

ISOTOPE TRACERS IN CATCHMENT HYDROLOGY

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Dedication

To Vance C. Kennedy, now retired from the U. S. Geological Survey, for having gotten Kendall interested in watersheds in the first place by inviting her to visit his field area at the Mattole River (California, USA) in 1983 and become involved in the grand puzzles of stormflow generation. His obvious fascination with the linkages between watershed hydrology and geochemistry was highly contagious.

About the Editors

Carol Kendall is a research hydrologist in the Water Resources Division of the U.S. Geological Survey. Since 1990, she has been chief of the "Isotope Tracers of Hydrologic and Biogeochemical Processes" project in Menlo Park, California. The purpose of this research project is to develop new methods, concepts, and applications of environmental isotopes to solve problems of national importance. She received her B.S. and M.S. in Geology from the University of California (Riverside), and her Ph.D. in Geology from the University of Maryland. Her main background is in isotope hydrology and aqueous geochemistry. Kendall is coordinator and main instructor of the 5-day Isotope Hydrology training course taught almost yearly for the USGS, and frequently teaches other short-courses. The main focus of Kendall's recent research has been on small forested catchments: investigating the impact of isotopic heterogeneity in shallow systems on determining recharge mechanisms, tracing sources and reactions of nitrate in surface waters and groundwaters using oxygen and nitrogen isotopes, and applying a multi-isotope (O, H, C, N, S, Sr) approach to studying watershed hydrology and biogeochemistry. She has recently become fascinated with "isotope biomonitoring" -- the idea of using isotopes of organisms as integrators of environmental conditions at the landscape-scale, including providing information about sources of nutrients in human-impacted environments.

Jeffrey J. McDonnell is Professor of Hydrology at the State University of New York, College of Environmental Science and Forestry. He received his B.Sc. from the University of Toronto, M.Sc. from Trent University, and Ph.D. from the University of Canterbury. His background is in physical hydrology and geomorphology. His particular interests relate to the age, origin and pathway of subsurface stormflow and runoff processes in catchments. While working as an Assistant Professor at Utah State University, McDonnell began a working relationship with Kendall that has continued for several years -- one that exploits their very different backgrounds and perspectives on catchment hydrology. McDonnell has been a Research Fellow at NASA, the Japanese Forestry and Forest Products Research Institute and Landcare New Zealand. He has received the Gordon Warwick Award from the British Geomorphological Research Group, the Horton Research Grant from the American Geophysical Union, Warren Nystrom Award from the Association of American Geographers, and the Commonwealth Scholarship and Fellowship from Canada. Prof. McDonnell was an Associate Editor for Water Resources Research (1996-1998) and is now an Associate Editor for Journal of Hydrology and Editorial Board member of the journals Hydrological Processes and Progress in Environmental Science. He has published about 50 papers on catchment hydrology.

Preface

Of all the methods used to model hydrologic processes in small catchments over the past 20 years, tracers -- in particular isotope tracers -- have provided the best new insights into the age, origin, and pathway of water movement. Isotope hydrograph separations determined by simple conservative-mixing models have shown repeatedly, in a variety of climatic and hydrogeologic environments, that streamflow generated during rainfall or snowmelt is derived primarily from water stored in the catchment prior to the event, a surprising insight that has profoundly changed how hydrologists view the runoff process. Use of other isotopes to trace solute sources and reactions has revolutionized the way that we view catchment biogeochemical processes. And recent advances in water age-dating using chlorofluorocarbons and in tracing sources of nitrate have instigated new developments in hydrology, and helped forge new links between hydrology, ecology, and biogeochemistry.

The use of isotope tracers in catchment hydrology has increased dramatically since we first envisioned this book. This increased usage has been facilitated by the formation of the International Committee on Tracers (ICT), in association with the International Association for Hydrological Sciences (IAHS); numerous sessions devoted to isotope tracers in catchment hydrology at meetings convened by the American Geophysical Union (AGU), the European Geophysical Society (EGS), and the IAHS; and the continued support of the International Atomic Energy Agency (IAEA) for the development of new tools for water resources management. The long gestation period of our text, while sometimes frustrating our contributing authors, has enabled several of these new developments to be incorporated into different chapters.

Several isotope hydrology/biogeochemistry books have been published recently, including *Environmental Isotopes in Hydrogeology* (1997, CRC Press) by Clark and Fritz, *Chemical and Isotopic Groundwater Hydrology: The Applied Approach* (1997, Marcel Dekker) by Mazor, *Stable Isotopes: Integration of Biological, Ecological and Geochemical Processes* (1998, Bios Scientific) edited by Griffiths, *Stable Isotopes in Ecology and Environmental Science* (1994, Blackwell Scientific) edited by Lajtha and Michener, and others being prepared. The first two are textbooks aimed at classes in isotope hydrogeology and field methods, respectively. While our book is intended more as a reference text than as a textbook, we hope that it is suitable for use in senior undergraduate and graduate courses in hydrology and hydrochemistry that focus on catchment processes or tracers. Because of its broad coverage of environmental isotope geochemistry, this book may also serve as an update for some chapters in volumes 1 and 2 of the venerable *Handbook of Environmental Isotope Geochemistry* (1980, 1986; Elsevier) edited by Fritz and Fontes.

Isotope Tracers in Catchment Hydrology represents a new "earth systems" approach to catchments. Modern isotope hydrology requires a multi-disciplinary approach that examines the entire landscape. Catchment hydrology is more than just the study of water, or rocks, or biota -- it encompasses the physical and biogeochemical interactions that control the hydrology and biogeochemistry of the system. This book reflects the evolution of our perspective over the years. Our initial vision of this book centered on the connection between physical hydrology

and isotope geochemistry. We then added more biologically-oriented chapters in the final stages. Interestingly, the U. S. Geological Survey underwent similar changes during this same time, redefining itself to better combine its expertise in hydrology, geology, and now biology to focus on modern environmental concerns. If we had not exceeded our page allowances, we would have added a chapter on environmental controls on foodweb structures or ecosystem restoration. We think the real strength of this book is its broad definition of what "catchment hydrology" entails; this reflects the merging of the editors' very different perspectives on catchment hydrology -- Kendall with her interests in isotope biogeochemistry and McDonnell with his focus on physical hydrology.

The editorial decision to emphasize research at the catchment scale rather than at the regional groundwater-basin scale was made partly because of the vast amount of existing literature devoted to isotope hydrology/geochemistry of groundwater basins. A broader book would necessarily be largely review and we wanted to emphasize cutting-edge research -- and research trends that we think are the "wave of the future." Hence, we have chosen to focus the book on the more specific topic of applications of isotope hydrology and geochemistry to understanding how catchments "work." Most of the processes that affect the use of isotopes in larger groundwater systems are also addressed in this book -- and physical and biogeochemical reactions during recharge cause most of the isotope fractionations and source-related isotope variations that affect their use as tracers in systems at all scales.

We instructed our chapter authors to cover the fundamentals of isotope geochemistry and catchment hydrology in enough detail so that readers unfamiliar with the specifics of either field could rapidly feel comfortable with more technical material. The focus of the book, however, is research that we think represents an important component of future hydrological science. We selected authors who are both experts in their fields and who, from our personal knowledge, are actively involved in catchment-related research and would bring to the book a wealth of published and in-progress studies of isotopic applications. Each chapter is self-contained and yet builds on the earlier chapters in Parts I and II. This has resulted in non-uniform coverage of topics and some overlap. Each of the chapters received at least two formal technical reviews and, in some cases, many more, and several editorial reviews. We hope that the rigorous reviews ensure accuracy, perspective, cohesiveness, and up-to-date science.

Part I (Chapters 1 and 2) provides sufficient background in hydrology and isotope geochemistry for a reader at the senior undergraduate or beginning graduate-student level to comprehend and make good use of the rest of the book. Part II (Chapters 3-7) provides a very detailed look at the important topic of variability in the isotopic compositions of water and, to a lesser degree, some solute sources. The thorough discussions of the various hydrologic and biogeochemical processes responsible for this variability include practical guidelines for dealing with the problem of isotopic variability in catchment research. These spatial and temporal variations in water and solute sources reveal much process information that is the topic of active study in the field at present.

Parts III and IV are the core of the book: discussions of specific case studies of applications of isotopes to understanding catchments. Part III emphasizes isotope hydrological studies, and Part IV emphasizes isotope geochemical applications to catchment research. Keeping in mind the process-related variability and problems raised in Part II, the case studies explore a broad

range of well-tested and new applications of isotopes. Each chapter includes a very brief review of fundamentals of hydrology and isotope geochemistry required to understand the chapter (with appropriate references to Chapters 1 and 2). The chapters in Part III are organized by types of catchment environments and have very similar formats. The chapters in Part IV focus on different types of geochemical applications. Part V contains two synthesis chapters, one that reviews the use of isotopic and geochemical data in catchment hydrology, and one that describes the uses of isotopic techniques for understanding environmental change.

We resisted the usual tendency to divide the chapters by isotopes, and instead tried to focus the chapters on catchment types and catchment processes. We provided the authors with a semi-detailed outline of our ideas, a statement of the philosophy of the book, and a very detailed plan for chapter format and terminology. We hope that this has resulted in a cohesive volume that is both a handbook of tools in isotope hydrology and a guide for future research developments in this ever-expanding field. The challenges of future research are to apply our understanding of small catchment hydrology to the ever-increasing problems in larger watersheds, including those from urban development and agricultural landuses, and to develop new isotopic techniques to trace anthropogenic pollutants through the landscape and biosphere.

Carol Kendall and Jeffrey J. McDonnell

Menlo Park and Syracuse

August 1998

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Chapter 1

Fundamentals of Small Catchment Hydrology

James M. Buttle

1.1 Introduction to Small Catchments

This chapter seeks to provide an overview of hydrological processes relevant at the catchment scale, and to identify areas where environmental isotopes have assisted the study of such processes. This will form the backdrop for subsequent chapters examining the use of environmental isotopes in specific hydrological subsystems (in particular Chapters 10 to 14). Beginning with an outline of the general components of the water balance equation, we will review the salient physical principles associated with each component. The related issue of spatial and temporal scale in small catchments will be examined. This will be followed by a survey of the use of isotopes in examining the nature of hydrological processes, and some suggested issues for future research.

We will concentrate on hydrological processes operating in small catchments. A glossary of terms relevant to hydrological processes discussed in this and subsequent chapters is presented in Table 1.1. An operational definition of "small" would encompass catchments ranging in size from 10^{-2} to 10^2 km²; most isotopic hydrograph separations have been conducted in catchments $< 10^2$ km² (Buttle, 1994). Such catchments tend to be located in headwater areas and possess a number of attributes that distinguish them from "large" catchments, such as the Seine, the Potomac, and the Ottawa. Small catchments have relatively steep channel gradients and valley sideslopes, absent or minor floodplains, groundwater inputs from local or intermediate flow systems (cf. Tóth, 1963), and a comparatively uniform regional climate.

1.2 The Catchment Water Balance

The catchment water balance is an appropriate starting point for our discussion of small catchment hydrology, because it provides the conceptual framework within which hydrologists conduct their research, and is the vehicle by which people working in various subdisciplines can relate their findings to each other. In addition, closure of the water balance is used as a check on the validity of results from hydrological studies.

1.2.1 General components of the water balance

The water balance is based on the equation of continuity:

$$I - O = \frac{dS}{dt} \quad (1.1)$$

where I = inputs (m/s), consisting of precipitation (P) in solid (snow, ice) and liquid (rain) forms, as well as the deposition of water from fog and clouds (occult water); O = outputs (m/s), including evapotranspiration (ET) and runoff (R); and dS/dt = changes in storage (S) per unit time t (m/s).

Runoff consists of both surface runoff and subsurface flow. These are separated for convenience, but frequently there is interaction between the two. The storage term (S) incorporates the retention of water in a number of stores within the terrestrial portion of the hydrological cycle, such as the soil, aquifers, surface depressions, snowcover, and glaciers. This revised water balance is given by Equation 1.2, and is illustrated using canonical structures in Figure 1.1:

$$P - R - ET = \frac{dS}{dt} \quad (1.2)$$

Any hydrological system can be studied using a water balance approach. If we look at the system for a period of a year or more (in order to integrate seasonal fluctuations in the various terms), change in net storage is usually small relative to the size of the other terms and can often be ignored, such that

$$P - R = ET \quad (1.3)$$

At first glance the water balance looks very simple; however, this can be misleading, because the terms in the equation cannot always be quantified adequately or easily, particularly at the scale of large catchments. Many hydrological studies have been conducted at the small catchment scale partly for this reason, since these smaller areas simplify application of the water balance equation, particularly in terms of the assessment of net groundwater fluxes (e.g. Robertson and Barry, 1985).

1.2.2 Precipitation, interception, net precipitation

Precipitation (rainfall, snowfall) is generated by storms that possess structural properties discernable at the micro- and mesoscales, and which can be described in terms of their "exterior" and "interior" characteristics (Bras, 1990). The former relate to the depth and duration of precipitation as well as the time between storms, while the latter comprise the spatial and temporal distribution of precipitation intensities throughout a storm. Table 1.2 presents some characteristics of general storms relevant to small catchment hydrology. Despite the importance of these properties to hydrological processes in small catchments and to their overall water balance, and in spite of the advent of radar and remote sensing approaches to precipitation measurement, precipitation characteristics are usually measured with a rain gage, which is "more or less a glorified tin can, or receptacle, placed on the ground" (Bruce and Clark, 1966). Standard, or non-recording, gages can be used to estimate the depth of water collected between sampling periods, while various types of recording gages (usually weighing or tipping-bucket designs) can monitor temporal properties of the storm, such as the start and end of precipitation and short-term intensities. Snowfall depth can be measured using a graduated ruler inserted into snow that has accumulated onto a reference surface (snow board).

Table 1.1. Glossary of terms.

aerodynamic resistance	"The bulk meteorologic descriptor of the role of the atmospheric turbulence in the evaporation process" (Oke, 1978). It is dependent upon wind speed, surface roughness and atmospheric stability.
albedo	"The ratio of reflected solar radiation to the total incoming solar radiation where both streams are measured across the complete wavelength range of solar radiation ($\sim 0.3 - 4.0 \mu\text{m}$)" (Henderson-Sellers and Robinson, 1986).
anisotropy	The condition of having different physical properties (e.g. K_H) in different directions.
aquifer	"A saturated permeable geologic unit that can transmit significant quantities of water under ordinary hydraulic gradients" (Freeze and Cherry, 1979).
aquitard	"The less-permeable beds in a stratigraphic sequence" (Freeze and Cherry, 1979).
baseflow	Sustained runoff that is the sum of deep subsurface flow and delayed shallow subsurface flow; however, it is not synonymous with groundwater flow (Ward and Robinson, 1990).
Bowen Ratio	The ratio of the sensible and latent fluxes over a surface.
capillary fringe	The area between the vadose and phreatic zones; all pores are filled with water, but the water is held under slight matric tension, such that the addition of a small amount of water will convert this zone to saturated conditions (Gillham, 1984).
capillary rise	Movement of water from the saturated zone upward into the unsaturated zone due to surface tension (Dingman, 1993).
catchment	"A unit of land on which all the water that falls (or emanates from springs) collects by gravity and fails to evaporate and runs off via a common outlet" (Black, 1991).
channel precipitation	Direct precipitation onto a water surface.
depression storage	The volume of water contained in small surface depressions during or shortly after rainfall or melt, none of which runs off (Horton, 1933).
detention storage	Rainwater or snowmelt held in temporary storage on the surface as it moves downslope by overland flow, and which either runs off, is evaporated, or is infiltrated after rainfall or melt ceases (Horton, 1933).
dew point	Temperature at which an air parcel becomes saturated if cooled without a change in pressure or moisture content (Henderson-Sellers and Robinson, 1986).
emissivity	Degree to which a real body approaches a black body radiator (i.e. a perfect emitter of radiation) (Henderson-Sellers and Robinson, 1986).
evaporation	Diffusion of water vapor into the atmosphere from exposed water surfaces.
evapotranspiration	Diffusion of water vapor into the atmosphere from vegetated surfaces. It represents the combination of evaporation from soil and plant surfaces with plant transpiration (Goudie et al., 1985).
event water	Water that is added to a catchment's surface as rainfall or snowmelt during a storm event.
exfiltration	The removal of water from the soil at the ground surface, together with the associated unsaturated upward flow (Freeze, 1974).
falling limb	That portion of the hydrograph where discharge is decreasing with time. Also known as the recession limb.
fractionation	"The separation of a mixture, usually of chemically related or otherwise similar components, into fractions of different properties" (Uvarov et al., 1979).

Table 1.1. Glossary of terms (continued).

groundwater flow	That part of streamflow that has infiltrated the ground, has entered the phreatic zone, and has been discharged into a stream channel as spring or seepage water (Chorley, 1978b).
Horton flow	"Direct surface runoff across saturated soils where rainfall intensity exceeds infiltration plus depression storage" (Chorley 1978b).
hydraulic conductivity	The constant term in Darcy's Law expressing the ability of a soil or rock to transmit water under a given hydraulic gradient (Chorley, 1978b).
hydraulic diffusivity	The ratio of the hydraulic conductivity to the volume of water that a unit volume of saturated soil or rock releases from storage per unit decline in hydraulic head. It is a parameter that combines transmission characteristics and the storage properties (Goudie et al., 1985).
hydraulic gradient	The change in total potential over the change in flow length.
hysteresis	The property whereby a dependent variable exhibits different values according to whether the independent variable is increasing or decreasing (Goudie et al., 1985).
immobile water	Soil water that remains in place in soil matrix during infiltration through vadose zone.
infiltration	Entry of water through the soil surface, via pores or small openings, into the soil mass.
infiltration capacity	The maximum rate at which a given soil can absorb water when it is in a specified condition (Horton, 1933).
interception	"The process by which precipitation is trapped on vegetation and other surfaces before reaching the ground" (Goudie et al., 1985).
isothermal	At the same temperature throughout. In snowmelt hydrology, this condition implies that the snowpack is at the melting point (273.2K or 0°C) throughout.
isotropy	The condition of having uniform physical properties in all directions.
kriging	A statistical estimation technique used for spatial interpolation and integration.
lag-to-peak	The time difference between the centre of mass of rainfall and the peak discharge rate (Dunne and Leopold, 1978).
latent heat	That part of the thermal energy involved in a change of state (e.g. 2.4 MJ/kg released when water vapor condenses to liquid) (Goudie et al., 1985).
leaf area index	The proportion of the surface area of one side of all leaves to the plan-view area of the entire plant.
litter	"The surface layer of fallen, dead vegetation lying on the mineral soil" (Chorley, 1978b).
litter flow	"Downslope flow of water in the litter layer" (Chorley, 1978b).
local evaporation line	The relationship describing parallel variations in ^{18}O and D in water that has undergone evaporation. Water that has undergone evaporation will plot below the mean water line in ^{18}O -D space.
macropore	Large soil pores that may result from biological activity (earthworms, plant root extension and subsequent decay) as well as structural cracks and fissures (Ward and Robinson, 1990).
micropore	Small soil pores between individual mineral grains.
meteoric water line	The relationship describing parallel variations in ^{18}O and D in precipitation: $\delta\text{D} = 8\delta^{18}\text{O} + 10$ (‰) (Craig, 1961).

Table 1.1. Glossary of terms (continued).

mixing models	"Models used to explain or predict temporal variations in the solute concentrations of streamflow by taking account of the mixing of water from different sources or the mixing of water within a store" (Goudie et al., 1985).
net radiation	"The resultant flux of the solar and terrestrial radiation through a horizontal surface" (Goudie et al., 1985).
occult precipitation	Precipitation in liquid (fog drip) and solid (rime) forms that is induced when clouds encounter trees or other vegetation (Dingman, 1993).
overland flow	"Water that, failing to infiltrate the surface, travels over the ground surface towards a stream channel either as quasi-laminar sheet flow or, more usually, as flow anastomosing in small trickles and minor rivulets" (Ward and Robinson, 1990).
partial area runoff	Storm runoff generated by only part of the surface of a catchment (Betson, 1964).
phreatic zone	The volume of soil and bedrock below the water table that is saturated (i.e. pores and void spaces are completely filled with water).
pipe flow	Concentrated subsurface flow of water in natural pipes (Jones, 1971).
piping	Formation of natural pipes in unconsolidated material by eluviation or other processes of differential subsurface erosion (Jones, 1971).
pre-event water	Water that was held in a catchment prior to, and has been discharged into the stream channel during, a storm event.
quickflow	The sum of channel precipitation, surface runoff and rapid subsurface flow, also referred to as direct runoff. Quickflow is the major runoff contribution during storm periods and most floods; however, it is not synonymous with surface runoff (Ward and Robinson, 1990).
return flow	Infiltrated water which returns to the surface having flowed for a short distance in the upper soil horizon (Dunne and Black, 1970a).
rising limb	That portion of the hydrograph where discharge is increasing with time.
saturation overland flow	Surface runoff over saturated soil, the infiltration capacity of which has not been exceeded (Carson and Kirkby, 1972).
sensible heat	The addition or subtraction of energy to a body that is sensed as a rise or fall in its temperature (Oke, 1978).
stemflow	That portion of the gross rainfall intercepted by the vegetation canopy which reaches the litter or soil surface by running down stems or trunks (Helvey and Patric, 1965).
stomata	"The leaf orifices through which water vapor escapes to the atmosphere" (Ward and Robinson, 1990).
stomatal resistance	Resistance to diffusion of water vapor through a plant's stomata.
sublimation	"The conversion of a solid direct into vapor, and subsequent condensation, with melting" (Uvarov et al., 1979).
subsurface runoff	The sum of shallow and deep subsurface flow, normally equal to the total flow of water arriving at the stream as saturated flow into the stream bed itself and as percolation from seepage faces on the stream bank (Freeze, 1972).
subsurface stormflow	That fraction of stormflow generated by lateral subsurface flow of water above water-impeding layers, which reaches the channel without entering the groundwater zone (Whipkey, 1967).

Table 1.1. Glossary of terms (continued).

surface runoff	That part of total runoff that reaches the catchment outlet via overland and channel flow (Ward and Robinson, 1990).
throughfall	That portion of gross rainfall which directly reaches the forest litter through spaces in the canopy and as drip from leaves, twigs and stems (Helvey and Patric, 1965).
throughflow	Water that infiltrates the soil surface and then moves laterally through upper soil horizons towards the stream channels, either as unsaturated flow or, more usually, as shallow perched saturated flow above the main groundwater level" (Ward and Robinson, 1990).
time of rise	The time difference between the initial rise in streamflow in response to water inputs and the occurrence of peak discharge.
translatory flow	Lateral throughflow of 'old' water stored in the soil and released to channel flow by a process of displacement by 'new' water inputs (Hewlett and Hibbert, 1967).
transpiration	Loss of water vapor mainly from leaf cells through pores but also from the leaf cuticle and through lenticels of the stem (Goudie et al., 1985).
vadose zone	The volume of soil and bedrock above the water table that is generally unsaturated (i.e. pores and void spaces are not completely filled with water).
vapor pressure	"The force per unit area created by the motions of the vapor molecules treated in isolation from all other gases in the atmosphere" (Henderson-Sellers and Robinson, 1986).
variable source areas	Areas contributing to storm runoff. These can vary in size between storms and during the course of a single storm (Chorley, 1978b).
wetlands	"Usually flat areas which are covered either periodically, regularly or permanently by shallow water up to a depth of around 6 m. They include swamps and marshes, bogs, fens, peatlands, seasonally flooded land around lakes and rivers or level, ill-drained plains" (Goudie et al., 1985).
watersheds	Synonymous with catchments, large basins or collections of catchments in this book.

The equivalent depth of water (snow water equivalent) can be obtained by melting the accumulated snow and expressing the water volume as a depth over the board's area. Snowfall can also be measured with various recording and non-recording gages, which are usually shielded in order to reduce wind turbulence over the gage orifice. Rainfall and snowfall gages have been described by Bruce and Clark (1966), Dunne and Leopold (1978), and Goodison et al. (1981). Regardless of the type and number of gages employed, only a minute fraction of the precipitation falling on the entire catchment is actually sampled.

Precipitation estimates from recording and non-recording gages are subject to 2 types of errors:

- (1) Systematic errors, which result from the influence of gage itself upon the amount of precipitation it records; for example gage exposure, gage inclination, evaporation and wetting losses, and rain splash, both into and out of the gage.
- (2) Random errors, which are due to micrometeorological variations in the immediate vicinity of the gage, slight differences in gage manufacture, and the spatially and temporally variable nature of precipitation.

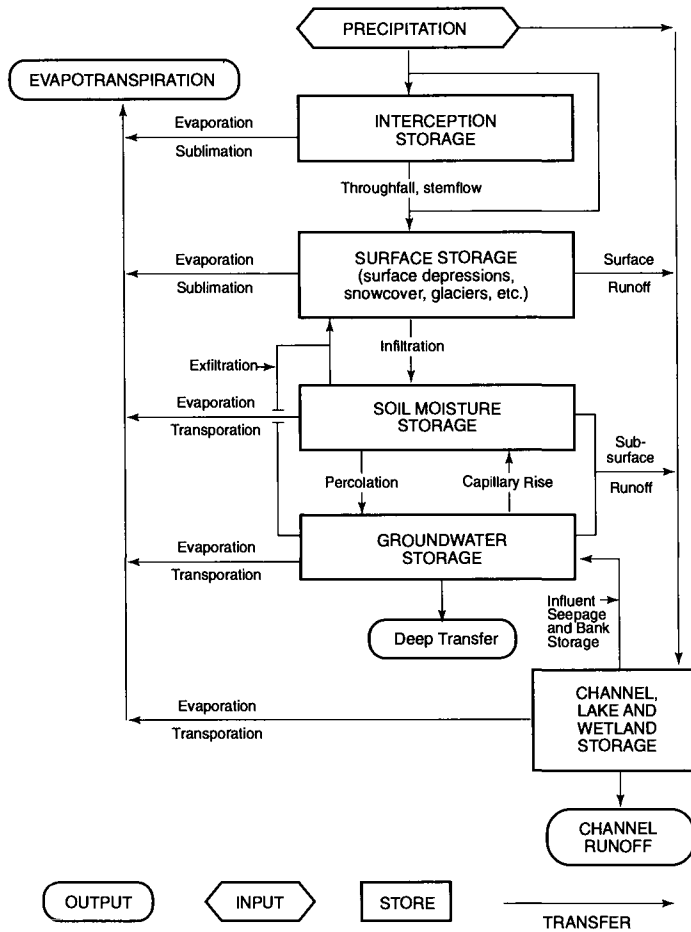


Figure 1.1. Major water balance components and fluxes within a small catchment.

Table 1.2. Characteristics of general storms relevant to small catchment hydrology (from Graymon and Eagleson, 1971). "Cell" refers to a convective cell or thunderstorm, "intensity" refers to rainfall intensity, and a small mesoscale storm "consists of a unit of developing cells, each at different developmental stages and moving in unison in a preferred direction" (Bras, 1990).

STORM TYPE	SIZE (km ²)	INTENSITY	DURATION	DENSITY
cellular	8	~ 2 - 10 times that of small mesoscale	~ linearly related to cell intensity	1 - 7 cells per small mesoscale
small mesoscale	130-390	~ 2 times that of the large mesoscale level (2300 - 4600 km ²)	1/3 - 3 h	2 - 5 small mesoscales per 2600 km ²

The approximate errors introduced into point rainfall measurements by systematic and random errors are summarized in Table 1.3. Uncertainty associated with use of these precipitation estimates is exacerbated by the need to move from point to areal estimates of precipitation. There are a number of methods available to extrapolate point precipitation to the mean over a catchment, ranging in complexity from arithmetic averages of the point values, through the use of Thiessen polygons and isohyetal mapping, to such methods as kriging (Smith, 1993). Regardless of the method employed, it must be recognized that most catchments tend to experience persistent patterns of precipitation, largely in response to interactions between topography and the dominant storm tracks over the catchment. Thus, precipitation often increases with elevation within a region, while windward slopes receive more precipitation than leeward ones. These patterns may frequently go undetected in areas of rugged relief, owing to a topographic bias in precipitation measurement whereby there are relatively fewer precipitation stations in areas of high elevation (Briggs, 1991).

Interception refers to the temporary storage of precipitation on natural (e.g. vegetation) or artificial (e.g. buildings) ground cover. Most research into interception has been concerned with the interaction between precipitation and vegetation rather than with urban surfaces, and our discussion will also focus on this process. Water that impinges on the vegetation surfaces can be partitioned between interception loss, throughfall and stemflow. Interception loss refers to the amount of water retained on the vegetation which is subsequently evaporated back to the atmosphere or absorbed by the plant. The capacity of these surfaces to retain precipitation (interception storage) is greatest at the beginning of a storm but may be quickly satisfied by initial precipitation inputs; nevertheless, evaporation of this stored water during the storm means that there is continual retention of a small fraction of incident precipitation (the importance of this is discussed in Chapter 3). For this reason, total canopy interception loss (I) during a storm is frequently estimated using relationships of the form:

$$I = C + LAI \cdot E \cdot T \quad (1.4)$$

where C = interception storage capacity of the vegetation (m), LAI = leaf area index (dimensionless), E = index of evaporation rate from the leaf surface (m/s), and T = time duration of the rainfall event (s).

Interception loss for a particular vegetation type during an event is largely a function of storm conditions (e.g. size, intensity, duration, wind speed, air temperature), and I can equal 100% of incident precipitation in small storms. In addition to intra- and inter-event changes in I , interception loss varies on a seasonal basis for a given vegetation type, and between vegetation types. Thus, annual interception as a fraction of annual precipitation in middle to high latitudes ranges from 0.1 to 0.5 for conifers, while the corresponding range for non-conifers is only 0.1 to 0.35 (Figure 1.2a). This difference is an expression of different leaf habits and the fact that conifers intercept at relatively constant levels year round. One source of the large variations in I/P ratios at a given latitude for conifers is the tendency for these trees to intercept a smaller fraction of precipitation as P increases (Figure 1.2b). This trend is not apparent from the limited data for non-coniferous species, and $I/P > 0.4$ has been reported for low-latitude angiosperms receiving more than 5 m of rainfall annually (Figure 1.2b).

Throughfall refers to water that has either fallen through openings in the canopy or has come into contact with the canopy before falling to the ground. Stemflow is the transfer of water

Table 1.3. Approximate errors in point rainfall measurements (from Kurtyka, 1953; Dreaver and Hutchinson, 1974).

SYSTEMATIC ERRORS	% ERROR
evaporation	-1.0
adhesion	-0.5
colour	-0.5
inclination	-0.5
splash	+1.0
Subtotal	-1.5
exposure	-5.0 to -80.0
RANDOM ERRORS	up to ± 10.0 , depending on storm size

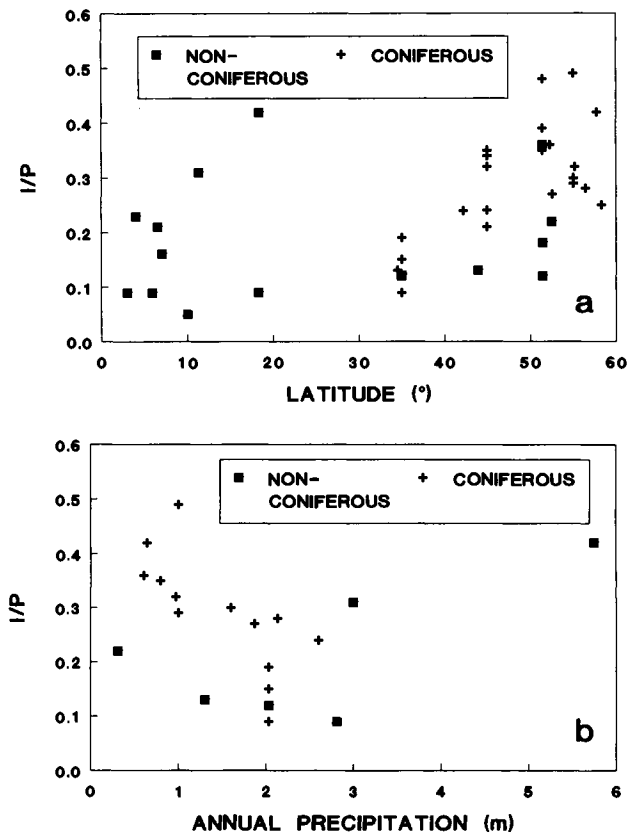


Figure 1.2. Variations in the ratio of annual interception (I) to annual precipitation (P) with latitude (a) and annual precipitation (b) for coniferous and non-coniferous tree types. Data from Dingman (1993).

down leaf stems and branches to the ground along the main stem or trunk of the plant. The sum of throughfall and stemflow is often referred to as net precipitation. The effect of both processes is a redistribution of water reaching the ground surface relative to the precipitation field above the canopy. Differences in the architecture of the vegetation canopy produce variations in the amount of throughfall and stemflow between species. Neary and Gizyn (1994) found throughfall/mean annual precipitation ratios of 0.84 and 0.74 for hardwoods and conifers, respectively, in south-central Ontario, while the ratio was as low as 0.66 for beech in the eastern U.S.A. (Helvey and Patric, 1965). Black (1991) reported that stemflow as a fraction of annual precipitation is generally ~ 0.001 , although this ratio can reach 0.01 or 0.02 for some tree species.

Snowfall is also intercepted by vegetated surfaces; however, this temporary storage is generally held to be a minor loss of water from the catchment, since intercepted snow often is blown down to the ground following the storm or melts and drips onto the ground, both processes reducing the opportunity for evaporative and sublimative loss of intercepted snow (Ward and Robinson, 1990; isotopic fractionation of snow is treated in Chapter 4). Nevertheless, recent work indicates that evaporation and sublimation of intercepted snow can be appreciable in some environments (Golding, 1982; Calder, 1990).

Intercepted water is usually viewed as a loss of water out of the catchment system. Calder (1990) contends that evaporative loss of intercepted water forms a major part of total evaporation, and may be twice that due to transpiration in some upland forests in the U.K. However, despite considerable experimental study, hydrologists have only recently reached a consensus on the quantitative significance of interception to a catchment's water balance. Some early workers (e.g. Burgy and Pomeroy, 1958) contended that the amount of water intercepted and later evaporated reduces water loss from vegetation due to evapotranspiration by the same amount. More recent work has demonstrated that intercepted precipitation evaporates at a much greater rate than transpired water, such that total water loss from wet vegetative surfaces exceeds transpiration rates from unwetted vegetation under the same environmental conditions (Ward and Robinson, 1990). The significance of evaporation of intercepted water to a catchment's water balance is exemplified by the work of Pearce et al. (1980), who observed night-time evaporation of intercepted water in an evergreen mixed forest in New Zealand (when transpiration was zero) similar to daytime wet canopy evapotranspiration rates. Conversely, vegetation can collect occult precipitation, enhancing water inputs to the surface via throughfall and stemflow. For example, fog drip is ~ 880 mm/yr ($\sim 30\%$ of annual precipitation) in a Douglas fir forest in Oregon, U.S.A. (Harr, 1982), and fog-water deposition to a blanket bog in Newfoundland, Canada, averaged 1.8 mm/d during summer months (Price, 1992).

1.2.3 Snowmelt

Much of the snow that falls in high-altitude and mid- to high-latitude environments accumulates due to low winter temperatures. This represents a large reservoir of water in some regions that is released to the ground surface over a relatively short period during the spring. Since evaporation rates at this time are usually low, snowmelt inputs have little abstraction, resulting in high rates of soil water and groundwater recharge and enhanced water inputs to stream channels.

Direct measurements of snowmelt are often obtained from short-term (e.g. daily) differences in the snowpack's water equivalent using snow tubes (Goodison et al., 1981), from snowmelt lysimeters (e.g. Price and Hendrie, 1983) that record meltwater runoff from a known area, or as the product of the decrease in mean elevation of the snow surface and mean density of the surface snow layer (Heron and Woo, 1978). Snowmelt can also be estimated from the snowpack's energy balance:

$$Q_{\theta} = Q^* + Q_H + Q_E + Q_G + Q_P - Q_m \quad (1.5)$$

where Q_{θ} = change in energy stored in the snowpack (W/m^2), Q^* = net radiation (W/m^2), Q_H = sensible heat flux (W/m^2), Q_E = latent heat flux (W/m^2), Q_G = ground heat flux (W/m^2), Q_P = energy flux delivered to the snowpack by rainfall (W/m^2), and Q_m = energy used to melt snow (W/m^2). Methods for measuring or estimating these stores and fluxes are given by Anderson (1968), Male and Gray (1981), and Price (1988). Melt occurs at the snowpack's surface; nevertheless, meltwater does not reach the ground surface until energy inputs have reduced Q_{θ} to 0 (isothermal condition), and have coated the snow crystals with a thin layer of water in order to allow liquid water to percolate through the snowpack to the ground ("ripe" condition). It is often assumed that meltwater flux is spatially uniform down through the snowpack; however, Gerdell (1954) observed preferential flow of meltwater down vertical channels of coarse-grained snow, and dye tracing studies (e.g. Marsh and Woo, 1984) have shown that the presence of high-density ice layers in the snowpack can induce horizontal water movement and meltwater percolation down discrete "fingers" within the snow.

The energy balance approach provides the most accurate means of estimating snowmelt at a point; however, data required to determine the various fluxes in Equation 1.5 are often unavailable. Therefore many operational estimates of snowmelt use air temperature as an index of energy available for melt, since air temperatures are measured in many areas (Male and Gray, 1981). These temperature-index expressions are usually of the form:

$$M = M_f \cdot (T_i - T_b) \quad (1.6)$$

where M = melt (m of water) produced per unit time, M_f = melt factor (m/K unit/time), T_i = index air temperature (usually the maximum or mean daily temperature), and T_b = base temperature (usually 273.2K (0°C)). Price (1988) notes that temperature-index methods generally work better in forests, since Q^* is dominated by longwave radiative fluxes, which in turn are linked to air temperature. However, such expressions work poorly in open areas due to the greater importance of fluxes of shortwave radiation and sensible and latent heat in these environments, none of which are well correlated with air temperature.

1.2.4 Infiltration and soil water storage

Movement of precipitation into the ground consists of a series of hydrological processes: (1) entry of water across the soil-atmosphere interface; (2) filling of storage; (3) transmission of water through the soil profile; (4) deep drainage; and (5) recharge of the underlying groundwater system.

Processes (1) - (4) generally occur in unsaturated soil (vadose zone), where soil pores are occupied by water and soil atmosphere in varying proportions. The water table separates the unsaturated zone and the underlying saturated (phreatic) zone of groundwater where all pores are filled with water. The capillary fringe represents an intermediate region between the unsaturated and saturated zones (Figure 1.3). The reader must bear in mind that sequence (1) - (5) is a continuum which has been divided into distinct units only in order to aid discussion.

All of these processes relate to the potential energy of water in the soil, which in turn is comprised of several component potentials. These can be expressed as energy per unit mass (J/kg); they are also expressed as energy per unit weight, which is obtained by division by the acceleration of gravity g , giving dimensions of length (m).

- (1) Matric potential ψ : caused by the attraction of water to solid surfaces (adhesion), as well as the attraction of water molecules to each other (cohesion). Water held in the soil above the water table possesses a negative soil water potential; therefore, unsaturated soil matric potentials are negative. Zero matric potential occurs when all the pores are filled with water (e.g. below the water table). Films of water around the soil pore walls become thinner as a soil dries, and remaining soil water is held under a greater tension, or increasingly negative matric potential. Figure 1.4 shows moisture characteristic curves for different soil textures during drainage, relating a soil's volumetric water content (θ) to its corresponding matric potential (ψ). In the field θ will vary for any given ψ depending on whether the soil is being wetted or dried, a property referred to as hysteresis. θ will be greatest at a given ψ in the case of a drying soil, and least for a soil being wetted. Ward and Robinson (1990) review the various explanations advanced to account for this hysteresis.
- (2) Gravity potential z : due to the elevation difference between the soil water and the reference pool (water table, sea level, soil surface, etc.).
- (3) Pressure potential p : due to the weight of water or gas pressure. Beneath the water table, pressure potential is equal to, and the opposite sign of, the gravity potential. We only consider pressure potential when dealing with saturated soil; p equals zero when the soil is unsaturated.
- (4) Osmotic potential o : caused by salts dissolved in the soil water. This component is related to the process of osmosis, whereby water will move from a weaker to a stronger solution in order to balance the solution concentrations. Osmotic potential can be important in certain circumstances, such as in studies of water uptake by plants; however, osmotic potential and temperature effects on a soil's hydraulic properties are generally ignored in studies of soil water movement (Nielsen et al., 1986).

Total potential (Φ) can be defined as:

$$\Phi = \psi + z + p + o \quad (1.7)$$

Definition of soil water in terms of total potential assists an examination of water movement into and through soils, since water moves from areas of high to low total potential.

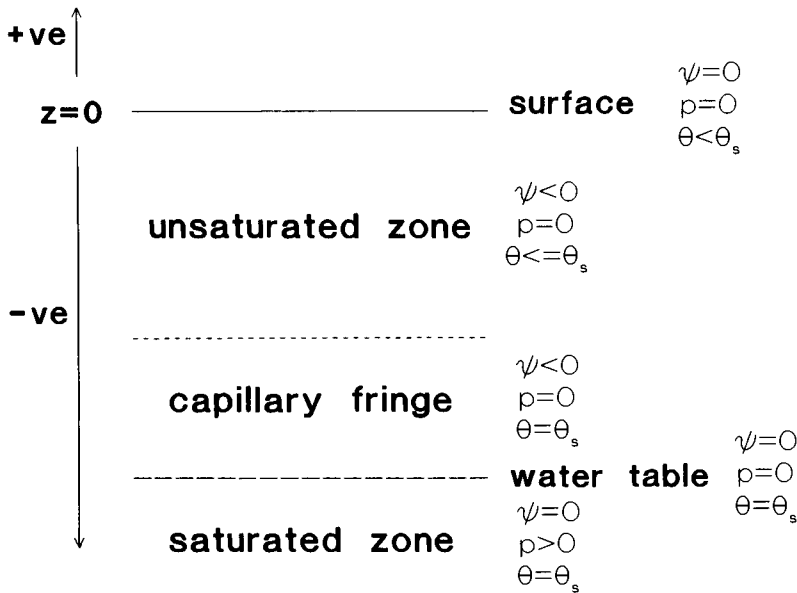


Figure 1.3. Schematic of ψ , p and θ conditions during drainage in the unsaturated zone, capillary fringe and saturated zone. Terms are defined in the text.

Infiltration is the entry of water past the soil surface. The gravity potential of a thin sheet of water at soil surface is greater than that a slight distance below the surface. In addition, matric potential of water at the surface equals zero, while ψ is less than zero below the surface, by virtue of its unsaturated state. Thus, water enters the soil in response to a gradient of total potential. The subsequent treatment of infiltration follows that of many other studies (e.g. Philip, 1957; Hillel, 1982), in that uniform delivery of water to the soil surface over space is assumed, such as under ponded irrigation conditions or delivery of meltwater from the base of an overlying snowpack. However, infiltration in the field often occurs under conditions of marked spatial variations in the flux of water to the surface. These may arise during rainfall due to microscale variations in precipitation as well as the effects of throughfall and stemflow, whereas structural heterogeneities in snowpacks (e.g. ice lenses) can induce nonuniform meltwater inputs to the underlying soil (cf. Marsh and Woo, 1984).

The infiltration rate is the actual flux of water across the atmosphere-soil interface at any given time, while the absolute maximum rate at which water can enter the soil at any specific time has been termed the infiltration capacity. Infiltration capacity generally exhibits an exponential decay with time (Figure 1.5). The initial decline in infiltration capacity represents filling of available storage in the soil, leading to a decrease in the gradient of total potential ($d\Phi/dz$) as the soil becomes wetter and θ and therefore ψ become more uniform with depth. It also reflects reductions in the permeability of the soil surface (surface sealing) due to dispersal of clays, swelling of colloids, and clogging of pores by suspended solids transported in the infiltrating water. The portion of the curve that asymptotically approaches a constant infiltration rate reflects transmission of water through the subsoil and deep drainage out of the profile.

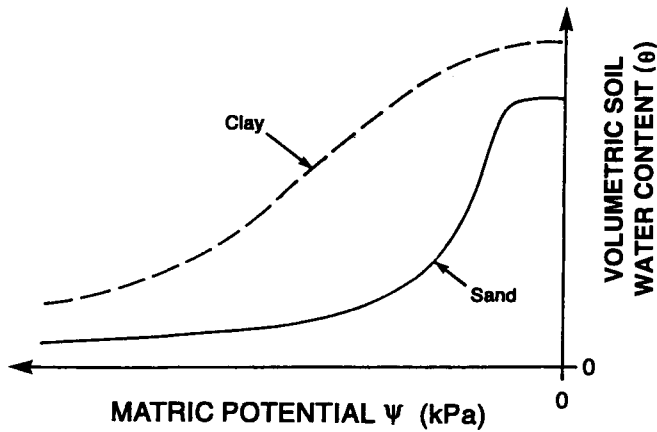


Figure 1.4. Hypothetical moisture characteristic curves for a sand and a clay, showing the relationship between θ and ψ for soils that have drained from saturation.

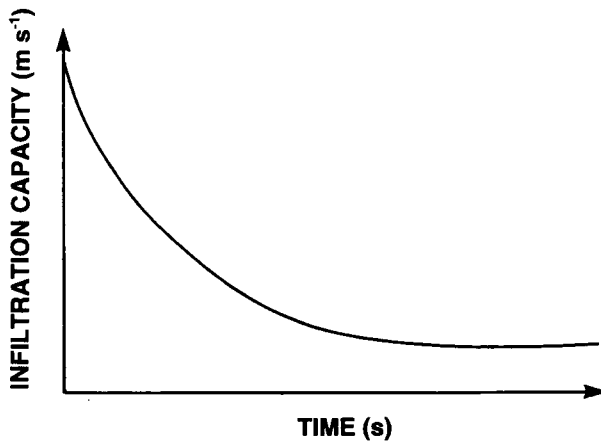


Figure 1.5. Exponential decline in a soil's infiltration capacity with time.

The link between the rate of change of soil water content and infiltrating water flux (or specific discharge R) can be expressed as an abridged form of the Richards equation (Richards, 1931):

$$\frac{\partial \theta}{\partial t} = \frac{\partial R}{\partial z} \quad (1.8)$$

In turn, the specific discharge depends on the ability of the soil to conduct water (the hydraulic conductivity K_H) and the gradient of total potential often referred to as the hydraulic gradient (i.e. Darcy's Law):

$$R = K_H \frac{\partial \Phi}{\partial z} \quad (1.9)$$

Given that total potential (Φ) equals the sum of ψ and z under unsaturated conditions, then R can be expressed in terms of the matric potential and the hydraulic conductivity:

$$R = K_H \frac{\partial \psi}{\partial z} + K_H \quad (1.10)$$

This relationship can be reexpressed with θ as the independent variable:

$$R = D \frac{\partial \theta}{\partial z} + K_H \quad (1.11)$$

where D is the hydraulic diffusivity (m^2/s):

$$D = K_H \frac{\partial \psi}{\partial \theta} \quad (1.12)$$

All soil pores are filled with water under saturated conditions ($\theta = \theta_s$ = soil porosity) and K_H is constant for a given depth and specified direction in a particular soil. The saturated hydraulic conductivity of geologic materials can range quite widely (Table 1.4), even within well-sorted media. Unconsolidated deposits tend to have larger K_H values than rocks, although the presence of fractures in the latter can result in conductivities comparable to those observed in gravels and coarse sands. Regardless of the degree of consolidation, K_H is primarily dependent on the pore size distribution: large pores exert little drag on water passage, while small pores slow down water movement. Thus, saturated K_H is greater in sands than in clays, even though the porosity (and therefore θ_s) of clays tends to exceed that of sands (~ 0.6 vs. ~ 0.4). K_H tends to decrease with depth for a given soil texture, due to the influence of compaction on reducing pore sizes and the reduced influence of various pedogenic processes that serve to increase the fraction of large pores in the topsoil.

The situation is more complicated under unsaturated conditions, where water movement occurs in water films lining the soil pores. Total flux is dependent on the thickness and continuity of these films, which will decrease as soil water content drops. Therefore K_H cannot be treated as a constant, but is a function of the soil's matric potential: $K_H(\psi)$. Figure 1.6 shows the relationship between unsaturated K_H and ψ for two different soil types. In sands the pores are large, and the water flux is also large at high ψ . K_H drops rapidly as θ decreases and the water films become thin and discontinuous. Conversely, clays tend to possess small pores and the water flux is small relative to that of sands at high ψ due to greater resistance to water movement. However, the flux in clays does not decrease as much as in sands during drainage, because the small pores are able to maintain reasonably thick and continuous water films.

The preceding approach is standard in treatments of infiltration theory in soil physics (e.g. Hillel, 1982) and hydrology (e.g. Knapp, 1978; Bras, 1990). Equations 1.10 to 1.12 can be solved analytically assuming simplified boundary conditions, or numerically using finite-difference and finite-element approaches (e.g. Campbell, 1985). These equations have been

Table 1.4. Ranges of saturated hydraulic conductivities (K_H) for various geologic materials.

MATERIAL	RANGE IN K_H (m/s)
<u>Unconsolidated deposits</u>	
gravel	$1 - 10^{-3a}$ $3 \times 10^{-2} - 3 \times 10^{-4c}$
well-sorted gravel	$10^{-2} - 10^{-4b}$
clean sand	$10^{-2} - 2 \times 10^{-6a}$
silty sand	$10^{-3} - 10^{-7a}$
well-sorted sand, glacial outwash	$10^{-3} - 10^{-5b}$
silty sand, fine sand	$10^{-5} - 10^{-7b}$
coarse sand	$6 \times 10^{-3} - 9 \times 10^{-7c}$
medium sand	$5 \times 10^{-4} - 9 \times 10^{-7c}$
fine sand	$2 \times 10^{-4} - 2 \times 10^{-7c}$
silt, loess	$2 \times 10^{-5} - 10^{-9ac}$
silt, sandy silts, clayey sands	$10^{-6} - 10^{-8b}$
glacial till	$10^{-6} - 10^{-12a}$ $10^{-6} - 10^{-8b}$ $2 \times 10^{-6} - 10^{-12c}$
unweathered marine clay	$2 \times 10^{-9} - 8 \times 10^{-13ac}$
clay	$10^{-8} - 10^{-11b}$ $4.7 \times 10^{-9} - 10^{-11c}$
<u>Rocks</u>	
<i>Sedimentary</i>	
karst and reef limestone	$2 \times 10^{-2} - 10^{-6ac}$
limestone and dolomite	$2 \times 10^{-6} - 5 \times 10^{-10a}$ $2 \times 10^{-6} - 10^{-9c}$
sandstone	$2 \times 10^{-6} - 10^{-10a}$
siltstone	$1.4 \times 10^{-8} - 10^{-11c}$
salt	$10^{-10} - 10^{-12c}$
anhydrite	$2 \times 10^{-8} - 4 \times 10^{-13c}$
shale	$10^{-9} - 5 \times 10^{-14a}$ $2 \times 10^{-9} - 10^{-13c}$
<i>Crystalline</i>	
permeable basalt	$2 \times 10^{-2} - 4 \times 10^{-7ac}$
fractured igneous and metamorphic rocks	$3 \times 10^{-4} - 8 \times 10^{-9ac}$
weathered granite	$5.2 \times 10^{-5} - 3.3 \times 10^{-6c}$
weathered gabbro	$3.8 \times 10^{-6} - 5.5 \times 10^{-7c}$
basalt	$4.2 \times 10^{-7} - 2 \times 10^{-11c}$
unfractured igneous and metamorphic rocks	$2 \times 10^{-9} - 5 \times 10^{-14ac}$

^a Freeze and Cherry (1979)^b Fetter (1994)^c Domenico and Schwartz (1990)

thoroughly and rigorously tested on uniform homogeneous soils (Towner, 1989), and provide an adequate description of the infiltration process when water is transmitted through the soil matrix in response to hydraulic gradients. Water motion under these conditions is via piston displacement (Horton and Hawkins, 1965), whereby incoming water displaces previously-stored water deeper into the profile. However, methods for direct measurement or calculation of water flux through the unsaturated zone, based on unsaturated zone properties, are presently unavailable (Nielsen et al., 1986). Therefore estimation of infiltration and soil-water redistribution using Equations 1.10 to 1.12 requires data on θ , ψ and K_H at various depths within the soil. θ can be determined gravimetrically, by neutron thermalization, gamma attenuation, or by time-domain reflectometry (Topp, 1993). Matric potential can be measured using resistance blocks, tensiometers, or thermocouple psychrometers (Livingston, 1993). Saturated K_H can be estimated in the laboratory using falling and constant head permeameters (Freeze and Cherry, 1979), or in the field using piezometer tests (Freeze and Cherry, 1979) or the Guelph permeameter (Reynolds et al., 1983). Unsaturated K_H can be measured on soil columns in the laboratory (Klute, 1965) or in the field using the instantaneous profile method (Hillel, 1982).

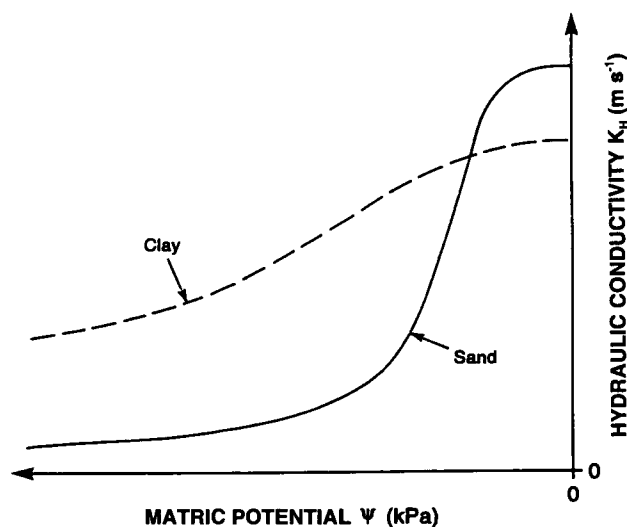


Figure 1.6. A log-log plot of unsaturated hydraulic conductivity (K_H) vs. soil matric potential (ψ) for a sand and a clay.

Despite the theoretical soundness of the Richards equation, it may not provide an adequate description of water movement in field situations (e.g. Espeby, 1992). A major restriction on the applicability of classical soil physics to the field is due to heterogeneity in soil properties. For example, Price and Bauer (1984) noted that subtle textural changes induced pronounced microscale vertical and lateral variations in θ (and consequently K_H) in nominally well-sorted sands. It is not clear as to how such spatial variations in key soil properties can be incorporated into soil-water transport theory. Philip (1980) examined an obvious approach to flow in heterogeneous systems: (i) use measured parameters of the system to estimate parameters of a substitute homogeneous flow system which produce equivalent gross flow behavior; and (ii)

estimate the errors associated with this approach. However, the use of "average" values ignores the effects that heterogeneity can have on water flow paths (Towner, 1989). In addition, it depends on the additivity of the system, whereby the means of the properties of the component parts represent the properties of the whole system (Philip, 1980). Philip showed that properties for a simple unsaturated flow system are not necessarily additive, such that "no conceivable process of averaging sample values of parameters can give a useful estimate of the flow behavior of the total system" (Philip, 1980).

The previous discussion is also based on the assumption that flow through soils is Darcian - i.e. laminar. The laminar condition is a function of the flow velocity, and can be distinguished from turbulent flow by using the Reynolds number (R_e) for flow through porous media:

$$R_e = \frac{\rho R d}{\mu} \quad (1.13)$$

where ρ = fluid density (kg/m^3), R = specific discharge, defined by Equation 1.9 (m/s), μ = dynamic fluid viscosity (kg/m/s), and d = a representative length dimension for the porous medium (e.g. mean grain diameter in m) (Freeze and Cherry, 1979). If mean grain diameter is used as a measure of the porous medium, laminar flow occurs when R_e is less than 10, and Darcy's Law is applicable. However, there is abundant evidence of turbulent flow through large cavities in the soil (Beven and Germann, 1982). Terms employed to describe these cavities include macrochannels and macropores, although other definitions have been used to describe pores capable of transmitting water by turbulent processes (e.g. Luxmoore, 1981). Turbulent flow allows infiltrating water to bypass the soil matrix and reach specific depths faster than water moving through soil micropores. Figure 1.7 is a simplified schematic of flows occurring in a "typical" block of soil containing macropores. Beven and Germann (1982) proposed the following sequence to describe the infiltration process in such a soil:

- (1) Matrix micropores that are connected to the surface absorb water arriving in precipitation or irrigation (P).
- (2) Water entry into micropores (I_1) and macropores (S_1) occurs simultaneously. Lateral infiltration from the macropore into the matrix (I_2) will reduce flow within the macropore (S_2), although some flow will always pass vertically through macropores due to their higher K_H relative to other parts of the soil (Anderson and Bouma, 1977). In addition, water losses from macropore to matrix may be reduced by the hydrophobicity of the macropore walls (Wilson et al., 1990). I_2 follows strong lateral hydraulic gradients formed due to the difference in Φ between the macropore and the matrix. Chen and Wagenet (1992) suggested that I_2 will also be affected by soil type, matrix antecedent θ , and the surface area of the macropore walls.
- (3) Increased θ in the upper soil layers will weaken lateral hydraulic gradients. This will increase the depth of water penetration along the macropore walls.
- (4) In the event that P exceeds the ability of the soil to take up water ($I_1 + S_1$), then overland flow (O) may occur. Bouma (1990) suggested that the latter is required to generate flow into macropores (S_1).

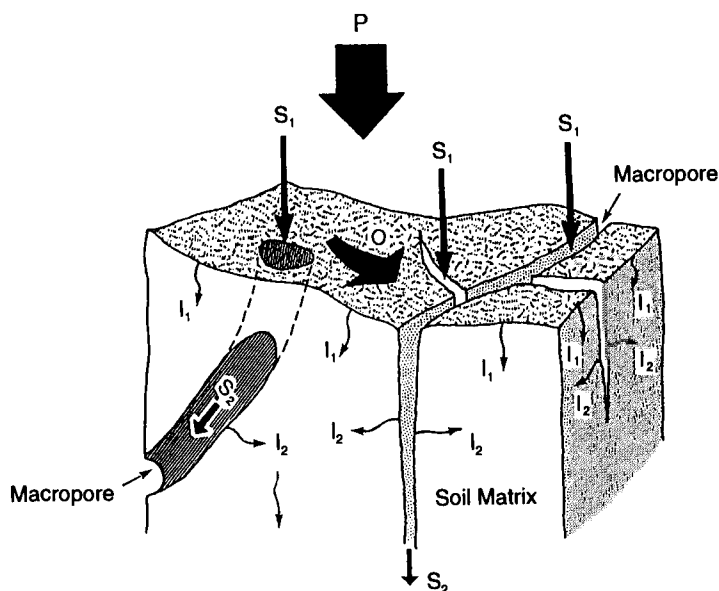


Figure 1.7. A simplified schematic of flow in macroporous soil: water input (P); overland flow (O); surface micropore infiltration (I_1); infiltration into macropores at the soil surface (S_1); lateral infiltration through macropore walls into the matrix (I_2); flow within the macropore (S_2). Modified after Beven and Germann (1982).

Richards' equation does not describe the infiltration process during macropore flow, since assumptions of homogeneous soil hydraulic properties and well-defined hydraulic gradients no longer apply (Bear, 1972; Beven and Germann, 1982). Flow in soil containing macropores can be represented by a two domain model: Darcian flow through soil micropores and turbulent bypassing flow via soil macropores (Nielsen et al., 1986). In reality, there are a range of flow velocities and Reynolds numbers encountered in the soil, and the two domain model is a gross simplification.

1.2.5 Evaporation and evapotranspiration

Evaporation (E) is "the physical process by which a liquid or solid is transferred to the gaseous state" (Glossary of Meteorology), while transpiration (T) is evaporation of water that has passed through living organisms such as plants. Direct evaporation from the soil (E_s) and T occur simultaneously in nature, and it is difficult to distinguish the water vapor produced by the two processes (Rosenberg et al., 1983). Thus, evapotranspiration (ET) is the total process of water transfer into the atmosphere from vegetated surfaces. Our discussion will separate evaporation and evapotranspiration only for convenience, and many of the concepts and models related to evaporation also apply to evapotranspiration.

"Evaporation in the natural environment can be considered to be the result of a balance between externally applied atmospheric demand and the availability of water at the evaporating surface" (Calder, 1990). Evaporation from a surface requires that three conditions be satisfied:

- (1) Presence of a gradient between the vapor pressure at the surface (e_o) and atmospheric vapor pressure (e). This is an expression of atmospheric demand for water vapor. Evaporation occurs when $e_o > e$, condensation occurs when $e_o < e$, while under saturated conditions $e = e_o = e_{sat}$ (the saturation vapor pressure at the surface temperature).
- (2) Input of energy to the surface. The net input of radiative energy (Q^*) to a water surface increases water temperature and therefore the kinetic energy of water molecules. It also increases the maximum amount of water vapor that the air can hold, thus influencing the vapor pressure gradient and hence atmospheric demand. Energy can also be supplied to a surface via advection, defined as the transport of energy in the horizontal plane in the downwind direction (Rosenberg et al., 1983). Rosenberg et al. (1983) distinguish between **regional** and **local** advection. An example of the former is the oasis effect produced by a lake in a desert, where warm air advected from upwind areas over the lake may increase evaporation above that attributable solely to Q^* . Local advection occurs when wind blows across a surface that is discontinuous in temperature, humidity or roughness, such as from a dry field to an adjacent wet one. As distance from the leading edge (the fetch) increases, the influence of local advection on ET decreases until horizontal homogeneity is established (Rosenberg et al., 1983), because atmospheric vapor pressure approaches e_{sat} .
- (3) Presence of a mechanism to remove saturated air away from the surface. Continued evaporation in a closed system will saturate the air immediately above the surface, thereby eliminating the vapor pressure gradient and terminating net evaporative loss from the surface. This mechanism can be supplied via two processes. **Free convection** is generated by energy inputs to the surface which result in a surface temperature (T_o) $>$ air temperature (T) some distance above the surface. Warming a layer of air immediately above the surface reduces its density, causing it to rise under unstable conditions. This rising air transfers energy from the surface to the overlying atmosphere in the form of sensible (Q_H) and latent (Q_E) heat fluxes. The latent heat flux is the product of the evaporation rate E (m/s), the latent heat of vaporization of water λ ($\sim 2.4 - 2.5$ MJ/kg within the range 313.2K - 273.2K (40° - 0°C)), and the density of water ρ (1000 kg/m³). Free convection is a relatively minor means of moving air away from surfaces relative to the second mechanism of **forced convection**, which involves the transfer of parcels of air towards and away from the surface as a result of turbulent movements of air. These turbulent movements are the dominant means of moving air towards and away from surface, and both Q_H and Q_E are often referred to as turbulent transfers.

This section will examine some of the main ways in which the previously-mentioned controls have been incorporated into methods of calculating E . As Calder (1990) notes, a generalized model of evaporation from natural systems has not yet been achieved.

The aerodynamic/mass transfer approach

Dalton (1801) showed that evaporation rates from water warmed in small containers were closely related to the difference between the vapor pressure of water in the container and the vapor pressure of water at the dew point temperature of the air. He also recognized the importance of air circulation in promoting evaporation, such that:

$$E = (e_o - e) \cdot f(u) \quad (1.14)$$

where $f(u)$ is some function of windspeed u (i.e. the aerodynamic function). We can think of the aerodynamic function as a resistance (r_a) to the transfer of water vapor from the evaporating surface to the atmosphere. The evaporation rate can be expressed as the equivalent latent heat flux Q_E :

$$Q_E = \frac{\left[\frac{\rho c_p}{\gamma} (e_o - e) \right]}{r_a} \quad (1.15)$$

where ρ = density of moist air (approximately 1.2 kg/m^3); c_p = specific heat of air at constant pressure ($1.01 \times 10^3 \text{ J/kg/K}$); γ = psychrometric constant $= P c_p / \lambda \epsilon$, where P = atmospheric pressure; and $\epsilon = M_w / M_a$, where M_w and M_a are the mole weights of water vapor and air, respectively. γ is $\sim 0.066 \text{ kPa/K}$ at 293.2 K (20°C) and 100 kPa .

A major problem with this approach is determining r_a . We can assume that it is some function of wind speed, such that $1/r_a \propto u$. A similar relationship can be used to describe the flux of sensible heat Q_H :

$$Q_H = \frac{\rho c_p (T_o - T)}{r_a} \quad (1.16)$$

where T_o = surface temperature (K) and T = air temperature (K).

The energy balance equation

This approach is based on the fact that it takes approximately 2.5 MJ of energy to evaporate 1 kg of water. The energy balance of a water body, such as a lake, can be defined as:

$$Q_\theta = Q^* - Q_H - Q_E + Q_v - Q_{ve} \pm Q_{sed} \quad (1.17)$$

where Q_θ = change of energy stored in lake (W/m^2); Q^* = net radiation input (W/m^2); Q_H = sensible heat transfer (W/m^2); Q_E = latent heat transfer (W/m^2); Q_v = net energy advected into the lake by flows of water (W/m^2); Q_{ve} = energy advected out of the lake in the evaporated water (W/m^2) - the loss of heat content in the layer of water that has been evaporated equals $[Q_E / \lambda] \cdot T_o \cdot c_{pw}$, where c_{pw} is the specific heat of water; and Q_{sed} = net energy lost or gained from lake sediments (W/m^2).

Each term can be measured in theory; however, surface temperature and therefore surface vapor pressure are generally unknown, and aerial resistances to heat and vapor transfer must be determined. The Bowen ratio β (Bowen, 1926) can be employed to avoid trying to measure Q_H when using the energy balance approach to solve for Q_E . β is the ratio of sensible to latent heat fluxes (Q_H / Q_E), and is based on the **principle of similarity**, whereby the transfer coefficients for heat and water vapor are equal:

$$\beta = \frac{Q_H}{Q_E} = \frac{c_p P}{0.662\lambda} \cdot \frac{T_o - T}{e_o - e} = \gamma \frac{T_o - T}{e_o - e} \quad (1.18)$$

where P is barometric pressure (kPa). Substitution of βQ_E for Q_H in the energy balance equation and solution for Q_E gives:

$$Q_E = \frac{\lambda[Q^* + Q_v - Q_\theta]}{[\lambda(1 + \beta) + [T_o - T_e]c_p]} \quad (1.19)$$

where Equation 1.18 can be substituted for β .

Evapotranspiration (ET) is the combination of evaporation of water from plant and soil surfaces and transpiration from the plant. ET regulates plant temperature, powers the uptake of nutrients from the soil, and maintains plant turgor. Only ~1% of water taken up by plants is actually involved in metabolic activity (Rosenberg et al., 1983). The rate at which water is taken up by the plant is a function of the availability of water and the rate of transpiration at the top of the plant. Transpiration occurs through stomata, which are openings on the leaf or plant needle. An average leaf may possess between 50 and 500 stomata/mm² (Oke, 1978). These are lined with guard cells, which open and close in response to light, the CO₂ content of air, and the presence or absence of moisture. The purpose of the guard cells is to prevent the plant from losing too much moisture as a result of atmospheric demand for water vapor.

The dominant factors controlling evapotranspiration can be resolved into those associated with soil water content, plant characteristics, and meteorological conditions.

- (1) **Water availability.** So long as there is adequate water, ET will proceed at the maximum possible rate depending only on the amount of energy available and the control (if any) exerted by the vegetation. ET will decrease when soil water becomes limiting, although there is considerable debate as to the nature of the relationship between ET and θ (e.g. van Bavel, 1967; Meyer and Green, 1981). Dew and intercepted water evaporate at the maximum rate, and can result in greatly increased ET (e.g. Stewart, 1977; McNaughton and Black, 1973; Calder, 1976). Thus, evaporation of free-standing water on plant surfaces reduces the energy available to drive transpiration, and helps to conserve soil water.
- (2) **Plant factors.** These include stomatal resistance (r_s), leaf area index, plant height, and plant morphology. For plants to transpire at potential rates, they must behave as passive wicks (e.g. *Sphagnum* mosses); however, this condition is rare (Penman and Schofield, 1951). Stomata may have a strong influence on transpiration, and the factors influencing stomatal resistance have been noted above. Increases in LAI tend to be positively associated with the ratio of actual ET to the theoretical maximum ET (Kristensen, 1974). Plant height may influence ET , since taller plants have a relatively greater aerodynamic roughness, which increases their extraction of energy from the ambient air (Rosenberg et al., 1983). Plant morphology has several implications for ET since, all things being equal, broad-leaved plants transpire more than grasses (Fritschen,

1965); larger leaves tend to be less efficient in dissipating heat through convective transfer, and have more energy available for evaporation than will smaller leaves (Rosenberg et al., 1983). In addition, factors such as leaf color and shape may alter the plant's energy balance, leaf and canopy boundary layer resistance to energy and mass exchange, or the way in which dew is deposited on plant surfaces.

- (3) **Meteorological factors.** These include **net radiation**, which is a major source of energy for ET and which generally sets the upper limit on the amount of energy consumed as Q_E in humid regions; **sensible heat advection**; **wind**, which drives advection and enhances turbulence, thereby reducing boundary layer resistance and promoting movement of water vapor near the surface into the atmosphere; **humidity**, such that ET increases with increasing vapor pressure deficit; and **temperature**, which influences the vapor pressure deficit, the amount of advected sensible heat, the energy required to evaporate a given amount of water, and stomatal resistance.

ET can be measured directly using a variety of drainage and weighing lysimeters (Pruitt and Lourence, 1985); more commonly, however, it is calculated. The water balance approach (e.g. Robertson and Barry, 1985) requires measurement of all elements in the water balance and calculation of ET as the residual. Unfortunately, errors associated with the measured quantities (e.g. P , R in Equation 1.2) propagate into the calculated ET , giving the estimate a large relative uncertainty (Dingman, 1993). There are numerous empirical methods for estimating ET (e.g. Thornthwaite, 1948; Blaney and Criddle, 1950); the more physically-based ones are essentially combination models, in that they combine the aerodynamic approach to estimating sensible heat flux with the energy balance equation to calculate ET as the residual. The most popular of these is Penman's (1948) equation, which employs the Bowen ratio β . Evaporation over open water (E_o , mm/d) is given as:

$$E_o = \frac{\Delta H + \gamma E_a}{\Delta + \gamma} \quad (1.20)$$

where H = evaporation equivalent of net radiation over open water (mm/d); E_a = empirical aerodynamic term = $2.6 (e' - e)(1 + 0.537u_2)$, where e' is the saturation vapor pressure at the present air temperature, e is the atmospheric vapor pressure, and u_2 is the average daily wind speed at a height of 2 m (m/s); and Δ = slope of the saturation vapor pressure curve (kPa/K).

Penman defined "potential" evapotranspiration (ET_p) as the evaporation from short vegetation (grass) when well supplied with water (Calder, 1990), and found that it was related to E_o by:

$$ET_p = fE_o \quad (1.21)$$

where the factor f was 0.8 in summer, 0.7 in spring and autumn and 0.6 in winter. According to Monteith (1973), these factors are valid to within $\pm 15\%$ for all temperate climates. Monteith (1965) introduced a canopy resistance parameter (r_s) to deal explicitly with the ability of plants to resist the transfer of water through their stomata. When this stomatal resistance term is combined with Penman's equation (with the aerodynamic term written in the form of Equation 1.15) the result is:

$$Q_E = \frac{\Delta Q^* + \frac{\rho c_p (e' - e)}{r_a}}{\Delta + \gamma \left(1 + \frac{r_s}{r_a}\right)} \quad (1.22)$$

The assumption that water vapor diffuses out of the leaves against stomatal resistance (r_s) and then into the overlying atmosphere against aerodynamic resistance (r_a) has been described as the "big leaf" approximation (Calder, 1990). The Penman-Monteith model provides a realistic basis for studies of ET (Shuttleworth, 1992); however, it has been limited primarily to use in research applications, largely because of difficulties in obtaining estimates of r_a and r_s .

The Priestley-Taylor equation (Priestley and Taylor, 1972) is an attempt to simplify the Penman equation for use in situations where data are limited. It was developed for use over land sites which were not experiencing water stress and significant advection. The Priestley-Taylor equation assumes that the aerodynamic term in the Penman equation (γE_a) is a constant fraction (α) of the equilibrium evaporation rate determined by the available radiative energy ($Q^* - Q_G$), where Q_G is the soil heat flux, thus:

$$Q_E = \alpha \frac{\Delta(Q^* - Q_G)}{\Delta + \gamma} \quad (1.23)$$

Values of α range from 1.08 to 1.34, with an overall mean of 1.26 (Priestley and Taylor, 1972).

Some sense of the control that the surface exerts on evaporation rates in small catchments is provided by Table 1.5. Q_E was estimated using the Penman-Monteith model for simple surface types with representative surface properties and uniform micrometeorological conditions to facilitate comparisons. A number of simplifying assumptions have been made (e.g. uniform surface temperature, unlimited water supply, negligible heat storage, no advection of energy); nevertheless, the results appear reasonable. Q_E is greater for water compared to bare soil, despite similar r_a and r_s . This is due to water's lower albedo, and thus more Q^* available for evaporation. Bare soil has a lower Q^* and higher r_a relative to the grassed surface; yet it has greater Q_E , due to the influence of stomatal resistance in limiting water loss from vegetation. When comparing the vegetated surfaces, the coniferous forest receives more Q^* , has a lower r_a due to enhanced turbulence over rough surfaces, and has a lower r_s ; the result is higher Q_E compared to grass. This spatial variability in Q_E between surface types highlights the challenges facing hydrologists attempting to extrapolate point E values to catchment-wide estimates.

1.2.6 Storage in lakes, wetlands and stream channels

These landscape features may act as stores of water by delaying the passage of flood peaks through the catchment. The influence of lakes and stream channels on storage and routing of flood waters is well documented (Dunne and Leopold, 1978; Bras, 1990; Dingman, 1993). Wetlands are popularly thought to act as streamflow regulators; however, Bay's (1969) work

Table 1.5. Hypothetical micrometeorological and surface conditions, and fluxes of latent heat (Q_E) predicted by the Penman-Monteith model (Equation 1.22), for common surface types in small catchments.

PARAMETER	SURFACE TYPE			
	WATER	BARE SOIL	GRASS	CONIFEROUS FOREST
INCOMING SHORTWAVE RADIATION (W/m^2)	600	600	600	600
INCOMING LONGWAVE RADIATION (W/m^2)	300	300	300	300
ALBEDO	0.1	0.4	0.25	0.15
EMISSIVITY	0.97	0.98	0.94	0.97
AIR TEMPERATURE (K)	288.2	288.2	288.2	288.2
SURFACE TEMPERATURE (K)	288.2	288.2	288.2	288.2
OUTGOING LONGWAVE RADIATION (W/m^2)	379	383	368	379
NET RADIATION (W/m^2)	461	277	382	431
HEIGHT OF VEGETATION (m)	0	0	0.1	10
WIND SPEED AT 2 m ABOVE VEGETATION (m/s)	5	5	5	5
ATMOSPHERIC PRESSURE (kPa)	101.33	101.33	101.33	101.33
ATMOSPHERIC VAPOR PRESSURE (kPa)	1.2	1.2	1.2	1.2
r_a (s/m)	97.9	85.3	45.0	6.5
r_s (s/m)	0	0	200.0	22.3
Q_E (W/m^2)	323	214	118	353

on small peatland catchments in northern Minnesota showed that "at least some types of peatlands do not provide long-term storage of water nor do they make any substantial contribution to streamflow during dry periods". Nevertheless, wetlands may provide short-term storage of rainfall inputs following drying periods when water tables are low. An example of wetland effects on hydrograph properties is Taylor and Pierson's (1985) comparison of runoff from a small wetland with that from a downstream sideslope zone in south-central Ontario. During spring snowmelt, peak runoff and the time lag between peak rainfall intensity and peak runoff for the wetland were similar to those of the sideslopes. However, a decline in wetland groundwater levels as the season progressed resulted in a substantial decrease in peak runoff and an increase in hydrograph time lag relative to the sideslope zone. Thus, antecedent wetness exerts an important control on the influence of routing through channels, lakes and wetlands and, consequently, on hydrograph form in small catchments. This influence depends on the

proportion of the catchment occupied by these surface features and their relative position in the landscape. Bras (1990) suggests that the effect of routing through channels, lakes and wetlands upon the stream hydrograph is greatest in catchments where the flow time on hillslopes is small relative to the residence time of water in these surface stores. An additional hydrological effect of these stores in small catchments is through their influence on E and ET losses from the catchment, because they maintain wet surfaces which enhance evaporative losses. For example, Roulet and Woo (1986) observed evaporation losses of up to 7 mm/d from subarctic lake and wetland surfaces during the snow-free period. There is a current debate regarding the relative magnitude of evaporation from wetlands compared to free water surfaces (Idso and Anderson, 1988). Thus, small lysimeter experiments suggest that the presence of vegetation increases evaporation relative to that from open water (Idso, 1981), while field experiments by Rouse et al. (1977) showed that wetland evaporative loss was less than that from a small lake in the Canadian subarctic. In addition to providing local zones of enhanced evaporation from small catchments, these areas may directly convert precipitation into surface water available to runoff.

1.2.7 Runoff outputs via streamflow

Streamflow can be defined as the gravity movement of water in channels (Ward and Robinson, 1990). Streamflow is measured at a point on the drainage system known as a gauging station. This measurement normally involves (i) obtaining a continuous record of water level (stage) in the stream above a datum; (ii) establishing the relationship between stage and discharge (the rating curve); and (iii) using this relationship to transform the stage record to a continuous record of discharge (Mosley and McKerchar, 1992). Streamflow can be measured at natural channel cross-sections, or at artificial controls such as weirs and flumes. Provided there is sufficient storage in the catchment, streamflow output is usually continuous in all but the driest areas, while precipitation inputs are discrete and often widely separated in time. Therefore the annual streamflow comprises short periods of discharge increases associated with inputs (rainfall, snowmelt, glacier melt), and intervening longer periods when flow is dominated by release of water from storage. Figure 1.8 shows a hypothetical hydrograph (the temporal behavior of discharge measured at the gauging station) produced by a rainstorm (terms are defined in Table 1.1). During the release of water from storage in the catchment, the hydrograph's falling limb takes the exponential form of the typical exhaustion curve:

$$Q_t = Q_p e^{-t/K} \quad (1.24)$$

where Q_t = discharge at time t (h) following peak discharge Q_p (m^3/s), and K = decay constant of the hydrograph falling limb (h).

Rainfall and snowmelt may arrive in a stream channel by one of a number of flowpaths (Figure 1.9): (1) direct precipitation onto the water surface (channel precipitation); (2) overland flow; (3) shallow subsurface flow; and (4) deep subsurface flow. Figure 1.9 is modified from Ward and Robinson (1990) and the terms are defined in Table 1.1; however, terms like "throughflow" and "groundwater flow" have been avoided due to the potential for overlap or confusion. For example, throughflow may result from saturated transport through a perched aquifer, which raises the question of whether this water is groundwater since all the soil pores are temporarily

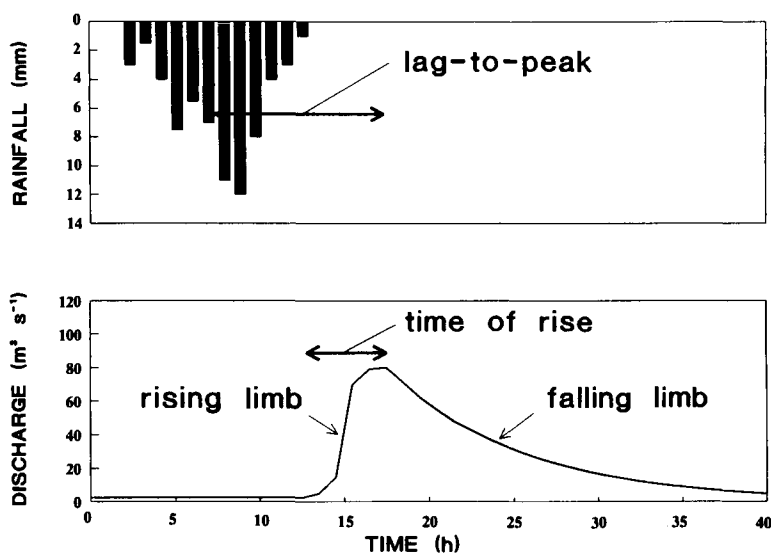


Figure 1.8. Idealized hydrograph produced by a rainstorm.

filled with water. It is important to recognize that not all of these sources of runoff are of equal importance in terms of the hydrograph produced by a rainfall or snowmelt event in any catchment (Ward and Robinson, 1990); nevertheless the processes by which water is induced to follow one or more of the flowpaths in Figure 1.9 to the stream channel merit a more detailed examination.

1.2.8 Mechanisms of Stormflow Generation

An examination of these mechanisms is most useful at the small catchment scale, because "in large river systems lag effects, both within and outside channels, and the multiplicity of flow contributions to the main channel from numerous tributary streams make it more difficult to interpret hydrograph response to precipitation" (Ward and Robinson, 1990).

Horton flow

This mechanism has also been termed "infiltration excess" overland flow (Church and Woo, 1990). Two conditions must be satisfied for production of Horton flow (Freeze, 1980): first, delivery of precipitation to the soil surface in excess of the K_H of the surface soil; and secondly, a rainfall duration longer than the time required to saturate the surface for a given initial soil moisture profile (ponding time). Excess water accumulates at the soil surface in small depressions (depression storage). Some of this water is lost via evaporation and infiltration, and these losses are partially offset by contributions from water in transit down the slope (detention storage). Overflow and coalescence of these surface pondings promotes the downslope movement of a thin sheet of water; however, "embedded within a widespread sheet of overland flow are preferred veins of high discharge meandering around grass tussocks, leaf litter and occasional dead tree logs and branches" (Bonell and Williams, 1986).

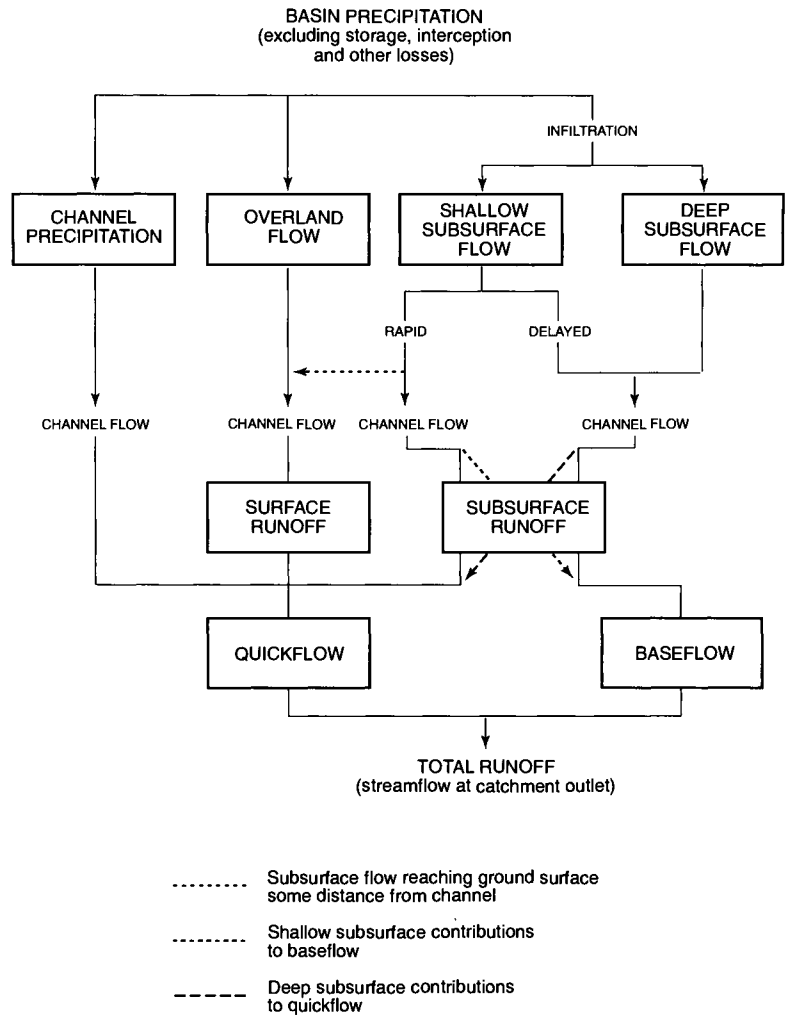


Figure 1.9. Pathways that rainfall and snowmelt may follow to reach the catchment outlet as streamflow (modified after Ward and Robinson, 1990).

Figure 1.10 presents the response of runoff produced by Horton flow to rainfall. Under certain slope and pedological conditions, local concentration of flow may result in the creation of a network of minute channels known as rills. These in turn may be incised to depths > 0.3 m, forming more pronounced channels known as gullies. The hydrological significance of the channel structures is their reduced flow resistance relative to sheet flow and enhanced ability to convey water quickly from the hillslope. Thus, Horton flow implies a rapid response of runoff to rainfall, and Dunne (1978) cites overland flow velocities of 0.03 - 0.15 m/s and time lags between rainfall bursts and hydrograph peaks ranging from 0.15 to < 2 h for catchments up to 148 km².

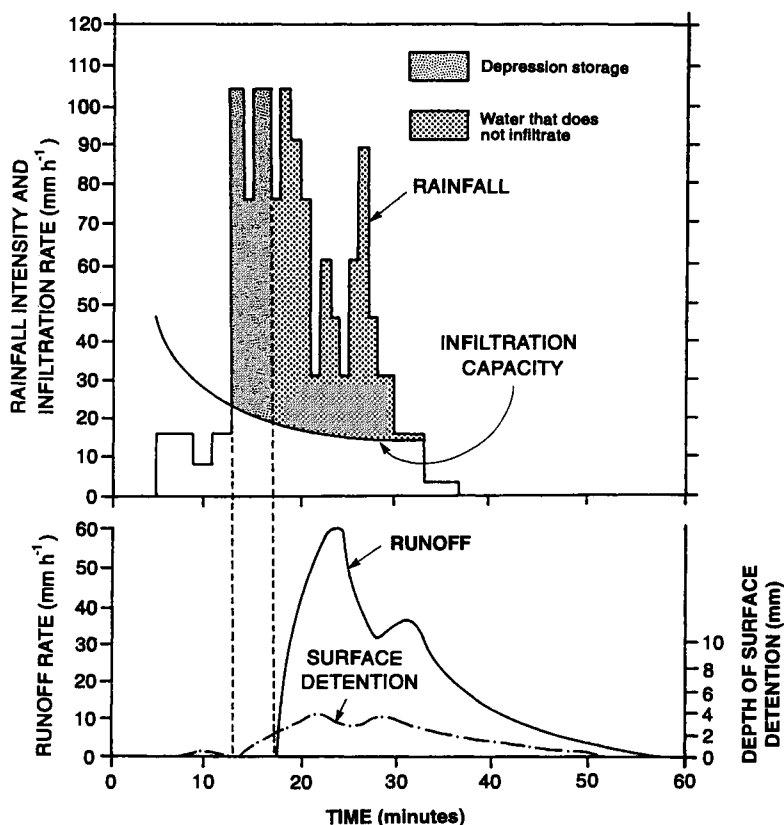


Figure 1.10. Infiltration capacity, Horton flow and surface detention for a storm of varying intensity (modified after Dunne, 1978). Note that depression storage must be exhausted before Horton flow is produced.

Horton flow is linked to Horton's (1933) concept that infiltration capacity goes through a definite cycle for each storm (Figures 1.5 and 1.10). The decline in infiltration capacity with time means that a given amount of rain falling late in a storm or storm sequence will generate more overland flow and therefore greater streamflow response than the same amount of precipitation falling early in the storm. Whereas Horton (1933) envisaged flow occurring over entire catchments, it is now recognized that its occurrence in humid temperate areas is somewhat localized. Betson (1964) proposed the partial area model for humid regions, whereby only a small portion of the catchment produces Horton flow in particular areas. In addition, redistribution of rainfall under forest cover results in drip points, isolated ponding and local Horton flow (Bonell et al., 1984). The exception to localized Horton flow in temperate areas occurs on exposed bedrock (Allan and Roulet, 1994) or where the near-surface saturated hydraulic conductivity has undergone substantial reduction. This reduction may result from climatic conditions such as frozen soil and permafrost (Woo and Steer, 1983); anthropogenic effects such as urban development (Dunne, 1978), agriculture (Dingman, 1993) and removal of vegetation due to air pollution (Pearce, 1976); and particular soil conditions, such as the hydrophobic nature of some very dry and sodic soils (Morin et al., 1981; Agassi et al., 1985).

Rainfalls of small-to-moderate size frequently produce a streamflow response; however, comparison of saturated K_H values and rainfall intensity-duration curves demonstrated that generation of Horton flow on unfrozen soils in humid areas in eastern North America is restricted to high intensity, long duration rainfalls (Freeze, 1972). In contrast, Pilgrim (1983) observed widespread Horton flow in a number of Australian catchments under a variety of climatic and vegetative conditions. Horton flow was initially produced on catchment ridges and extended downslope until the entire catchment generated runoff. Bonell and Williams (1986) showed that on gentle slopes underlain by semi-arid tropical soils Horton flow can be expected for a wide range of rainfall intensities, because the surface fabric is continually changing due to both biological activity and raindrop impact. Such overland flow is redistributed and subsequently infiltrates as consequence of short storm durations, low slope angle and the relatively high saturated hydraulic conductivity of the soils. These observations illustrate the danger of extrapolating findings from Britain and eastern North America to other environments.

Subsurface stormflow

The history of hydrological research into rapid movement of water via subsurface routes to stream channels has been summarized elsewhere (Dunne, 1978; O'Brien, 1983; Ward and Robinson, 1990). Subsurface stormflow is the term coined by Hursh (1936) to describe the rapid lateral movement of water occurring through the soil above the water table. Generation of subsurface stormflow is favored by the anisotropic nature of the soil profile (Ward and Robinson, 1990), where the near-surface lateral conductivity is often much greater than the overall vertical hydraulic conductivity. Two basic models have been developed to account for rapid lateral movement of water downslope: translatory flow and macropore flow.

"Translatory flow" was coined by Hewlett and Hibbert (1967) to describe the lateral throughflow of "old" rainwater and snowmelt (water stored in the soil prior to the storm event) that is displaced into the channel by precipitation inputs. This displacement process was supported by the laboratory results of Horton and Hawkins (1965). Thus, channel flow responds rapidly to precipitation inputs, even though the individual water molecules are only moving a short distance, perhaps at rates of cm or m per day. Translatory flow is essentially a diffuse process involving the flux of water stored in soil micropores (Chorley, 1978a). The process is most effective when soil water contents are close to saturation values (Bonell et al., 1984; Ward and Robinson, 1990), and is assisted by the frequently-observed decrease in saturated hydraulic conductivity with depth in soil profiles (e.g. Buttle, 1989; Bishop, 1991). Although the decrease in hydraulic conductivity may not be abrupt, when combined with large water inputs to the soil surface it may be sufficient to result in the formation of transient perched aquifers during prolonged rainstorms and spring snowmelt. Water tables in these perched aquifers tend to parallel the ground surface, so there is little change in the hydraulic gradient driving water downslope (Buttle, 1989). However, there is a pronounced increase in K_H as the saturated zone extends upwards into the near-surface area, resulting in increased water flux (Rodhe, 1987; Bishop, 1991; Nyberg, 1995). This process was termed "transmissivity feedback" by Bishop (1991) and may be assisted by the capillary fringe effect (Rodhe, 1987), whereby infiltration in areas where the capillary fringe is at or near the ground surface (footslopes, valley bottoms) results in conversion of the tension-saturated zone to phreatic water and a disproportionately large rise in the perched aquifer's water table (Gillham, 1984).

There may be several depths at which subsurface stormflow occurs within the soil, corresponding to textural changes between horizons and to the junction between the weathered

mantle and the bedrock (Whipkey, 1965). Displacement from the hillslope into the channel occurs from the near-stream portion of the catchment, and Hewlett and Hibbert (1967) suggest that the degree of displacement of "old" water increases with depth in the soil profile and with distance downslope (cf. Mulholland et al., 1990).

Macropore flow involves the turbulent movement of water through large conduits in the soil, as noted in our examination of infiltration. However, in the context of runoff generation, we are now concerned with the vertical and lateral movement of water downslope via such macropore structures as animal burrows, root cavities, soil pipes, and voids produced by eluviation of soil particles (Jones, 1971; Whipkey, 1969). The physical considerations discussed regarding infiltration through macropores also apply to lateral flow: namely that the delivery of water to the macropore must exceed the rate at which water is abstracted through the macropore walls into the soil matrix (Beven and Germann, 1982). Water fluxes smaller than this abstraction rate will be conveyed by the soil's micropores. "It therefore seems that the existence of macropores is not in itself evidence of a significant role in the runoff process" (Ward and Robinson, 1990). Nevertheless, there is abundant evidence for macropore flow on slopes (e.g. Hursh, 1944; Beasley, 1976; Mosley, 1979; Bonell et al., 1984; Roberge and Plamondon, 1987; McDonnell, 1990; Renzetti et al., 1992; Peters et al., 1995). Quoted flow velocities range from $\leq 1.5 \times 10^{-3}$ m/s (Hammermeister et al., 1982) to $\leq 9.8 \times 10^{-3}$ m/s (Mosley, 1982), which are sufficiently high to allow rapid translation of precipitation and snowmelt water from hillslopes to channels. In practice, both piston flow through the soil matrix and preferential flow can occur simultaneously in heterogeneous structured soils under wet conditions (Bonell et al., 1984). Regardless of whether subsurface stormflow is through the matrix or macropores, delivery of water to the stream is by an expanding and contracting subsurface saturated wedge usually located above a relatively impermeable subsoil horizon (Hewlett and Hibbert, 1967; Weyman, 1973).

Saturation overland flow

This mechanism combines infiltrated water which returns to the land surface having flowed for a short distance in the upper soil horizon (return flow - Dunne and Black, 1970a,b) with direct precipitation or melt onto the saturated discharge zone (Kirkby and Chorley, 1967). The saturated zone is produced by a rising water table intersecting the ground surface. The principal mode of recharge to the water table may vary (Bonell et al., 1984): macropore flow through root channels from sideslopes (Whipkey, 1965, 1967); translatory flow through the soil matrix (Hewlett and Hibbert, 1967); or vertical infiltration (Dunne and Black, 1970a,b). However, the presence of macropores may counteract formation of saturated areas in upslope zones, because the macropores may conduct large discharges and locally prevent the water table from reaching the surface (Bonell et al., 1984). The proximity of the water table and capillary fringe to the ground surface in many near-channel zones, areas of flow convergence and thin soil zones means that only small amounts of water are required to saturate the soil (Gillham, 1984) and induce emergence of return flow. Unlike Horton flow, saturation overland flow occurs where or when the precipitation rate is less than K_H , and surface saturation results from a rising water table (Freeze, 1980).

The spatial extent of areas that are saturated from below fluctuates in response to changes in catchment wetness over time and space, and the resulting temporal variations in the extent of surface saturation in a catchment have been termed the **variable source area model** (TVA, 1964; Freeze and Cherry, 1979). According to this model, near-channel areas are capable of

supplying both saturation overland flow and subsurface stormflow. Source areas also include upslope zones where various subsurface conditions can cause saturated conditions to occur (O'Brien, 1983). If such disjunct areas have effective hydrological connections with valley bottoms or lower slopes, they will also contribute quickflow to the channel (Jones, 1979; Ward and Robinson, 1990). Variations in the size of the source area are dictated by initial soil moisture content, storage capacity, and rainfall duration and intensity (Chorley, 1978). Thus, the variable source area can be viewed as an expanded stream system which is spatially and temporally dynamic (Dunne, 1978), fluctuating in extent both within and between storms. The variable source area model posits that it is only the saturated areas of the catchment that supply quickflow; all other areas of the catchment absorb rainfall and either store it or transfer it beneath the ground surface.

Groundwater ridging

Several studies have demonstrated the importance of groundwater flow to total streamflow (e.g. O'Brien, 1980; Zaltsberg, 1987). The question remains: how can groundwater make a rapid and significant contribution to stormflow, given the small saturated K_H of many geologic media (Table 1.4) relative to the large velocities observed for overland flow? The groundwater ridging mechanism has been suggested as the appropriate means, and is linked to the role of the capillary fringe in streamflow generation (Gillham, 1984). Saturation of the capillary fringe during infiltration was discussed in the context of subsurface stormflow, and the resulting disproportionate and rapid rise in the water table has been noted in a number of field and laboratory studies (Abdul and Gillham, 1984, 1989; Novakowski and Gillham, 1988). This in turn increases the hydraulic gradient to the stream and/or the size of the seepage face, both of which enhance the flux of groundwater to the stream channel. This effect is augmented by "transmissivity feedback" discussed above, where a rise in the water table results in the transport of water through relatively more conductive near-surface layers.

1.2.9 Groundwater flow

Groundwater is discharged from the saturated zone through seepage faces (saturated areas) at various locations on hillslopes and at the margins and beds of lakes, wetlands and stream channels. It supplies the major component of streamflow in highly permeable catchments and in the lowland areas of larger drainage catchments. Water fluxes in the phreatic zone can be quantified by Darcy's Law (Equation 1.9), where total potential (Φ) is the sum of the elevation and pressure potentials and where K_H is the saturated hydraulic conductivity of the porous material. Pressure potential at a point in an aquifer can be measured using a piezometer, which is simply a pipe that is sealed along its length and is open to water flow at the bottom and the atmosphere at the top (Freeze and Cherry, 1979). The pressure potential p at the bottom of the piezometer is the height to which water rises in the pipe. By installing several piezometers to different depths in a geologic formation at a variety of horizontal locations, it is possible to define the pressure field in the aquifer and therefore the components of groundwater flow. A confined aquifer is saturated throughout and is overlain by a layer of relatively low K_H (an aquitard), which may form the upper boundary of the groundwater flow system. The upper boundary of an unconfined aquifer is formed by the water table, where the pressure potential p is 0 relative to atmospheric pressure (Figure 1.3). The water table elevation is measured using a well, which is a pipe that is perforated along its length and extends just deep enough below the ground surface to meet standing water (Freeze and Cherry, 1979).

Short-term oscillations in precipitation are often muted during passage through the unsaturated zone due to the latter's storage potential, such that the time lag between precipitation inputs and groundwater outputs to the stream channel can be considerable, ranging from days to years. Residence times in the saturated zone are also relatively longer than in other catchment stores due to slow flow rates in groundwater bodies. The exception to this occurs in local circumstances that produce increased values of K_H and/or the hydraulic gradient, such as fracture zones in bedrock (Dunne, 1980) and near-stream areas prone to the development of groundwater ridges (Sklash and Farvolden, 1979). Because it represents outflow from a slowly changing reservoir of moisture in soil and rock layers, groundwater flow tends to be very regular, acting as the main long-term component of total runoff and often serving as the sole source of streamflow during dry spells when surface runoff is absent (Ward and Robinson, 1990).

1.3 Questions of Spatial and Temporal Scale in Catchment Hydrology

A major advantage in studying small catchments is that spatial extrapolations from point measurements can be made with a greater degree of confidence than for large catchments. However, that does not necessarily mean that these extrapolations are realistic or meaningful. Much of the issue of spatial scale in hydrology has concentrated on the identification of the scale of spatial variability associated with hydrological parameters and processes, such as rainfall (Berndtsson, 1987), infiltration (Rogowski, 1972), saturated hydraulic conductivity (Nielsen et al., 1973), and channel travel times (Pilgrim, 1983). There have been at least two major outcomes of this work:

- (1) Incorporation of spatial data in hydrological models. For example, Binley et al. (1989a,b) studied the effect of spatially heterogeneous K_H on hillslope drainage using a 3-d finite element model. They found that hillslopes with highly permeable soils and exclusively subsurface drainage could be modeled in a lumped fashion using an effective K_H value. However, spatially heterogeneity in K_H for soils of low permeability that generate surface flow generally increased runoff volumes and peak flows, especially when K_H exhibited spatial correlation. This condition precluded lumped modeling of the hillslope's hydrology.
- (2) Identification of the maximum scales at which assumptions of homogeneity may reasonably apply. This work follows from Bear's (1972) concept of the **representative elementary volume** of a porous medium, which is sufficiently large to permit the determination of meaningful statistical averages of hydrological properties such as porosity and hydraulic conductivity (Freeze and Cherry, 1979). For example, Towner (1989) suggested that infiltration into a soil containing macropores can be analyzed using established soil-water transport theory (Equations 1.8 - 1.12), provided that the macropores are distributed densely and uniformly throughout the soil and that a representative elementary volume can be defined by a sufficiently large sampling volume.

In terms of temporal scale, we must distinguish between random and systematic/cyclical temporal variations. Certain hydroclimatic processes are seasonal, such as snowmelt in nival environments and subsurface drainage in humid environments. Seasonal oscillations in precipitation and energy inputs to hydrological systems are of particular importance, for these variations cascade through the entire system. For example, Figure 1.11 shows how precipitation deficiencies during a hypothetical 4-year period are translated in delayed fashion, over time,

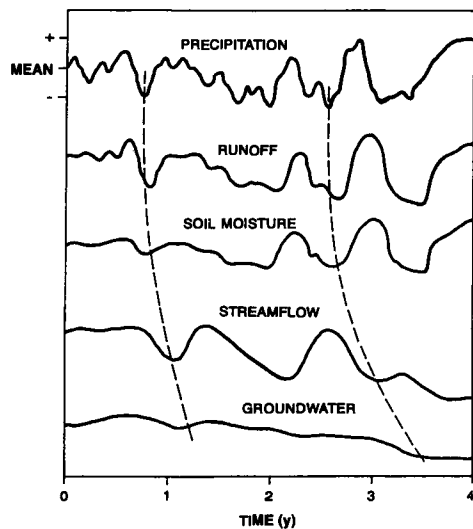


Figure 1.11. Hypothetical variations in precipitation, and resultant changes in other components of a catchment's water balance (modified after Chagnon, 1987). Dashed lines suggest how precipitation deficiencies may manifest themselves in the behavior of these components after an appropriate time lag.

through other components of the hydrological cycle (Rasmusson et al., 1992). As the zonal climate becomes more arid, terrestrial hydrological phenomena become less regular and predictable, and more dominated by isolated events (Church and Woo, 1990).

Figure 1.12 presents time and space scales of various hydrological phenomena. These temporal and spatial scale factors are largely responsible for introducing observed variability in the terrestrial phase of the hydrological cycle (Church and Woo, 1990). The issue of scale is even more fundamental than this, because our insights into physical processes are strongly controlled by the spatial and temporal scale of study we adopt. "In nature, scales of things are not arbitrary, but arise as a function of their material substance and of the balance between interacting forces. As far as nature is concerned, we cannot impose scales but have to search for those which exist and try and understand their interrelationships and patterns" (Klemeš, 1983).

As Klemeš noted, each level of scale is dominated by a different set of physical laws which appear anti-intuitive when viewed from a different scale. Thus, Pilgrim (1983) observed that maximum constant evapotranspiration loss from 22 catchments in New South Wales, Australia showed a positive relationship with catchment size. He attributed this to two main processes: (1) limited retention of water in smaller catchments, resulting in a lower opportunity for evapotranspiration; and (2) increased channel transmission losses for larger catchments, resulting in increased apparent evapotranspiration. Interactions of numerous elements at one level of scale result in a single element at a higher level, such that laws at the higher level express averages or integrals of those dominant at a lower level. A process may be seen as random if viewed from a higher scale; deterministic if viewed from a lower scale level (Figure 1.12). Klemeš observed that different forces tend to dominate at different scale levels, complicating the transfer of mathematical relationships derived from data at a given scale to other levels. He

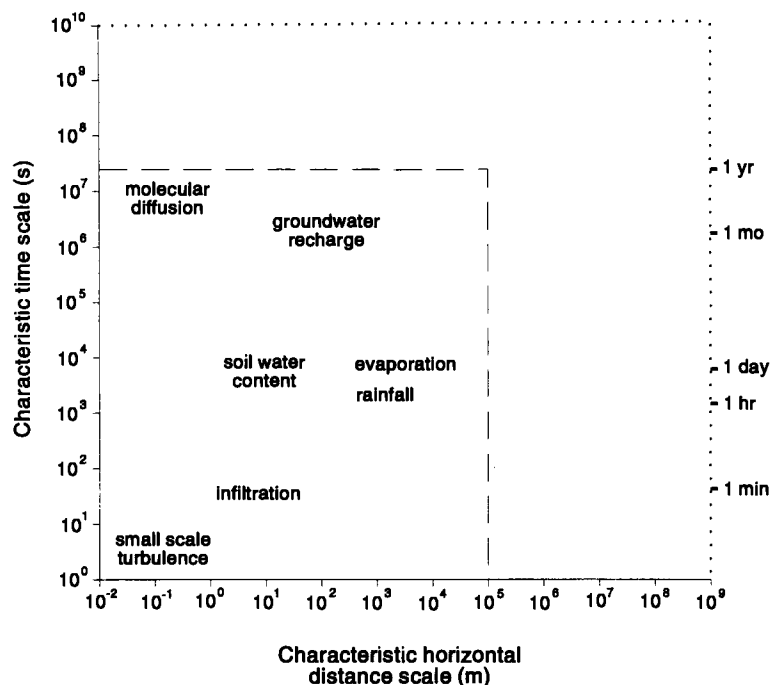


Figure 1.12. Spatial and temporal scales of variability relevant to various hydrological phenomena studied in small catchments (modified from Henderson-Sellers and Robinson, 1986). The dotted line indicates the outer bounds of hydrological scale suggested by Klemeš (1983), while the dashed line indicates the outer time and space scale boundaries suitable for most hydrological studies in small catchments.

used the concept of "catchment scale" as an example of hydrologists' indifference to these scaling problems: "Can we expect a greater similarity in behaviour between a 5-km² catchment of a creek and the Orinoco Catchment than between a kitchen sink and the Aswan Dam? Our approaches often suggest that we believe so" (Klemeš, 1983). Another important point raised by Klemeš is the interconnectedness of scales in space and time, which is often ignored in scientific research. Spatial scale determines the relationships and processes that may be identified for a given time scale. A spatial unit with a "memory" longer than the selected time interval is necessary if the dynamic effects of the spatial unit are not to be "swallowed" by integration over a single time interval.

1.4 Use of Isotopes in Catchment Research

Having outlined current conceptualizations of the major hydrological processes functioning in small catchments and some of the approaches used to measure or estimate them, we now turn our attention to the use of isotopes in hydrological research. Our aim is to present examples of how isotopes can be used to increase our understanding of catchment hydrology, focusing on the isotopes of elements making up the water molecule, namely deuterium (D), tritium (T), and oxygen-18 (¹⁸O). These examples are expanded upon in latter sections of the book.

1.4.1 Evaporation, evapotranspiration, interception

Classical soil physical and meteorological methods can be used in conjunction with equations presented in Section 1.2.5 to estimate evaporative fluxes over short time periods; however, they are difficult to use over longer time periods appropriate for water balance studies (Allison and Barnes, 1983). Isotopes provide a useful means of obtaining evaporation estimates under these circumstances. The principles of isotopic fractionation are covered in Chapter 2, and the most important fractionation governing the occurrence of D and ^{18}O is caused by evaporation-condensation. Water undergoing evaporation into undersaturated air masses will plot on a local evaporation line (LEL) with a slope less than 8 (the slope of the meteoric water line MWL (Craig, 1961) in D- ^{18}O space). This "is a well-exploited tool to identify water that has been subjected to evaporation since the raindrop formation" (Rodhe, 1987). In transpiration and evaporation from soil, fractionation is prevented or diminished due to incomplete mixing (e.g. Zimmermann et al., 1967). Thus, studies of the degree of fractionation of intercepted water, soil water, standing water (e.g. Allison et al., 1979; Saxena, 1986; Zimmermann et al., 1967) have been employed to estimate evaporative fluxes from various surface types.

Zimmermann et al. (1967) used isotope concentrations in soil water to estimate evaporation rates from saturated soils. The isotope profile in soil water is generally exponential, as δ becomes more depleted with depth. Zimmermann et al. (1967) attributed this to competition between convective and diffusive fluxes. The convective flux drawing depleted water to the soil surface due to evaporation at the surface is balanced by the diffusion of enriched soil water from the surface deeper into the profile at equilibrium:

$$D^* \frac{d\delta}{dz} = E(\delta - \delta_{res}) \quad (1.25)$$

where D^* = effective liquid diffusivity of isotopes (m^2/s), δ = isotope content of liquid water, E = evaporation rate (m/s), δ_{res} = isotope content of water entering the soil column from below, and z = depth coordinate, positive downwards (m).

Solution in terms of E gives:

$$E = - \frac{D^* \ln \left[\frac{\delta/\delta_{res}}{\delta_o - \delta_{res}} \right]}{z} \quad (1.26)$$

where δ_o is the isotope content of water at the soil surface ($z = 0$). This approach was extended to evaporation from unsaturated soils (e.g. Barnes and Allison, 1983), and the method provides an integrated estimate of evaporation over relatively long time periods.

It is also possible to use δ in surface water to estimate the amount of evaporation from water bodies. Gibson et al. (1993) combined the water and isotopic mass balances to obtain evaporation as a fraction of precipitation for well-mixed headwater lakes at steady-state:

$$\frac{E}{P} = \frac{(\delta_p - \delta_L)}{(\delta_E - \delta_L)} \quad (1.27)$$

where E = evaporation, P = precipitation, δ_p = isotopic content of mean weighted local precipitation, δ_L = isotopic content of lake water, δ_E = isotopic content of evaporating moisture. δ_p and δ_L can be obtained directly from sampling, while δ_E can be estimated from evaporation pan experiments (Allison et al., 1979), through calibration against a lake with known water balance (Dinçer, 1968), or from theoretical relations requiring an estimate of the isotopic content of atmospheric vapor, δ_A (Gibson et al., 1993). The method provided estimates of mean daily evaporation and evaporation over a 23-day period comparable with those obtained from evaporation pans and mass transfer approaches (e.g. Equation 1.15). However, the method did not work well for lakes that experienced significant evaporative drawdown, because the steady-state assumption was thereby violated. A $\pm 10\%$ range in the isotopic separation between δ_A and δ_p induced variations in evaporation estimates of up to $\pm 20\%$ for observed levels of isotopic enrichment. "Owing to seasonal variations in lake level and rates of runoff and evaporation, isotopic monitoring of ungauged catchments is best suited to longer-term studies encompassing complete annual cycles (and hence approximating conditions of consistent water balance)" (Gibson et al., 1993). Nevertheless, the approach provides valuable water balance information for ungauged areas.

Use of isotopes in studies of evaporation and other hydrological processes discussed below often requires samples of soil water in order to measure their isotopic signature and chemistry. Soil water samples for chemical and isotopic analysis can be obtained from coring and subsequent centrifugation or azeotropic distillation (Buttle and Sami, 1990), tension or suction lysimeters (Stewart and McDonnell, 1991), and zero-tension lysimeters (Wels et al., 1991). Soon and Warren (1993) and Steele and Buttle (1994) discuss some of the problems associated with these sampling methods when attempting to assess soil water chemistry. There is relatively little information on the implications of these methods for the isotopic signature of the soil water that is recovered; however, Hemmen (1990) found that the $\delta^{18}\text{O}$ of soil water sampled from intact soil cores by azeotropic distillation was generally more negative than water obtained from tension lysimeters. He attributed this difference to the inability of tension lysimeters to sample more strongly bound (and isotopically more negative) water held in micropores. Interactions between soil water sampling methods and the resulting isotopic signature of the extracted soil water are the subject of current research.

1.4.2 Pore-water mixing (the mobile-immobile water issue)

Biggar and Nielsen (1962), de Smedt et al. (1986), and others have noted the existence of an immobile soil water phase, consisting of water held in thin films around soil particles (Bengtsson et al., 1987), in dead-end pores or intraaggregate micropores (Nielsen et al., 1986), which is not displaced during infiltration. The concept has been used to model unsaturated hydraulic conductivity in soils (e.g. van Genuchten, 1980). The immobile water content (i.e. the moisture content at which hydraulic conductivity is assumed to be zero) can be derived from soil moisture retention data (Bengtsson et al., 1987); however, it has also been obtained using environmental isotope tracers (Gvirtzman and Magaritz, 1986; Buttle and Sami, 1990). In the latter study, the pronounced difference in the isotopic signatures of infiltrating snowmelt water and pre-melt soil water were used to estimate the volume of pre-melt water that was not displaced during recharge. The method provides an *in situ* means of assessing immobile water content. The degree of mixing of these mobile and immobile water phases can also be assessed by comparing the time series of isotope levels in incoming precipitation with that in soil water samples (e.g. Stewart and McDonnell, 1991).

1.4.3 Soil and groundwater recharge rates

A major advantage to using environmental isotopes to study water movement in the unsaturated zone is that the relevant isotope diffusivities vary slowly with water content, in contrast to marked dependence of soil water diffusivity (Equation 1.12) on water content (Barnes and Allison, 1988). The temperature effect on isotopic concentrations of precipitation (Dansgaard, 1964) means that the isotopic signature of precipitation may be seasonally tagged in areas experiencing a marked seasonal temperature cycle as outlined in detail in Chapters 5 and 21. "Thus recharge waters from successive seasons can be identified in deep unsaturated profiles where piston flow is the dominant mechanism of water movement, although diffusive attenuation of the signal is to be expected" (Barnes and Allison, 1988). Figure 1.13 shows the cyclical variation in $\delta^{18}\text{O}$ in soil water with depth obtained by Saxena (1984) in his study of recharge in sandy overburden. Oscillations in the profile may be attributed to inputs of isotopically-light meltwater and heavier summer and fall rains. By observing the displacement following one year's infiltration, annual recharge can be estimated by integrating the θ profile over that interval (Barnes and Allison, 1988). Saxena (1984) found that rates of moisture movement ranged from 2.2×10^{-7} to 8×10^{-7} m/s; and annual recharge varied from 170 to 336 mm for different sites in Sweden. Similar meltwater particle velocities and recharge depths were obtained for moraine deposits in south-central Ontario using this method (Labadia and Buttle, 1996).

An alternative approach suggested by Dinçer et al. (1974) is to record the isotopic signature of precipitation so as to identify the passage of water from a particular event through the soil profile. This method was used by Buttle and Sami (1990) to examine recharge through aeolian sands during snowmelt. They measured average water particle velocities up to an order of magnitude greater than those found by Saxena (1984), which may reflect bypassing flow in the organic-rich topsoil during the initial snowmelt. Bypass flow presents a particular limitation to the use of isotopic tracers in recharge studies, since the isotopic signature of recharge water will not be adequately assessed by sampling the soil matrix (Darling and Bath, 1988; Hemmen, 1990). Sami and Buttle (1991) used data on the displacement of an isotopic tracer to estimate unsaturated K_H for a sandy soil, which was estimated to be 2.6 to 4.5 times greater than values obtained from the instantaneous profile method. They suggested that this was because the tracer method was used during recharge when macropores were active, while the instantaneous profile method was used during drainage when macropores were nonconductive. Thus, isotopic tracers provide a means of obtaining realistic field K_H values during infiltration that incorporate macropore effects, while avoiding the instrumentation and assumptions required when applying classical infiltration theory (Equations 1.10 to 1.12) in the field.

Stable isotopes have also been used to estimate groundwater recharge in arid and semi-arid regions, where recharge is thought to be dominated by the heavier rainfall events (Barnes and Allison, 1988). Evaporation causes enrichment in $\delta^{18}\text{O}$ and δD of the residual soil water. Sites with high recharge rates should have soil water that is more similar to the isotopic signature of the incoming precipitation than sites with lower recharge, greater evaporation, and consequently enhanced isotopic enrichment of soil water. Barnes and Allison (1988; and in Chapters 5 and 7) presented results for four dunes in the Australian arid zone which suggest that the displacement of deep unsaturated zone water from the MWL is proportional to the inverse of the square root of an independent estimate of the recharge rate. This hypothesis deserves testing in a variety of recharge environments, because the measured displacement of soil water from the MWL may serve as a convenient means of obtaining regional recharge estimates.

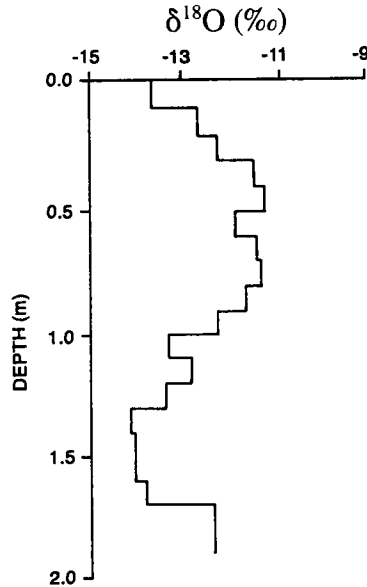


Figure 1.13. $\delta^{18}\text{O}$ profile of soil moisture in moraine material at Kloten, Sweden, 23 September 1983 (modified after Saxena, 1984).

1.4.4 Soil water, groundwater and surface water residence times

Environmental isotopes have been used in conjunction with a number of models to estimate residence times for various stores of water within the catchment (e.g. Maloszewski et al., 1983; also Chapter 21). Residence time is the elapsed time between a water particle's entry to, and exit from, a store or reservoir in the catchment. Knowledge of the residence times of water in various catchment stores may be useful in interpreting water chemistry (Nyström, 1985). Estimates of water residence times using isotopic tracers have been made at a variety of scales. For example, Brown (1961) used the T balance to examine the hydrology of the Ottawa River catchment (62,160 km²). He estimated a mean storage reservoir of 2.1 m (surface, soil and groundwater storage), 27% of which is replaced annually. At a smaller scale, Pearce et al. (1986) used D variations in rainfall and runoff in conjunction with the method of Maloszewski et al. (1983) to estimate the mean residence time (t) of water in the M8 catchment, South Island, New Zealand:

$$t = \omega^{-1} \left[\left(\frac{A}{B} \right)^2 - 1 \right]^{0.5} \quad (1.28)$$

where ω = period ($2\pi/y$), A = amplitude of sine curve describing δD variations in rainfall (‰), and B = amplitude of sine curve describing δD variations in streamflow (‰).

They found that catchment outflow reflected a well-mixed reservoir with a mean residence time of approximately 4 months. Lindström and Rodhe (1992) combined a simple water balance model with the $\delta^{18}\text{O}$ in precipitation and the drainage from three soil lysimeters. The best

simulations of $\delta^{18}\text{O}$ in lysimeter drainage occurred when mixing was assumed in the upper soil horizons, combined with piston flow at greater depths. Residence time distributions ($g(t)$) were determined following Maloszewski and Zuber (1982):

$$g(t) = \frac{C_I(t)}{\int_0^\infty C_I(t) dt} = \frac{C_I(t)Q}{M} \quad (1.29)$$

where $C_I(t)$ = tracer concentration observed at the measuring point as a result of an instantaneous injection to the system at $t = 0$, Q = discharge, and M = mass or activity of the injected tracer. The mean residence time of water in a 0.8 m long lysimeter ranged from ~3 to 6 months, with an average value of 4 months. Nyström (1985) used a similar approach with injected T in two small Swedish catchments. 40% of the water stored in the catchments appears to be replaced annually, suggesting a "shallow" groundwater circulation. Nyström also estimated storage volumes (soil and shallow groundwater) in the catchments. Stewart and McDonnell (1991) used a variety of models (including Equation 1.28) to estimate soil water residence times based on D levels in soil water in the M8 catchment. They found that a dispersion model yielded the most accurate mean residence times and indicated the presence of bypass flow.

Nyström (1985) noted that the residence time distribution concept is often limited to long residence times, and that the uncertainty associated with $g(t)$ becomes large for short residence times. In addition, all of these methods are based on assumptions (e.g. perfect mixing of tracer inputs with resident water, bypassing flow when inputs exceed a critical threshold) that may not be met in the field. Therefore it would be useful to perform such tracer studies in conjunction with hydrometric data (e.g. θ , K_{μ}) that can identify the dominant flow processes, which in turn can guide the appropriate model to be used to estimate residence times.

1.4.5 Storm runoff components

Environmental isotopes such as ^{18}O and D are applied naturally over entire drainage catchments, are not subject to chemical reactions during contact with mineral matter at temperatures encountered at or near the earth's surface (Drever, 1988), and undergo fractionation during evaporation and condensation (Section 1.4.1). Variations in the isotopic content of precipitation may be dampened as water passes through the vadose zone to the water table, with the result that groundwater δ values can approach uniformity in time and space, and are changed only by mixing with waters with different isotopic contents (Sklash, 1990). This greater temporal variability in the isotopic content of precipitation relative to that of soil and groundwater means that there is frequently a difference between the δ of water input to the catchment's surface and water stored in the catchment prior to the event. It is this difference that permits use of the following mass balance and mixing equations to separate a stormflow hydrograph into its event and pre-event components:

$$Q_t = Q_p + Q_e \quad (1.30)$$

$$C_t Q_t = C_p Q_p + C_e Q_e \quad (1.31)$$

where Q_t is streamflow; Q_p and Q_e are contributions from pre-event (soil water, groundwater)

$$X = \frac{C_t - C_e}{C_p - C_e} \quad (1.32)$$

and event (rainfall, snowmelt) water; C_t , C_p and C_e are δ values in streamflow, pre-event and event waters, respectively; and X is the pre-event fraction of streamflow.

Isotopic hydrograph separations have been performed in a variety of environments around the world, although mainly in mid- and high-latitude regions (Buttle, 1994). The vast majority of studies have shown that pre-event water supplies at least 50% of streamflow at peak discharge. Some of the lowest pre-event contributions to stormflow have been noted in urban, agricultural, bedrock and permafrost environments, which are conducive to generation of Horton flow and enhanced delivery of event water to stormflow.

Use of these mixing equations to solve for the event and pre-event components of streamflow rests on several assumptions (discussed in detail in Chapter 10):

- (1) there is a significant difference between the isotopic content of the event and pre-event components;
- (2) the isotope signature of event water is constant in space and time, or any variations can be accounted for;
- (3) the isotope signature of pre-event water is constant in space and time, or any variations can be accounted for;
- (4) contributions of water from the vadose zone to stormflow must be negligible, or the isotopic content of soil water must be similar to that of groundwater; and
- (5) contributions to streamflow from surface storage are negligible.

Rodhe (1987), Sklash (1990) and Buttle (1994) discuss these assumptions and their implications for the reliability of isotopic hydrograph separations. These reviews indicate that the assumptions underlying the isotope hydrograph separation technique may be violated as often as they are satisfied, and suggest that the method has been used inappropriately in some cases (Buttle, 1994). Nevertheless, violations of some of the more important assumptions, such as (2), (3) and (4), do not compromise the essential finding that pre-event water comprises a large component of stormflow (Bishop, 1991).

1.4.6 Water sources versus water flowpaths

Sklash et al. (1976) noted that isotopic hydrograph separations reveal the **time source** components of runoff - the relative contributions of event and pre-event water to stormflow. However, such separations in isolation can say nothing about the flowpath that the event and pre-event water followed in order to reach the stream channel.

A variety of runoff mechanisms and associated flowpaths have been invoked in order to account for rapid delivery of pre-event water from drainage catchments during storm or melt events, including groundwater ridging (Blowes and Gillham, 1988; Sklash and Farvolden, 1979), translatory flow (Bishop et al., 1991), macropore flow (McDonnell, 1990), and saturation overland flow (Beven, 1989). Buttle (1994) notes two major problems associated with attempts to link the isotopic behavior of streamflow to causal runoff mechanisms: (1) intra-catchment processes have often been inferred solely on the basis of the isotopic output from the catchment; and (2) the isotopic response of catchments to rainfall and snowmelt inputs can potentially be generated from a variety of alternative mechanisms. Advances in linking runoff processes to isotopic responses depend on careful integration of hydrometric and isotopic techniques. An example of progress in this area is McDonnell's (1990) reconciliation of the apparently contradictory results obtained by Mosley (1979) and Sklash et al. (1986) from the Maimai catchments in New Zealand. The former found rapid movement of dye through lateral macropores at the base of the soil profile, leading Ward and Robinson (1990) to conclude that "the high velocity of conduited, macropore subsurface flow ... means that the water arriving in the stream channel by this route will almost certainly be 'new' water ... rather than 'old' water ...". Nevertheless, isotopic separations conducted at the same sites by Sklash et al. (1986) found that the bulk of the macropore flow on the slopes was pre-event water. It was only through McDonnell's (1990) simultaneous application of hydrometric and isotopic methods that macropore flow routing of appreciable quantities of pre-event water from these hillslopes was identified. In addition to the inclusion of hydrometric methods in isotopic studies, there has been considerable progress in the use of multiple tracers, particularly reactive compounds that may indicate the flowpath that water followed as it moved from the soil surface to the sampling point (e.g. Peters et al., 1995).

1.4.7 Sources of solutes

A fundamental premise of many hydrochemical studies in catchments is that the source, pathway and residence time of water in a catchment exert a strong control on the water chemistry (e.g. Kleissen et al., 1990; Robson and Neal, 1990; Mulholland et al., 1990). Water that moves rapidly through a catchment will have a shorter contact time with soil and regolith than water that moves via slower pathways and has a greater opportunity to undergo chemical transformation through such processes as adsorption, oxidation, reduction, dissolution and cation exchange (Whitehead et al., 1986; Joslin et al., 1987). Environmental isotope hydrograph separations have been used to provide information on the sources and relative residence times of water reaching the stream channel and to explain stream hydrochemistry (e.g. Wels et al., 1990). However, assumptions frequently made with regard to environmental isotopes (e.g. well-mixed reservoirs with uniform isotopic signatures) may not apply to the solutes of interest, which do not necessarily exhibit these uniform concentrations in event or pre-event waters (e.g. Hooper et al., 1988; Bishop et al., 1990). Explanations of stream hydrochemical behavior will continue to require careful integration of the results from hydrometric, isotopic and geochemical methods, rather than the use of any one approach in isolation.

1.5 New Research Directions

Subsequent chapters will detail recent progress in specific areas where isotopes have been used to improve our understanding of small catchment hydrology, and will also suggest new research

directions within these areas. In addition to these more focussed topics, there are two broader and related issues that should receive attention in future research in all areas of the application of isotopic techniques to hydrology.

The first issue concerns the implications of spatial and temporal changes in isotopic levels in water for isotopic methods. Many of the applications of isotopes to small catchment hydrology have assumed spatial and/or temporal homogeneity of the isotopic signature of water. The degree to which these assumptions hold, and the implications of these assumptions for the conclusions drawn from applications of isotopes to hydrological research, need to be examined. Research into two fundamental questions is required:

- (1) what is the spatial and temporal scale of variations in the isotope signature of water held in various stores in the hydrological system?; and
- (2) what is the maximum degree of nonhomogeneity in these signatures that will still permit valid applications of the various isotopic methods that have been discussed?

The second issue that needs to be addressed in future work is the degree to which isotopic methods can be transferred over various spatial and temporal scales. Intuitively, some of the methods that were presented in Section 1.4 are more appropriate at some scales rather than others. For example, Equation 1.26 (Zimmermann et al., 1967) is appropriate for estimating evaporation from a saturated soil at a point, whereas Gibson et al.'s (1993) use of Equation 1.27 provides whole lake estimates of evaporation. Both methods provide long-term (i.e. annual) rates of evaporation; however, the ability to employ these and similar methods at different spatial and temporal scales needs to be explored.

1.6 Summary

Small catchments provide a convenient framework within which to examine hydrological processes, and the water balance equation forms the backdrop for the examination of most if not all of these processes. This chapter has highlighted the dominant processes operating in small catchments, methods used to study these processes, and some of the ways in which isotopes have been used to improve our understanding of small catchment hydrology. Advances in our efforts to measure and model hydrological processes, using both hydrometric and isotopic methods, will depend to a great extent upon our ability to come to grips with some of the questions of spatial and temporal scale that have been raised here.

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Chapter 2

Fundamentals of Isotope Geochemistry

Carol Kendall and Eric A. Caldwell

2.1 Introduction

Of all the methods used to understand hydrologic processes in small catchments, applications of tracers--in particular isotope tracers--have been the most useful in terms of providing new insights into hydrologic processes. This is because they integrate small-scale variability to give an effective indication of catchment-scale processes (McDonnell and Kendall, 1992; Buttle, 1994). In contrast, internal watershed *point* measurements, such as those of water level or groundwater composition, cannot be used without extrapolation or additional assumptions about catchment behavior. Isotopes are also "applied" at the watershed scale (i.e., they are within all components of the hydrologic cycle). In particular, ^{18}O , ^2H , and ^3H are integral parts of natural water molecules that fall as rain or snow (meteoric water) each year over a watershed and, consequently, are ideal tracers of water. This no cost, long-term, and wide-spread *application* of these natural tracers allows hydrologists to study runoff generation on scales ranging from macropores to hillslopes to first- and higher- order streams (Sklash, 1990).

Environmental isotopes are natural and anthropogenic isotopes whose wide distribution in the hydrosphere can assist in the solution of hydrogeochemical problems. Typical uses of environmental isotopes in hydrology include:

- identification of mechanisms responsible for streamflow generation
- testing flowpath and water-budget models developed using hydrometric data
- characterization of flowpaths that water follows from the time precipitation hits the ground until discharge at the stream
- determination of weathering reactions that mobilize solutes along those flowpaths
- determination of the role of atmospheric deposition in controlling water chemistry
- identification of the sources of solutes in contaminated systems and
- assessment of biologic cycling of nutrients within an ecosystem.

Environmental isotopes can be used as tracers of waters and solutes in catchments because:

- Waters recharged at different times, in different locations, or that followed different flowpaths are often isotopically distinct; in other words, they have distinctive "fingerprints".
- Unlike most chemical tracers, environmental isotopes are relatively conservative in reactions with catchment materials. This is especially true of oxygen and hydrogen isotopes in water; meteoric waters retain their distinctive fingerprints until they mix with waters of different compositions or, in the case of isotopes of dissolved species, there are reactions with minerals or other fluids.
- Solutes in catchment waters that are derived from atmospheric sources are commonly isotopically distinct from solutes derived from geologic and biologic sources within the catchment.
- Both biological cycling of solutes and water/rock reactions often change isotopic ratios of the solutes in predictable and recognizable directions; these interactions often can be reconstructed from the isotopic compositions.
- If water from an isotopically distinctive source (e.g., rain with an unusual isotopic composition) is found along a flowpath, it provides proof for a hydrologic connection, despite any hydraulic measurements or models to the contrary.

Given all these powerful applications, why do environmental hydrogeologists continue to under utilize isotopes? The most probable explanations are fear of the unknown and the sometimes awkward terminology used in this field. We hope to address and redress these problems in this book.

Before embarking on the fundamentals of isotope geochemistry, we would like to close this introduction with a cautionary note first presented in 1983 at a short-course on Isotope Hydrology co-taught by Tyler B. Coplen and Carol Kendall to scientists at the U.S. Geological Survey. This very appropriate note has been repeated at each subsequent USGS course we have taught:

Fretwell's Law: "Warning! Stable isotope data may cause severe and contagious stomach upset if taken alone. To prevent upsetting reviewers' stomachs and your own, take stable isotope data with a healthy dose of other hydrologic, geologic, and geochemical information. Then, you will find stable isotope data very beneficial." (Marvin O. Fretwell, pers. comm. 1983).

Environmental isotopes *can* be a useful tool to help deduce geochemical processes. However, to avoid breaking Fretwell's Law, make sure that isotopic measurements are used along with measurements of major and minor trace elements and judicious amounts of hydrologic data to test hypotheses about hydrologic and geochemical mechanisms. In fact, one of the most powerful applications of isotopic measurements is their use in confirming or rejecting models derived from the use of other techniques. Isotopic measurements can also provide input for mass-balance calculations and quantitative constraints on reaction progress.

2.2 Fundamentals of Isotope Geochemistry

The following section presents a very brief discussion of the fundamentals of stable and radio-isotope geochemistry, intended to provide readers with the necessary background information to understand the succeeding chapters. Many of the topics below are discussed in more detail in individual chapters. For more information on isotope systematics, the readers are encouraged to examine the following isotope reference books: Clark and Fritz (1997), Dickin (1995), Faure (1986), and Gat and Gonfiantini (1981). The first of these is a textbook intended for upper-division and graduate hydrogeology students, and contains problem sets.

2.2.1 Definitions

Isotopes are atoms of the same element that have different numbers of *neutrons*. Differences in the number of neutrons among the various isotopes of an element mean that the various isotopes have different masses. The superscript number to the left of the element designation is called the *mass number* and is the sum of the number of protons and neutrons in the isotope (Figure 2.1). For example, among the hydrogen isotopes, deuterium (denoted as D or ^2H) has one neutron and one proton. This mass number of 2 is approximately equal to twice the mass of protium (^1H), whereas tritium (^3H) has two neutrons and its mass is approximately three times the mass of protium. Isotopes of the same element have the same number of protons. For example, all isotopes of oxygen have 8 protons; however, an oxygen atom with a mass of 18 (denoted ^{18}O) has 2 more neutrons than oxygen with a mass of 16 (^{16}O). Isotope names are usually pronounced with the element name first, as in "oxygen-18" instead of "18-oxygen." In many texts, especially older ones typeset without superscripts, the mass number is shown to the right of the element abbreviation, as in C-13 or C^{13} for carbon-13.

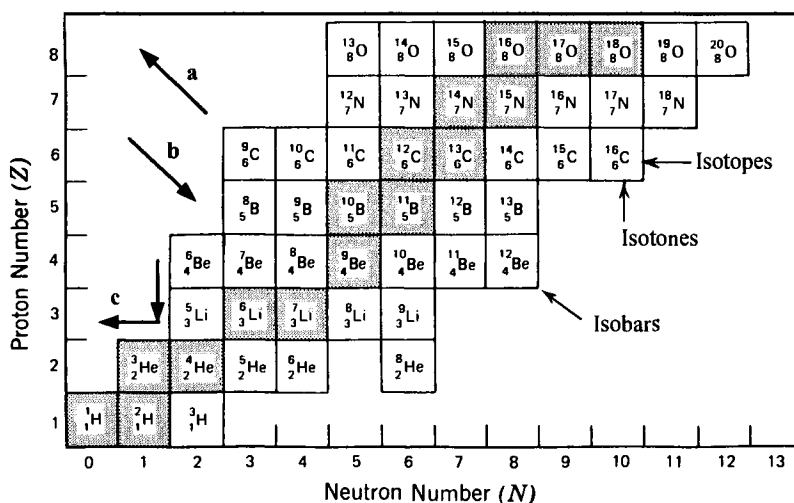


Figure 2.1. Partial chart of the elements. Each square represents a particular nuclide. The shaded squares are stable atoms and the unshaded squares are unstable or radioactive nuclides. Arrows at the left side of the diagram show the shifts in proton and neutron number caused by different decay mechanisms: beta decay (a), positron decay and beta capture (b), and alpha decay (c). Modified from Faure (1986).

The original isotopic compositions of planetary systems are a function of nuclear processes in stars. Over time, isotopic compositions in terrestrial environments change by the processes of radioactive decay, cosmic ray interactions, mass-dependent fractionations that accompany inorganic and biological reactions, and anthropogenic activities such as the processing of nuclear fuels, reactor accidents, and nuclear-weapons testing. *Radioactive* (unstable) isotopes are *nuclides* (isotope-specific atoms) that spontaneously disintegrate over time to form other isotopes. During the disintegration, radioactive isotopes emit *alpha* or *beta* particles and sometimes also *gamma rays*. *Stable* isotopes are nuclides that do not appear to decay to other isotopes on geologic time scales, but may themselves be produced by the decay of radioactive isotopes.

Naturally occurring nuclides define a path in the chart of nuclides, corresponding to the greatest stability of the neutron/proton (N/Z) ratio. For nuclides of low atomic mass, the greatest stability is achieved when the number of neutrons and protons are approximately equal ($N = Z$); these are the so-called *stable* isotopes (denoted as shaded nuclides in Figure 2.1). However, as the atomic mass increases, the stable neutron/proton ratio increases until $N/Z = 1.5$. Radioactive decay occurs when changes in N and Z of an unstable nuclide cause the transformation of an atom of one nuclide into that of another, more stable nuclide; these radioactive nuclides are called *unstable* nuclides (denoted as the non-shaded nuclides in Figure 2.1).

Atoms produced by the radioactive decay of other nuclides are termed *radiogenic*. A few nuclides are produced by cosmic ray bombardment of stable nuclides in the atmosphere and are termed *cosmogenic*. Other nuclides may be created by the addition of neutrons produced by the alpha decay of other nuclides (neutron activation). Alternatively, the neutron addition can displace a proton in the nucleus, creating a nuclide of the same atomic mass but lower atomic number. Nuclides produced by these two processes are termed *lithogenic*. If the daughter product is radioactive, it will decay to form an isotope of yet another element. This process will continue until a stable nuclide is produced. For example, uranium and thorium decay to form other radionuclides that are themselves radioactive and decay to other radionuclides, and so on until stable lead isotopes are formed (see Chapter 20 for uranium decay chains). Although the terms *parent* and *daughter* nuclides are commonly used, these terms can be misleading. Only *one* atom is involved during radioactive decay; that is, the daughter nuclide is the same nuclide as the parent atom. However, after radioactive decay it has a different number of neutrons in its nucleus.

The change in the number of neutrons can occur in a variety of ways (Figure 2.1). However, the four mechanisms described below are the most common and produce the radiogenic nuclides most relevant to hydrologic and geologic studies:

Beta decay occurs when nuclides deficient in protons transform a neutron into a proton and an electron, and expel the electron from the nucleus as a negative β particle (β^-), thereby increasing the atomic number by one while the number of neutrons is reduced by one.

Positron decay occurs when nuclides deficient in neutrons transform a proton into a neutron, an electron (β^+), and a neutrino, thereby decreasing the atomic number by one and increasing the neutron number by one. The daughters are *isobars* (nuclides of equal mass) of their parent and are isotopes of different elements.

Beta capture (or electron capture) occurs when nuclides deficient in neutrons transform a proton into a neutron plus neutrino by the capture of an electron by a proton, thereby decreasing the number of protons in the nucleus by one. Both this and positron decay yield a radiogenic nuclide that is an isobar of the parent nuclide.

Alpha decay occurs when heavy atoms above $Z = 83$ in the nuclide chart emit an alpha particle, which consists of a helium nuclei with two neutrons, two protons, and a 2^+ charge. This radiogenic daughter product is *not* an isobar of its parent nuclide because its mass is reduced by four (see Figure 2.1).

For example, the radioisotope (radioactive isotope) ^{14}C is produced in the atmosphere by cosmic ray neutron interaction with ^{14}N . ^{14}C has a half-life of about 5730 years, and decays back to stable ^{14}N by emission of a beta particle. The *decay equation* below expresses the change in the concentration (activity) of the nuclide over time:

$$A_t = A_0 \cdot e^{-\lambda t} \quad (2.1)$$

where A_0 is the initial activity of the parent nuclide, and A_t is its activity after some time "t." The decay constant " λ " is equal to $\ln(2/t^{1/2})$. Note that the decay rate is only a function of the activity of the nuclide and time, and that temperature and other environmental parameters appear to have no effect on the rate.

2.2.2 Terminology

Stable isotope compositions of low-mass (light) elements such as oxygen, hydrogen, carbon, nitrogen, and sulfur are normally reported as δ values. The term " δ " is spelled and pronounced **delta** not **del**. The word del describes either of two mathematical terms: an operator (∇) or a partial derivative (∂). δ values are reported in units of parts per thousand (denoted as ‰ or permil, or per mil, or per mille -- or even recently, per mill) relative to a standard of known composition. δ values are calculated by:

$$\delta \text{ (in ‰)} = (R_x / R_s - 1) \cdot 1000 \quad (2.2)$$

where R denotes the ratio of the heavy to light isotope (e.g., $^{34}\text{S}/^{32}\text{S}$), and R_x and R_s are the ratios in the sample and standard, respectively. For sulfur, carbon, nitrogen, and oxygen, the average terrestrial abundance ratio of the heavy to the light isotope ranges from 1:22 (sulfur) to 1:500 (oxygen); the ratio $^2\text{H}:^1\text{H}$ is much lower at 1:6410. A positive δ value means that the isotopic ratio of the sample is higher than that of the standard; a negative δ value means that the isotopic ratio of the sample is lower than that of the standard. For example, a $\delta^{15}\text{N}$ value of +30‰ means that the $^{15}\text{N}/^{14}\text{N}$ of the sample is 30 parts-per-thousand or 3% higher than the $^{15}\text{N}/^{14}\text{N}$ of the standard. Many isotope geochemists advocate always prefacing the δ value with a sign, even when the value is positive, to distinguish between a true positive δ value and a δ value that is merely missing its sign (a frequent occurrence with users unfamiliar with isotope terminology).

There are several commonly used ways for making comparisons between the δ values of two materials. The first two are preferred because of their clarity, and the fourth should be avoided:

- (1) high vs. low values
- (2) more/less positive vs. more/less negative (e.g., -10‰ is more positive than -20‰)
- (3) heavier vs. lighter (the "heavy" material is the one with the higher δ value)

(4) enriched vs. depleted (always remember to state *what* isotope is in short supply, e.g., a material is enriched in ^{18}O or ^{16}O relative to some other material, *and* that the enrichment or depletion is a result of some reaction or process). For example, to say that "one sample is enriched in ^{34}S relative to another because of sulfate reduction" is proper usage. Phrases such as "a sample has an enriched $\delta^{15}\text{N}$ value" are misuses of terminology.

2.2.3 Standards

The isotopic compositions of materials analyzed on mass spectrometers are usually reported relative to some international *reference standard*. Samples are either analyzed at the same time as this reference standard or with some internal laboratory standard that has been calibrated relative to the international standard. Alternatively, the absolute ratios of isotopes can be reported. Small quantities of these reference standards are available for calibration purposes from either the National Institute of Standards and Technology (NIST) in the USA (Web site: <http://www.nist.gov/>), or the International Atomic Energy Agency (IAEA) in Vienna (Web site: <http://www.iaea.or.at/>).

Various isotope standards are used for reporting light stable-isotopic compositions (Table 2.1). The δ values of each of the standards have been defined as ‰. δD and $\delta^{18}\text{O}$ values are normally reported relative to the SMOW standard (Standard Mean Ocean Water; Craig, 1961) or the equivalent VSMOW (Vienna-SMOW) standard. $\delta^{13}\text{C}$ values are reported relative to either the PDB (Pee Dee Belemnite) or the equivalent VPDB (Vienna-PDB) standard. $\delta^{18}\text{O}$ values of low-temperature carbonates are also commonly reported relative to PDB or VPDB.

Table 2.1. Abundance ratios and reference standards for some environmental isotopes.

Isotope	Ratio measured	Reference Standard	Abundance ratio of standard
^2H	$^2\text{H}/^1\text{H}$	VSMOW	$1.5575 \cdot 10^{-4}$
^3He	$^3\text{He}/^4\text{He}$	atmospheric He	$1.3 \cdot 10^{-6}$
^6Li	$^6\text{Li}/^7\text{Li}$	L-SVEC	$8.32 \cdot 10^{-2}$
^{11}B	$^{11}\text{B}/^{10}\text{B}$	NBS 951	4.04362
^{13}C	$^{13}\text{C}/^{12}\text{C}$	VPDB	$1.1237 \cdot 10^{-2}$
^{15}N	$^{15}\text{N}/^{14}\text{N}$	atmospheric N_2	$3.677 \cdot 10^{-3}$
^{18}O	$^{18}\text{O}/^{16}\text{O}$	VSMOW, or VPDB	$2.0052 \cdot 10^{-3}$ $2.0672 \cdot 10^{-3}$
^{34}S	$^{34}\text{S}/^{32}\text{S}$	CDT	$4.5005 \cdot 10^{-2}$
^{37}Cl	$^{37}\text{Cl}/^{35}\text{Cl}$	SMOC	0.324
^{87}Sr	$^{87}\text{Sr}/^{86}\text{Sr}$	Absolute ratio, or various materials	

VSMOW and VPDB are virtually identical to the SMOW and PDB standards. Use of VSMOW and VPDB is supposed to imply that the measurements were calibrated according to IAEA guidelines for expression of δ values relative to available reference materials on *normalized* permil scales (Coplen, 1994; 1995; 1996). Laboratories accustomed to analyzing synthetic compounds that are highly enriched in the heavy (or, less commonly, the light) isotope may report absolute isotope abundances in atomic-weight percent or ppm, instead of relative ratios in permil. In general, radioisotopes are reported as absolute concentrations or ratios. Tritium (^3H) values are typically reported as absolute concentrations, called Tritium Units (TU) where one TU corresponds to 1 tritium atom per 10^{18} hydrogen atoms. Tritium values may also be expressed in terms of activity (pico-Curies/liter, pCi/L) or decay (disintegrations per minute/liter, dpm/L), where $1 \text{ TU} = 3.2 \text{ pCi/L} = 7.2 \text{ dpm/L}$. ^{14}C contents are referenced to an international standard known as “modern carbon” and are typically expressed as a percent of modern carbon (pmc).

2.3 Stable Isotope Fractionation

2.3.1 Properties of isotopic molecules

The various isotopes of an element have slightly different chemical and physical properties because of their mass differences. Under the proper circumstances, such differences can manifest themselves as a *mass-dependent* isotope fractionation effect. Nuclear interactions, on the other hand, lead to a *non-mass-dependent* effect in the sense that they depend on the nuclear structure, rather than on the weight difference per se. In the first case, for example, the properties of molecules with ^{17}O will be intermediate between those of molecules with ^{16}O and ^{18}O ; this is not necessarily the case for the non-mass-dependent effects. For elements of low atomic numbers, these mass differences are large enough for many physical, chemical, and biological processes or reactions to *fractionate* or change the relative proportions of different isotopes of the same element in various compounds. As a result of fractionation processes, waters and solutes often develop unique isotopic compositions (ratios of heavy to light isotopes) that may be indicative of their source or the processes that formed them.

Two main types of phenomena produce isotopic fractionations: *isotope exchange reactions* and *kinetic processes*. Isotope exchange reactions can be viewed as a subset of kinetic isotope reactions where the reactants and products remain in contact in a closed, well-mixed system such that back reactions can occur and chemical equilibrium can be established. Under such circumstances, isotopic equilibrium can be also established. Detailed discussions of isotope fractionations are found in O’Neil (1986), Gat and Gonfiantini (1981), Gat (1980), and other texts.

2.3.2 Fractionation accompanying chemical reactions and phase changes

The strength of chemical bonds involving different isotopic species will usually be different. Molecules containing heavy isotopes are more stable (i.e., have a higher dissociation energy) than molecules with lighter isotopes. Hence, isotopic fractionations between molecules can be explained by differences in their *zero point energies* (ZPE). For example, there is about a 2 kcal/mole difference in ZPE associated with the breaking of the H-H bond compared to the D-D bond (Figure 2.2). Hence, H-H bonds are broken more easily and D-D bonds are more stable. Chemical reaction rates where such a bond is broken will also show an isotope effect. These are quantum effects that become appreciable at low temperatures and disappear at higher temperatures.

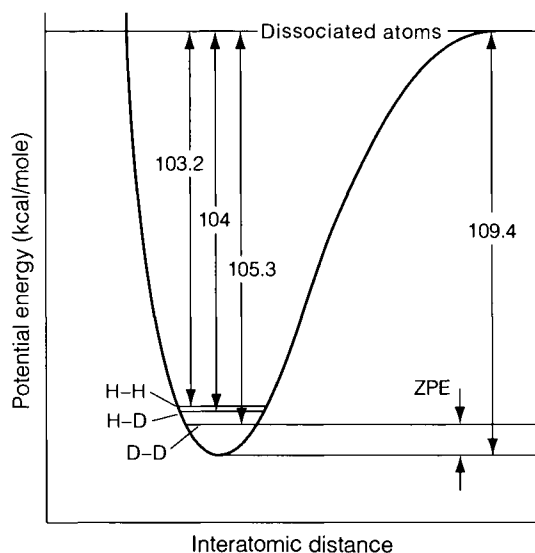


Figure 2.2. The interatomic distance - potential energy relationship for stable hydrogen isotopes of a molecule. Higher zero point energies (ZPE) result in molecules being less stable. Modified from O'Neil (1986).

The energy differences associated with isotope effects are about 1000 times smaller than the ΔG for chemical reactions, and hence cannot be the driving force for chemical equilibrium.

Equilibrium fractionations

Equilibrium isotope-exchange reactions involve the redistribution of isotopes of an element among various species or compounds (in a strict sense, this only occurs in a closed, well-mixed system at chemical equilibrium). At isotopic equilibrium, the forward and backward reaction rates of any particular isotope are identical. This does not mean that the isotopic compositions of two compounds at equilibrium are identical, but only that the ratios of the different isotopes in each compound are constant for a particular temperature.

During equilibrium reactions, the heavier isotope generally preferentially accumulates in the species or compound with the higher oxidation state. For example, sulfate becomes *enriched* in ^{34}S relative to sulfide (i.e., has a more positive $\delta^{34}\text{S}$ value); consequently, the residual sulfide becomes *depleted* in ^{34}S . As a "rule of thumb," among different phases of the same compound or different species of the same element, the more dense the material, the more it tends to be enriched in the heavier isotope. For example, for the various phases of water, at equilibrium, $\delta^{18}\text{O}_\text{s} > \delta^{18}\text{O}_\text{l} > \delta^{18}\text{O}_\text{v}$. Also, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of $\text{CO}_2 < \text{HCO}_3^- < \text{CaCO}_3$.

During phase changes, the ratio of heavy to light isotopes in the molecules in the two phases changes. For example, as water vapor condenses in rain clouds (a process typically viewed as an equilibrium process), the heavier water isotopes (^{18}O and ^2H) become enriched in the liquid phase while the lighter isotopes (^{16}O and ^1H) remain in the vapor phase. In general, the higher the temperature, the less the difference between the equilibrium isotopic compositions of any two species (because the differences in ZPE between the species become smaller).

The fractionation associated with the equilibrium exchange reaction between two substances *A* and *B* (i.e., the fractionation of *A* relative to *B*) can be expressed by use of the isotope fractionation factor α (alpha):

$$\alpha_{A-B} = R_A / R_B \quad (2.3)$$

where R = the ratio of the heavy isotope to the lighter isotope (i.e., D/H, $^{18}\text{O}/^{16}\text{O}$, $^{34}\text{S}/^{32}\text{S}$, etc.) in compounds *A* and *B*.

The value of such an *equilibrium* fractionation factor can be calculated on the basis of spectral data of the isotopic molecular species, at least for simple molecules. The α values generally differ by just a few percent from the equal-energy value of 1.00, except for exchange reactions involving hydrogen isotopes where α values may be as large as 4 at room temperature (see Friedman and O'Neil, 1977). The sign and magnitude of α are dependent on many factors, of which temperature is generally the most important. Other factors include chemical composition, crystal structure, and pressure.

The equilibrium fractionation factors (α_{l-v}) for the water liquid-vapor phase transition are 1.0098 and 1.084 at 20°C and 1.0117 and 1.111 at 0°C for ^{18}O and ^2H , respectively (Majoube, 1971). In both cases, $\alpha_{l-v} > 1$, which means that the first phase (the liquid water) is "heavier" than the second phase (e.g., for $\alpha_{l-v} = 1.0098$, the $\delta^{18}\text{O}$ of water is +9.8‰ higher than the $\delta^{18}\text{O}$ value of vapor at equilibrium). For the ice-water transition (0°C), the values are 1.0035 and 1.0208, respectively (Arnason, 1969).

A useful equation that relates δ values and fractionation factors is:

$$\alpha_{A-B} = (1000 + \delta_A) / (1000 + \delta_B) . \quad (2.4)$$

Other common formulations for fractionation factors include:

$$\alpha^* = 1/\alpha = \alpha_{B-A} = R_B / R_A \quad (2.5)$$

and

$$\epsilon_{A-B} = (\alpha_{A-B} - 1) \cdot 1000 . \quad (2.6)$$

For small values of ϵ (epsilon), $\epsilon_{A-B} \approx \delta_A - \delta_B$. For example, if $\delta_B = +10\text{‰}$ and if $\alpha_{A-B} = 1.020$, then $\epsilon = 20\text{‰}$ and $\delta_A \approx +30\text{‰}$. The difference in isotopic composition between two species *A* and *B* is defined as:

$$\epsilon_{A-B} \approx \delta_A - \delta_B \approx 1000 \ln \alpha_{A-B} . \quad (2.7)$$

Fractionation factors are commonly expressed as " $10^3 \ln \alpha$ " because this expression is a very close approximation to the permil fractionation between the materials (ϵ), especially for the values of α near to unity typical of most elements of interest (O'Neil, 1986), and because the value " $10^3 \ln \alpha$ " is nearly proportional to the inverse of temperature ($1/T$) at low temperatures (°K). Graphical plots of the temperature dependency of α are typically given as $10^3 \ln \alpha$ versus $1/T$ (Friedman and O'Neil, 1977).

Kinetic fractionations

Chemical, physical, and biological processes can be viewed as either reversible *equilibrium* reactions or irreversible unidirectional *kinetic* reactions. In systems out of chemical and isotopic equilibrium, forward and backward reaction rates are not identical, and isotope reactions may, in fact, be unidirectional if reaction products become physically isolated from the reactants. Such reaction rates are dependent on the ratios of the masses of the isotopes and their vibrational energies, and hence are called **kinetic** isotope fractionations.

The magnitude of a kinetic isotope fractionation depends on the reaction pathway, the reaction rate, and the relative bond energies of the bonds being severed or formed by the reaction. Kinetic fractionations, especially unidirectional ones, are usually larger than the equilibrium fractionation factor for the same reaction in most low-temperature environments. As a rule, bonds between the lighter isotopes are broken more easily than equivalent bonds of heavier isotopes. Hence, the light isotopes react faster and become concentrated in the products, causing the residual reactants to become enriched in the heavy isotopes. In contrast, reversible equilibrium reactions can produce products heavier or lighter than the original reactants.

Many reactions can take place either under purely equilibrium conditions or be affected by an additional kinetic isotope fractionation. For example, although isotopic exchange between water and vapor can take place under more-or-less equilibrium conditions (i.e., at 100% humidity when the air is still and the system is almost chemically closed), more typically the system is out of chemical equilibrium (i.e., < 100% humidity) or the products become partially isolated from the reactants (e.g., the resultant vapor is blown downwind). Under these conditions, the isotopic compositions of the water and vapor are affected by an additional kinetic isotope fractionation of variable magnitude (see below).

Isotope fractionation factors can be defined as:

$$\alpha = R_p / R_s \quad (2.8)$$

where R_p and R_s are the ratios of the heavy to light isotope in the *product* and *substrate* (reactant), respectively. An isotope enrichment factor, ϵ , can be defined as:

$$\epsilon_{p-s} = (\alpha - 1) \cdot 1000 . \quad (2.9)$$

If the reactant concentration is large and fractionations are small,

$$\epsilon_{p-s} \approx \Delta = \delta_p - \delta_s \quad (2.10)$$

where Δ (del) is another term for the enrichment factor. Note that Equations 2.8 - 2.10 for kinetic fractionations are the same as Equations 2.3, 2.6, and 2.7 (respectively) for equilibrium fractionations, except for the differences in subscripts. One should be especially careful with the superscripts, subscripts, and units of all fractionation factors; different authors may define them differently. The use of p and s (or r) for kinetic fractionations like Equation 2.10 reflects the unidirectional nature of these reactions.

The same formulations apply not only when part of the system is removed by a chemical or biological reaction, but also when material escapes by diffusion or outflow (e.g., by effusion through an aperture). In the latter cases the term *transport* fractionation factor may be preferred.

The transport fractionation, like the *equilibrium* factors, is temperature dependent. However, unlike true *kinetic* fractionation factors, which can be quite appreciable, transport fractionations have only slight (positive) temperature coefficients.

2.3.3 The Rayleigh equations

The isotopic literature abounds with different approximations of the **Rayleigh equations**, including the three equations below. These equations are so-named because the original equation was derived by Lord Rayleigh (pronounced "raylee") for the case of *fractional distillation of mixed liquids*. This is an exponential relation that describes the partitioning of isotopes between two reservoirs as one reservoir decreases in size. The equations can be used to describe an isotope fractionation process if: (1) material is continuously removed from a mixed system containing molecules of two or more isotopic species (e.g., water with ^{18}O and ^{16}O , or sulfate with ^{34}S and ^{32}S), (2) the fractionation accompanying the removal process at any instance is described by the fractionation factor α , and (3) α does not change during the process. Under these conditions, the evolution of the isotopic composition in the residual (reactant) material is described by:

$$(R / R_0) = (X_1 / X_{1_0})^{\alpha-1} \quad (2.11)$$

where R = ratio of the isotopes (e.g., $^{18}\text{O}/^{16}\text{O}$) in the reactant, R_0 = initial ratio, X_1 = the concentration or amount of the more abundant (lighter) isotope (e.g., ^{16}O), and X_{1_0} = initial concentration. Because the concentration of $X_1 \gg X_h$, X_1 is approximately equal to the amount of original material in the phase. Hence, if $f = X_1/X_{1_0}$ = fraction of material remaining, then:

$$R = R_0 f^{(\alpha-1)} \quad (2.12)$$

Another form of the equation in δ -units is:

$$\delta \approx \delta_0 f^{(\alpha-1)} \quad (2.13)$$

which is valid for α values near 1, δ_0 values near 0, and ϵ values less than about 10.

In a strict sense, the term "Rayleigh fractionation" should only be used for chemically *open* systems where the isotopic species removed at every instant were in thermodynamic and isotopic equilibrium with those remaining in the system at the moment of removal. Furthermore, such an "ideal" Rayleigh distillation is one where the reactant reservoir is finite and well mixed, and does not re-react with the product (Clark and Fritz, 1997). However, the term "Rayleigh fractionation" is commonly applied to equilibrium closed systems and kinetic fractionations as well (as described below) because the situations may be computationally identical.

2.3.4 Isotopic fractionation in open and closed systems

The Rayleigh equation applies to an open system from which material is removed continuously under condition of a constant fractionation factor. However, such processes can proceed under different boundary conditions, even when the fractionation factors are the same. One such

system is the so-called "closed" system (or 2-phase equilibrium model), where the material removed from one reservoir accumulates in a second reservoir in such a manner that isotopic equilibrium is maintained throughout the process (Gat and Gonfiantini, 1981). An example is the condensation of vapor to droplets in a cloud where there is continuous exchange between the isotopes in the vapor and water droplets.

The isotope enrichment achieved can be very different in closed vs. open systems. For example, Figure 2.3 shows the changes in the $\delta^{18}\text{O}$ of water and vapor during evaporation (an *open*-system process) where the vapor is continuously removed (i.e., isolated from the water) with a constant fractionation factor $\alpha_{l,v} = 1.010$ (i.e., the newly formed vapor is always 10‰ lighter than the residual water). As evaporation progresses (i.e., $f \rightarrow 0$), the $\delta^{18}\text{O}$ of the remaining water (solid line A), becomes heavier and heavier. The $\delta^{18}\text{O}$ of the instantaneously formed vapor (solid line B) describes a curve parallel to that of the remaining water, but lower than it (for all values of f) by the precise amount dictated by the fractionation factor for ambient temperature, in this case by 10‰. For higher temperatures, the α value would be smaller and the curves closer together. The integrated curve, giving the isotopic composition of the accumulated vapor thus removed, is shown as solid line C. Mass balance considerations require that the isotope content of the total accumulated vapor approaches the initial water $\delta^{18}\text{O}$ value as $f \rightarrow 0$; hence, any process should be carried out to completion (with 100% yield) to avoid isotopic fractionation.

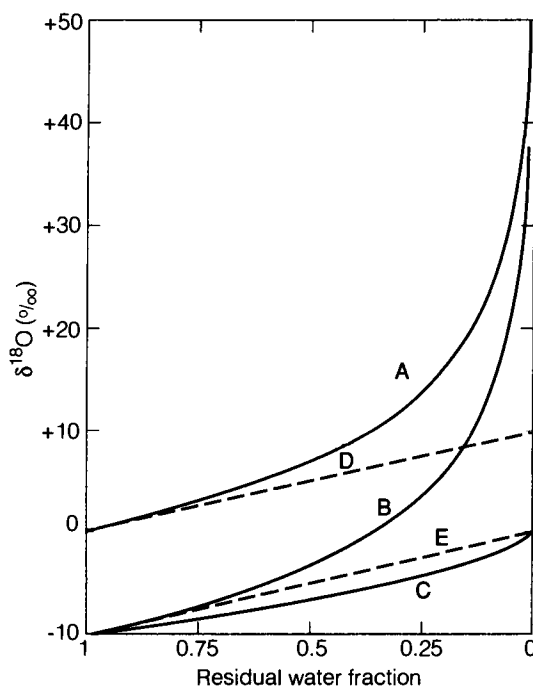


Figure 2.3. Isotopic change under open- and closed-system Rayleigh conditions for evaporation with a fractionation factor $\alpha = 1.01$ for an initial liquid composition of $\delta^{18}\text{O} = 0$. The $\delta^{18}\text{O}$ of the **remaining water** (solid line A), the **instantaneous vapor** being removed (solid line B), and the **accumulated vapor** being removed (solid line C) all increase during single-phase, open-system, evaporation under equilibrium conditions. The $\delta^{18}\text{O}$ of water (dashed line D) and vapor (dashed line E) in a two-phase closed system also increase during evaporation, but much less than in an open system; for a closed system, the δ values of the instantaneous and cumulative vapor are identical. Modified from Gat and Gonfiantini (1981).

The dashed lines in Figure 2.3 show the $\delta^{18}\text{O}$ of vapor (E) and water (D) during equilibrium evaporation in a *closed* system (i.e., where the vapor and water are in contact for the entire phase change). Note that the $\delta^{18}\text{O}$ of vapor in the *open* system where the vapor is continuously removed (line B) is always heavier than the $\delta^{18}\text{O}$ of vapor in a *closed* system where the vapor (line E) and water (line D) remain in contact. In both cases, the evaporation takes place under equilibrium conditions with $\alpha = 1.010$, but the cumulative vapor in the closed system *remains* in equilibrium with the water during the entire phase change. As a rule, fractionations in a true "open-system" Rayleigh process create a much larger range in the isotopic compositions of the products and reactants than in closed systems. This is because of the lack of back reactions in open systems. Natural processes will produce fractionations between these two "ideal" cases.

Other non-equilibrium fractionations may behave like Rayleigh fractionations in that there may be negligible back reaction between the reactant and product, regardless of whether the system is open or closed, because of kinetics. Such fractionations typically result in larger ranges of composition than for equivalent equilibrium reactions. An example of this process is biologically mediated denitrification (reduction) of nitrate to N_2 in groundwater; the N_2 is lost so it can't re-equilibrate with the nitrate, even if there was a back reaction by this organism, which there isn't. Figure 2.4 shows how Rayleigh-type fractionations affect the compositions of residual substrate, instantaneous product, and cumulative product (curved lines) during a *closed*-system kinetic reaction (e.g., denitrification, uptake of N by plants, or nitrification). Note that at all times, the δ values of instantaneous product are " ϵ ‰" less than the corresponding δ values of residual substrate. The parallel straight lines are the compositions for an *open*-system kinetic reaction where the supply of substrate is infinite and, hence, is not affected by the conversion of some substrate to product with a constant fractionation of ϵ .

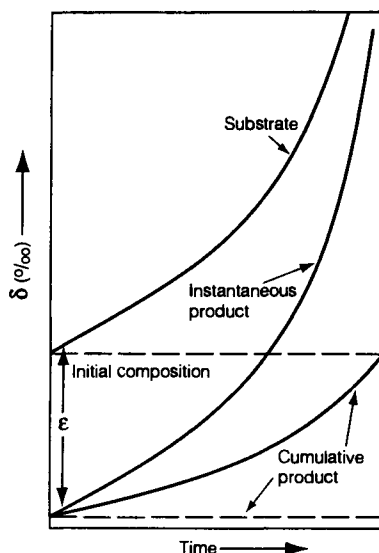


Figure 2.4. Relative changes in δ values of substrate, instantaneous product and cumulative product during closed-system (solid curved lines) and open-system (dashed straight lines) kinetic fractionation processes. In an open system, the supply of reactant is infinite; in a closed system, it is finite. At all times, the compositions of the instantaneous product and substrate differ by ϵ , the enrichment factor. For the open system, both the instantaneous and the cumulative product fall along the same line, parallel to the substrate-composition line but lower than it by ϵ . Modified from Högberg, 1997.

The curved lines on Figure 2.4 are very similar to the curved lines on Figure 2.3, which is reasonable since they are both solutions of the same Rayleigh equations. However, the ones in Figure 2.3 describe an *open*-system equilibrium process whereas the ones in Figure 2.4 describe a *closed*-system kinetic process. Furthermore, the straight lines in Figure 2.3 depict a *closed* system and the dissimilar but also straight lines in Figure 2.4 depict an *open* system. What is going on here? How can the same Rayleigh equations be used to produce fractionation curves described so differently?

The answer lies with where the *boundary lines* are drawn between the system being studied and the rest of the universe. In the case of the *equilibrium* fractionations illustrated in Figure 2.3, "open" means that the product, once formed at equilibrium, escapes to outside the system and does not interact again with the residual substrate (and, consequently, is no longer in equilibrium with the substrate). And "closed" means that the reactant and product remain in close contact, in their own closed (finite) system during the entire reaction, so that the two reservoirs are always in chemical and isotopic equilibrium. For the *kinetic* fractionations illustrated in Figure 2.4, "open" means that the supply of substrate is infinite (which it can't be in a closed system). The use of "closed" for kinetic reactions suggests that there is a limited supply of reactant, which is undergoing irreversible, quantitative, conversion to product in an isolated system.

Thusfar, a constant fractionation factor was assumed to apply throughout the process. However, this is not always the case. For example, rainout from an air mass is usually the result of a continuous cooling of the air parcel. The cooling increases the fractionation factor for the vapor-to-water (or vapor-to-ice) transition. Another conspicuous example of a changing "effective" fractionation factor is that of the evaporation of water from a surface water body to the atmosphere. As will be shown, the change in this situation is the result of the changing conditions (in this case, of the isotopic gradient) at the water-atmosphere boundary, rather than a change of the fractionation factors themselves.

Almost everyone finds the Rayleigh equations a bit confusing. Hence, we will now give some examples of how to calculate open- and closed-system fractionations, and how they affect the compositions of the residual substrate and the newly formed products of a reaction. Because much of the book focuses on *water* and its isotopes, we will demonstrate how to apply the Rayleigh equations by using the fractionations during water phase changes (i.e., during the condensation of vapor and the evaporation of water) as examples. For a more rigorous discussion of the topic, see Gat and Gonfiantini (1981) or Gat (1996); chapter 2 of Clark and Fritz (1997) provides a well-illustrated and exceptionally clear discussion of this fascinating topic. Many other reactions (e.g., sulfate reduction, methane oxidation, ammonia volatilization, and nitrification) can also be modeled with Rayleigh-type models; the same principles described here apply to these kinetic reactions.

Condensation of water

The isotopic composition of moisture in the marine atmosphere is controlled by the air-sea interaction processes as described by Craig and Gordon (1965), Merlivat and Jouzel (1979), and others. As air masses move across continents and lose water by rainout, they become *depleted* in the heavy isotopic species (H_2^{18}O and HDO) because the liquid phase is *enriched* in the heavy isotopic species relative to the vapor phase (see Chapter 3). The evolution of the isotopic composition is adequately described by a Rayleigh process (in this case it is condensation) in those cases where rainout is the only factor in the atmospheric-moisture budget (Dansgaard, 1964; Gat, 1980). A Rayleigh fractionation plot for condensation would

be very similar to Figure 2.3, except that all the curves would bend down instead of up because the residual vapor and water condensed would become progressively *lighter* over time, not heavier (as they do for evaporation).

When the isotopic compositions of precipitation samples from all over the world are plotted relative to each other on $\delta^{18}\text{O}$ versus δD plots, the data form a linear band of data that can be described by the equation (Craig, 1961):

$$\delta\text{D} = 8 \delta^{18}\text{O} + 10 \quad (2.14)$$

and is called the *Global Meteoric Water Line* (GMWL) or just the *MWL*, or even the *Craig Line*. The slope is 8 (actually, different data sets give slightly different values) because this is approximately the value produced by equilibrium Rayleigh condensation of rain at about 100% humidity. The value of 8 is also close to the ratio of the equilibrium fractionation factors for H and O isotopes at 25–30°C. At equilibrium, the δ values of the rain and the vapor both plot along the MWL, but separated by the ^{18}O and ^2H enrichment values corresponding to the temperature of the cloud base where rainout occurred.

The y-intercept value of 10 in the GMWL equation is called the *deuterium excess* (or d-excess, or d parameter) value for this equation. The term only applies to the calculated y-intercept for sets of meteoric data "fitted" to a slope of 8; typical d-excess values range from 0 to 20 (see Chapter 3). The fact that the intercept of the GMWL is 10 instead of 0 means that the GMWL does not intersect $\delta^{18}\text{O} = \delta\text{D} = 0$, which is the composition of average ocean water (VSMOW). The GMWL does not intersect the composition of the ocean, the source of most of the water vapor that produces rain, because of the $\approx 10\%$ kinetic enrichment in D of vapor evaporating from the ocean at an average humidity of 85%.

The Rayleigh law is formulated in approximate differential form and using δ notation as:

$$d\delta \approx \epsilon^* \cdot d\ln f \quad (2.15)$$

where $f = N_f/N_0$ is the fraction of remaining water (N_0 and N_f being the water content of the air mass before and after the rain, respectively) so that $(N_0 - N_f)$ is the total water loss (rainout) from the air mass. The term ϵ^* is related to α^* , the unit equilibrium isotope fractionation factor between water and its vapor at the ambient near-surface air temperature, as follows:

$$\epsilon^+ = (\alpha^+ - 1) \cdot 10^3. \quad (2.16)$$

Note that this equation is the same as Equation 2.6, except for the superscripts. Why the change? Because of some historical choices made to simplify mathematical expressions.

The equilibrium fractionation factor α between liquid and vapor can be defined in two ways, which are mathematical inverses: $\alpha = R_l/R_v$ or $\alpha = R_l/R_v$, where R_l and R_v are the isotopic ratios of the liquid and vapor, respectively. However, Craig and Gordon (1965) defined equilibrium fractionation factors such that $\alpha^+ = 1/\alpha^*$, so that $\alpha^+ = R_l/R_v > 1$ and $\alpha^* = R_v/R_l < 1$ (and, consequently, $\epsilon^+ > 0$ and $\epsilon^+ \approx -\epsilon^*$). This usage has become traditional when discussing atmospheric processes. In general, α^+ (often abbreviated to simply α) is used for condensation problems, whereas α^* is commonly preferred for evaporation problems. Values for α^+ can be calculated from Majoube (1971). Although the use of α^+ vs. α^* may simplify calculations, many other people find it more convenient to use the definition of fractionation factor that produces $\alpha > 1$, despite tradition.

As rain condenses, the heavier isotopes of water (mainly HD^{16}O and H_2^{18}O) are preferentially removed from the air mass (and into the rain), and the air mass consequently becomes progressively lighter in isotopic composition (i.e., higher concentrations of H_2^{16}O). Hence, the isotopic compositions of successive aliquots of rain become progressively lighter in the heavier isotope due to continuing rainout of the heavy isotopes. As will be described in Chapter 3, this is why the δ values of rain become lighter as storms move inland from the ocean. At any point along the storm trajectory (i.e., for some specific fraction f of the total original vapor mass), the $\delta^{18}\text{O}$ of the residual fraction of vapor in the air mass can be calculated by:

$$\delta \approx \delta_o + \epsilon \ln(f) \quad (2.17)$$

$$\delta^{18}\text{O}_v \approx \delta_o^{18}\text{O}_v + \epsilon_{l-v} \cdot \ln f \quad (2.18)$$

where $\delta_o^{18}\text{O}_v$ is the initial δ value of the vapor (remember that $\ln x < 0$ for $x < 1$, so that the residual vapor is lighter than the initial vapor). The $\delta^{18}\text{O}$ of the of the rain produced at this point can be determined by:

$$\delta^{18}\text{O}_l \approx \delta^{18}\text{O}_v + \epsilon_{l-v} \quad (2.19)$$

where ϵ_{l-v} (the enrichment of liquid relative to vapor, equivalent to ϵ^+ in the discussion above) is constant. For a system with changing temperature, the relation has to be integrated to account for the change in ϵ as a function of temperature.

Another commonly used formulation of the Rayleigh equation for systems with a constant fractionation factor is: $\delta \approx \delta_o - \epsilon \ln(f)$. In this case, the enrichment factor in the Rayleigh equation has a negative sign, instead of the positive sign shown earlier (Equation 2.17), because of different definitions for α (and hence for ϵ values). The choice of either α^* or its reciprocal value α^+ for the equilibrium fractionation factor is dictated only by convenience; there is no "right" way. If there is any confusion about how the fractionation terms are defined in some paper, just try a few test calculations to make sure the δ values for a reaction change in the "right" direction (e.g., with biological reactions, residual reactants get heavier; during condensation of rain, residual vapor gets lighter; etc); if the δ values don't change as expected, this probably means that the fractionation factor being used is the inverse of what should be used in the equation.

Evaporation of water

Evaporation from an open-water surface fractionates the isotopes of hydrogen and oxygen in a manner which depends on a number of environmental parameters, the most important of which is the ambient humidity. This is illustrated for various relative humidities in Figure 2.5. The higher the humidity, the smaller the change in $\delta^{18}\text{O}$ and δD during evaporation. For example, at 95% humidity, the δ values are constant for evaporation of the last 85% of the water. Evaporation results in lines with slopes < 8 on a $\delta^{18}\text{O}$ vs. δD plot (i.e., the data plot on lines *below* the MWL that intersect the MWL at the composition of the original water).

Evaporation at 0% humidity describes open-system evaporation ("open" in terms of the definitions for Figure 2.3). Note that the two upper diagrams on Figure 2.5 are Rayleigh-type plots, similar to Figure 2.3 but with larger changes in $\delta^{18}\text{O}$ during open-system evaporation on Figure 2.5. The δ values on the curved fractionation lines on the upper diagrams plot along nearly straight lines on the lower $\delta^{18}\text{O}$ vs. δD plot. The "length" of the evaporation lines on the

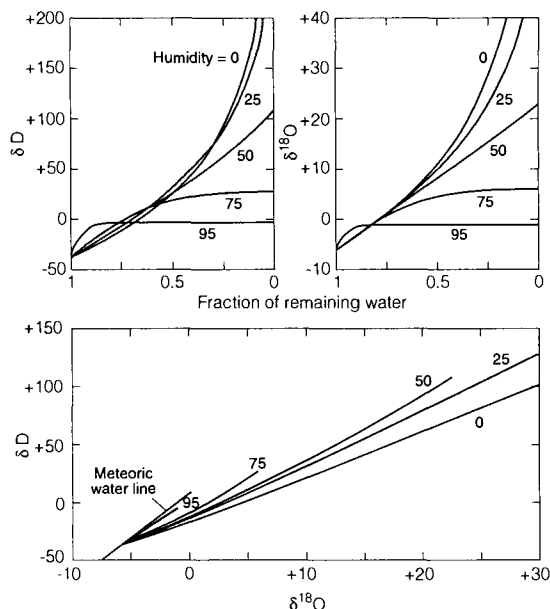


Figure 2.5. The effect of humidity on the $\delta^{18}O$ and δD values of the residual water fraction during evaporation. Higher humidities result in less fractionation because of back exchange between the water and the vapor, and evaporation lines with higher slopes. Modified from Gat and Gonfiantini (1981).

$\delta^{18}O$ vs. δD plot reflect the range of values of water produced during total evaporation under different humidities. For example, the short line for 95% humidity indicates that the water changes little during the entire evaporation process.

Evaporation under almost 100% humidity conditions is more-or-less equivalent to evaporation under closed-system conditions (i.e., isotopic equilibrium is possible), and data for waters plot along a slope of 8 (i.e., along the MWL). However, the shapes of the curves in the upper diagrams for 95% humidity are not the same as for closed-system *equilibrium* fractionation (Figure 2.3); instead, they are similar to the infinite-reservoir *kinetic* fractionation shown on Figure 2.4. This is because the curves in Figure 2.5 were calculated using both an equilibrium fractionation for the phase change and a kinetic fractionation (Equation 2.20) for the diffusion of water vapor across the water-atmosphere interface (Gat and Gonfiantini, 1981). This is also the explanation for the larger open-system fractionations on Figure 2.5 than on Figure 2.3.

The most useful model for the isotope fractionation during evaporation is that of Craig and Gordon (1965). It is schematically shown in Figure 2.6 (redrawn from Gat, 1996). This model assumes that equilibrium conditions apply at the air/water interface (where the humidity is 100%), that there is a constant vertical flux, and that there is no fractionation during fully turbulent transport. For a detailed derivation, see Craig and Gordon (1965) or Gat (1996).

At the water-air interface, there is a balance between two opposing water fluxes: one upward from the water surface and one downward consisting of atmospheric moisture. When the humidity is 100% (i.e., the air is saturated), the upward and downward physical fluxes can

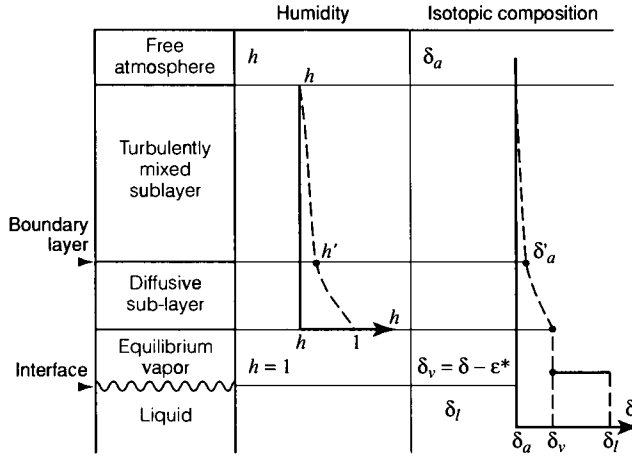


Figure 2.6. The Craig-Gordon model for isotopic fractionation during the evaporation of water, showing how isotopic composition and humidity change across different layers above the water. Modified from Gat (1996).

become equivalent and their isotopic compositions may then reach equilibrium (note that equilibrium does *not* mean that the δ values of the two reservoirs are identical, only that they differ by the equilibrium enrichment factor); see Clark and Fritz (1997) pages 26-27.

The changes in humidity and corresponding changes in the isotopic composition of vapor across the transition between the water and the free atmosphere are given as dashed lines in Figure 2.6. Note that where $h = 1$ (in the so-called "equilibrium vapor" layer between the interface and the boundary layer where the humidity is 100%), the vapor is in equilibrium with the liquid (i.e., $\delta_v = \delta - \epsilon^*$). When the air is undersaturated (i.e., $h < 1$), a net evaporative flux is produced. The rate determining step for evaporation is the diffusion of water vapor across the air boundary layer, which occurs in response to the humidity gradient between the surface and the fully turbulent ambient air (Figure 2.6).

The isotopic composition of the evaporated moisture (for either oxygen or hydrogen isotopes) can be formulated as:

$$\delta_E = (\alpha^* \delta_w - h \delta_a - \epsilon) / [(1 - h) + \Delta \epsilon / 1000] \approx (\delta_w - h \delta_a - \epsilon) / (1 - h) \quad (2.20)$$

where $\epsilon = \epsilon^* + \Delta \epsilon$, $\epsilon^* = (1 - \alpha^*) \cdot 10^3$, $\alpha^* < 1$, and the variable $\Delta \epsilon$ is an additional diffusive (kinetic) isotope fractionation which results from the different diffusivities of the water molecules of various isotopic compositions in the liquid-air boundary layer (i.e., an additional fractionation caused by diffusion across the humidity gradient between the "equilibrium vapor layer" and the turbulently mixed vapor sublayer on Figure 2.6). Hence, the total fractionation ϵ equals the sum of the equilibrium and kinetic fractionations. δ_w and δ_a are the isotopic compositions of the surface water and the atmospheric moisture (vapor), respectively, with all parameters in ‰ units. Relative humidity, h , is normalized to the saturated vapor pressure at the temperature of the lake surface water, and is written as a fraction < 1 . According to the Craig and Gordon (1965) model, $\Delta \epsilon$ has the form:

$$\Delta\epsilon = (1 - h) \cdot \theta \cdot n \cdot \epsilon_k \quad (2.21)$$

where ϵ_k is a "kinetic" constant with values of 25.1‰ and 28.5‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively (Merlivat, 1978), and $0.5 \leq n \leq 1$. The weighting term θ can be assumed equal to 1 for small bodies of water whose evaporation flux does not perturb the ambient moisture significantly (Gat, 1995), but has been shown to have a value of 0.88 for the North American Great Lakes (Gat et al., 1994) and a value of about 0.5 for evaporation in the eastern Mediterranean Sea (Gat et al., 1996). For an open water body, a value of $n = 0.5$ seems appropriate (Gat, 1996). However, for evaporation of water through a stagnant air layer such as in soils (Barnes and Allison, 1988) or leaves (Allison et al., 1985), a value of $n \approx 1$ fits the data reasonably well. See Chapters 5 and 6 for discussion of evaporation in soils and plants. Note that in some articles the ϵ_k values in Equation 2.21 are modified by multiplication by 1000 (or need to be) because the values for ϵ_k may not be in ‰.

The values of δ_E and δ_w define a line in $\delta^{18}\text{O}$ vs. δD space called the *evaporation line* (Figures 2.5 and 2.7) whose slope is given by:

$$S = [h(\delta_a - \delta_w) + \epsilon]_{2\text{H}} / [h(\delta_a - \delta_w) + \epsilon]_{18\text{O}} \quad (2.22)$$

To preserve mass balance, the initial water composition, the evaporated moisture, and the residual water (such as lake waters or soil waters) must all plot along this same line. The slope of the evaporation line is determined by the air humidity (Figure 2.5), and the equilibrium and kinetic fractionations (ϵ^* and $\Delta\epsilon$), which are dependent themselves on temperature and boundary conditions, respectively. The slopes of evaporation lines on Figure 2.5 range from 3.9 (for humidity = 0) to 6.8 (for humidity = 95%). The δ_E value plots above the MWL (Figure 2.7). This evaporated vapor will mix with ambient vapor δ_a to produce vapor with a higher d-excess value than the original vapor, and can affect the δ values of later rain from the airmass.

When part of the rained-out moisture is returned to the atmosphere by means of evapo-transpiration, then a simple Rayleigh law no longer applies. The downwind effect of the evapo-transpiration flux on the isotopic composition of the atmospheric moisture and precipitation

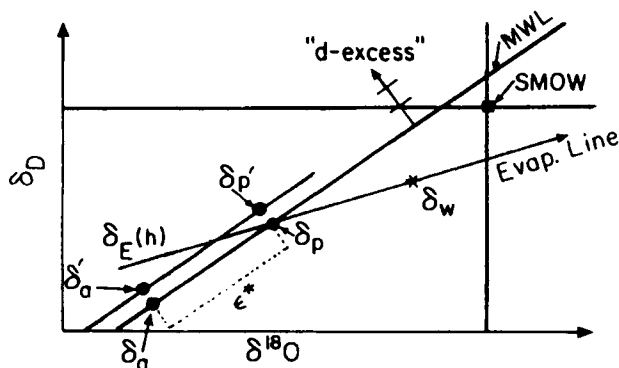


Figure 2.7. The isotopic compositions of evaporated surface water (δ_w), the original precipitation prior to evaporation (δ_p), and the evaporated vapor (δ_E) all plot along the same evaporation line. Both the precipitation (δ_p) and the atmospheric vapor (δ_a) in equilibrium with it plot along the MWL, separated by the enrichment factor for the environmental temperature (ϵ^*). When the evaporate (δ_E) mixes with the local atmospheric vapor (δ_a), a new vapor (δ_a') is formed that plots above the MWL. If rain later condenses from this vapor, it would plot along a new line parallel to the MWL but with a higher *d-excess* value. (From Gat et al., 1994).

depends on the details of the evapo-transpiration process. Transpiration returns precipitated water essentially unfractionated to the atmosphere, despite the complex fractionations in leaf water (see Chapter 6). Thus, transpiration cancels out the effect of the rainout process. In other words, admixture of transpired waters moves the isotopic composition of the atmospheric moisture back towards more positive δ values (i.e., enriched in the heavy isotopic species), as if rain never took place. Under such circumstances, the change in the isotope composition along the air-mass trajectory measures only the net loss of water from the air mass, rather than being a measure of the integrated total rainout. On the other hand, evaporated vapor (δ_e) is usually depleted in the heavy isotopic species relative to that of transpired water (δ_T) and is actually closer to the composition of the atmospheric moisture. Hence mixing of moisture derived from the evaporation of lake water back into the atmospheric moisture reservoir has a somewhat smaller effect than the addition of transpired water in restoring isotopic composition of the original air mass.

2.3.5 Biological fractionations

Biological processes are generally unidirectional and are excellent examples of *kinetic* isotope reactions. Organisms preferentially use the lighter isotopic species because of the lower energy "costs" associated with breaking the bonds in these molecules, resulting in significant fractionations between the substrate (heavier) and the biologically mediated product (lighter). Kinetic isotopic fractionations of biologically-mediated processes vary in magnitude, depending on reaction rates, concentrations of products and reactants, environmental conditions, and -- in the case of metabolic transformations -- species of the organism. The variability of the fractionations makes interpretation of isotopic data difficult, particularly for nitrogen and sulfur. The fractionations are very different from, and typically larger than, the equivalent equilibrium reaction. The magnitude of the fractionation depends on the reaction pathway utilized (i.e., which is the rate-limiting step) and the relative energies of the bonds severed and formed by the reaction. In general, slower reaction steps show greater isotopic fractionation than faster steps because the organism has time to be more selective (i.e., the organism saves internal energy by preferentially breaking light-isotope bonds).

If the substrate concentration is large enough that the isotopic composition of the reservoir is insignificantly changed by the reaction (O'Leary, 1981) or if the isotopic ratio of the product is measured within an infinitely short time period (Mariotti et al., 1981), the fractionation factor can be defined as in Equation 2.8 (i.e., the straight lines on Figure 2.4 for the "open system model"). For unidirectional reactions (Figure 2.4, curved lines), the change in the isotope ratio of the substrate relative to the fraction of the unreacted substrate can be described by the Rayleigh equation:

$$R_s / R_{s0} = f^{(\alpha-1)} \quad (2.23)$$

where R_s and R_{s0} are the ratios of the unreacted and initial substrate, respectively, and f is the fraction of unreacted substrate. Figure 2.8 shows the changes in compositions of residual NO_3 , incremental N_2 produced, and cumulative N_2 for denitrification with a fractionation factors of $\beta = 1.005, 1.010$, and 1.020 (i.e., the organism preferentially utilizes the lighter isotope), which are equivalent to $\alpha = 0.995, 0.99$, and 0.98 , respectively. In the final stages of the reaction, when the NO_3 is almost gone, the isotopic compositions of the residual reactant and incremental product increase dramatically, reaching very high values when the reaction is almost complete (see Chapter 16).

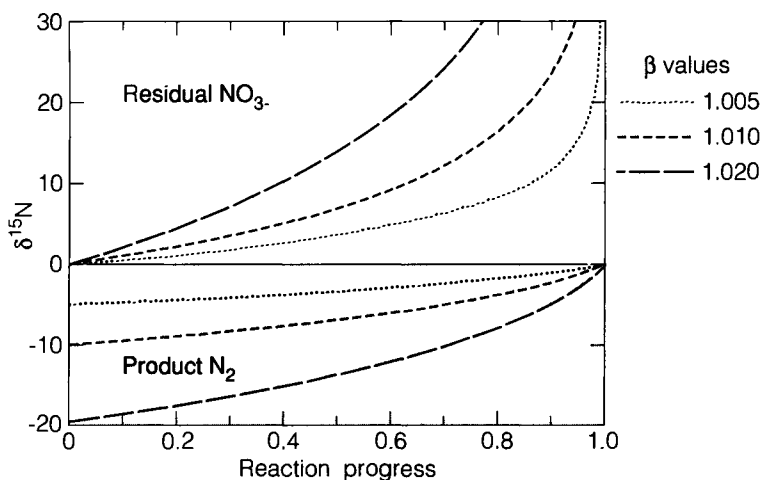


Figure 2.8. Reaction progress vs. the $\delta^{15}\text{N}$ values of residual reactant (NO_3^-) and cumulative product (N_2) resulting from denitrification with fractionation factors (β) of 1.005, 1.010, and 1.020. The higher the β value, the higher the $\delta^{15}\text{N}$ of the NO_3^- and the lower the $\delta^{15}\text{N}$ of the N_2 .

Readers of this book and articles dealing with isotope fractionations must be careful: both fractionation and enrichment factors are defined in various ways by different authors, especially in the biological literature. Kinetic fractionation factors are typically described in terms of enrichment or discrimination factors, using such symbols as β , ϵ , or D . In particular, the enrichment factor is sometimes defined in reverse (i.e., $\epsilon_{s/p}$), and some researchers define a "discrimination factor" $D_{s/p} = (\alpha_{s/p} - 1)1000$, where s/p denotes "substrate relative to products." Good discussions of fractionations associated with biological processes include Hübner (1986) and Fogel and Cifuentes (1993).

A good example of the complexities of kinetic reactions is given by the fractionation between CO_2 and photosynthetic organic carbon. The fractionation can be described by the model (Fogel and Cifuentes, 1993):

$$\Delta = A + (C_i / C_a)(B - A) \quad (2.24)$$

where Δ is the isotopic fractionation, A is the isotope effect caused by diffusion of CO_2 into the plant (-4.4‰), B is the isotope effect caused by enzymatic (photosynthetic) fixation of carbon (-27‰), and C_i/C_a is the ratio of internal to atmospheric CO_2 contents. The magnitude of the fractionation depends on the values of the above parameters. For example, when there is unlimited CO_2 (i.e., $C_i/C_a = 1$), the enzymatic fractionation controls the $\delta^{13}\text{C}$ of the plant, with plant $\delta^{13}\text{C}$ values as low as -36‰ (Fogel and Cifuentes, 1993). Alternatively, if the CO_2 content is limiting ($C_i/C_a \ll 1$) and the diffusion of CO_2 into the cell is rate determining, $\delta^{13}\text{C}$ values will be strongly affected by the smaller diffusional isotope effect, resulting in more positive $\delta^{13}\text{C}$ values (-20 to -30‰).

2.4 Sample Collection, Analysis, and Quality Assurance

2.4.1 Sampling guidelines

Considerable field effort is often required to collect a sample that adequately represents the average composition of the medium being sampled, at the time it is sampled. For small streams, this can be as simple as collecting water as it flows over a weir or rock ledge. For large rivers, lakes, soils, and organisms, mass-integrated composites may be required. Adequate coverage of this vital topic is beyond the scope of this chapter. The reader is advised to look at the references given in subsequent chapters, or consult colleagues who routinely collect such samples. Other useful sources of information include: Clark and Fritz (1997; chapter 10: "Field methods for sampling"), Mazor (1997), and the Web pages of various isotope laboratories.

Below is a potpourri of guidelines and suggestions related to collecting, bottling, and preserving samples for analysis of the most commonly-used environmental isotopes. The reader should keep in mind that the optimum methods often depend on the laboratory chosen for analysis and their preferred preparation methods, and should always inquire before planning the field campaign. Collection of duplicates is always advisable -- in case of breakage of samples during transport and to use as checks of the reproducibility of the laboratory (i.e., submit 5-10% of these as "blind duplicates," with different sample ID numbers than their duplicates).

$\delta^{18}O/\delta^2H$ of water

Natural waters are easy to collect. The water sample is put in a clean dry bottle, which is filled almost completely to the top, and capped tightly. The main objective is to protect the sample from evaporation and exchange with atmospheric water vapor. Samples should not be filtered unless they contain oil (e.g., mineral oil added to rain collectors to help prevent evaporation) or contain abundant particulate matter. Bottle rinsing, chilling, and addition of preservatives are unnecessary. Freezing does not affect the composition of the water but can break the bottles in transit; for this reason, many users prefer plastic bottles. Our experience suggests that caps with conical plastic inserts (e.g., "poly-seal" caps) are the most reliable, followed by teflon-lined caps. For extended storage, use of glass bottles and waxing of the caps is advisable. Sample-size is lab-dependent; typical volumes range from 10-60 mL. In some laboratories, samples as small as a few μL can be analyzed.

Determinations of both hydrogen and oxygen isotope ratios are usually made on the same bottle of water. It is wise to collect many more samples than one can afford to analyze at the present; samples have a long shelf life if bottled correctly, and can be archived for future analysis. One should make sure that the laboratory chosen to analyze the samples normalizes their values according to IAEA guidelines (Coplen, 1994), and reports values relative to VSMOW. If the samples are saline, one should check whether the lab is preparing samples by an equilibration or quantitative-conversion method (see below). Waters with high contents of volatile organic matter may require distillation.

For many purposes, especially hydrograph separations (see Chapter 1), analysis for all samples for both oxygen and hydrogen isotopes is unnecessary because of the high correlation coefficient between these isotopes (see Chapter 3). A sensible alternative is to have some smaller percentage analyzed for both isotopes, either initially or after the data for the first

isotope are evaluated. For hydrograph studies in arid environments or studies that involve evaporated water in ponds or wetlands, analysis of samples for both isotopes is probably advisable. Because most labs have fewer problems analyzing waters for $\delta^{18}\text{O}$ than for $\delta^2\text{H}$, if the samples are not analyzed in duplicate and will only be analyzed for one isotope, it is usually better to choose $\delta^{18}\text{O}$.

Solid and vapor samples are more difficult to collect for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Snow and ice samples can be collected in tightly sealed bags or jars, melted overnight, and then poured into bottles. Plant and soil samples should be collected in air-tight containers matched to the sample size. Common procedures include waxing of soil cores, use of heat-sealed bags, or insertion into tiny tree-core-size vials. Water vapor samples are collected by pumping vapor through a cold-trap where the vapor is quantitatively retained. For more information on various sampling procedures, see Chapters 3-6.

Tritium

The amount of water needed for tritium analysis depends on the age of the water (old waters contain little tritium) and the sensitivity of analysis needed. Typical sample sizes range from 10 mL to 1L. Samples are collected in unrinsed glass or high-density polyethylene bottles and should not be filtered. The bottles should then be sealed and returned to the laboratory for analysis. The collection date should be noted on the bottle to obtain an accurate determination of the tritium concentration for the time of collection.

$\delta^{13}\text{C}$ and ^{14}C of dissolved inorganic carbon

There are two main methods in common use for the collection of DIC (dissolved inorganic carbon) for the measurement of ^{13}C or ^{14}C , depending on which of two laboratory preparation methods is being used: gas stripping or carbonate precipitation. Both preparation methods insure quantitative removal of the DIC and provide a $\delta^{13}\text{C}$ or ^{14}C value for total DIC. Analysis for $\delta^{13}\text{C}$ generally requires 10-100 μM of carbon. Analysis of ^{14}C by conventional beta-counting methods requires as much as 1 g of C; analysis by AMS usually requires about 1 mg of C.

For laboratories that use a gas-stripping method to extract the CO_2 , samples are usually collected in sample-rinsed glass bottles with septa-caps, or in vessels with stopcocks or valves. Such samples should be filtered to remove particulate carbon, and perhaps poisoned (using mercuric chloride, acid, or organic biocide) to prevent biological activity; the bottles should be kept chilled until analyzed to prevent biological fractionations.

The alternative technique is the precipitation method. Samples should be pre-filtered if there might be suspended carbonate particulate material in the water. The carbonate is precipitated by adding a strongly basic solution of strontium or barium chloride (Gleason et al., 1969) to the sample in a sample-rinsed bottle. The base increases the pH to 10-11 where all the inorganic carbon is CO_3^{2-} , and the Ba or Sr precipitates all the DIC in the water. This reagent and the treated samples must be protected against contamination by atmospheric CO_2 . Glass bottles are best because CO_2 diffuses through most plastic bottles. Bottles should have poly-seal caps that are taped securely. Bottles should be individually wrapped in bubble paper and shipped in insulated boxes or coolers filled with artificial "peanuts" to insure against breakage.

$\delta^{15}\text{N}$ of dissolved inorganic nitrogen

A number of different preparation methods are in common use; inquire what collection method is preferred by the contract laboratory for their particular preparation method. In particular, it

is important to verify that the laboratory is accustomed to analyzing *natural abundance* samples. Laboratories that primarily analyze agricultural samples often use methods that are appropriate for labeled (^{15}N -spiked) samples but have unacceptable analytical precisions for natural abundance studies. Check that the laboratory has a good track record for natural abundance samples. Samples can be analyzed for the $\delta^{15}\text{N}$ of ammonium and/or nitrate; analysis of total nitrogen is probably worthless. Generally, samples are filtered through 0.1 micron filters, put in rinsed glass bottles, poisoned (with sulfuric acid, mercuric chloride, or chloroform), chilled or frozen, wrapped in insulating packing material, and sent to the laboratory in ice chests. Sample-size requirements are in the range of 10-100 μM of N. Nitrate samples can also be analyzed for $\delta^{18}\text{O}$ in a few laboratories.

An alternate method is to concentrate the NO_3 or NH_4 on anion or cation exchange resins (Garten, 1992; Silva et al., submitted; Chang et al., in review). Collection of nitrate on anion exchange resins eliminates the need to send large quantities of chilled water back to the laboratory, eliminates the need for hazardous preservatives, makes it easier to archive samples, and allows analysis of extremely low-nitrate waters.

$\delta^{34}\text{S}$ of dissolved sulfate

Depending on the sulfate concentration, samples are filtered directly into glass bottles or are first pre-concentrated on an exchange resin. Sulfate from dilute waters should be collected on ion exchange resin in the field if the concentration of sulfate in the water is believed to be less than 20 mg/L. Similar to collection methods for NO_3 or NH_4 on ion exchange resins, collection of sulfate on exchange resins avoids problems of incomplete precipitation of BaSO_4 in dilute samples, eliminates the need to send large quantities of chilled water back to the lab, eliminates the need for hazardous preservatives, makes it easier to archive samples, and allows analysis of extremely low-sulfate waters.

Low-sulfate water samples are first acidified before passing through ion exchange columns. The sulfate is then eluted from the resin using a relatively small volume of concentrated barium chloride solution. The final volume of the solution is much less than that of the original water sample and the sulfate from the sample is thus concentrated in this much smaller volume (generally 10-500 μM of SO_4 is required). The solution is reacidified and sulfate is precipitated by adding BaCl_2 . BaSO_4 is then collected by filtration and analyzed for $\delta^{34}\text{S}$. Sulfate can also be analyzed for $\delta^{18}\text{O}$ in some laboratories. Large quantities of sulfate can also be analyzed for ^{35}S , a natural radioisotope with a half-life of 87 days, using liquid scintillation counting.

C, H, N, O, and S isotopes of solid samples

Solid organic and inorganic samples (e.g., animals, plants, minerals, and soils) and liquids (such as oils) can also be analyzed for their isotopic composition. Particulate matter in water can be captured on fiberglass filters and processed similar to methods used for other solid samples. Requirements for solid samples are similar to the requirements for solute samples of the same element (i.e., 1-100 μM of the element of interest). Biologically labile samples (e.g., leaves, fish, manure) should be kept cold until processed. Freeze-drying is an ideal means for preserving the samples; air-drying results in loss of volatile organic matter and probably some isotopic fractionation.

Lithogenic (metals and semi-metals) isotopes

The sample size is dependent on the species being analyzed. Analysis of Sr, Li, or B requires a minimum of 1 μg ; Pb and Nd require a minimum of 0.1 μg . Aqueous samples should be

filtered; 0.1 micron filters are best for Nd and Pb, and 0.45 micron filters are best for Sr, Li, and B (Thomas D. Bullen, pers. comm. 1997). Aqueous samples are collected in rinsed plastic bottles and acidified to $\text{pH} \approx 2$ using Ultrex HNO_3 . Blanks should be sent to the laboratory along with your samples, including the triple distilled water used for filtering and the clean water run through the processing equipment. One must be careful about possible contamination with lithium grease, borate soaps or detergents, and strontium chloride reagents.

2.4.2 Analytical methods and instrumentation

Stable isotopes are analyzed either on *gas-* or *solid-source* mass spectrometers, depending on both the masses of the isotopes and the existence of appropriate gaseous compounds stable at room temperature. Radioisotopes can be analyzed by counting the number of disintegrations per unit time on gamma ray or beta particle counters, or analyzed on mass spectrometers.

Gas-source mass spectrometers

Many methods are used to prepare gases for C, H, N, O, and S (CHNOS) stable isotope content, but in all the cases the basic steps are the same. Sample preparation involves the quantitative conversion or production of pure gas from solely the compound of interest, cryogenic or chromatographic purification of the gas, introduction of the gas into the mass spectrometer, ionization to produce positively charged species, dispersion of different masses in a magnetic field, impaction of different masses on different collector cups, and measurement of the ratios of the isotopes in the ionized gas. In general, hydrogen is analyzed as H_2 , oxygen and carbon are both analyzed as CO_2 , nitrogen is analyzed as N_2 , and sulfur is usually analyzed as SO_2 . The analytical precisions are small relative to the ranges in δ values that occur in natural earth systems. Typical one standard deviation analytical precisions for oxygen, carbon, nitrogen, and sulfur isotopes are in the range of 0.05 to 0.2‰; typical precisions for hydrogen isotopes are poorer, from 0.2 to 1.0‰, because of the lower $^2\text{H}:^1\text{H}$ ratio.

Although the topic is rarely discussed, the activity coefficients of isotopic species are not all equal to 1 (i.e., the isotope *concentration* of a sample is not necessarily equal to the isotope *activity*). The activity coefficient for a particular isotope can be positive or negative, depending on solute type, molality, and temperature. The isotopic compositions of waters and solutes can be significantly affected by the concentration and types of salts because the isotopic compositions of waters in the hydration spheres of salts and in regions farther from the salts are different (see Horita (1989) for a good discussion of this topic). In general, the only times when it is important to consider isotope activities is for low pH, high SO_4 , and/or high Mg brines because the activity and concentration δ values of these waters (δ_a and δ_c) are significantly different. For example, the difference ($\delta D_a - \delta D_c$) between the activity and concentration δ values for sulfuric acid solutions in mine tailings is about +16‰ for 2 molal solutions. For normal saline waters (e.g., seawater), the activity coefficients for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are essentially equal to 1.

Virtually all laboratories report $\delta^{18}\text{O}$ activities (not concentrations) for water samples. The $\delta^2\text{H}$ of waters may be reported in either concentration or activity δ values, depending on the method used for preparing the samples for analysis. Methods that involve *quantitative conversion* of the H in H_2O to H_2 , produce δ_c values. Methods that *equilibrate* H_2O with H_2 (or H_2O with CO_2) produce δ_a values. "Equilibrate" in this case means letting the liquid and gas reach isotopic equilibrium at a constant, known temperature. To avoid confusion, laboratories and research papers should always report the method used.

Most conventional CHNOS mass spectrometers are *dual inlet* machines that have both a sample and a standard inlet or introduction port. In such instruments, the ratios of the isotopes of interest (e.g., $^{13}\text{C}/^{12}\text{C}$) in the sample gas are measured relative to the same ratios in a gaseous standard that is analyzed more-or-less simultaneously. Such instruments usually have either "double collectors" or "triple collectors," meaning that either two or three masses of the ionized gas can be measured simultaneously. For example, N_2 contains three species: $^{14}\text{N}^{14}\text{N}$, $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}^{15}\text{N}$ (i.e., masses 28, 29, and 30). A triple-collecting mass spectrometer would measure the abundances of all these species relative to the abundances in a gaseous standard introduced through the "standard" inlet. A double-collecting mass spectrometer would only measure the 28 and 29 masses (actually m/e is measured since the molecules are ionized, with positive charges).

Another type of stable isotope mass spectrometer is the so-called *continuous flow* mass spectrometer. Such instruments may lack a dual inlet, and usually have triple collectors. These instruments represent a "marriage" of chromatography and mass spectrometry, and are similar to conventional organic mass spectrometers in that gas samples are introduced into the mass spectrometer within a stream of helium gas, usually from an automated sample preparation unit (e.g., an elemental analyzer or gas chromatograph). In general, the analytical precision available for continuous flow mass spectrometers is slightly poorer than with conventional methods, but this may change in the next few years. The main advantage of the continuous flow method is that such instruments are very easily combined with various on-line preparation systems, dramatically lowering the manpower cost of isotope analyses. For an exceptionally thorough discussion of modern stable isotope mass spectrometry see Barrie and Prosser (1996).

Solid-source mass spectrometers

Elements analyzed as solids (e.g., strontium, lithium, boron, lead, etc.) are prepared by precipitating selected compounds on wire filaments, loading the filaments into the source of a thermal ionization (solid-source) mass spectrometer, ionizing the compounds to produce gases (negative or positive charged), and measuring the abundances of selected isotopes in the gas on multiple collectors. Some light-mass solids (e.g., boron and lithium) are reported in the standard δ units. Generally, the heavier-mass elements are reported in terms of the relative abundances of two isotopes (e.g., $^{207}\text{Pb}/^{206}\text{Pb}$); however, strontium isotope abundances ($^{87}\text{Sr}/^{86}\text{Sr}$) are occasionally reported in δ notation relative to some arbitrary standard. Solid-source mass spectrometry has been shown to give a more accurate analysis of certain radium and uranium isotopes that conventionally were measured by decay counting methods.

Gas and liquid scintillation counters

Radioactive isotopes can be measured by a number of methods, depending on the mass, abundance, type of decay involved, accuracy desired, and money available. Some, of course, can be analyzed on solid source mass spectrometers (e.g., uranium-series isotopes). Otherwise, radioisotopes are analyzed on liquid scintillation counters (LSC) and gas proportional counters (both with enrichment), and on accelerator mass spectrometers (see below). Liquid scintillation and gas proportional systems are the most common systems used for light isotopes with beta decays. Gas proportional counting usually requires that the isotope being analyzed form a suitable counting gas, so that elements with high electronegativities, such as chlorine and sulphur, are not suitable for this type of analysis. The two isotopes most commonly used in hydrology, tritium and ^{14}C , have generally been analyzed using liquid scintillation or gas proportional counting. Radon is analyzed either by gas Geiger or proportional counting in the field, or sent to a laboratory for liquid scintillation counting, depending on the accuracy desired. For isotopes that decay by gamma and alpha emission, and beta emissions where the

target isotope cannot be reduced to a suitable chemical form for LCS or gas counting, the use of solid scintillation-counting using crystals, or more advanced systems like lithium-germanium drift counters, have been utilized.

Accelerator mass spectrometry

Accelerator mass spectrometers (AMS), sometimes called "tandem" accelerators, are very large (> 10m), expensive, high-resolution, mass spectrometers (with either gas or solid-sources) that accelerate charged particles through very high (mega-volt) electrical fields to separate different isobars and isotopes (Figure 2.1). These instruments can analyze some radioactive species more rapidly, with greater accuracy, and/or with much smaller sample sizes (e.g., mg rather than g samples) than previous counting methods. For example, tritium can now be analyzed using the helium ingrowth method, although it frequently requires long delays (6 months) to accrue enough ^3He to obtain an accurate analysis. AMS has become the method of choice for some isotopes, such as ^{14}C , ^{36}Cl and ^{129}I . It will give accuracies close to those obtained by traditional methods, and samples can be analyzed much more rapidly by AMS.

2.4.3 Quality assurance of contract laboratories

How does one find a good contract laboratory for analyzing samples? Choices include university laboratories, private commercial companies, and government laboratories that can accept contract (or collaborative) work. A primary selection criterion should be that the laboratory has been making the desired type of analysis for several years on a routine basis (e.g., samples submitted to some university laboratories may be analyzed by temporary student help, who do not perform analyses on a routine basis). Make inquiries among colleagues about the long-term track record of the laboratory. Good laboratories have active QA/QC programs, with documentation generally available on request. In our opinion, the laboratory should analyze about 5-15% of the samples in duplicate, as an internal verification that "everything" is operating correctly. Furthermore, laboratories with automated preparation systems and computer-controlled data management systems probably produce better and more reliable data on a long-term basis than laboratories where everything is done manually. The reader is cautioned to beware of bargains (*caveat emptor*); quality work usually costs more than the average price. Furthermore, the potential long-term cost of **wrong** interpretations, due to bad data, should be factored into the total cost of the analyses when evaluating laboratory choices.

One should also consider collecting duplicates in case the sample bottle is broken or lost in transit. Most laboratories routinely analyze each sample only once; if high precision data are required, either request duplicate analysis of each sample (and triplicates if the duplicates do not agree within some predetermined range) or send in "blind" duplicates. Sending in 10-15% blind duplicates is advisable, in any case. If any result seems questionable, immediately request a repeat. Most laboratories keep analyzed samples for a couple months before discarding them and will reanalyze modest numbers of samples at no additional cost.

For water samples, immediately plot the data on a δD vs. $\delta^{18}\text{O}$ diagram; outliers, especially ones that plot appreciably above the GMWL (the line defined by " $\delta\text{D} = 8 \delta^{18}\text{O} + 10$ " -- see Figure 2.7), should be viewed with skepticism and possibly reanalyzed. Few natural processes produce waters that plot significantly above the GMWL; exceptions include methanogenesis in landfills (Baedecker and Back, 1979) and silicate hydrolysis.

2.5 Applications of Isotope Tracers in Catchment Hydrology

The applications of environmental isotopes as hydrologic tracers in low temperature ($< 40^{\circ}\text{C}$) systems fall into two main categories:

- tracers of the water itself: *water isotope hydrology*
- tracers of the solutes in the water: *solute isotope biogeochemistry*.

These classifications are by no means universal but they are conceptually useful and often eliminate confusion when comparing results using different tracers. This book uses this classification for dividing chapters into Part III (Chapters 10 - 14) and Part IV (Chapters 15 - 20). Because the main emphasis of this book is watershed *hydrology* not *biogeochemistry*, much of the discussion in Part II (Chapters 3 - 9) focuses on uses of environmental isotopes to understand sources, ages, and transport of **water**, with extra attention given to understanding the sources of variability in water isotopes because of their leading role as tracers of water. Part V contains two synthesis chapters, one which reviews the "art and science of modeling of environmental isotope and hydrochemical data in catchment hydrology," and one which describes the uses of isotope techniques for understanding environmental change.

Chapters 10 - 22 provide an overview of some of the myriad applications of environmental isotopes to catchment hydrobiogeochemistry. Most of the chapters focus on a particular type of catchment and how isotopes can be used to understand the functioning of the catchment, or on specific kinds of uses of isotopes in catchments (e.g., on determining flowpaths or obtaining climatic information). For general information on uses of isotopes of some particular element, especially for applications "beyond the catchment," useful Web sources of information include:

<http://www.iaea.or.at/> The Web site for the IAEA (International Atomic Energy Agency). This page contains information on IAEA publications, how to order isotope reference materials, and how to access the IAEA isotope databases.

<http://www.nist.gov/> The Web site for the National Institute of Standards and Technology (formerly NBS) provides information on ordering isotope reference materials.

<http://wwwrcamnl.wr.usgs.gov/isoig/> The Web site of the USGS Isotope Interest Group (IsoIG). This page contains a variety of links to isotope-related resources, including short notes on isotope fundamentals and applications, information about isotope reference standards, links to several search engines for finding publications, and a link to the Web site for the **ISOGEOCHEM** email discussion group. The **ISOGEOCHEM** listserv primarily focuses on the stable isotope community, contains links to many isotope laboratories, and contains an archive of previous emails with a full search engine. If any of the other URLs listed here have changed, check the IsoIG Web site for updated links.

<http://wwwrcamnl.wr.usgs.gov/isoig/period/> This Web site contains a "clickable" periodic table that provides information about many isotopes, including lists of noteworthy publications, and descriptions of the uses of these isotopes to hydrology, geology, and biology; it contains a search engine.

<http://wwwrcamnl.wr.usgs.gov/isoig/isopubs/> The Web site for this book.

The sections below are intended as a brief introduction to the many uses of environmental isotopes in catchment hydrology, for readers who might be unfamiliar with what various isotopes have to offer, and a lead-in to the more thorough discussions in succeeding chapters.

2.5.1 Water isotope hydrology

Isotope Hydrology addresses the application of the measurements of isotopes that form water molecules: the oxygen isotopes (oxygen-16, oxygen-17, and oxygen-18) and the hydrogen isotopes (protium, deuterium, and tritium). These isotopes are ideal tracers of water sources and movement because they are integral constituents of water molecules, not something that is dissolved *in* the water like other tracers that are commonly used in hydrology (e.g., dissolved species such as chloride). Water isotopes can sometimes be useful tracers of water flowpaths, especially in groundwater systems where a source of water with a distinctive isotopic composition forms a "plume" in the subsurface (see Chapter 18 or Bullen et al., 1996).

In most low-temperature environments, stable hydrogen and oxygen isotopes behave conservatively in the sense that as they move through a catchment, any interactions with oxygen and hydrogen in the organic and geologic materials in the catchment will have a negligible effect on the ratios of isotopes in the water molecule. Although tritium also exhibits insignificant reaction with geologic materials, it does change in concentration over time because it is radioactive and decays with a half-life of about 12.4 years. The main processes that dictate the oxygen and hydrogen isotopic compositions of waters in a catchment are: (1) phase changes that affect the water above or near the ground surface (evaporation, condensation, melting), and (2) simple mixing at or below the ground surface.

Stable oxygen and hydrogen isotopes can be used to determine the contributions of old and new water to a stream (and to other components of the catchment) during periods of high runoff because the rain or snowmelt (new water) that triggers the runoff is often isotopically different from the water already in the catchment (old water). Chapters 3-7 discuss the sources of variability in the isotopic compositions of water in rain, snow, soil water, plants, and groundwater (respectively) and explain why the old and new water components often have different isotopic compositions. Tritium (^3H) is an excellent tracer for determining time scales for the mixing and flow of waters, and is ideally suited for studying processes that occur on a time scale of less than 100 years (see Chapters 3, 7, and 9). Chapters 10-14 explore how isotopes can be used to investigate hydrologic processes in various catchment types (rain-dominated temperate and tropical catchments, snowmelt-dominated catchments, arid basins, and lake-dominated systems, respectively).

2.5.2 Solute isotope biogeochemistry

Isotope Biogeochemistry addresses the application of isotopes of constituents that are dissolved in the water or are carried in the gas phase. Isotopes commonly used in solute isotope **bio**chemistry research include the isotopes of: sulfur (Chapter 15), nitrogen (Chapter 16), and carbon (Chapters 17 and 18). Less commonly applied isotopes in **geo**chemical research include those of: strontium, lead, uranium, radon, helium, radium, lithium, and boron (see Chapters 8, 9, 18, 19, and 20).

Unlike the isotopes in the water molecules, the ratios of solute isotopes can be significantly altered by reaction with biological and/or geological materials as the water moves through the catchment. Although the literature contains numerous case studies involving the use of solutes (and sometimes solute isotopes) to trace *water* sources and flowpaths, such applications include an implicit assumption that these solutes are transported conservatively *with* the water. In a strict sense, *solute isotopes only trace solutes*. Solute isotopes also provide information on the

reactions that are responsible for their presence in the water and the flowpaths implied by their presence.

As discussed above, water isotopes often provide relatively unambiguous information about residence times and relative contributions from different water sources; these data can then be used to make hypotheses about water flowpaths. Solute isotopes can provide an alternative, independent isotopic method for determining the relative amounts of water flowing along various subsurface flowpaths. However, the least ambiguous use of solute isotopes in catchment research is tracing the relative contributions of potential solute sources to groundwater and surface water. Although there has been extensive use of carbon, nitrogen, and sulfur isotopes in studies of forest growth and agricultural productivity, solute isotopes are not yet commonly used for determining weathering reactions and sources of solutes in catchment research. This book attempts to remedy that situation.

2.5.3 Mixing

Isotopic compositions mix conservatively. In other words, the isotopic compositions of mixtures are intermediate between the compositions of the endmembers. Despite the awkward terminology (i.e., the δ notation and units of ‰) and negative signs, the compositions can be treated just like any other chemical constituent (e.g., chloride content) for making mixing calculations. For example, if two streams with known discharges (Q_1 , Q_2) and known $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_1$, $\delta^{18}\text{O}_2$) merge and become well mixed, the $\delta^{18}\text{O}$ of the combined flow (Q_T) can be calculated from:

$$Q_T = Q_1 + Q_2 \quad (2.25)$$

$$\delta^{18}\text{O}_T Q_T = \delta^{18}\text{O}_1 Q_1 + \delta^{18}\text{O}_2 Q_2 \quad (2.26)$$

Another example: any mixing proportions of two waters with known $\delta^{18}\text{O}$ and δD values will fall along a tie line between the compositions of the endmembers on a $\delta^{18}\text{O}$ vs. δD plot.

What is *not* so obvious is that on many types of X-Y plots, mixtures of two endmembers will not necessarily plot along lines but instead along *hyperbolic curves* (Figure 2.9a). This is explained very elegantly by Faure (1986) using the example of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The basic principle is that mixtures of two components that have different *isotope ratios* (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{15}\text{N}/^{14}\text{N}$) and different *concentrations* of the element in question (e.g., Sr or N) form hyperbolas when plotted on diagrams with coordinates of isotope ratios versus concentration. As the difference between the elemental concentrations of two components (endmembers) approaches 0, the hyperbolas flatten to lines. The hyperbolas are concave or convex depending on whether the component with the higher isotope ratio has a higher or lower concentration than the other component. Mixing hyperbolas can be transformed into a straight lines by plotting isotope ratios versus the inverse of concentration ($1/C$), as shown in Figure 2.9b.

Graphical methods are commonly used for determining whether the data support an interpretation of *mixing* of two potential sources or *fractionation of a single source*. Implicit in such efforts is often the idea that mixing will produce a "line" connecting the compositions of the two proposed endmembers whereas fractionation will produce a "curve." However, as shown in Figure 2.10a, both mixing and fractionation (in this case, denitrification) can produce curves (Mariotti et al., 1988), although both relations can look linear for small ranges of

concentrations. However, the equations describing mixing and fractionation processes are different and under favorable conditions, the process responsible for the curve can be identified. This is because Rayleigh fractionations are *exponential* relations (Equation 2.13), and plotting δ values versus the natural log of concentration will produce a straight line (Figure 2.10b). If an exponential relation is not observed and a straight line is produced on a δ vs $1/C$ plot (like Figure 2.9b), this supports the contention that the data are produced by simple mixing of two endmembers.

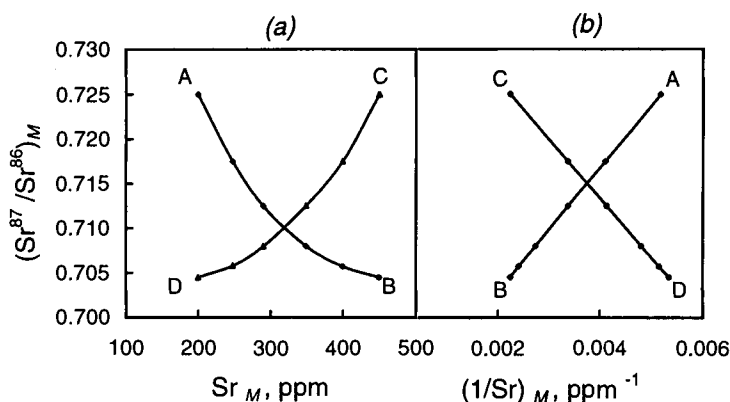


Figure 2.9. (a) Hyperbolas formed by the mixing of components (waters or minerals) A and B with different Sr concentrations and Sr isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$). If the concentrations of Sr in A and B are identical, the mixing relation would be a straight line; otherwise, the mixing relations are either concave or convex curves, as shown. (b) Plotting the reciprocals of the strontium concentrations transforms the mixing hyperbolas into straight lines. If the curves in (a) were the result of some fractionation process (e.g., radioactive decay) that is an exponential relation, plotting the reciprocals of the Sr concentrations would not produce lines. Modified from Faure (1986).

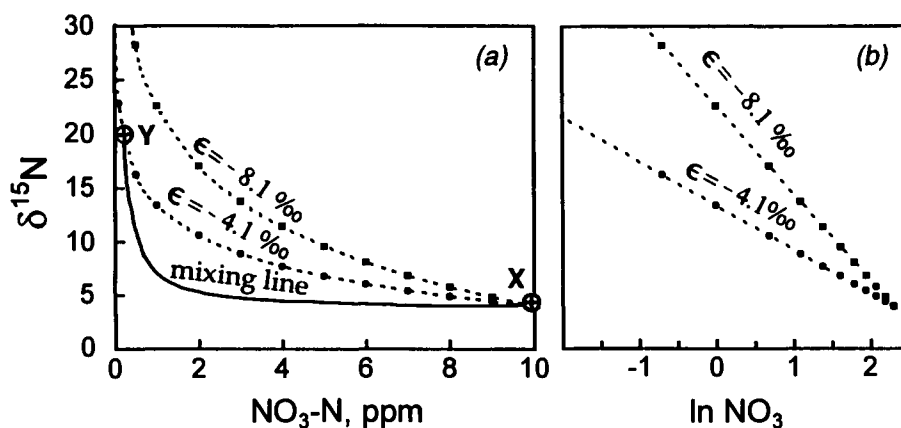


Figure 2.10. (a) Theoretical evolution of the $\delta^{15}\text{N}$ and the nitrate-N concentration during mixing (solid line) of two waters X and Y, and during an isotope fractionating process (e.g., denitrification of water X with a NO_3 concentration of 10 ppm). Denitrification for $\epsilon = -4.1\text{‰}$ results in a curve (dashed line) that ends at Y. Two different enrichment factors are compared: $\epsilon = -4.1\text{‰}$ and $\epsilon = -8.1\text{‰}$. The data points represent successive 0.1 increments of mixing or denitrification progress. (b) Plotting the natural log of the concentrations for a fractionation process yields straight lines, different for different ϵ values. Modified from Mariotti et al. (1988).

2.5.4 Isotopically labeled materials

Man-made materials with isotopic compositions that are not observed in nature are called "spiked" or isotopically labeled materials. There are many commercial suppliers of isotopically labeled liquids, gases, and solids -- some with multiple-labeled atoms (e.g., water with unusual $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios, or organic molecules with various percentages of the elements of specific functional groups labeled with uncommon isotopic compositions). The most common watershed use of spiked tracers is for agricultural studies of plant uptake of nutrients. Other applications include whole-catchment experiments where labeled NH_4 , NO_3 , or SO_4 is sprinkled in artificial rain (see Chapters 15 and 16), and plot studies where labeled H_2O is applied to the land surface to make it easier to trace the movement of "new" water into the subsurface.

Materials can be enriched in either the common or less common isotope. Advantages of the former include low price, ready availability, and absence of potential contamination problems. The main disadvantage is that the lowest possible δ value for a material is -1000‰ . In contrast, materials enriched in the less common isotope with δ values greater than $+10 \cdot 10^6 \text{‰}$ are commonly available. Why the lower limit of the permil scale is -1000‰ is illustrated by the following example for a water with no deuterium (i.e., all the hydrogen is protium):

$$\delta^2\text{H} = [({}^2\text{H} / {}^1\text{H})_x / ({}^2\text{H} / {}^1\text{H})_s - 1] \cdot 1000 \quad (2.27)$$

$$\delta^2\text{H} = [(0/{}^1\text{H})_x / ({}^2\text{H} / {}^1\text{H})_s - 1] \cdot 1000 = (0 - 1) \cdot 1000 = -1000\text{‰} . \quad (2.28)$$

The isotopic compositions in "labeled tracer" catalogs are generally in units of atom weight percent (at.%). For accurate conversion of these values to δ values, one must know the R_s value of the appropriate standard used for that isotope. Unfortunately, the absolute R_s values are not known for all international standards; the average terrestrial abundance ratios can be used for rough estimates. For example, the $\delta^2\text{H}$ value of a bottle of "95 at.% ^2H " water is calculated as follows (using the absolute ratio of VSMOW from Table 2.1):

$$\delta^2\text{H} = [(95/5) / (156 \cdot 10^{-6}) - 1] \cdot 1000 = +122 \cdot 10^6 \text{‰} . \quad (2.29)$$

Although δ values are additive for natural abundance studies, mass balance calculations for labeled materials should be done using fractional isotopic abundances where $F = R/(1 + R)$ and R is the ratio of isotopes of interest. For the general case where the *concentrations* of labeled material in the waters mixed together might be different (e.g., a water with 20 mg/L of 75 at.% ^{15}N -labeled NO_3 added to water with 5 mg/L of NO_3 with a $\delta^{15}\text{N}$ value of $+2\text{‰}$), the isotopic composition of the solute in the mixed solution is:

$$F_T C_T n_T = F_1 C_1 n_1 + F_2 C_2 n_2 \quad (2.30)$$

where C is the concentration of the species of interest, n is the number of liters of solution, and the subscripts T , 1 , and 2 refer to the total, 1st, and 2nd waters, respectively.

2.5.5 Stable isotopes in geochemical modeling

In chemical reaction modeling, usually several reaction models can be found that satisfy the data. For each model reaction path, calculations are used to predict the chemical and isotopic composition of the aqueous phase as well as the amounts of minerals dissolving or precipitated

along a flow path. The power of the stable isotope technique in groundwater modeling lies in the fact that we have added one more thermodynamic component to our system for each isotope ratio that is measured (Plummer et al., 1983). These isotopic compositions can be used along with chemical data in geochemical mass balance and reaction path models (e.g., BALANCE, PHREEQE, NETPATH, etc.) to deduce geochemical processes, test hypotheses on hydrology and geochemical mechanisms, and eliminate possible reaction paths (Plummer et al., 1991).

For example, the $\delta^{13}\text{C}$ of total dissolved inorganic carbon (DIC) is generally a function of the $\delta^{13}\text{C}$ of the rocks and extent of reaction with the rocks in a system. Thus, $\delta^{13}\text{C}$ can be a good indicator of which geochemical reactions are occurring (Chapter 18). Sulfur is similar to carbon in this respect, and changes in $\delta^{13}\text{C}$ along a flowpath sometimes can reflect reactions that also cause changes in $\delta^{34}\text{S}$ (e.g., progressive calcite precipitation along a flowpath in response to degassing of CO_2 causes gypsum to dissolve). Changes in ^{14}C content along a flowpath are useful for indicating changes in residence time. On the other hand, there is little change in δD and $\delta^{18}\text{O}$ of water during reactions with minerals along shallow, low-temperature flowpaths. Therefore, sulfur and carbon isotope data along a flowpath can sometimes be used to eliminate one or more plausible reaction models developed from chemical data, by comparing the observed changes in isotopic compositions with reaction progress (Figure 2.8) along a flowpath. Other useful stable isotope tracers include $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrates (Chapter 16) and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfates (Chapter 15). Useful radiogenic isotopes include carbon-14, strontium-87, and various uranium-series isotopes (Chapter 7-9, 18, and 20).

2.5.6 Use of a multi-isotope approach for the determination of flowpaths

Flowpaths are the individual pathways contributing to surface flow in a catchment (see Chapter 1). These result from runoff mechanisms that include, but are not limited to, saturation-excess overland flow, Hortonian overland flow, near-stream groundwater ridging, hillslope subsurface flow through the soil matrix or macropores, and shallow organic-layer flow. Knowledge of hydrologic flowpaths in catchments is critical to the preservation of public water supplies and the understanding of the transport of point and non-point source pollutants (Peters, 1994). The need to incorporate flowpath dynamics is recognized as a key ingredient in producing reliable chemical models (Robson et al., 1992). In other words, if the model used gets the hydrology wrong, it is unlikely to correctly predict the geochemical response.

Stable isotopes such as ^{18}O and ^2H are shown throughout this book to be an improved alternative to traditional non-conservative chemical tracers because waters are often uniquely labeled by their isotopic compositions (Sklash and Farvolden, 1979), often allowing the separation of waters from different sources (e.g., "new" rain vs. "old" pre-storm water). However, studies have shown that flowpaths commonly cannot be identified to a high degree of certainty using $\delta^{18}\text{O}$ or δD data and simple hydrograph separation techniques because waters within the same flowpath can be derived from several different sources (Ogunkoya and Jenkins, 1991). Furthermore, an underlying theme of many of the chapters in Part 2 of this book is that the isotopic composition of rain, throughfall, meltwater, soil water, and groundwater are commonly variable in time and space. If such variability is significant at the catchment scale (i.e., if hillslope waters that are variable in composition actually reach the stream during the storm event) or if transit times are long and/or variable, then simple two- and three-component, constant composition, mixing models may not provide realistic interpretations of the system hydrology.

One solution is to include alternative, independent isotopic methods for determining the relative amounts of water flowing along different subsurface flowpaths into hydrologic models. Reactive solute isotopes such as ^{13}C , ^{34}S , and ^{87}Sr can provide valuable information about flowpaths (not water sources) useful for geochemical and hydrologic modeling precisely because they *can* reflect the reactions characteristic of and taking place along specific flowpaths (see Bullen et al., 1996; Chapter 18). In many instances, the waters flowing along mineralogically distinctive horizons can be distinctively labeled by their chemical composition and by the isotopic compositions of solute isotopes like ^{13}C , ^{87}Sr , ^{34}S , ^{15}N , etc. For example, waters flowing through the soil zone often have $\delta^{13}\text{C}$ values that are depleted in ^{13}C relative to deeper groundwaters because of biogenic production of carbonic acid in organic soils; these same shallow waters can also have distinctive Pb and Sr isotopic compositions.

2.6 Summary

The dominant use of isotopes in catchment research in the last few decades has been to trace sources of waters and solutes. Generally, such data were evaluated with simple mixing models to determine how much was derived from either of two (sometimes three) constant-composition sources. The world does not seem this simple anymore. With the expansion of the field of isotope hydrology in the last decade, made possible by the development and increased availability of automated preparation and analysis systems for mass spectrometers, we have documented considerable heterogeneity in the isotopic compositions of rain, soil water, groundwater, and solute sources. We are still grappling with how to deal with this heterogeneity in our hydrologic and geochemical models. A major challenge is to use the variability as *signal*, not noise, in our models (Kendall et al., 1995); the isotopic and chemical compositions are providing very detailed information about sources and reactions in shallow systems, if only we can develop appropriate models to use the data. This integration of chemical and isotopic data with complex hydrologic models constitutes an important frontier of catchment research.

Acknowledgments

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Isotopic Variations in Precipitation

Neil L. Ingraham

3.1 Introduction

Precipitation is of major interest in the hydrologic cycle as it is the ultimate source of water to catchments. The terrestrial portion of the hydrologic cycle to the hydrologist, then, begins when precipitation reaches the ground. Therefore, an understanding of the formation of precipitation, and knowledge of temporal and geographic variations in the amount and mode of precipitation are important to hydrologists and critical for basin-wide water balance studies. Similarly, understanding how the stable isotopic composition is controlled by the formation of precipitation, and knowledge of the temporal and geographic variations in stable isotopic ratios of precipitation are equally important to the isotope hydrologist. Although precipitation is the source of groundwater, the study of the relationship between the two is complicated. While groundwater is typically an integration of precipitation over a large area and usually over a long time period, precipitation occurs episodically with each event often having different meteorological histories, and in many forms (e.g. rain, snow, hail and fog).

As discussed previously in Chapter 2, when water undergoes a change of state the various isotopic molecules present in the water (H_2^{16}O , HDO , H_2^{18}O) distribute themselves between the phases such that the heavier molecules (HDO , H_2^{18}O) are preferentially concentrated in the more condensed phase (solid rather than liquid and liquid rather than vapor), while the lighter molecule (H_2^{16}O) is concentrated in the remaining phase. In this way, quantification of the hydrologic importance of certain forms of precipitation is possible.

The D and ^{18}O content of water vapor within a condensing air mass is determined by several factors, including the isotopic compositions of the ocean surface that provides the vapor and the isotopic fractionation that occurs during the change of state from liquid to vapor (evaporation). The trajectory of air masses also has an important affect on the isotopic composition of precipitation, and can account for observed differences in compositions between storm events at an individual site, and for climatically-induced changes over long time periods. The next step in the formation of precipitation occurs as the parcel of air reaches saturation and water in the liquid or solid state forms. Again this change of physical state results in isotopic fractionation between the phases. As rain falls from the cloud, its composition can be modified by evaporation and reaction with atmospheric water vapor between the cloud base and the ground. In arid regions, certain types of precipitation either rapidly evaporate and may not reach the ground (virga), or evaporate on the ground providing no groundwater recharge (see Chapter 13). Heavier rains may drain off rapidly and recharge an aquifer that is remote from the precipitation event. In this chapter we will consider all of the

factors that are important in determining the isotopic composition of different forms of precipitation and their relationship to catchment hydrology.

Historic Perspective

Shortly after the discovery of oxygen-18 (Giauque and Johnston, 1929) and deuterium (Urey, 1932) various investigators attempted to determine the isotopic content of natural waters by the measurement of density and other physical properties of water. These determinations were unsuccessful for a variety of reasons. The first accurate determinations of the deuterium content of natural waters were a byproduct of the wartime Manhattan project that led to the development of the atomic bomb, and were made using mass spectrometry by Kirschenbaum (1951). Their method and instrumentation were refined by Friedman (1953) who published deuterium data on a large number of samples of natural waters. The covariance of deuterium and oxygen-18 was also described in this paper. Beginning in 1961, and continuing to the present, the International Atomic Energy Agency (IAEA) in cooperation with the World Meteorological Organization (WMO) began the deuterium and oxygen-18 analysis of precipitation samples collected monthly at 100 meteorological stations world wide. The number of stations has almost doubled over the years, although some of the original stations have ceased collecting. Dansgaard (1964) analyzed samples collected at 70 IAEA-WMO stations for one year and explained the variations in isotopic compositions at these stations in terms of known fractionation processes. Friedman et al. (1964) analysed over 1000 samples of natural waters collected on the North American continent and adjacent oceans, and developed preliminary theories to explain the regional character of the surface waters of North America.

3.1.1 Global hydrologic cycle

There are myriad pathways for the precipitated water to take once it reaches the ground; however, assuming steady-state conditions (no climate change) all pathways ultimately lead either to runoff in the liquid phase, or a return of the water to the atmosphere in the vapor phase. Runoff, which occurs without a change in phase, is a non-fractionating process; return to the atmosphere which requires a phase change, indeed involves an isotopic fractionation, but the resultant vapor may not be measurably different from the liquid. Water returning to the atmosphere by direct evaporation is isotopically fractionated, resulting in a vapor with an isotopic composition usually more depleted than that of the remaining water. Water returning to the atmosphere by transpiration is not substantially different than the soil or ground water available to the plant (Wershaw, et al., 1966; White, et al., 1985) in spite of the fact that the process of transpiration is simply evaporation occurring from the leaf and thus is indeed a fractionating process. Transpiration is a steady state process in which soil water is transported to the leaf, where evaporation occurs. During this process isotopic fractionation enriches the leaf water relative to the incoming soil water. Once a steady state is established in which the amount of water entering the plant equals that exiting by transpiration, the isotopic compositions of the entering and exiting waters will be equal. However, the water within the plant leaf will be enriched in the heavier isotopes. Hydrologists commonly combine the processes of evaporation and transpiration into one consumptive use process and use the term evapotranspiration (ET). However, isotopically, the two processes behave differently such that the isotope hydrologist must recognize the different isotopic effects and not always combine the two processes. Chapter 6 provides a more detailed discussion on plant-water interactions and their possible effects on the resultant isotopic compositions.

Condensation

Humidity is the term used to describe the amount of water vapor held in a parcel of air. Absolute humidity refers to the amount of water contained in a parcel of air and is commonly measured in grams of water per kg of dry air. The value is termed the mixing ratio. Relative humidity is the ratio of the amount of water vapor held in a parcel of air to the amount of water vapor that the air can actually hold. Relative humidity, RH, is usually reported in percent and is a measure of the saturation of the air. The amount of water vapor that a parcel of air can hold is temperature dependent, thus, a given absolute humidity does not correspond to a unique relative humidity unless a temperature of the air is identified. The dew point is the temperature at which the absolute humidity is equal to the amount of water that the air can actually hold, or the temperature at which the absolute humidity equals the relative humidity of 100%. Because the dew point is the temperature of saturation, it is the temperature at which condensation will normally occur.

The decrease in temperature with increasing atmospheric height is called the lapse rate. Several lapse rates can be identified. An adiabatic lapse rate is when the change in temperature is caused solely by a change in pressure; that is, without heat being added to, or lost by, the system. A normal dry adiabatic lapse rate of 1°C per 100 m can be derived for the atmosphere by first principles from the first law of thermodynamics (Oliver and Fairbridge, 1987). It is called a dry adiabatic lapse rate, as it represents the natural change in temperature of an air parcel due to changes in pressure with no effects from the condensation of water. A moist adiabatic lapse rate can also be identified. This lapse rate is termed a pseudo-adiabatic lapse rate as it describes the change in temperature of an air mass maintained at the dew point as water is being condensed due to continued cooling. The value of this lapse rate ranges from between 0.3°C per 100 m and 1°C per 100 m but is usually reported to be about 0.6°C per 100 m (Oliver and Fairbridge, 1987). The lesser change in temperature with altitude, and the prefix pseudo result from the release to the system of latent heat of vaporization (540 cal/gm) or fusion (80 cal/gm) by the condensing water. An environmental lapse rate, reflecting more closely the actual change in temperature with change in altitude, has been identified as approximately 0.65°C per 100 m (Rogers and Yau, 1989). Knowing the temperature, absolute humidity, and the dry adiabatic lapse rate, a lifting condensation level can be identified. The lifting condensation level is the altitude at which, by adiabatic cooling, the temperature of a parcel of air will be lowered to the dew point and condensation will occur. The lifting condensation level defines the altitude of the cloud base.

Precipitation systems

There are several atmospheric processes which may lower the temperature of an air mass to below the dew point causing condensation and precipitation to occur. Most involve adiabatic cooling due to an increase in the altitude of the air mass. The three most common atmospheric systems are Frontal, Orographic and Convective systems.

Frontal systems

A front is simply the interface between two air masses of different temperatures. Given this situation, the less dense air mass will move over the more dense air mass. When this occurs, the rising air mass may cool to the dew point and produce precipitation. This can be accomplished either by cold air invading a region occupied by warm air and producing a cold front, or by warm air invading a region occupied by cold air to produce a warm front. In either

case, the warm air is less dense and will rise over the cold air and cool adiabatically. These advective systems are generally associated with mid-latitude atmospheric-low disturbances.

Orographic systems

An orographic system is another type of advective system when an air mass is blown over a mountain range instead of over a cooler air mass. Precipitation formed by this method is associated with mountainous regions. The air is adiabatically cooled by increasing altitude in the same manner as with the frontal system except this increase in altitude is due to orographic relief.

Convective systems

A convective system results when air heated near the surface of the earth rises because the density decreases with an increase in temperature. As the air mass rises, it adiabatically cools and precipitation will occur if the air mass rises enough to adiabatically cool below the dew point. These systems are common in desert regions in the summer when the surface of the earth may get quite hot. This process differs from advective (horizontal transport) systems where water vapor is transported in from other regions, as occurs with the frontal and orographic systems. Thermal convective systems, being local phenomena, tend to recycle local atmospheric vapor instead of being a source of new water to the region or catchment basin.

Types of precipitation

There is a variety of precipitation types, but only a few will be discussed here. Rain and snow are the most common with rain being formed in either the solid or liquid phase, but reaching the ground in the liquid phase, while snow is formed and remains in the solid phase. Less common is hail, which is a solid precipitation which can be 50 mm in diameter or larger (Wixon, 1987) and is usually composed of concentric ice spheres. The concentric spheres are commonly alternately bubbly and clear, or show different degrees of opacity. The concentric spheres observed in hail are caused by continual accretion in the cloud. The accretion of the spheres may occur when water accumulates in the lower, warmer levels of the cloud and freezes subsequently when it is updrafted into the higher, colder reaches, with continual accretion during recycling in updrafts and downdrafts in the cloud. In this model, the various layers in the hailstone would have been formed at different altitudes and temperature. An alternative explanation has been proposed which relates the spheres to the rate of ice deposition in a steady updraft. This model does not require the hailstone be accreted at greatly differing altitudes or temperatures within the cloud. The stable isotopic composition of the concentric layers in hail yields information concerning its formation.

Fog

Fog is a stratus cloud that generally lies very close to the ground, envelops the observer, and is produced when an air mass is cooled to the dew point (Day, 1987). Advective fogs are produced when moist air blows into a cooler region. When this commonly occurs near coastal regions where moist air blows landward over cool ocean water that has upwelled to replace surface water driven offshore, the air mass cools to produce coastal fog, a special type of advection fog. When moist air is blown upslope orographically, it produces mountain or upslope fogs, while radiation cooling at night produces radiation fogs. Advection and mountain fogs yield water which has been transported in from other areas, in contrast to radiation fog, which is produced from local water vapor.

Most fog droplets range in size from 0.01 to 0.1 mm in diameter and have a slow settling rate (Goodman 1977, 1982). The rate at which fog droplets reach the ground may be enhanced when blowing fog coalesces on foliage to produce large drops that rain to the ground. This water is termed 'fog drip', or mist precipitation. Unlike rain or snow where the amount reaching the ground is mainly dependent on atmospheric conditions and is fairly uniform within a small region, the amount of fog drip reaching the ground is more dependent on surface effects such as the duration of fog; type, density, and cross-sectional area of collecting vegetation; and wind prevalence (Ingraham and Matthews, 1988). At locations where fog is prevalent and conditions permit, fog drip has been considered a measurable source of water to the local water budget.

3.2 Natural Fractionation of Isotopes in Precipitation

As was shown by Stewart (1975), the isotopic composition of raindrops in clouds is primarily determined by equilibrium fractionation processes. Therefore, there are two major factors that control the stable isotopic composition of precipitation at any given location: the isotopic composition of the condensing parent vapor and temperature. The composition of the condensing vapor is the result of the meteoric history of the original air mass, the most important being upwind losses by precipitation and additions by evapotranspirational recycling. The temperature of condensation and the physical state of the condensate (liquid versus solid) determines the isotopic partitioning during condensation.

3.2.1 Co-variance of hydrogen and oxygen isotopes in precipitation

In general, the systematics of stable hydrogen and oxygen isotopic fractionation are similar, thus their behavior in the hydrologic cycle is also similar. This similarity gives rise to a co-variance between the stable hydrogen and oxygen isotopic concentrations found in most meteoric water and observed first by Friedman (1953). The co-variance may be described by the relationship:

$$\delta D = 8 \delta^{18}O + 10 \quad (3.1)$$

as defined by Craig (1961) and has been given the term global meteoric water line (GMWL). This regression line of the covariance was derived from the isotopic analysis of precipitation samples and not derived from first principles. Nevertheless, the slope and intercept of this equation are useful in understanding the systematics of isotopic fractionation as controlled by the hydrologic cycle.

The GMWL may be explained by the condensation of water vapor under conditions close to equilibrium that was evaporated under conditions of nonequilibrium (Dansgaard, 1964). During condensation of water vapor under equilibrium conditions, the resulting condensate should have isotopic compositions equal to the ratio of the vapor pressures of HDO and $H_2^{18}O$ at the temperature of condensation (or equal to $\alpha_D/\alpha^{18}O$). This process should yield a slope for the regression line that is greater than 8 when HDO/ H_2O is plotted against $H_2^{18}O/H_2O$ (or when δD is plotted against $\delta^{18}O$). The observed slope of the GMWL of 8 is related to the ratios of the fractionation factors, the minor dissimilarity is caused by a kinetic fractionation effect during evaporation. The intercept of +10 of the GMWL is mostly a factor of the lack of isotopic equilibrium during evaporation.

The kinetic effect imparts an additional fractionation to the equilibrium fractionation (α), and these additional fractionation factors observed during evaporation are nearly the same for the isotopes of both elements. However, because the equilibrium fractionation factors are less for oxygen than hydrogen, the additional kinetic effects have a commensurately greater affect on the oxygen isotopic ratios. The stable isotopic composition of the evaporating water body, then, may be explained by kinetic fractionation and would lie on a (evaporation) line with a slope less than that explained by the equilibrium fractionation factors (approximately 8 of the GMWL), and thus be more enriched in deuterium and oxygen-18. As a result of this process, the composition of the evaporating vapor must shift to a composition more depleted in deuterium and oxygen-18 along a line of similar slope as for the remaining evaporating water. Evaporation from the ocean, or any water body, is subjected to this process. However, unlike a smaller water body, the ocean, due to its size and continuous return of meteoric water, is buffered by the isotopic affects of the vapor loss. Thus a vapor evaporating from the ocean may show a kinetic effect that the remaining water in the ocean would not.

Thus the GMWL is the result of kinetic fractionation during evaporation from the ocean producing a vapor isotopically more depleted than the ocean, but above (positive deuterium excess, 'd' parameter) a line of a slope of 8 ($\alpha D/\alpha^{18}O$), followed by subsequent equilibrium condensation of the vapor along a slope described by $\alpha D/\alpha^{18}O$. This process is illustrated in Figure 3.1.

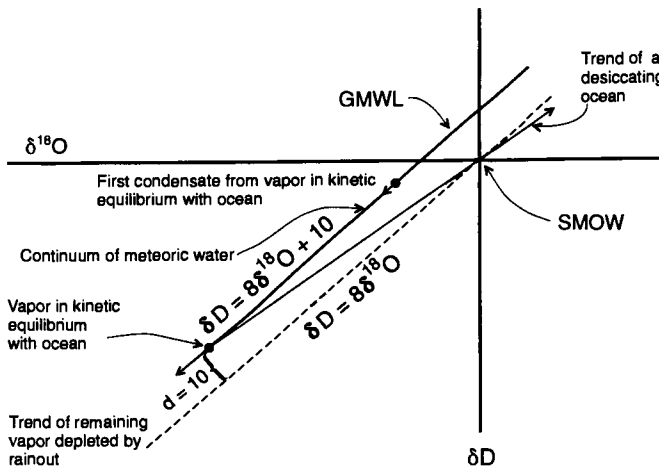


Figure 3.1. The Global Meteoric Water Line may be explained by the condensation of a vapor under conditions close to equilibrium producing a slope of 8 (related to $\alpha D/\alpha^{18}O$). The vapor however was evaporated under conditions of nonequilibrium resulting in a 'd' parameter of +10 (after Dansgaard, 1964). The inflow/outflow mass balance of the ocean precludes remaining water trending on an evaporation line.

Evaporation lines

Unlike in the ocean, the remaining water in smaller water bodies is isotopically affected by fractionation during the loss of the evaporating vapor. Because the evaporating vapor, compared to the remaining water, is isotopically depleted, the remaining water must become enriched. Because the isotopic compositions of the remaining water becomes enriched by a

ratio of less than that described by equilibrium fractionation ($\alpha_D/\alpha^{18}O$) resultant water will plot below the GMWL. The resultant slopes of water undergoing evaporation are less than 8, commonly between 4 to 7.

Local meteoric water lines

The GMWL was developed as a world-wide average and is useful as a baseline comparison of stable isotopic data. However, the stable isotopic ratios of a local region may represent different meteoric conditions and be described by a local meteoric water line (LMWL) of a slightly different slope and intercept. These lines are useful in describing the stable isotopic composition of precipitation or meteoric water in a specific region for the purpose of comparison. A LMWL was developed from the IAEA network stations for North America and is described by the equation: $\delta D = 7.95 \delta^{18}O + 6.03$ (Yurtsever and Gat, 1981). The small difference in slope between this LMWL and the GMWL is insignificant. However, the smaller intercept probably reflects smaller kinetic effects during evaporation over the North Pacific Ocean or over North America than for the worldwide average. Reliance on smaller-scale site specific LMWLs may mask any understanding of the meteoric history of the water in question (Ingraham and Matthews, 1990). In addition, LMWLs produced strictly by precipitation commonly cross the global meteoric water line in the region of interest as the enriched precipitation is commonly effected by the amount effect (see Section 3.3.3). Thus, the mathematical expression and extension of the LMWL may have more significance to the amount effect than large-scale meteoric history. This phenomenon is shown in Figure 3.2 (Ingraham et al., 1991).

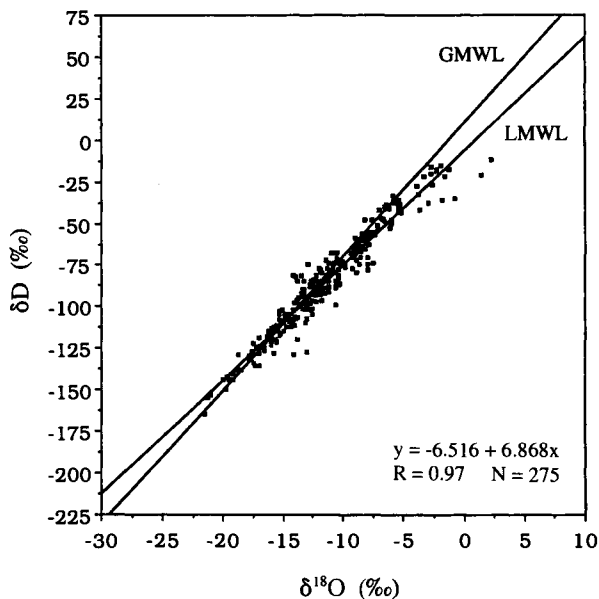


Figure 3.2. The stable isotopic compositions of 275 precipitation samples collected in southern Nevada and their resultant Local Meteoric Water Line of $\delta D = 6.87 \delta^{18}O - 6.5$ (Ingraham et al., 1991). Also shown is the GMWL: $\delta D = 8 \delta^{18}O + 10$. The data fit the GMWL reasonably well in the region of interest despite the mathematical difference between the two lines.

3.3 Systematics of Isotope Variations in Precipitation

The natural fractionation of stable isotopes and the co-variance of deuterium and oxygen-18 are continually operating during the formation of precipitation. However, the observed geographic and temporal variations in the stable isotopic composition of precipitation is complicated by the systematics of the hydrologic cycle which include evaporation, transpiration and the mixing of air masses. In addition, understanding the isotopic compositions of precipitation is complicated by the physical state of the precipitation (liquid or solid), mode and location of the formation of the precipitation, and the possible changes in precipitation during descent.

3.3.1 System fractionation

The importance of losses by precipitation and additions by evapotranspirational recycling in the meteoric history of the air mass has been demonstrated by observing geographic variations in the stable isotopic composition of precipitation (Salati et al., 1979; Ingraham and Taylor, 1991). Four distinct systems may be identified based on the degree of precipitation losses and evapotranspirational recycling to the air mass shown in Figure 3.3.

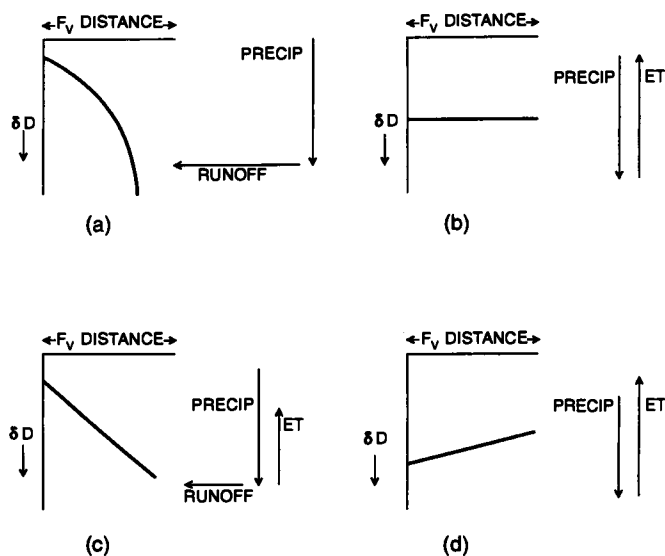


Figure 3.3. Diagrammatical sketch of the four identified systems: a) open, b) closed, c) partially closed and d) desiccating, based on the geographic variations in the stable isotopic composition of precipitation. The four systems, based on Ingraham and Taylor (1986), are the result of different degrees of precipitation and the partitioning of precipitation between runoff and evapotranspirational recycling as shown by the vectors. In the open system, all water leaves the system in the liquid state as runoff and precipitation and consequent runoff down wind becomes progressively depleted in D and ^{18}O and may be modeled by simple Rayleigh fractionation. A completely closed system results when all of the precipitation is returned to the atmosphere in the vapor phase by evapotranspiration, and no geographic variation in the isotopic composition of ground water occurs. A partially closed system is governed by the partitioning of precipitated water between runoff and evapotranspiration. A desiccating system is an unstable situation that may occur if evapotranspirational recycling exceeds the amount of water provided by precipitation.

1) Open system

In an open system water, drops are removed from the system and, once formed, cannot reequilibrate with the water vapor. In addition, no water vapor is added from an outside source, such as locally derived evapotranspired water vapor. The isotopic relationship between vapor and precipitate in this end-member system may be explained by the Rayleigh distillation (see Chapter 1).

The ultimate fate of all water in this system is runoff, leaving none for evapotranspirational recycling back to the atmosphere. The open system results in the greatest depletion in the isotopic composition of precipitation. Any depletion in the stable isotopic ratios of precipitation of less than that predicted by Rayleigh distillation implies some evapotranspirational recycling; local temperature fluctuations modify the values only slightly (Rozanski et al., 1982a). However, it is difficult to quantify evapotranspirational recycling by using isotopic ratios (Ingraham and Craig, 1993).

2) Closed system

Rayleigh distillation is still operating in this system, but the precipitation is not removed, so the bulk composition of the system remains the same. All of the precipitation is ultimately returned to the atmosphere by evapotranspiration, and no geographic variation in the isotopic composition of ground water is observed. Assuming no climate change (change in storage), the ultimate fate of all of the water in this simple system is evapotranspiration, leaving none for runoff.

3) Partially closed system

In nature, neither the open nor the closed system operates exclusively. Deviation from the variation in the isotopic composition of precipitation with distance predicted by simple Rayleigh fractionation is therefore an indication of a 'partially closed' system, in which some evapotranspired water is returned to the atmosphere and recycled. The 'degree of closure' of the system is governed by the partitioning of precipitated water between runoff and evapotranspiration. Runoff removes water from the cloud-ground water system, while evapotranspiration retains water in the system by returning it to the atmosphere. The resultant geographic variation in the isotopic composition lies between the Rayleigh depletion of the open system and the lack of depletion of the closed system.

4) Desiccating system

A desiccating system may occur if evapotranspirational recycling exceeds the amount of water lost by precipitation. This is an unstable situation that may only occur for short periods of time (seasonally) or during periods of a drying climate (climate change). The geographical variations in the stable isotopic compositions of meteoric water in a desiccating system would become progressively more enriched downwind.

Observed geographic variations

The geographic variation in stable isotopic composition of three of the four special systems is best shown in Figure 3.4. The hydrogen isotopic composition is shown as a function of distance

from the Pacific Ocean and the isotopic variation within each segment appears continuous and each segment adjoins another. The first segment shows a marked, curvilinear decrease of about 60‰ per 100 km and most closely approximates an open system. A partially closed system is shown in the second segment that displays an isotopic depletion with distance of about 12‰ per 100 km. These segments represent partially closed systems where precipitation is partitioned between runoff and evapotranspiration to varying degrees. Abrupt changes in either precipitation or evapotranspiration may produce new segments with different slopes of δD vs. distance which are also partially closed systems. Qualitatively, steeper slopes in the stable isotopic-distance trends are developed in regions where precipitation dominates evapotranspiration.

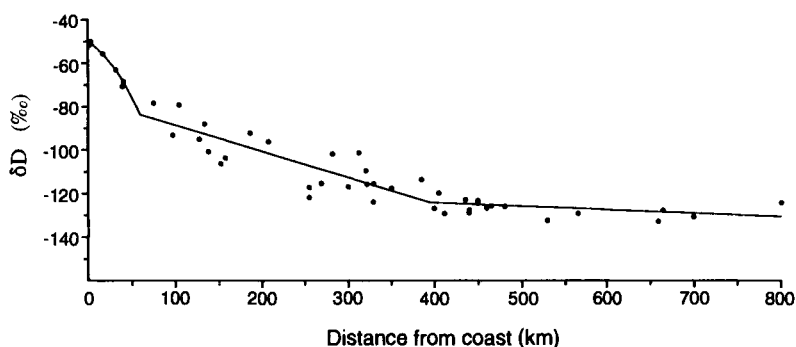


Figure 3.4. The stable hydrogen isotopic composition of meteoric waters is shown as a function of distance from the Pacific Ocean showing the geographic variation of three of the systems (Ingraham and Taylor, 1991). The coastal segment displays a curvilinear decrease of about 60‰ per 100 km and best approximates an open system. The partially closed system displays an isotopic depletion of about 12‰ per 100 km. A closed system is approximated by the third segment where only about 2‰ per 100 km depletion is observed.

The lack of isotopic depletion in meteoric waters with increasing distance has been observed and explained as representing a closed hydrologic system (Ingraham and Taylor, 1986, 1991), where evapotranspirational recycling serves to maintain downwind precipitation (Salati et al., 1979). A closed system is shown by the third segment (Figure 3.4) where little depletion in δD with increasing distance (2‰ per 100 km) from the coast is observed. The variations in δD collectively represent the isotopically closed hydrologic nature of the Great Basin, a vast area of interior drainage.

3.3.2 Unique types of precipitation

Hail

Solid precipitation retains the stable isotopic composition of the atmospheric conditions during condensation (or sublimation) as, unlike liquid precipitation, it is not subjected to evaporation and isotopic exchange and fractionation during its descent. Thus the isotopic composition of solid precipitation may provide significant information about atmospheric conditions. Hailstones are of particular interest (Jouzel et al., 1975) because large kinetic effects have been

observed during the formation of snow from super-cooled vapor (Jouzel and Merlivat, 1984; Gedzelman and Lawrence, 1982). Models to demonstrate the formation and growth of hailstones have successfully used equilibrium fractionation factors and forms of the Rayleigh distillation equation, indicating that the formation of the condensate occurs close to equilibrium conditions and that subsequent alteration of the isotopic composition of the liquid phase precipitation must occur by evaporation during descent to the ground.

The mean altitude of formation of each concentric hailstone sphere has been determined by modeling using the isotopic composition of the concentric layers. The concentric layers have alternating isotopic compositions indicating that the hailstones were formed under alternating temperature conditions. Thus they must have been formed during a series of upward and downward movements in the cloud. The isotopic composition of concentric rings of hailstones, then, records the vertical path of the stone in the cumulonimbus cloud during formation (Jouzel et al., 1975).

The change in deuterium content with radius is generally a simpler and much more accurate gauge of changes in hailstone growth than is bubble content, opacity or crystal size. The opacity of the ice is thought to indicate whether the ice has formed during wet growth (condensation) or dry growth (sublimation). The isotopic ratio is also a much better indicator of growth altitude than are the structural features such as crystal size (Knight et al., 1975). These results give credence to the proposal that the concentric spheres are a result of upward and downward cycling in the cloud.

Fog

The importance of fog and fog-drip (the coalescing of blowing fog droplets on foliage to produce large drops that rain to the ground) has received little attention in the field of hydrology. However, by the use of the stable isotopic compositions of fog, it has been shown that in unique environments fog drip may be an important addition to the local water budget. The stable isotopic composition of fogs has been observed to be enriched in D and ^{18}O relative to rain at the same location. This enrichment is related to the origin and history of the water vapor producing the precipitation as well as the meteoric conditions during condensation (Ingraham and Matthews, 1990). Fogs are generally early stage condensates produced when moist air blows either landward over cool upwelled ocean water (as with coastal fogs) or upslope (as with mountain fogs). The moist air mass does not condense as fog until it is cooled to the dew point which usually does not occur until the air mass is close to the point of observation. Rain however (from frontal or orographic systems) is generally continuously produced for great distances across the ocean or land mass prior to reaching the point of interest. This continued loss of water from the cloud system (rain-out) produces rain with isotopic compositions indicative of a continuous process of isotopic fractionation resulting in a precipitate of more advanced stages. In addition, fog condensation occurs near the surface of the earth and thus under warmer conditions than that of rain which may partially retain the stable isotopic ratios of a cooler higher altitude of condensation. These two processes (temperature of condensation and stage of condensate) have similar effects on the stable isotopic composition of the condensate, producing an isotopically enriched fog, and an isotopically depleted rain as observed by Gonfiantini and Longinelli (1962). The differences in the stable isotopic compositions of fog and rain have been observed to be consistent and predictable and have allowed the tracing of fog water movement through the hydrologic cycle and perhaps to the ground water system.

The stable isotopic compositions of mountain fogs from Kenya and coastal fogs from California (from the Point Reyes Peninsula) have been reported by Ingraham and Matthews (1988; 1990) and Chilean fogs have been reported by Aravena et al. (1989). The stable isotopic results yield information concerning the origin of fog water and provide a means to trace fog water through the hydrosphere.

The California coastal fogs plot below the GMWL ($\delta < +10$) indicating a lower kinetic fractionation effect during evaporation from the ocean than is observed for rain. In addition, local rains are predictably and consistently more depleted than the fog by up to 30‰ (Figure 3.5). A similar difference has been observed between the stable isotopic compositions of fog and rain in fog-laden areas in Chile (Aravena et al., 1989). The coastal fogs on the west coast of the Americas are an early stage condensate, having experienced no rainout of the heavier isotopes prior to reaching the coast. Friedman et al. (1964) observed similar effects for coastal fog collected at Woods Hole, Massachusetts. The stable isotopic compositions of the fogs are produced by a single stage evaporation-condensation cycle. Local coastal rain is a later stage condensate that has experienced considerable rainout with loss of the heavier isotopes during precipitation over the ocean prior to reaching the coast.

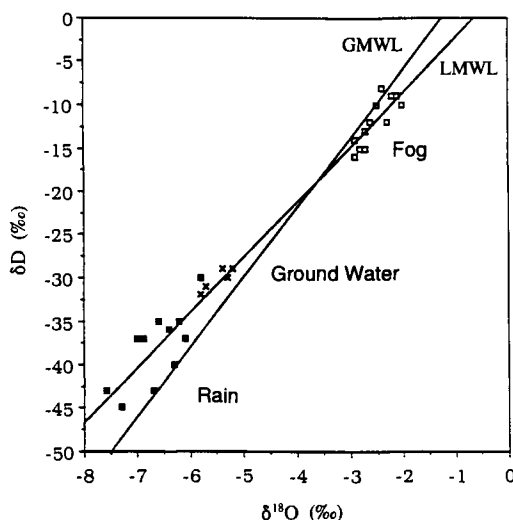


Figure 3.5. The stable isotopic composition of fog, rain and ground water collected on the Point Reyes Peninsula on the coast of California. The ground water plots on a mixing line (LMWL) between the compositions of fog and rain and shows no effects of evaporation (after Ingraham and Matthews, 1990).

Local ground water on the Point Reyes Peninsula in California plots on a mixing line between the compositions of local fog and rain and shows no effects of evaporation (Figure 3.5). A similar mixing line for the ground water has been observed in fog-laden areas in Chile (Aravena et al., 1989), although the ground water from these regions exhibit some effects of evaporation. One interpretation that can be made based on these mixing lines is that fog-drip water infiltrates the soil zone and recharges the local ground water system as proposed by Ingraham and Matthews (1988; 1990), a conclusion not supported by Aravena et al. (1989).

Mountain fogs collected in Kenya plot above the GMWL and have been observed to commonly be more enriched in deuterium than V-SMOW. These mountain fogs contain water that has been terrestrially evapotranspired and recycled upwind. The stable isotopic compositions of water vapor produced by terrestrial evaporation may plot as shown in Figure 3.6, while those of transpiration will be similar to the ground water. Together these processes serve to produce a vapor, that when condensed, will be isotopically more enriched, and of a larger deuterium excess, than the original ground water. This evapotranspired vapor then mixes with water vapor already present in the atmosphere, which blows upslope and condenses to produce the observed stable isotopic composition of the mountain fog.

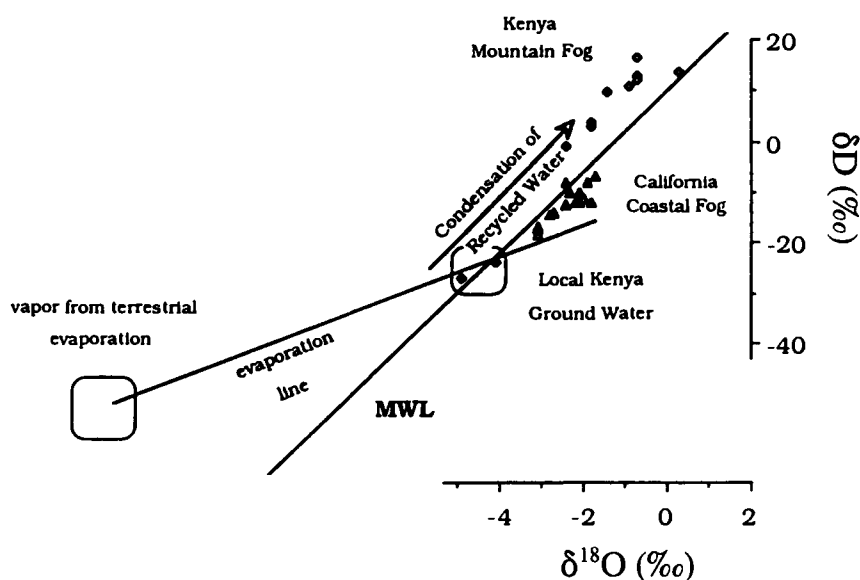


Figure 3.6. The stable isotopic compositions of the California coastal fog and Kenyan mountain fog. The coastal fogs are produced from a single stage cycle of evaporation over the open ocean and condensation over the coast, and represent an early stage condensate. The Kenyan mountain fogs contain water that has been terrestrially recycled by evapotranspiration. This evapotranspired vapor mixes with water vapor already in the atmosphere and is blown upslope and condensed as fog (after Ingraham and Matthews, 1990).

Occult Precipitation

Dew, rime, or frost is the condensate formed on a solid surface by temperature gradients between the air and the surface. These temperature gradients are usually caused by radiation cooling of the surface at night. Because it generally occurs at night and is not readily observed, the process is sometimes called occult precipitation. The importance of dew, rime or frost has been recognized in the ecological community (Stone, 1957; Kerfoot, 1968), but has had only minimal attention in the field of hydrology. Went (1955) estimated that up to 38 cm of precipitation per year can be produced by occult precipitation, whereas Monteith (1963), using more rigorous energy balance equations, calculated that perhaps only 10 percent of this amount could be produced.

Friedman et al. (1964) discussed the deuterium content of samples of dew and frost collected at Woods Hole, Mass. and concluded:

"The deposits of dew and frost, which were obtained on clear nights during late winter and early spring, were evidently the result of radiative cooling of comparatively dry air. The deuterium content of both forms of deposit varies over a wide range. Although these deposits appear to have risen for the most part from continental polar air that has descended from high altitude and latitudes, and analysis such as was applied to the samples of dew from La Jolla, California, indicates that the samples have d values 50 to 100 per mil greater than would be expected if they were determined simply by pseudo-adiabatic ascent of moist air from over the tropical ocean, followed by adiabatic descent and radiative cooling to the point of depositions. Apparently the d ratio of the moisture in the air has been modified to varying degrees during the flow of air over the land surface."

Little attempt has been made to use isotopic measurements to understand the hydrologic importance of occult precipitation. Moser and Stichler (1975) explained the daily fluctuations in δD of 6‰ in surface layers of a fresh snowfall in the Swiss Alps. During the daytime the snow would become isotopically more enriched due to evaporation and commonly more depleted at night. The isotopic depletion at night was probably caused by the addition of condensation in the form of hoarfrost. In certain environments of minimal precipitation or of extreme diurnal temperature variations caused by nighttime radiative cooling (e.g. cold deserts or high elevations), occult precipitation may play an important role in the local hydrologic budget. Stable isotopes of water might be the only possible way of quantifying water types and determining their importance.

3.3.3 Observed effects

Two major factors control the stable isotopic composition of precipitation at any location: temperature (which controls the fractionation factor, α), and the proportion of the original water vapor that still remains in the parcel of air that is undergoing precipitation (F_v); these are also the two variables in the Rayleigh distillation equation. Geographic and temporal variations are observed in the stable isotopic compositions of meteoric water and are the result of these two controlling factors; the variations are the effects. The systematic geographic and temporal observations that have been made concerning the stable isotopic compositions of meteoric water (Dansgaard, 1964; Friedman et al., 1964) related to the controlling factors are discussed below.

The continental effect

The continental effect is the observation that meteoric water is more depleted farther from the source (the ocean) of the water vapor (Figure 3.7). The isotopic composition of the condensing precipitation is more enriched than that of the remaining vapor due to isotopic fractionation during condensation. As an air mass travels inland, this fractionation continues to remove the heavier isotopes from the air mass leaving the air mass more depleted. Subsequent precipitation forming from this more depleted air mass must also be progressively depleted. The continued raining out of the heavier isotopes upwind produces precipitation that is more and more depleted down wind. Thus, this effect is the result of the evolution of the parent condensing vapor becoming depleted by the continued raining out of the heavier isotopes. Ingraham and Taylor (1986; 1991) have observed a continental effect from as large as 45‰ in δD per 100 km on the north coast of California to as little as only 2‰ across the Great Basin in northern

Nevada. Salati et al. (1979) observed only a 0.075‰ depletion in $\delta^{18}\text{O}$ per 100 km across the Amazon Basin. This lack of depletion in the Amazon is thought to be the result of isotopic complexities introduced by the recycling of evapotranspired vapor.

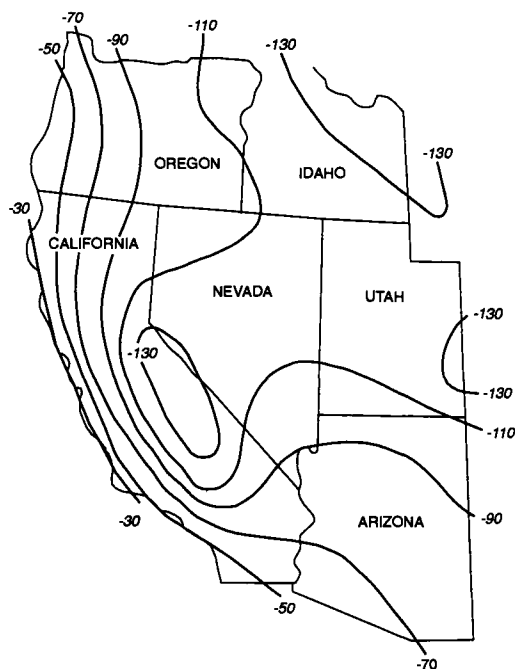


Figure 3.7. The stable hydrogen isotopic composition in meteoric water in Western U.S. The observed inland isotopic depletion, the 'Continental Effect', is caused by the raining out of the heavier isotopes leaving the vapor, and subsequent precipitation, isotopically lighter.

Elevation effect

The elevation effect is the observation that the stable isotopic compositions of meteoric water are more depleted at higher elevations. This effect is caused by increased rain at the higher elevations due to continuous cooling of the air mass pseudo-adiabatically to below the dew point in an orographic precipitation system. The progressive isotopic depletion of the rain is exacerbated by increased fractionation between liquid and vapor at cooler temperatures. The elevation effect is caused by both the evolution of the parent condensing vapor and the temperature of condensation, and in large measure can not be entirely separated from the continental effect. Values of the elevation effect have been reported by Friedman and Smith (1970) to be approximately 40‰ in δD per 1000 m increase in elevation on the west slope of the Sierra Nevada. Siegenthaler and Oeschger (1980) report an elevation effect of precipitation collected in Switzerland of 0.56‰ in $\delta^{18}\text{O}$ per degree Celsius or a 3.2‰ decrease in $\delta^{18}\text{O}$ per 1000 m increase in elevation. Elevation effects are well defined on the windward side of mountain ranges but as found by Friedman and Smith (1970) not well defined on leeward sides probably caused by spillover of precipitation that formed in the rising air along, and slightly downwind of, the crest of the range to the lee side.

Latitude effect

The latitude effect is the observation that the stable isotopic composition of meteoric water is more depleted at higher latitudes (Figure 3.8). This effect is caused by increased rainout at higher latitudes and by greater isotopic fractionation at the cooler temperatures prevalent at the higher latitudes. The latitude effect results from increased evolution of the air mass due to increased isotopic fractionation at the cooler temperatures of condensation in a manner similar to that responsible for the elevation effect. An additional factor causing increased depletion in the compositions of high latitude precipitation may be lesser amounts of more enriched evapotranspired vapor being recycled back to the air mass system in the higher latitudes. Dansgaard (1964) reports a good world-wide correlation for coastal and polar stations between mean δD and $\delta^{18}O$ values of precipitation and temperature with an average variation of 5.6 and 0.7‰, respectively, per degree Celsius. These observed variations are consistent with the temperature dependence of the equilibrium fractionation factors again indicating that condensation is an equilibrium process.

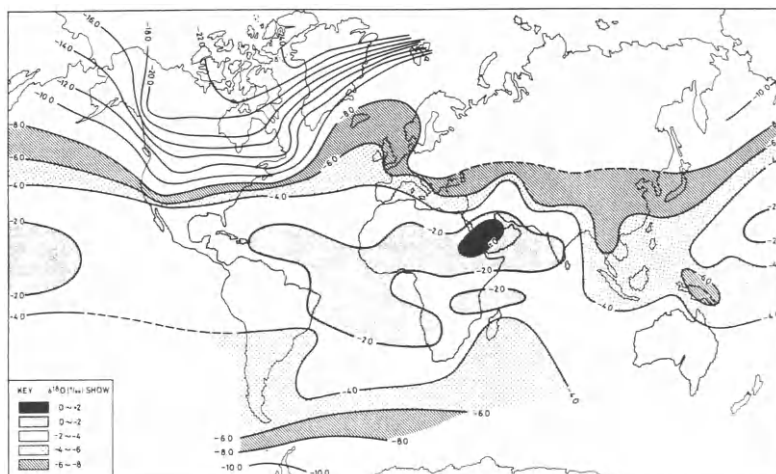


Figure 3.8. The world-wide distribution of $\delta^{18}O$ in precipitation. The observation that precipitation is lighter at higher latitudes, the 'Latitude Effect' is apparent (from IAEA, 1981).

Amount effect

The amount effect is the observation that the water collected during smaller rainstorms is generally more enriched than the water collected during larger rainstorms. During brief rain showers, the liquid reaching the ground may have become more enriched by evaporation during its descent. This effect may be observed in light rains or in rain from the early part of the storm, as in both cases the rain evaporates as it falls to the ground through an atmosphere of low relative humidity. During longer rainstorms, the air below cloud base may become more saturated which reduces the amount of evaporative loss of the raindrops, resulting in the lesser enrichment of the rain reaching the ground during later periods of the storm. The amount effect is also less pronounced at higher latitudes because more precipitation is in the form of snow, which is not subjected to isotopic fractionation by exchange or evaporation. In addition, the liquid phase at higher latitudes is also subjected to lesser degrees of evaporation during descent.

The amount effect may be viewed as a reversal of the depletion of the isotopic composition of the parent condensing vapor caused by the return of water to the cloud by evaporation.

3.3.4 Temporal variation in precipitation

Extreme differences have been observed in the stable isotopic composition of precipitation both during the course of a single storm and between storms. Large differences have also been observed on a seasonal scale and to a lesser degree on a yearly scale. The stable isotopic data of short-duration rain samples, then, do not reflect the stable isotopic composition of the average precipitation. Shallow groundwater may reflect a longer term isotopic average of precipitation, however it may also be biased due to selective recharge. In order to determine the long term average isotopic composition of precipitation, numerous samples of precipitation must be collected and analyzed.

The systematic collection of world-wide precipitation for isotopic analysis has been attempted by the International Atomic Energy Agency (IAEA, 1969, 1970, 1971, 1973, 1975, 1979, 1983, 1986, 1990). This organization collected and analyzed samples from numerous precipitation collection stations around the world in the early 1960's in an attempt to obtain background data on the tritium and stable isotopic composition of precipitation. Unfortunately, only seven widely separated stations in North America are included in the network, and the collection of precipitation from many stations is either short-lived or incomplete.

Observed differences

Smith et al. (1979) observed highly variable deuterium contents in precipitation in the Sierra Nevada in central California. Differences ranging up to 114‰ in δD between sequential samples were measured at one station during one storm, while the mean δD value of individual storms from 13 stations varied up to 37‰. Siegenthaler and Oeschger (1980) report variations of over 10‰ in $\delta^{18}O$ between summer and winter precipitation in the Swiss Alps. Friedman and Smith (1972) report a difference of 20‰ in δD in the total seasonal snow pack between two separate, consecutive years in the Sierra Nevada. The precipitation totals in these two years differed by two to three times, which they believed had an effect on the stable isotopic results.

Similar large variations have been observed in desert regions. Nativ and Mazor (1987) report differences in δD of between -62 and +33‰ for rain from 46 individual rain events over a two year period in the Makhtesh Ramon Basin in Israel. The more enriched samples ($\delta^{18}O = +5.6$ and $\delta D = +33$ ‰) no doubt are the result of evaporation during rain fall. A difference of 5.5‰ in $\delta^{18}O$ was also observed between the two 1-year collection periods.

Ingraham et al. (1991) reported maximum differences in $\delta^{18}O$ of 2.3‰ for five different years of collection of over 400 precipitation samples from 14 locations in southern Nevada. Considerable variation was also observed on a seasonal basis. The stable isotopic composition of summer and winter precipitation commonly differed by 13‰ and differed by as much as 15‰ in $\delta^{18}O$ (Figure 3.9). This large variation in the stable isotopic compositions of precipitation represents differences in storm origins, atmospheric flow paths of the storm trajectories, and temperatures.

Simpson et al. (1972) have also demonstrated a substantial and predictable seasonal difference in the stable isotopic composition of precipitation in Arizona. Winter precipitation is produced

from mid latitude frontal systems migrating eastward off the Pacific Ocean. This precipitation condenses at cooler temperatures from an air mass of more advanced stages, and thus is isotopically more depleted than summer precipitation. Summer rains occur primarily as localized high-intensity convective storms (French, 1983; 1985) resulting from subtropical disturbances from the Gulf of California (Hales, 1972; 1974). Summer precipitation may contain more recycled water condensed at a warmer temperature and may experience more evaporation during the rain's descent, resulting in an isotopically enriched precipitation.

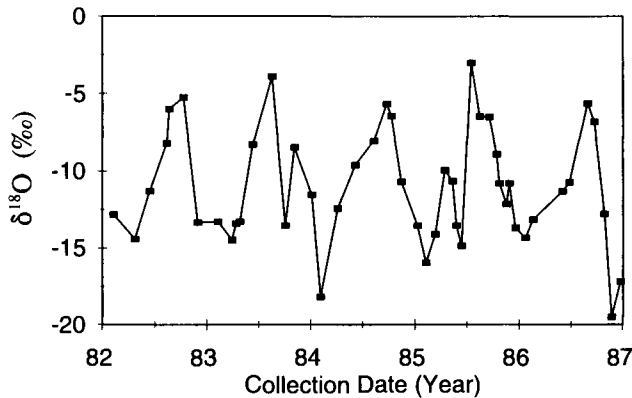


Figure 3.9. The stable oxygen isotopic composition of precipitation collected periodically over five years at 14 locations in southern Nevada. The large difference in the stable oxygen isotopic composition between summer and winter precipitation represents seasonal differences in storm origin and trajectory, and temperature (phase) of condensation. Each data point represents the accumulated precipitation since the previous sample (after Ingraham et al., 1991).

3.3.5 Geographic variation in precipitation in convective systems

Large variations in the stable isotopic ratios have been observed for precipitation from convective precipitation systems on a small geographic scale that can not be related to the continental effect (Miyake et al., 1968). Precipitation collected from a single convective storm in southern Nevada produced differences in δD and $\delta^{18}O$ of 15 and 1.5 ‰, respectively, within the range of less than 3 km. (Metcalf, 1995). Ephemeral runoff was produced in two separate wash systems by this summer precipitation event. The isotopic compositions of the flash flood water from both of the wash systems were similar and, in addition, may be described by mass balance calculations of the collected precipitation indicating geographic isotopic homogenization of the storm water once on the ground.

The large variations in the stable isotopic compositions of precipitation produced from convective storms on such a small scale illustrate the necessity to collect numerous samples of temporal and geographic proximity in order to determine a reasonable isotopic average.

3.3.6 Continental effect in precipitation

Surface and shallow ground waters, which generally represent an average of precipitation over time, have been observed to display a continental effect. However, this similar systematic

geographic variation has not been observed in precipitation from an individual storm as it moves inland. The stable isotopic composition of discrete precipitation events collected across central California were reported by Ingraham and Taylor (1991) as shown in Figure 3.10a-d. A general pattern of decreasing δD with distance inland is apparent in each case, however, the patterns do not appear systematic. The equilibrium relationship between the oxygen-hydrogen isotope ratios and the systematic continental effect has frequent interruptions in the form of excursions of the data along, and from, the GMWL. These deviations may represent different degrees of local recycling of the storm water which may include the effects of non-equilibrium fractionation of the evaporated water. These data also show variations of up to 40‰ in δD between the discrete systems emphasizing the large temporal variation observed in precipitation.

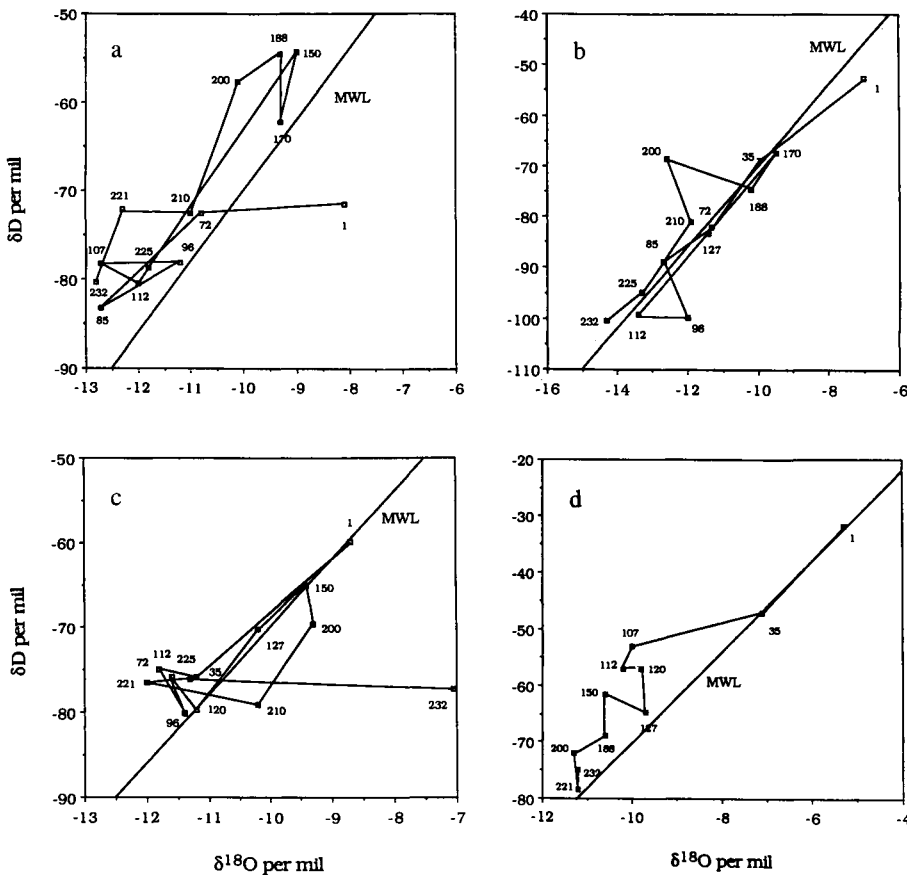


Figure 3.10a-d. The isotope data of collected rain from discrete precipitation events from frontal systems passing across central California. The compositions of the rain samples shown in each figure were produced from the same storm system and are identified by their distance, in km, from the Pacific coast. The samples for each event are connected in a fashion tracking the eastward migration of the storm as it passes across the landscape (after Ingraham and Taylor, 1991).

The weighted average hydrogen isotope composition of precipitation is compared with the hydrogen isotope compositions of surface- and shallow ground waters in Figure 3.11. The large-scale variations in the weighted average δD values of precipitation correspond more closely with those of the surface- and shallow ground waters. The yearly, seasonal, as well as in-storm variations in the isotopic composition of precipitation averages out and is not observed in surface and shallow ground waters. The minor difference between the compositions of precipitation and ground waters at the same locations are attributed to slight evaporation of the water prior to infiltration (Gat and Tzur, 1967).

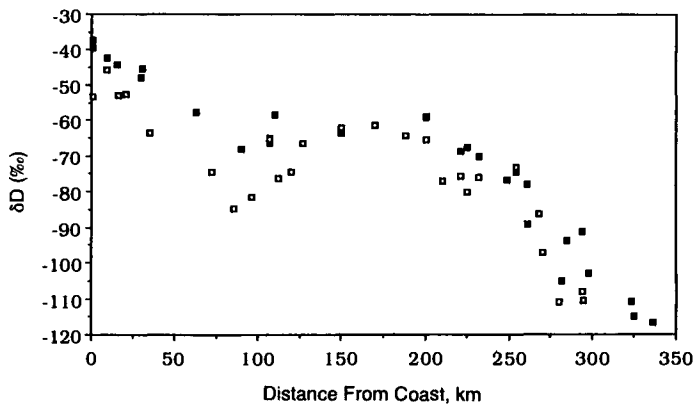


Figure 3.11. The weighted average hydrogen isotope composition of precipitation (open squares) compared with those of surface- and shallow ground waters (solid squares). The large-scale variations in the weighted average δD values of precipitation correspond closely with those of the surface- and shallow ground waters (after Ingraham and Taylor, 1991).

3.3.7 Dependence of rain on ambient temperature

Dansgaard (1964) reports a good world-wide correlation between mean δD and $\delta^{18}O$ values of precipitation and temperature for coastal and polar stations with an average variation of 5.6 and 0.7‰, respectively, per degree Celsius. Rozanski et al. (1992) have observed a latitude dependence of this relationship and report that the slope of $\delta^{18}O$ of precipitation from the IAEA network varies from 0.9‰ for the Antarctic Peninsula to virtually zero for tropical regions. Other authors (Yurtsever and Gat, 1981) report good correlation between ground temperature and the stable isotopic composition of precipitation. The observed correlation between surface temperature and isotopic composition is noteworthy because a correlation with altitude of formation might be more expected. Indeed, the stable isotopic compositions of precipitation samples collected by Smith et al. (1979) in eastern California indicate that the altitude of formation of the precipitation in low lying desert regions is about 2000 m above the surface while precipitation in the Sierra Nevada Mountains was formed between 1000 and 1500 meters above the surface.

3.3.8 Exchange with atmospheric vapor

Isotopic exchange processes exert the primary control in many systems and for example include ^{18}O and ^{13}C exchange of atmospheric CO_2 with the oceans (Bottinga and Craig, 1969; Inoue and Sugimura, 1985). Isotopic exchange is also assumed to be an important factor in controlling

the isotopic compositions of all natural water bodies in the hydrosphere. Continental, latitudinal and elevational variations in the isotopic compositions of natural waters are observed, as described by Dansgaard (1964) and Friedman et al. (1964). However, natural meteoric waters and water vapors in the same geographical area are generally not excessively out of isotopic equilibrium. This isotopic equilibrium must be maintained by continuous isotopic exchange between the various bodies of meteoric water.

Isotopic exchange between water bodies occurs through the vapor phase and varies exponentially with time (McKay, 1938; Harris, 1951; Stewart, 1975). When allowed to progress to completion, the various water bodies will attain a common isotopic ratio as shown in Figure 3.12. The final composition is controlled by the initial compositions and volumes of the waters, while the isotopic exchange rate depends on the surface area to volume ratios of the various water bodies (Ingraham and Criss, 1993).

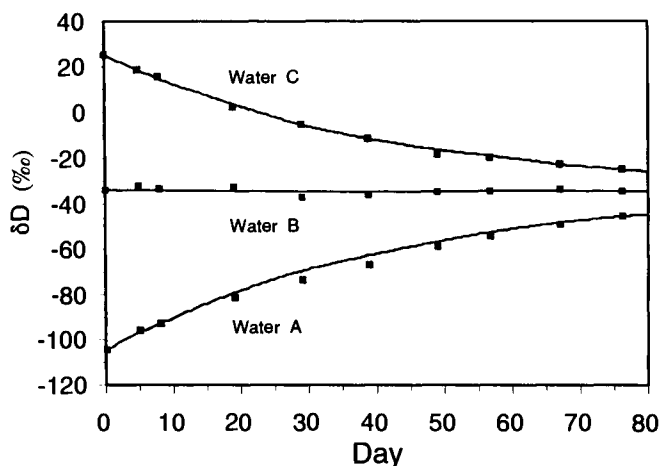


Figure 3.12. Observed hydrogen isotopic data of three waters experiencing isotopic exchange and calculated results for pure exchange shown by the curves (Ingraham and Criss, 1993). Isotopic exchange may be explained by $(\delta - \delta_{\infty})/(\delta_i - \delta_{\infty}) = e^{-kst/v}$ where: δ is the δ -value at time t , δ_i is the initial δ -value, δ_{∞} is the final δ -value after infinite time, and s and v refer to the surface area and volume of the water, respectively. The exchange constant, k , is observed to have the same value for all three (D/H, $^{18}\text{O}/^{16}\text{O}$, and T/H) isotopic systems.

Isotopic exchange has been previously observed in the interrelationships of cave waters (Ingraham et al., 1990) where the isotopic enrichment of cave waters by evaporation is limited by isotopic exchange with cave vapor as shown in Figure 3.13. The stable isotopic ratios of the evaporating drip waters and small pools are controlled by exchange with the water vapor in the cave, which, in turn, is controlled by larger pools nearby.

Isotopic exchange is also used to explain the amount effect (Friedman et al., 1964), the limited enrichment observed in waters undergoing evaporation (Craig and Gordon, 1965), and some isotopic changes observed in intercepted water (Saxena, 1986; Kendall, oral comm.). Isotopic exchange also explains the isotopic composition of grape berries (Roether, 1967), and perhaps the similarities between leaf water and fog (Aravena et al., 1989).

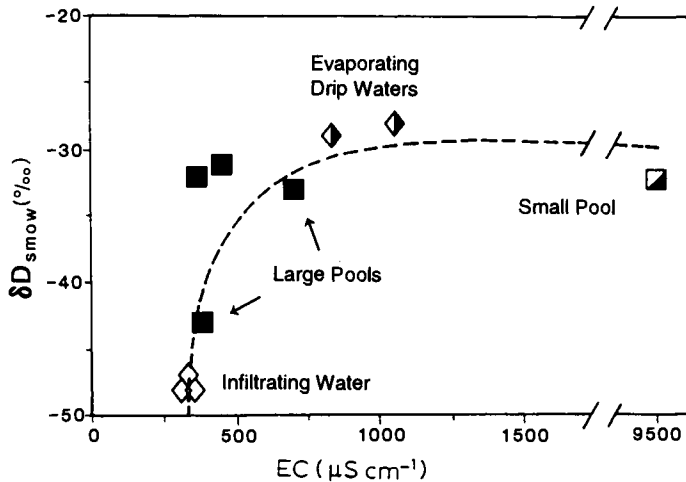


Figure 3.13. The stable isotope ratios and EC values of infiltrating water, evaporating drip water, small and large pools in Carlsbad Cavern are shown (after Ingraham et al., 1990). The EC of the small pool and drips have been elevated by evaporation (from less than 500 to 9500 $\mu\text{mhos/cm}$). However, the process of isotopic exchange with cave vapor limits isotopic enrichment obtainable by evaporation. The degree of stable isotopic enrichment of water in the cave is controlled by exchange with water vapor which, in turn, is controlled by large pools in the cave.

3.3.9 Evaporation on the canopy

Some precipitation is intercepted by tree canopies before it reaches the ground. This process continues until the leaf reservoir is saturated at which time the precipitation will fall through to the ground. The portion of precipitation that is caught in the leaf canopy is termed interception and may be as high as 40% in coniferous forests (Zinke, 1967), but is commonly about 20%. This intercepted water is subject to evaporation and isotopic exchange with the atmospheric vapor as well as with leaf water while residing on the forest canopy. Thus, the isotopic composition of throughfall, that portion that makes it to the ground, may not be the same as the original rain. Generally, the throughfall is enriched compared to the original rain as found by Saxena (1986) who reported oxygen isotope enrichment of from 0.1 to 1.2‰ in $\delta^{18}\text{O}$ in throughfall in a pine forest in Sweden. Conifer throughfall has also been reported to be generally more enriched in ^{18}O relative to deciduous throughfall regardless of season (Kendall, 1993). However, evaporative enrichment is not always the only contributing factor as in a few cases depletion has been observed. In addition, enrichment may be along a slope greater than 8 indicating that exchange with re-evaporated water during the storm is also a major control on the stable isotopic composition of throughfall (Kendall, 1993).

3.4 Mesoscale Circulation and Storm Trajectories

The depletion in the stable isotopic composition of meteoric waters along a storm path trajectory (the 'Continental Effect' described by Friedman et al., 1964; and Dansgaard, 1964) generally reflects a complex set of meteorological and hydrological processes. The most important processes controlling the stable isotopic composition at any location are the temperature of condensation and composition of the parent condensing vapor. Temperature

controls the fractionation factor during condensation, and also the phase of the condensate (solid or liquid). The composition of the parent condensing vapor is controlled by storm track trajectory, degree of upwind precipitation, temperature of that precipitation, and degree of evapotranspirational recycling. The sum total of the processes may be viewed as the degree of isotopic evolution of the condensing air mass. The isotopic composition of shallow ground waters in a small inland catchment basin, then, may be considered to represent a position on the continuum of the air mass trajectory and reflect the sum total of the upwind hydrologic conditions largely controlled by the evapotranspirational recycling of meteoric water.

Many investigators have used geographic differences in the isotopic composition of meteoric water to understand the horizontal flux of atmospheric water vapor. Gat and Carmi (1970), Leguy et al. (1983) and Rindsberger et al. (1983) studied the isotopic composition of precipitation in the Middle East. These researchers showed that changes in the isotopic composition of precipitation depended on whether the horizontal trajectory was primarily over Southern Europe, the Mediterranean Sea or North Africa. The differences may be attributed to the continental effect (raining out of the heavier isotopes) acting when the horizontal storm trajectories were over continents (Southern Europe or North Africa) and the continued exchange and replenishment of atmospheric vapor to the storm system when the horizontal storm trajectories were over the Mediterranean Sea. Differences between trajectories over Southern Europe or North Africa may be the result of differences in degrees of rain out and recycling. Lawrence et al. (1982) measured the hydrogen isotopic compositions of precipitation at Mohonk Lake, New York and also concluded that the results varied systematically with storm path trajectories. As the result of seven years of isotopic analysis of seasonally collected precipitation samples from 32 sites in eastern California, Friedman et al. (1992) also found seasonal differences in compositions which they relate to differences in calculated storm trajectories.

Some previous detailed studies have interpreted the stable isotopic compositions of meteoric water and their geographic variations primarily in terms of temperature and orographic effects (Smith et al., 1979; Yonge et al., 1989). Recently, investigators have considered all components of the hydrologic cycle including evapotranspiration which is shown to be an important component. Quantifying evapotranspirational recycling is critical to the quantification of the hydrologic cycle and is of great importance when considering natural or anthropogenic climate change, or the effects of changing vegetation patterns on precipitation.

Salati et al. (1979) proposed that the small geographic (0.075‰ per 100 km) depletion of the $\delta^{18}\text{O}$ of precipitation in the Amazon basin was a result of a large contribution of re-evaporated moisture to the basin's water balance. Gat and Matsui (1989, 1991) have recently attempted to determine the ratio of evaporation to transpiration in the Amazon Basin by using a steady-flux model incorporating deuterium excess values (defined as $d = \delta\text{D} - 8 \delta^{18}\text{O}$). These researchers report an increase of 3‰ in the 'd' parameter of precipitation across the Amazon Basin and attribute it to an isotopically fractionated evapotranspirational flux to the water balance. This 'd' parameter corresponds to 10-20% of the precipitation being evaporated, which represents an evaporative component of 20-40% of the total ET flux. Rozanski et al. (1982b) observed a decrease in δD of 3.3‰ per 100 km in winter precipitation and 1.3‰ per 100 km in summer precipitation in central Europe, which was explained by a ratio of winter precipitation to summer evapotranspiration.

The importance of evapotranspirational recycling was also demonstrated by Ingraham and Craig (1993) who used a climate model derived from a canonical analysis of the instrumental record to duplicate observed hydrogen isotopic compositions of meteoric water on a traverse across northern California. A best fit of the model to the data along most of the traverse was obtained when evapotranspiration was geographically constant at 20%, and no solution with an acceptable fit was ever obtained when the stable isotopic effects of terrestrially evapotranspired and recycled water were ignored. The isotopic effects of evapotranspirational recycling serve to enrich the isotopic compositions of inland meteoric waters over those predicted by simple Rayleigh distillation, and are required to explain the observed data. Thus the stable isotopic ratios of inland meteoric waters as well as the inland water balance can only be explained by including the effects of upwind evapotranspirational recycling.

3.5 Tritium

Tritium, ^3H or T, is a radioisotope of hydrogen with a mass of three. The variation in production and the radioactive nature of tritium renders the concentration of the isotope variable in the hydrosphere with time and no available standard concentration analogous to V-SMOW for reporting. Tritium is therefore reported in absolute concentrations or by radioactive decay. The concentrations of tritium are generally so small that tritium is reported in a special concentration called a 'tritium unit' or TU, defined as equal to 1 tritium atom per 10^{18} hydrogen atoms. This is an actual ratio (an R unit) and not analogous to a 'delta' unit. Tritium may also be reported in terms of activity (pico-Curies/liter, pCi/l) or decay (disintegrations per minute/liter, dpm/l). The tritium unit, can be related to the activity or decay by the following conversion factors: $1 \text{ TU} = 7.2 \text{ dpm/L} = 3.2 \text{ pCi/L}$.

3.5.1 Origin

Tritium is naturally produced in the upper atmosphere by the bombardment of nitrogen with cosmic-ray produced fast neutrons. This process also produces the stable isotope carbon-12:



Tritium formed in this way may be termed "cosmogenic", and the rate of natural production is about 0.25 atoms per cm^2 per second. Once tritium is formed it is quickly oxidized to form water and enters the hydrologic cycle. Tritium decays by soft-beta emission to ^3He by:



and has a half life of 12.43 years.

Tritium being an isotope of hydrogen follows similar systematics of isotopic fractionation from protium as does deuterium. The fractionation factors of tritium, T/H, (Jacobs, 1968; Sepal and Mason, 1960) are generally larger than those of deuterium, D/H, because of the larger mass difference. However, the behavior of tritium in the hydrologic cycle is dissimilar to that of deuterium.

Background (pre-bomb) levels of cosmogenic tritium have been determined to be between 5 and 10 TU. The pre-bomb tritium fallout and background levels in precipitation were determined by the analysis of bottled wines (Figure 3.14) (Kaufman and Libby, 1954) from Europe (Guerain and Tourlière, 1975) and Australia (Allison and Hughes, 1977). Similar to the results of Ingraham and Caldwell (1994) for D and ^{18}O , the tritium concentration in wines has been shown to relate to atmospheric conditions several weeks prior to harvest (Roether, 1967) and compare well with the average levels of tritium in rain for the year of bottling (Allison and Hughes, 1977). That the tritium concentration in meteoric water compares well to that of wine was shown to be the result of isotopic exchange between the grape and surrounding air moisture (Roether, 1967).

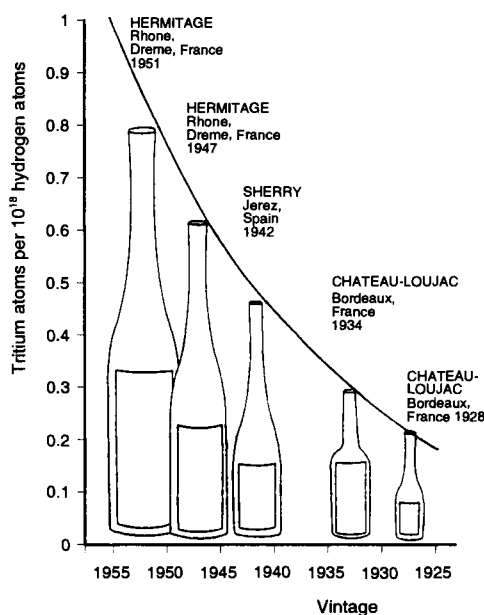


Figure 3.14. The tritium concentration observed in vintage wines (modified from Guerain and Tourlière, 1975).

3.5.2 Recent elevated levels and decline

Between the mid 1950's and 1963, a large amount of tritium had been produced by above ground thermonuclear testing. In 1963, the nuclear test ban treaty ended above ground testing. Extensive testing prior to the ban resulted in a peak concentration of tritium in precipitation measured to be as high as 10,000 TU in the northern Hemisphere (IAEA, 1969, 1970, 1971, 1973, 1975, 1979, 1983, 1986, 1990). Now only smaller amounts of 'technogenic' (or anthropogenic) tritium produced by nuclear power plants are being released into the atmosphere (Figure 3.15) and the peak of tritium concentration in meteoric water of the early 1960s is viewed as a tritium pulse.

This anthropogenic atmospheric tritium pulse provided a means by which the age of a water may be determined. Water containing amounts of tritium above background levels, indicates that at least some portion of the water was in equilibrium with the atmosphere since the early

1950's. However, since 1963, the concentration of tritium in precipitation and meteoric waters has significantly dropped. This reduction in concentration is due in part to radioactive decay, however, a larger factor is that the tritium is being lost to the oceans which are naturally tritium-free due to the mass of the oceans and long residence time of water in the oceans.

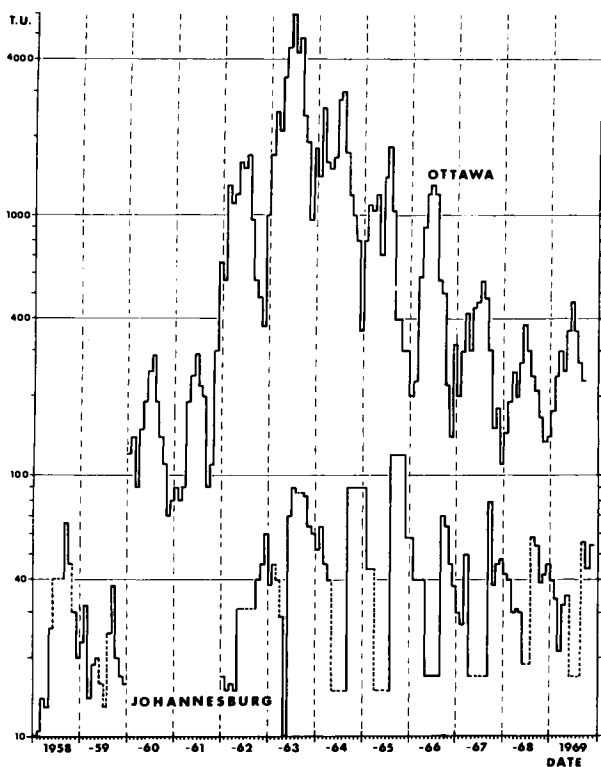


Figure 3.15. The tritium concentration in precipitation as observed in Ottawa and Johannesburg between 1958 and 1969. The 'pulse' of tritium production during the 1960's produced from above ground nuclear testing peaked before the nuclear test ban treaty of 1963 (from Ferronsky and Polyakov, 1982).

3.5.3 Observed terrestrial and marine distributions

Tritium has a different distribution than deuterium, mainly because the source of tritium is the upper atmosphere (and was also for the relevant years, above-ground thermonuclear testing), and the sink for tritium is the ocean. This difference gives rise to a reverse 'continental effect' as observed for the stable isotopes deuterium and oxygen-18 (Figure 3.16). The average residence time of the tritium in the atmosphere is only 1.6 years which is much shorter than its half-life.

3.5.4 Uses of tritium in catchment basin research

Tritium is the only real conservative tracer for determining the age of a water as tritium is the only radioactive isotope of a consequential half-life found in the water molecule. Unfortunately,

the natural background of tritium (cosmogenic source) is low and the half-life is relatively short, so the time-range of applicability is limited. In addition, recent elevated levels of tritium (anthropogenic/technogenic source) have fluctuated significantly, so the absolute age of a water in the nuclear age is difficult to ascertain.

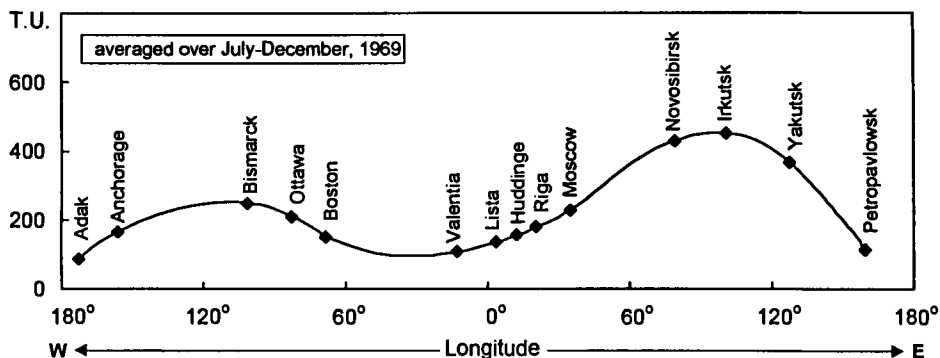


Figure 3.16. The reverse 'Continental Effect' for tritium. The different distribution is a result of the upper atmosphere being the source of tritium in meteoric water rather than the ocean as is the case with the stable isotopes (from Ferronsky and Polyakov, 1982).

3.6 Implications for Catchment Basin Research

3.6.1 Scale issues

Geographic variations as caused by rain-out (observed as the continental effect) are generally not a concern at the catchment basin scale. Most variations in the stable isotopic composition of precipitation at the catchment basin scale are related to elevational and temporal variations as have been observed by many researchers (Ingraham et al., 1991). At the catchment basin scale, the largest variation seems to be seasonal, the second largest is elevational while the smallest is geographic.

Nevertheless, these variations can be quite large thus an accurate measure of the isotopic composition of precipitation in a catchment basin requires the collection of numerous samples of precipitation. Short and usually incomplete records are available (IAEA, 1969, 1970, 1971, 1973, 1975, 1979, 1983, 1986, 1990) for a few locations, however because of the large geographic as well as temporal variation in the isotopic composition of precipitation, these databases are of little use for catchment studies.

3.6.2 Sample collection

Sample collection design should reflect the purpose of the study. Precipitation may be collected storm by storm, or monthly or yearly, depending upon the study.

Rain collection devices

The purpose of a rain collector is to simply obtain a sample for stable isotopic analysis and not to accurately gage the amount of rain. Thus in catchment basin studies a rain collector is used

rather than a rain gage, and the design and siting of the collector depends on isotopic considerations rather than meteorological considerations. Rain collectors might be located in places inappropriate for rain gages. If throughfall is of interest then a collector might be placed under a forest canopy, or if fog is of interest then the collector might be outfitted with a fog collecting screen.

Rain collectors are generally simple devices made of a funnel mounted on a collection tank. The size of the funnel and volume of the collection tank should be matched to accommodate the amount of rain expected during the collection period, perhaps a year, a season or a storm. The collection tank should be made of glass or some other material which will not allow isotopic exchange. Most plastics are not appropriate for this use as isotopic shifts may occur after only several months. Evaporation is controlled by the addition of an immiscible fluid that is less dense than water and thus will rise to the top of the mixture covering the water sample to protect it from evaporation. Mineral oil and silicon oil are common choices as they do not isotopically exchange with the water so the isotopic integrity of the precipitation sample is preserved. The water sample in the collection tank should be covered to a depth of at least 1/4 to 1/2 inch. Antifreeze can not be added to the collection tank to prevent the collected water sample from freezing as it can not be removed from the sample without interfering with the stable isotopic composition of the sample.

The practice of heating rain gages has been used to melt the snow on contact and insure its measurement in the tank. However a recent concern has been that heated devices may tend to create a thermal updraft effect and blow the smaller snowflakes or mist up and out of the collector. This would skew the water collected towards the larger flakes and drops. The smaller and lighter snow flakes that would be blown up and away, may be the result of colder precipitation, and thus may have a more depleted isotopic composition. The loss of this precipitation would render the sampled water isotopically more enriched. The isotopic effects of using a heated gage, however, have not been documented and thus should be investigated.

Standard tipping bucket and weighing bucket rain gages may be modified and used as rain collectors for stable isotopic analysis. Both would require the addition of mineral or silicon oil to the collection tank to prevent evaporation. It is recommended that precipitation be collected from both sides of the tipping bucket gage. Collecting precipitation from only one side of a tipping bucket gage is commonly assumed to be sufficient, but if variations exist between the accumulated 0.01 increments of precipitation, as might be expected during small precipitation events created by the amount affect, both sides of the tipping bucket gage should be piped to a collection tank and sampled. Comparison of sample volumes between various precipitation gages have been reported. It is unclear if the amounts collected by the different style gages translates to an isotopic difference in the collected samples. Indeed any variations in effectiveness of the gages to obtain accurate amounts may or may not be reflected in the stable isotopic compositions of the precipitation sample.

For atmospheric water vapor collection, samples are typically collected in vapor globes evacuated to 10^{-3} torr and vacuum sealed. Samples are obtained by releasing the vacuum seal on the globe, allowing the surrounding vapor to enter the globe. Each sample is allowed to equilibrate for several minutes, and then sealed and transferred to a laboratory vacuum line for extraction. A simple system for continuous vapor collection using an electrically operated cooling unit is described in Schoch-Fischer et al. (1983).

Snow Cores

The collection of snow may be made by the use of a snow corer which is simply a tube or pipe that is inserted down through the snow pack. When withdrawn, a core is obtained that preserves the stratigraphy of the snow pack. Snow coring allows for automatic integration of the individual layers of the snowpack if the isotopic composition of the entire snow pack is desired. Identifying the isotopic composition of snow is not a simple matter and will be discussed in Chapter 4.

3.7 Summary

Precipitation is probably the most important source of water to catchment basins. The stable isotopic composition of precipitation has been shown to be highly variable on temporal scales from intra-storm to years, and, depending on type and mode of precipitation, on geographic scales as little as kilometers and less. Any isotopic study at the catchment basin scale must start with an understanding of the formation of precipitation and the specific temporal and geographic variations in the stable isotopic ratios of precipitation.

The stable isotopic composition of precipitation is a function of various parameters, most of which indeed act at the catchment scale. Understanding these parameters and their effect on the stable isotopic ratios of precipitation yields information concerning the hydrology of catchments. Information concerning climate of recharge, mode and temperature of precipitation, seasonality of recharge and recharge area among other factors may be gained by studying the stable isotopic composition of precipitation.

The two major factors controlling the stable isotopic composition of precipitation are the composition of the condensing parent vapor and temperature. Temperature controls the phase of condensate as well as the fractionation factor. The fractionation factor describes the partitioning of the isotopic ratios between the condensing parent vapor and the resultant precipitate. The phase is of importance beyond indication of temperature because solid precipitation, unlike rain, is not subject to evaporation and exchange during its fall through air of ambient water vapor.

The composition of the parent condensing vapor is a larger factor in controlling the stable isotopic composition of precipitation than temperature because vapor controls the bank of isotopes available for partitioning to the liquid phase. The composition of the parent vapor can evolve by hydrologic and atmospheric processes upwind that are related to storm trajectory and evapotranspirational recycling of meteoric water.

These two major factors control the stable hydrogen as well as the stable oxygen isotope compositions in precipitation in a similar manner, yielding a covariance in the isotopic species in precipitation described by the Global Meteoric Water Line of $\delta D = 8 \delta^{18}O + 10$. This line was not derived from first principles, however the slope is related to the ratio of the fractionation factors ($\alpha_D/\alpha^{18}O$), while the intercept is a measure of the kinetic effects in the system.

The most significant caveat to studies involving the stable isotopic composition of precipitation is that extreme variations are observed. Temporal variations have been observed on the intra-

storm to year (and beyond) scale, whereas geographic variations have been observed on the scale of only kilometers. Thus, depending on the level of detail required and type of study, reliance on an existing data base is generally not possible, and instead, a copious number of samples of precipitation must be collected for a considerable length of time (at least 2 - 3 years) to obtain a credible isotopic average.

A secondary caveat to catchment basin studies is that precipitation may not be only in the form of rain or snow. There are a wide variety of modes of precipitation that may not be captured by the standard meteorological tool. These may include fog-drip, the coalescing of blowing fog droplets on foliage to produce large drops that rain to the ground; and occult precipitation, condensation on a solid surface caused by temperature gradients between the air and the surface due to radiation cooling at night. These modes of precipitation have been shown to represent significant fractions of the water budget in certain unique environments. In addition, surface effects such as interception and throughfall may also alter the stable isotopic composition of precipitation in a way that can not be measured by properly-sited conventional rain gages. Rain gages have been designed as meteorological tools to measure the amount of typical precipitation (rain and snow) reaching the ground, unobstructed by surface effects. Isotopic measurement of the water collected in the classical manner may not represent the isotopic composition of water which reaches the ground to become available for catchment basin studies conducted by an isotope hydrologist.

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Chapter 4

Isotopic Fractionation in Snow Cover

Lee W. Cooper

4.1 Introduction

Stable isotopes have been used for more than 25 years in the study of water flow resulting from snowmelt. The work of Dinçer et al. (1970) was among the earliest peer-reviewed tracer studies of snowmelt runoff, building upon the seminal work on isotope variations in natural waters by Epstein and Mayeda (1953), Dansgaard (1954), Craig (1961) and Friedman et al. (1964). The hydrological applications of natural stable isotope variability in snow were reviewed by Moser and Stichler in 1980. Since that review, studies utilizing the differences among the isotopic content of snow, summer rainfall, and groundwaters for estimating flowpaths and sources have continued to expand, becoming an important subset of the larger hydrological use of isotopic tracers.

The modeling of snowmelt contributions to streamflow or groundwater is complicated by isotopic fractionation during snow formation, accumulation, ablation, and phase change during melt. The isotopic content of any snowpack is in large part controlled by variations in the isotopic content of individual precipitation events, as discussed in Chapter 3. The formation of snow flakes, however, can involve additional isotopic fractionation. This is especially true in polar regions where snow is not formed by freezing of droplets, but rather as a vapor deposition process with an associated kinetic isotopic fractionation (Jouzel and Merlivat, 1984; and Chapter 2). This results in high deuterium excess values, ($d > 10\text{‰}$), where:

$$d = \delta D - 8\delta^{18}O \quad (4.1)$$

Prior to snowmelt, additional variation in stable isotopic content is introduced by the partial melt and re-freezing processes, changes in the crystal structure of snow, and the exchange with atmospheric and soil moisture. During snowmelt, additional isotopic fractionation associated with the phase change between liquid and solid phases of water may result in a decreased meltwater concentration of the heavier isotopes of ^{18}O and D relative to residual ice or snow. This chapter will focus on describing the fundamentals of isotopic fractionations in snow cover during accumulation and snowmelt, and presents an overview of isotopic water balance and evaporation; catchment scale and runoff considerations will also be addressed in this chapter. Several studies of meltwater isotopic tracing are presented in Chapter 12.

4.2 Isotopic Changes to a Snowpack

4.2.1 Changes during snow accumulation

Prior to melt, vapor in the snowpack can exchange with water in the soil and vegetation, and with atmospheric moisture. Isotopic exchange, combined with changes in the crystal structure of snow present will tend to dilute the specific isotopic signals contributed by individual storms over a winter season (Judy et al., 1970; Krouse and Smith, 1972; Krouse, 1973; Friedman et al., 1991; Claassen and Downey, 1995). Although annual cycles in variability of the stable isotope content of precipitation falling upon glacial ice sheets can be preserved sufficiently for historical climatic analyses (e.g. Hammer et al., 1978; Jouzel et al., 1983), isotopic fractionation following snowfall can often obscure seasonal or annual variations in the isotopic content of precipitation (Epstein and Sharp, 1959; Deutsch et al., 1966; Picciotto et al., 1968; Krouse and Smith, 1972; Jouzel and Souchez, 1982). In some catchments, high winds increase rates of ablation, snow crystallization, and water vapor exchange, causing increases in the $\delta^{18}\text{O}$ and δD values of upland slope snowpacks (Cooper et al., 1993; Nikolayev and Mikhalev, 1995), while preserving relatively negative $\delta^{18}\text{O}$ and δD values in snow in lower-lying, wind-sheltered areas. In catchments with large elevation changes, this effect is opposite to the expected orographic decrease in heavy isotope content with increasing elevation (Friedman and Smith, 1970; also see Chapter 3).

Claassen and Downey (1995) discussed in detail the potential changes in the isotopic composition of snow resulting from interception by vegetation. In forested catchments, more than one-half of precipitation may be lost to evaporation, largely due to the greater evergreen leaf area available for interception of precipitation. Claassen and Downey (1995) also point out that high evaporation of intercepted snow in forested catchments will result in isotopic modification of the remaining snow on branches and needles, and will have a significant influence on the isotopic composition of snowmelt available for groundwater discharge.

Studies of experimental and natural snowpacks (Sommerfield et al., 1991; Friedman et al., 1991) demonstrated that complex changes in isotopic content can be expected to occur between accumulation and melt. In an experimental snowpack study conducted in a freezer, Sommerfield et al. (1991) applied a vertical thermal gradient to induce formation of depth hoar (a re-crystallized form of snow) in an isotopically homogeneous snowpack. The change in both $\delta^{18}\text{O}$ and δD values over time were used to evaluate the specific mechanisms for shifts in the isotopic content of the snowpack. Both the upper and lower parts of the snowpack showed significant isotopic shifts of up to 10‰ in $\delta^{18}\text{O}$ and 50‰ in δD (Figure 4.1). The residual snow that lost mass through re-distribution generally became isotopically heavier, while frost that condensed on surrounding freezer walls was 10‰ lower in δD than the original snow (Sommerfield et al., 1991).

Friedman et al. (1991) investigated the effect of thermal gradients, derived from warmer underlying soil, on a natural snowpack. In one treatment, snowpacks were protected from exchange with underlying soil moisture by a plastic sheet; in a second treatment, snowpacks were resting on elevated tables such that the thermal gradient was eliminated; and in the control treatment, exchange between soil moisture and snowpack was unimpeded. The thermal gradient in the treatment with plastic barriers and in the control was crucial in the formation of depth hoar, and snow in the layers closest to the soil was isotopically heavier than corresponding

layers in the elevated table treatment. Although some exchange with isotopically heavier soil moisture was a contributing factor in the control treatment, the vertical distribution of stable isotopes in the plastic barrier treatment indicated that the isotopic content change had also resulted from upward migration of isotopically lighter moisture from the bottom layers of the snowpack. Although isotopic fractionation during sublimation is an apparent element in this process, the significant mechanism seems to have been fractional condensation of water vapor derived from sublimation upon growing snow crystals.

Direct evaporation and exchange with atmospheric water vapor significantly alter the isotopic composition of the upper snow layers. Enrichment in ^{18}O and D in snowpacks as a result of evaporation is a predictable outcome (Rodhe, 1987), and theoretical fractionation models developed for evaporation from well-mixed water bodies (e.g. Craig and Gordon, 1965) are reasonably successful at predicting the effects of simple evaporation once they are modified to account for the less than well-mixed conditions of natural snowpacks. However, isotopic change in snowpacks is more complicated than simple surface evaporation, and is dependent on variable conditions such as soil temperature, soil moisture, relative humidity, air temperature, vegetation cover, and the period of time the snowpack is present on the ground.

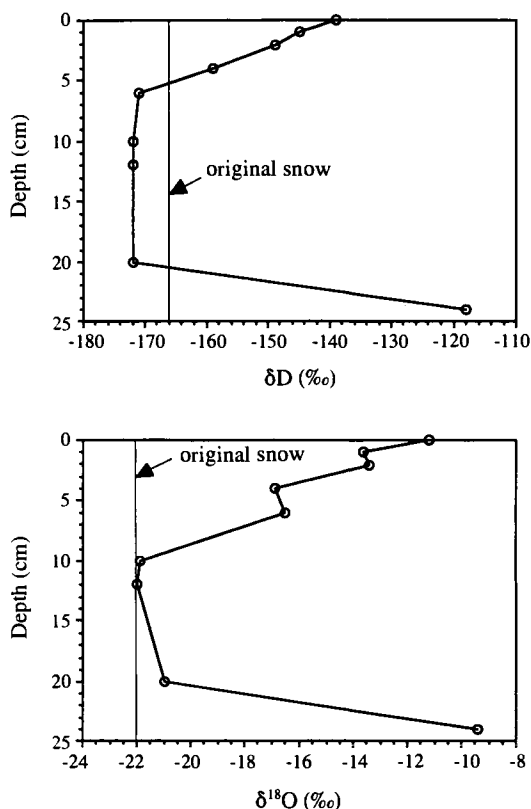


Figure 4.1. Isotopic profiles of δD and $\delta^{18}\text{O}$ for a homogenous snowpack after 31 days of heat (-1.2°C) applied at the bottom of the snowpack, stored in an open box in a freezer, in which a constant temperature of -24°C was maintained. Modified from Sommerfield et al., 1991.

Furthermore, rainfall during the period of snow accumulation results, in most cases, in a snowpack with heavier isotopes because the rain is usually enriched in ^{18}O and D relative to snow (Maclean et al., 1995). Each of these variables makes it difficult to quantify a priori how a particular snowpack will be altered isotopically between the time of snowfall and snowmelt.

Another complication in most snow covered areas is isotopic fractionation associated with partial melt, and re-freezing. Although a model has been developed for predicting the isotopic content of glacial ice where re-freezing processes have been significant (Souchez and Jouzel, 1984), additional research is needed to accurately predict the vertical (within snow profiles) and horizontal (spatial) variability in the isotopic content of snow within any specific catchment (Unnikrishna et al., 1998).

Despite the potential for changes in snowpack isotopic composition during the period of snow accumulation discussed above, snowpacks often are regarded as a record of the isotopic variability of winter precipitation (Rodhe, 1987). In work at Svartberget, Sweden in 1982, Rodhe was able to show good agreement between the isotopic composition of snowpacks and the equivalent amount of winter precipitation (Figure 4.2). Precipitation was most depleted in heavy isotopes in the middle of the winter, coinciding with the coldest air temperatures, and was less depleted during most early and late season snowfall events. At least in this case, the snowpack monitored on March 23 faithfully recorded the integrated trends in snowfall events (Figure 4.2).

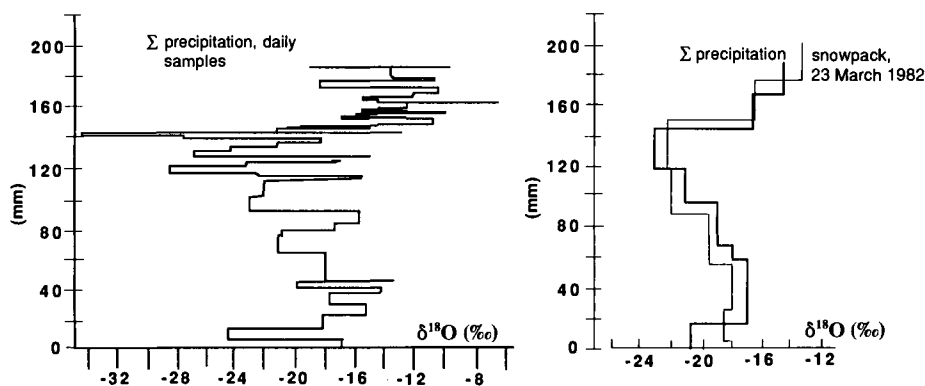


Figure 4.2. $\delta^{18}\text{O}$ values of snow compared with winter precipitation, for Svartberget, Sweden, March, 1982. Vertical axes are water equivalents of precipitation or snowpack. The vertical layering observed is a result of variability in precipitation during the snow accumulation period. Modified from Rodhe, 1987.

Isotopic fractionation effects prior to melt are not trivial; therefore, extreme care should be taken in snow sampling in order to obtain truly representative isotopic compositions. An adequate sampling scheme to characterize the isotopic content of a snowpack before melt would include sufficient sampling of snow, which must be completely melted and also kept covered to prevent isotopic fractionation during evaporation. In cases where significant snowmelt has occurred and water has re-frozen within surface soil layers, it should be

recognized that it could be very difficult to estimate accurately the isotopic signal contributed by the snowpack during melt. For this reason, comprehensive sampling of snowmelt, instead of snow, is generally recommended for hydrograph separations (see Chapter 12 for further discussion).

4.2.2 Changes during snowmelt

Snowmelt does not normally proceed under conditions of isotopic equilibrium, but the effective isotopic fractionation observed is often close to experimentally determined values. Hence, it is useful to begin any consideration of isotopic fractionation during snowmelt with an idealized treatment that assumes isotopic equilibrium during the phase change from snow to water.

Theoretical considerations

For a phase change of water at equilibrium, an equilibrium isotopic fractionation coefficient, α , can be defined (Friedman et al., 1964; also see Chapter 2):

$$\alpha = R_{\text{product}} / R_{\text{source}} \quad (4.2)$$

where R = the ratio of water containing ^{18}O or D relative to the isotopically lighter form of water ($^1\text{H}^1\text{H}^{16}\text{O}$). The product, for the purposes of this discussion, is meltwater for melting snow, vapor for evaporating liquid water, or ice for condensing vapor or re-freezing liquid water. Expressed in the more conventional " δ " units notation, this equation becomes:

$$\alpha = [1 + (\delta^{18}\text{O} \text{ or } \delta\text{D}_{\text{product}} / 1000)] / [1 + (\delta^{18}\text{O} \text{ or } \delta\text{D}_{\text{source}} / 1000)] \quad (4.3)$$

Let us assume equilibrium conditions during phase change of an isotopically homogeneous snow column melting as a closed system without significant evaporation or sublimation. In this case, the predicted isotopic fractionation during melt or freezing can be approached as a modification of Rayleigh-type relations used to describe changes in snowmelt isotopic composition (Stichler et al., 1981). In this modified form, changes in snowpack isotopic composition at equilibrium are primarily a function of the isotopic fractionation during phase change between the product (either ice or water), and the source (either water or ice), depending upon the phase change direction (Friedman et al., 1964; Herrmann et al., 1981; Jouzel and Souchez, 1982; Souchez and Jouzel, 1984):

$$(\delta_{\text{product}} + 1000) = (\delta_{\text{source}} + 1000) f^{(1/\alpha)-1} \quad (4.4)$$

where δ is $\delta^{18}\text{O}$ or δD , and f is the fraction of source (e.g. snowpack) remaining. In addition to assuming no evaporation or sublimation, this form of the Rayleigh distillation equation assumes that (1) snowmelt is slow (phase change at equilibrium), (2) the meltwater is immediately removed without exchange with remaining snow, and (3) no additional precipitation occurs during the melt. These are rather unlikely natural conditions; therefore, it is useful to consider the additional kinetic isotopic fractionation effects that can also affect the

isotopic composition of the reaction source. In this discussion, the source will be snow, the ultimate product will be meltwater and there will be fractionation through exchange with atmospheric water vapor. According to the model of Craig and Gordon (1965) and discussion in Chapter 2:

$$(\delta_{\text{meltwater}} + 1000) = 1/\alpha \{ f^\alpha [(\delta_{\text{snow}} + 1000)\alpha - (\delta_{\text{airvapor}} + 1000)b] + (\delta_{\text{airvapor}} + 1000)b \} \quad (4.5)$$

$$\text{where } \alpha = [1/\alpha^* - (1 - h)]/(1 - h) \text{ and } b = h/(1 - h) \quad (4.6)$$

with h = relative humidity and (α^*) = kinetic isotopic fractionation factor.

Practical considerations

Many of the terms in Equations 4.2 - 4.7 are difficult to measure, particularly the effective kinetic isotope fractionation (Equation 4.5). These terms vary dynamically in response to local humidity at the boundary layer of exchange between snow and atmospheric water vapor. As pointed out in Section 4.2.1, molecular exchange between snow crystals and water vapor is not limited to the top of the snowpack (Sommerfield et al., 1991; Friedman et al., 1991). This process can create or accentuate large variations in the snow profiles. In snowpacks sampled at the end of the winter in Svartberget, Sweden, $\delta^{18}\text{O}$ variations of 6 to 9‰ in individual profiles were observed (Rodhe, 1987). This variation obviously makes it more difficult to estimate the snowpack stable isotope content at any point during snowmelt. Even if snowpack isotopic heterogeneity induced by evaporation and condensation effects, or storm-to-storm variation is unimportant, a Rayleigh distillation-based treatment of melting snow assumes conditions that are uncommon in the field. As a result, it is not always certain if isotopic fractionation during phase change significantly alters the isotopic content of the source of the meltwater. There are many examples where phase change fractionation has been neglected when modeling snowmelt contributions to streamflow. This is done at some peril because water depleted in heavy isotopes is released first during melt and the residual snowpack normally becomes more and more enriched in heavy isotopes. As a snowpack continues to melt, the isotopic content of meltwater will continue to shift towards more positive δ values.

Isotopic fractionation during phase transition between ice and water

Many experimental and observational studies of the effective fractionation between ice and liquid water have been made, centering upon an approximate increase of 2 to 3‰ in $\delta^{18}\text{O}$ and 15 to 20‰ in δD for ice relative to water from which it freezes (Weston, 1955; Posey and Smith, 1957; Friedman et al., 1964; Merlivat and Nief, 1967; O'Neill, 1968; Árnason, 1969a; Suzuola and Kimuna, 1973). Most experimental studies of this isotopic fractionation have involved the freezing of rapidly stirred liquid water, rather than the melting of ice or snow. Therefore, the magnitude of the effective isotopic fractionation during natural snow melt is not necessarily known.

Jouzel and Souchez (1982) and Rodhe (1987) point out that compact ice should melt without observable isotopic fractionation because of the low diffusion coefficients of isotopically heavy water molecules in solid ice ($\sim 10^{-11} \text{ cm}^2 \text{ s}^{-1}$). Observations of heavy isotope-depleted meteoric

water preserved in undersea permafrost (Mackay, 1972) support the concept of very slow isotopic exchange in liquid-free solid ice or permafrost, probably on the order of geological time scales. By contrast, porous snows and firns are subject to isotopic fractionation during melt with an effective isotopic fractionation similar in magnitude to that observed for the phase transition from liquid water to ice (Árnason, 1969b; Buason, 1972; Moser and Stichler, 1980; Stichler et al., 1981; Herrmann et al., 1981; Ingraham and Taylor, 1989).

Detailed laboratory experiments with homogeneous snow cores showed that initial meltwater was depleted in deuterium by 15‰ relative to the snow in the pack (Herrmann et al., 1981). Although these experiments were performed in a closed cold room, the final integrated meltwater content was within 1.5‰ of the original snow. Since mass evaporation loss was approximately 7%, evaporative enrichment is probably the reason why the final integrated meltwater composition did not reach the original isotopic content of snow. Another possibility is molecular exchange with water vapor (which escaped the cold room) and related isotopic fractionation, which can occur even in the absence of evaporation (Rodhe, 1987). In any case, the discrepancy in the δD values between the integrated meltwater versus initial snow is rather small, just slightly larger than the analytical precision of the measurement ($\sim 1\%$). In an idealized closed Rayleigh distillation, the isotopic content of product (meltwater) integrated over the whole snowmelt period would be identical to source (snow) regardless of the isotopic fractionation associated with the phase change (Friedman et al., 1964; Dansgaard, 1964). These laboratory findings (Herrmann et al., 1981) suggest that evaporation losses may be a factor under field conditions and can affect the observed isotopic content of meltwater.

A field example is provided by snow core samples collected in the Loch Vale Watershed, Colorado during 1994 to evaluate mechanisms that control streamflow in an alpine watershed (Mast et al., 1995). The average $\delta^{18}O$ of the snowpack and the range of $\delta^{18}O$ values from 30-cm layers within the cores (shown in Figure 4.3) increased slightly during the accumulation, becoming progressively enriched in ^{18}O and the layers more uniform as melt continued. The $\delta^{18}O$ of meltwater (also shown in Figure 4.3) increased rapidly during the initial stages of melt, and then remained relatively constant throughout most of the melt period. The isotopically light meltwater values observed during the initial stages of the melting period were attributed to differences in the melting temperatures of waters with different isotope ratios, resulting in isotopically light meltwater relative to the bulk snowpack, whereas the isotopically heavy values observed at the end of the melt period coincide with several late spring snows. A simple mass balance calculation indicates the volume-weighted mean $\delta^{18}O$ of meltwater was 1.4‰ heavier than the average snowpack composition measured in early April (Mast et al., 1995).

Despite this example of isotopic fractionation during snowmelt, it should be pointed out that significant isotopic fractionation is not always observed in the field (e.g. Bottomley et al., 1986). In other cases, the isotopic content of snowmelt has been treated as not being appreciably different from the snow from which it melts (e.g. Lawrence, 1987; Cooper et al., 1991; Gibson et al., 1993b). Nevertheless, it is difficult to rigorously test this assumption.

Recent work in a catchment in a suburban area of Peterborough, Ontario (Buttle et al., 1995) illustrates some of the sampling complexities required for evaluating the appropriate $\delta^{18}O$ values of snowmelt to use in an isotopic hydrograph separation. Urbanization increases the rapidity of the hydrological response to snowmelt or rainfall events because of increased impermeable and otherwise modified surfaces. Buttle et al. (1995) found that the heterogeneity

of permeable surface areas, whether modified or natural, made it difficult to estimate the appropriate $\delta^{18}\text{O}$ value to use for the snowmelt (event) in the hydrograph separation. Although the spatial area of paved roads and other impermeable surfaces was constant, removal of snow from roads may have created spatial heterogeneity in the isotopic content of the snowpack. A larger problem seems to have been spatial variability in the delivery rate of snowmelt from variably permeable surfaces.

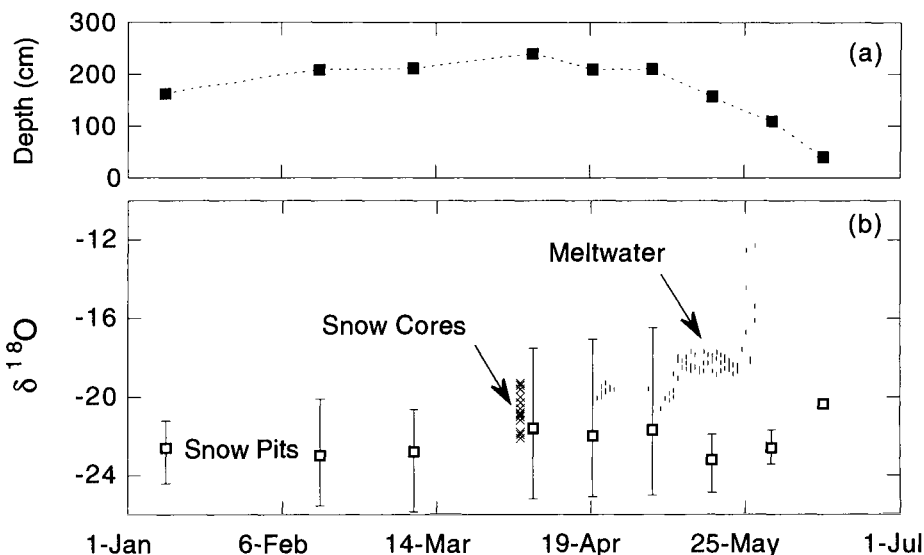


Figure 4.3. (a) Total snow depth at each snowpit collection. (b) average $\delta^{18}\text{O}$ values measured in the snowpit profiles (squares) with range of compositions in layers sampled (bars); snow cores collected during the annual snow survey (x's); and runoff collected from the melt lysimeters (dashes). From Mast et al., 1995.

Permafrost may represent an extreme case of impermeability that can provide insight into isotopic fractionation in melting snow cover in the absence of large-scale mixing with groundwater. Work at Imnavait Creek, Alaska (Cooper et al., 1993), within a catchment underlain by continuous permafrost and a seasonal active layer that remains totally frozen until after snow cover is completely gone, suggests that isotopic fractionation during snowmelt has a large cumulative impact on meltwater composition. Values of $\delta^{18}\text{O}$ in streamflow increased during a one-week snowmelt from -30‰ to -22‰ (Figure 4.4). A similar pattern, although less extreme, was observed at Apex River, Baffin Island (Obradovic and Sklash, 1986), where initial snowmelt was more depleted in ^{18}O than unmelted snow, and $\delta^{18}\text{O}$ values of streamflow increased over the period of melt. However, the two studies differed somewhat in their interpretation of these changes. Obradovic and Sklash (1986) estimated that approximately 50% of the snowmelt discharge was derived from "old" groundwater sources. In the case of the study in Alaska, the groundwater contributions were negligible. Independent physical measurements indicated that there was no significant mixing between snow and underlying frozen soil moisture before all snow was melted (Everett et al., 1989; Kane et al., 1989; Hinzman et al., 1991; Kane et al., 1991). Cooper et al. (1993) concluded that this isotopic shift

in streamflow resulted from an increasing heavy isotope content of residual snowpack during melt. This was consistent with observations of increasing $\delta^{18}\text{O}$ and δD values in snowpacks during melt that have been widely observed (Sharp et al., 1960; Deutsch et al., 1966; Árnason, 1969b; Krouse, 1973; Martinec et al., 1974; Stichler et al., 1981; Herrmann et al., 1981; Rodhe, 1981; Ingraham and Taylor, 1989; Moore, 1989).

Isotopic fractionation in the snowpack during melt may indeed be a dominant factor in determining the isotopic content of runoff. Therefore, adequate sampling of snowpack during melt (as well as meltwater) becomes crucial (see also discussions in Chapter 12). As a snowpack that is increasingly enriched in heavy isotopes continues to melt, the isotopic composition of meltwater will continue to increase. This is the same shift as would be expected due to mixing of early snowmelt with groundwater sources. Thus isotopic fractionation during snowmelt, unless otherwise accounted for, will tend to increase the apparent contribution of heavy isotope-enriched groundwaters to streamflow. Cooper et al. (1993) suggest that this may be the correct explanation for the estimates of remarkably high contributions of soil waters (50% or more) to streamflow that have been reported for several catchments that are underlain by presumably impermeable permafrost (Obradovic and Sklash, 1986; Cooper et al., 1991; Gibson et al., 1993b).

Studies of snowmelt contributions in permafrost catchments may serve a valuable function as a control indicator of isotopic fractionation during snowmelt that is unavailable in more temperate catchments underlain by unsaturated soils. Because of the presence of presumably

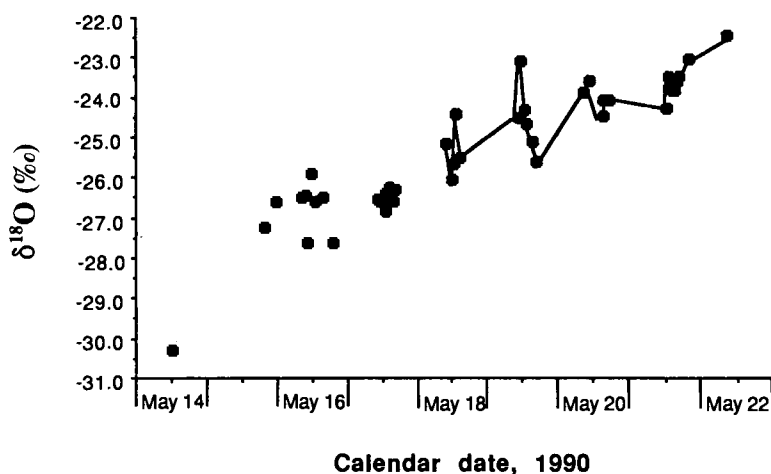


Figure 4.4. $\delta^{18}\text{O}$ values of streamflow during snowmelt at Imnavait Creek, Alaska, 1990. Snowmelt in this small 2.2 km² catchment north of the Brooks Range typically occurs over a one-to-two week period, and all snow is gone before any thawing of soil moisture. In 1990, streamflow began on 14 May (<1 L min⁻¹), and peak streamflow was observed on 17 May, reaching ~1000 L min⁻¹. Variability in $\delta^{18}\text{O}$ values of streamflow were muted on this date, suggesting a dilution of all variability in snowmelt contributions at the peak of streamflow. Early morning maxima in $\delta^{18}\text{O}$ values on 18 May–20 May, on the rising limb of the stream hydrograph, may have been due to the overnight retention of relatively ^{18}O -enriched meltwater due to re-hardening of the snowpack. Modified from Cooper et al., 1993.

impermeable permafrost, groundwater contributions to streamflow should be lower in this instance than in any other category of catchment. Consequently, at least for the Imnavait Creek study (Cooper et al., 1993), there must be either some unrecognized mechanisms for isotopic exchange between melting snow and underlying frozen soil ices with very low isotopic diffusivity, or, alternately, the apparent soil water contributions to streamflow during snowmelt are overestimates. Rodhe (1987) points out that molecular exchange during a slow, prolonged snowmelt might be a factor in increasing the heavy isotopic content of overland flow, but this is likely to be more significant in the case of liquid water within unsaturated soils, relative to molecular exchange with ice in frozen soils. It is uncertain if the conclusions drawn from the Imnavait Creek work are applicable to other catchments underlain by permafrost, or at temperate latitudes, since the prolonged snow accumulation period, short snowmelt, frozen soil conditions, low relative humidity, and apparently large loss of snow through ablation at Imnavait Creek (Kane et al., 1989) may result in an unusually large isotopic fractionation effect. Nevertheless, this study does indicate that adequate attention to snowcover sampling during melt might improve the utility of stable isotope measurements for calculating snowmelt contributions to runoff.

Freezing and repeated freeze/thaw cycles

The best documented isotopic effects associated with phase changes between ice and water involve the phase change from liquid to solid. Significant effects have been observed during the re-freezing of meltwater in temperate glaciers (Árnason, 1969b; Jouzel and Souchez, 1982), in the reaction between precipitated calcite and glacial meltwaters (Hanshaw and Hallet, 1978; Lemmens et al., 1982; Sharp et al., 1990), and in the relationship between sea ice and surface waters in the marine environment (Friedman et al., 1964; Tan and Fraser, 1976; Tan and Strain, 1980). Freezing of liquid water has a differential effect on δD values relative to $\delta^{18}O$ values in meteoric water (Souchez and Jouzel, 1984), leading to a decrease in the least-squares slope of the relation between δD and $\delta^{18}O$ that characterizes water of meteoric origin: $\delta D = 8\delta^{18}O + 10$ (Craig, 1961). In theory, this suggests that rain or meltwater that later becomes frozen within a snowpack can be distinguished from snow, but in practice, the characteristic isotopic "signature" of frozen water (i.e., enriched relative to water and plotting along a lower-slope meteoric water line) within ice has only found limited use. This is because evaporation produces a similar isotopic effect, when the lower mass species (HDO) evaporates slightly faster than higher mass species (HH¹⁸O), leaving the residual water pool with increased HH¹⁶O concentration (as discussed previously in Chapter 2). Consequently, it is difficult to separate isotope enrichment due to evaporation from isotope enrichment due to freezing of liquid water in snowpacks or permafrost, although it seems reasonable to assume that re-freezing effects must be dominant in solid glacial ice (Árnason, 1969b; Jouzel and Souchez, 1982).

4.2.3 Isotopic water balance and evaporation

The estimation of net evaporation during the ablation period was an early application of stable isotope studies in snow dominated systems (Moser and Stichler, 1980; Stichler et al., 1981). Essentially, the hydrologic mass balance, (with all units in cm) is:

$$R = W + P - E + C \quad (4.7)$$

Then, this is combined with the isotope mass balance to form:

$$I_R R = I_W W + I_P P - I_{E-C} (E - C) \quad (4.8)$$

where R = Runoff depth (from lysimeter), W = water equivalent of the melted snowcover, P = precipitation during ablation, E = evaporation during ablation, C = condensation during ablation, and where I_R , I_W , I_P , and I_{E-C} are the weighted, averaged isotopic contents during the ablation period.

Stichler et al. (1981) treated the snowmelt process as a Rayleigh-type distillation in their study of experimental plot lysimeters in Weissfluhjoch, Switzerland. They assumed an effective isotopic fractionation due to evaporation during snowmelt close to equilibrium values, as in Equation 4.4:

$$(\delta_R + 1000) = (\delta_{W+P} + 1000) f^{(1/\alpha)-1} \quad (4.09)$$

where f is the water equivalent fraction of snow and precipitation remaining, α is the equilibrium isotopic fractionation (Equation 4.2) between snow and water vapor, taken to be 1.132 for D/H and 1.01423 for $^{18}\text{O}/^{16}\text{O}$. The use of melt lysimeters in this study simplified the calculation of loss due to evaporation because there was no need to account for infiltration and storage. Kinetic isotopic fractionation effects during evaporation were then estimated to take into account relative humidity and atmospheric water vapor exchange, using forms of Equation 4.5 for both stable isotopes. The estimates of evaporation during ablation agreed with independent hydrological measurements within a few percent. This method can therefore provide an alternate estimate of evaporation in catchments where there is only limited water infiltration into soils, such as those underlain by permafrost.

Evapotranspiration is second only to surface runoff as a mechanism for water loss in watersheds underlain by permafrost. In practice, the loss due to evapotranspiration is difficult to measure accurately and directly (Kane et al., 1990, 1992; Gibson et al., 1993a). Recently, Gibson et al. (1993a) used δD and $\delta^{18}\text{O}$ covariance in lake waters to estimate catchment-scale evaporation in a northern Canadian catchment. Further work within permafrost regions is needed to fully develop the potential use of stable isotopes to estimate evaporation during ablation and snowmelt, as well as to estimate water residence times in catchments or lakes. Figure 4.5 presents an example of the potential for understanding annual hydrologic cycles using isotopic profiles of Toolik Lake, in northern Alaska over a summer season of open water. These profiles show (1) the initial overwinter mixed status of the lake (in May), (2) the distinct contributions of snowmelt that decrease the $\delta^{18}\text{O}$ values of lake water in June and July, and (3) surface water stratification in August. More positive $\delta^{18}\text{O}$ values in surface waters were associated with summer rainfall contributions and possibly evaporation.

4.2.4 Catchment scale and runoff considerations

The geographical distribution of $\delta^{18}\text{O}$ values in the Kuparuk River during snowmelt (Figure 4.6), into which Toolik Lake ultimately drains, provides insight into the problem of temporal

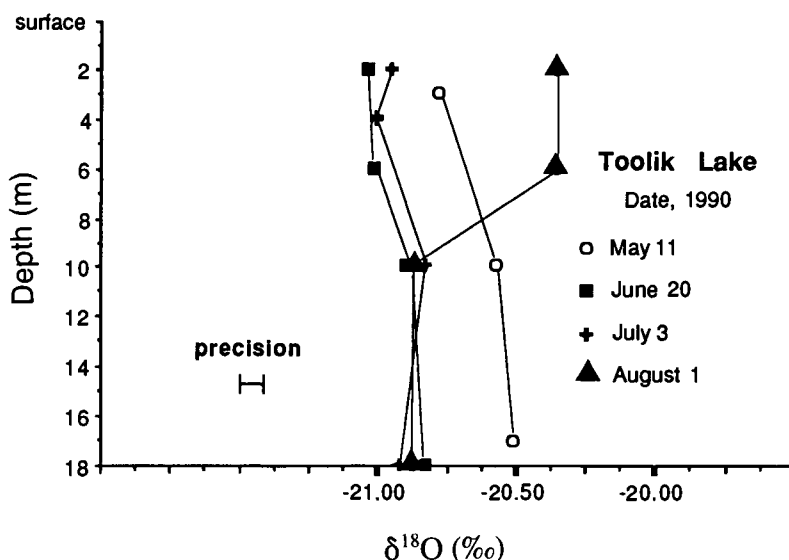


Figure 4.5. $\delta^{18}\text{O}$ values of lake water in Toolik Lake, Alaska, 1990, showing influence of snowmelt on annual hydrological cycle. In May, while the lake was still frozen, the water column was well mixed with little isotopic variability. Water profiles collected in June and July are shifted towards more negative $\delta^{18}\text{O}$ values, as a result of snowmelt contributions. Finally, by August, a thermocline developed, and surface water layers showed more positive $\delta^{18}\text{O}$ values, corresponding to storage of summer rainfall in the stratified surface layers.

and spatial scale when considering contributions of different isotopic sources in catchments during snowmelt. These river samples, collected contemporaneously with the Toolik Lake samples and the more detailed Imnavait Creek data set discussed in Section 4.2.1, show that natural springs that freeze overwinter into ice overflows (aufeis) provide water to the river that has a distinct isotopic content ($\delta^{18}\text{O} = -19.6$ to -19.9‰) relative to more negative $\delta^{18}\text{O}$ values contributed by direct snowmelt. These $\delta^{18}\text{O}$ values of water in aufeis are similar to summer precipitation at this location, suggesting overwinter storage, although isotopic modification during groundwater freezing cannot be excluded (Michel, 1986). The water contributed by the aufeis melts with the lack of isotopic fractionation characteristic of the melting solid ice (Jouzel and Souchez, 1982). It is not clear why there is good separation of contributions to streamflow during snowmelt in the Kuparuk basin, whereas more detailed but contemporaneous data from Imnavait Creek, the catchment immediately to the east, (Figure 4.4; Cooper et al., 1993) appear to raise fundamental questions about the stability of the isotopic signal contributed by snowmelt. Of course, the explanation lies partly in the duration of sampling, which extended over one day in the Kuparuk River catchment (Bruce Peterson, personal communication) but over the entire snowmelt period in the Imnavait Creek catchment. A more complex message would seem to be that stable isotopic analyses, while potentially powerful in application, can also be potentially misleading. Alternative tracers must be used and time consuming physical hydrologic measurements must still continue to be made.

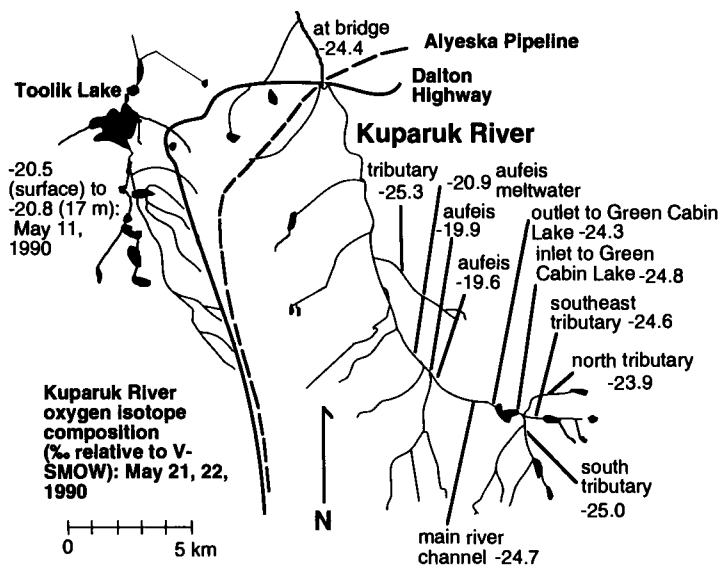


Figure 4.6. $\delta^{18}\text{O}$ values of surface waters in the Kuparuk River basin, Alaska, during the May, 1990 snowmelt. Water in the upper river tributaries and lakes had $\delta^{18}\text{O}$ values $\sim -25\text{‰}$, indicating contributions predominantly from melting snow. However, water in aufeis feature (ice overflow) contributed a more positive $\delta^{18}\text{O}$ signal, which led to an increase in the integrated river $\delta^{18}\text{O}$ value ($\sim -24\text{‰}$) downstream.

4.3 Future Directions for Research

Isotopic fractionation of hydrogen and oxygen isotopes during snow accumulation and melt can create complications for the study of snowmelt contributions to streamflow generation. These complications are not insurmountable and may in fact provide new insights into dynamics of the snow accumulation and melt process. Nevertheless, these complications suggest the need to explore and re-think the use of alternative tracers that can help validate and assure correct interpretations when δD and $\delta^{18}\text{O}$ are used to study snowmelt processes. Radioactive isotopes have always had a special appeal in this respect because the very low activities observed in environmental samples normally require only small or negligible adjustment to account for the same isotopic fractionation effects that can complicate use of stable isotopes. Of course, application of radioactive tracers to hydrological problems is not without its own complications, depending upon half-life, chemical reactivity, inputs from bomb fallout, and other factors (as discussed in Chapters 8 and 20). Nevertheless, radioisotope distributions in snowpacks and underlying soil could help unravel the extent of conservative behavior exhibited by stable isotopes in water.

One example of a study that combines examination of short-lived radionuclides present only in snowpack with stable isotopes is by Cooper et al. (1991). In this study, the contribution of ^{18}O -depleted snowmelt was assumed to be conservative and was used to confirm the particle-reactive behavior of radioisotopes such as ^7Be (half-life 53 d), during the high flux of snowmelt in an Arctic catchment. This study also examined for the first time fluxes of natural concen-

trations of ^{35}S (half-life 87 d) from snow to streamwater. This radioisotope, derived from cosmic ray spallation of ^{40}Ar , was apparently retained on tundra vegetation at a much higher proportion (~75%) within the catchment than indicated from analyses of sulfate concentrations in streamwater (Everett et al., 1989; Cooper et al., 1991).

Other potential natural and anthropogenic tracers that could be used under the right circumstances include ^{22}Na , ^{32}Si , ^{81}Kr , ^{85}Kr , and ^3H . Tritium, for example, might be a very useful tracer in catchments underlain by shallow permafrost. In such catchments, the water stored within permafrost has essentially no tritium content. In contrast, the concentrations of tritium in soil water in the seasonally thawed, active zone is likely to be heavily influenced by overlying snowcover (i.e., be relatively abundant). In such a catchment, the annual cycle of active zone thaw would be followed by freezing, which would effectively limit the infiltration of either cosmic ray-derived and bomb-fallout derived tritiated water into permafrost. Therefore, the presence or absence of tritium could be of practical use in monitoring changes in permafrost depth. This is an economically critical issue for protection of roads, bridges, pipelines and other infrastructure, especially considering current projections of global climate change in Arctic regions. This monitoring of permafrost status could be mounted on the scale of whole river basins, if a sufficient program of tritium concentration measurements could be made for snowpack, thaw zone moisture, and surface runoff. This is, potentially, a powerful indicator of recent shifts in active zone-permafrost boundaries, which may be influencing organic carbon accumulation in Alaskan North Slope tundra (Oechel et al., 1993).

A potentially large-scale experiment has been initiated in the former Soviet Union by injudicious disposal of nuclear materials (Yablokov et al., 1993). A large portion of Soviet nuclear research and development was undertaken in Arctic regions such as the Novaya Zemlya archipelago, which are underlain by permafrost. Among the chemically conservative or semi-conservative radionuclides that have been apparently released in relatively large amounts are ^3H , ^{36}Cl , ^{99}Tc , ^{129}I , and ^{237}Np . The tragedy of this radioactive contamination could contribute to a better understanding of hydrology in Arctic and boreal regions if national security sensitivities in Russia can be overcome, and adequate international financial resources permit joint research on this problem. Given the half-lives of some of the radionuclides involved (e.g. 15.7×10^6 y for ^{129}I), research opportunities derived from Soviet and other national nuclear development programs should continue to be available for periods reaching into geological time scales. Although the former Soviet Union was not alone in contributing conservative, long-lived tracers to groundwaters (e.g. Beasley et al., 1992, 1993), the potential applications for Arctic hydrology as a result of nuclear weapons programs are however concentrated in Russia.

It is somehow appropriate that this potential research opportunity, that follows the end of the Cold War era of competition in nuclear weapons development, could prove to be another link in the intertwined history of the use of radio and stable isotopic tracers in hydrological research. The first peer reviewed, published use of stable isotopes to follow snowmelt contributions to streamflow (Dinçer et al., 1970) also documented distributions of bomb fallout tritium in a mountain catchment in order to assess water residence time. The development of interest in stable isotopes of oxygen and hydrogen in the hydrological cycle during the period 1950 - 1970 (e.g. Epstein and Mayeda, 1953; Dansgaard, 1954; Craig, 1961; Friedman et al., 1964) paralleled the introduction of bomb fallout tritium into the hydrosphere. While it is not easy to predict the future utilization of stable isotope tracers in following snowmelt contributions to

catchments, the past record suggests that studies that combine varied tracers, whether radioactive or stable, will continue to provide powerful insights. Several dissolved constituents in snow cover for which stable isotope measurements could be made, including dissolved nitrate, ammonium, and sulfate, remain almost completely unexplored with respect to questions of transport and fate of snowmelt and its constituents.

Finally, much of the knowledge accumulated so far on the topic of isotopic fractionation in snowcover has been rather specific to individual catchments. It is reasonable to expect that the complexities of groundwater infiltration or snowfall interception in forested systems will not be present in catchments underlain by permafrost, or that patterns observed in paved suburban areas may provide significantly different insights to discharge during snowmelt. Therefore, additional studies in a diversity of catchments are needed before the work discussed in this chapter can be fully evaluated for applicability in following snowmelt contributions to catchments.

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Note Added in Proof

Three papers published while this chapter was in the final stages of preparation provide important additional insights over and beyond the topics already discussed:

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- Theakstone, W.H., Knudsen, N.T. 1996. Isotopic and ionic variations in glacial river water during three contrasting ablation seasons. *Hydrologic Processes*, 10: 523-539; and
- McNamara, J.P., Kane, D.L. and Hinzman, L.D., 1997. Hydrograph separations in an Arctic watershed using mixed model and graphical techniques. *Water Resour. Res.*, 33: 1707-1719.

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Isotopic Exchange in Soil Water

Christopher J. Barnes and Jeffrey V. Turner

5.1 Introduction

5.1.1 General discussion of isotopes

Investigations into the processes affecting the hydrological response of catchments typically revolve around interpreting a time record of the flux of water leaving the catchment outlet (the hydrograph) in response to a time record of precipitation intensity. Factors affecting the hydrograph are complex, and to some extent non-linear, and inevitably there is a confounding of the effects of different processes; that is, there is insufficient information in the hydrograph record to reconstruct the processes which gave rise to it. The degree to which the original processes can be reconstructed is greatly enhanced if additional independent information can be obtained. Measurements of chemical data, such as tracer concentrations, can provide such information, particularly if the tracer characteristics are carefully chosen so as to complement existing or more easily obtained data. However, additional data may not necessarily lead to more information. For example, for water balance it is enough to simply quantify bulk transpiration losses; for isotope balance it matters where these losses occur, as isotope concentrations are not uniformly distributed throughout the catchment. This requires further information, or additional assumptions (about mixing processes, etc.) whose validity needs to be assessed. In order to select the most appropriate tracer, it is necessary to understand how various catchment processes affect the range of potentially available tracers, and it is the aim of this chapter to explore the way in which isotopic tracers, and in particular oxygen-18 and deuterium, are affected by the range of processes commonly encountered in the soil water system.

Water falling as precipitation on a catchment will eventually leave the catchment after some finite time. Water which falls on vegetation or other non-porous surfaces may be rapidly re-evaporated, and has little direct impact on the isotopic composition of the remaining water in the catchment (Chapter 6). A proportion of the remaining water will fall on saturated areas directly connected to the stream network, and may leave the catchment rapidly as surface flow via the stream outlet (Chapter 1). The remainder will infiltrate the soil and, depending on catchment conditions and seasonal factors, will spend some time as soil water (including ground water) before leaving the catchment via transpiration, evaporation, groundwater flow or streamflow (Chapter 21). The isotopic signature of this water may initially be modified as it is partially re-evaporated during infiltration through the soil surface, and as it undergoes mixing and diffusional exchange with older water in the soil matrix. Deeper infiltration may result in mixing in a saturated zone, either as a perched water table or groundwater, where some

water is lost to transpiration prior to lateral movement and exfiltration in a saturated area. Evaporation and in-stream mixing may modify the isotopic signature still further before the water finally exits the catchment.

In this chapter we review the fundamentals of isotopic behavior in soil water, including processes of leading to variations in soil water concentrations, provide a simple conceptual model for explaining soil water movement, and present suggestions for new research directions. Discussion will be concerned principally with the environmental tracers deuterium (D) and oxygen-18 (^{18}O) as part of water molecules, and their distribution in the upper soil zone where partial water saturation occurs (the unsaturated or vadose zone). Exchange process modifications to the isotopic composition of soil water and the dependence of these processes on physical parameters of the catchment will also be presented.

5.1.2 Analytical considerations

Given the limited range of natural variation of oxygen-18 and deuterium in meteoric waters (see Section 5.2 below and discussion in Chapter 3), the usefulness of these tracers depends directly on the accuracy and precision with which they can be measured in the laboratory. We consider any process which affects the measured concentration of the isotope as a result of sampling, or during subsequent transport, storage or analysis as undesirable error. In this section we attempt to outline procedures for minimizing these errors, in particular errors associated with sampling, and to give estimates of the magnitude of the uncertainties introduced.

Soil water sampling for isotope profiles requires an estimate of the expected form of the profile to be successful, due to the high spatial gradients often encountered. An estimate of the length scale involved for an evaporation profile is given by the ratio of the effective diffusion coefficient of isotopes in the soil water, D^* to the anticipated evaporation rate E (see Section 5.3.2, Equation 5.4). This length scale ranges from about 2 mm for a wet soil evaporating at 20 mm/day, up to 1 m for water evaporating from a deep water table through very dry sandy soil (evaporation rate ~ 0.1 mm/day), but is typically in the range 1 - 10 cm for catchment soils. This implies relatively fine sampling intervals, and careful sampling to avoid cross contamination of adjacent samples, if the details of the isotope profile are to be preserved. With relatively high isotope concentration gradients, heterogeneity of the sampling area may also affect the measured profile significantly.

Soil samples should be stored rapidly in airtight containers in order to avoid sample modification due to evaporation and isotopic exchange. Because the rate of isotopic exchange is equivalent to that of evaporation into a dry atmosphere, care must be taken at all times to avoid unnecessary sample exposure, particularly in a humid atmosphere where exchange may be significant even though little net evaporation takes place. It is necessary to ensure that the sample bulk is sufficient so that evaporation and exchange during storage are not significant. It is also important to minimize contamination from external sources of water, especially for low water content samples, by oven drying sampling flasks prior to use, for example.

As even small amounts of evaporation can radically modify the isotopic composition of samples, it is important to weigh sample containers as soon as possible after storage. If samples are stored for any length of time before sampling, samples should be re-weighed before

analysis, and those with significant weight loss should be discarded. Typically, a 1% weight loss due to evaporation might result in a 1‰ and 0.4‰ increase in δD and $\delta^{18}O$, respectively, for the remaining sample.

5.1.3 Soil-water extraction techniques

Water samples obtained from catchment outflows in humid areas generally require no special treatment before standard preparation for mass-spectrometry (e.g. those studies outlined in Chapters 10 - 12). Exceptions are very saline water samples, or water from soil samples which must generally be processed before isotope analysis. There are basically four techniques commonly used for this purpose: vacuum distillation, azeotropic distillation, microdistillation with zinc, and immiscible displacement using centrifugation. Walker and Woods (1991) reported on a number of comparisons obtained from a number of laboratories worldwide using these techniques. The somewhat disturbing results reported there suggests that extraction techniques can have a large bearing on the measured isotope ratios. The observed range of up to 30‰ in δD and 3.5‰ in $\delta^{18}O$ was shown to be correlated with the temperature of extraction of the technique used, and was ultimately associated with incomplete extraction.

The results suggest that azeotropic distillation using paraffin oil (kerosene) was the best performed technique for non-gypseous soils, with particular care needed for clay rich soils. The reader is urged to consult more detailed accounts of the procedures and discussions of their relative merits in the published literature, especially Jusserand (1980), Revesz and Woods (1990), Walker and Woods (1991), Ingraham and Shadel (1992), and for gypseous soils, Woods (1990). Generally speaking, the consensus appears to be that all extraction techniques potentially result in some fractionation, and it is necessary to attempt to extract as much water as possible from a soil sample in order to obtain useful results. Fractionation effects appear to be more pronounced for the more strongly bound water which is produced toward the end of the extraction period (as for Raleigh distillation). For incomplete extraction, this results in a bias towards more positive δ -values in the extracted water sample. The effect is most pronounced for soils with a large fraction of small pores (i.e. high specific surface area), such as certain clays and clay minerals. Uncertain results are also obtained for soils which contain a high proportion of hydrated salts, such as gypsum, due to inconsistent partial dehydration on extraction. For azeotropic distillation using paraffin (kerosene) Walker and Woods (1991) found that repeated extractions on a number of soils yielded errors less than or equivalent to that due to mass spectrometry. Experience suggests that consistent results are obtained from a given technique itself applied consistently, and that errors due to the above extraction problems imply a consistent offset for the measured value. Extraction errors for soil water may therefore be more significant for comparison with rainfall analyses, than for determining stable isotope gradients within soil columns.

5.2 Processes Leading to Soil Water Concentration Variations: Meteorological Inputs

Stable isotopes are useful tracers in catchment hydrology because variations of their ratios in precipitated water and other catchment waters are measurable. Thus one can determine the isotopic composition of input precipitation and track changes due to evaporative fractionation and mixing processes such as hydrodynamic dispersion (see Chapter 3). In this section we consider the characteristics of the raw input isotope signal derived directly from precipitation, in order to understand the role of various exchange processes on modifying this signal.

Figure 5.1 shows oxygen-18 and deuterium concentrations from monthly rainfall and water vapor samples collected over an eight year period (1981-88) from Heidelberg, FRG, as reported by Jacob and Sonntag (1991). The global meteoric water line (MWL) of equation $\delta D = 8 \delta^{18}O + 10$ (Craig, 1961) is also shown. Excluding exceptional data from a single month (February, 1986) which effectively doubles the range, remaining rainfall data has a range of 10‰ in oxygen-18 and nearly 80‰ in deuterium, compared to analytical precision of about 0.2‰ and 1‰, respectively. These variations are fairly typical, although in mountainous or tropical regions somewhat greater ranges (up to double) can be found. This gives a maximum potential signal to noise ratio of about 50 - 100, which is useful though not ideal.

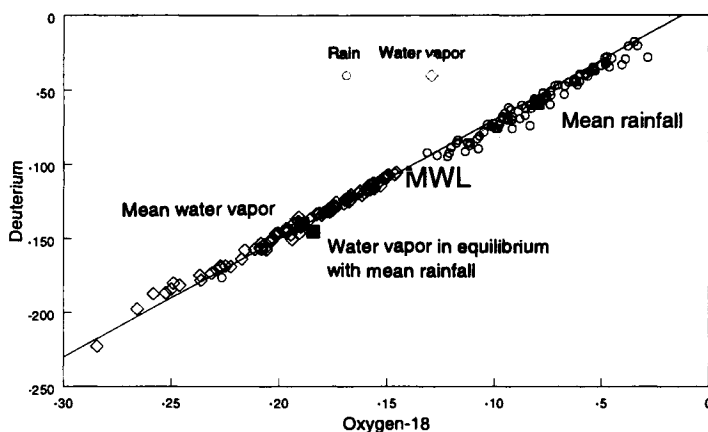


Figure 5.1. Global meteoric waters line (MWL) and monthly rainfall and water vapor data for Heidelberg, FRG (modified from Jacob and Sonntag, 1990).

The signal to noise ratio is also affected by the precision with which the input concentrations can be determined, both spatially and temporally. Temporal variations in the isotopic composition of precipitation at a particular station have been well studied in terms of seasonal effects, and are known to be loosely correlated with the ground level mean air temperature (cf. Jacob and Sonntag, 1991). On the scale of a single event, appropriate to catchment hydrology, variations have often been found to be of similar magnitude or greater than those between events. Barnes et al. (1989a) reported an event in which rainfall deuterium concentrations varied systematically by over 100‰ throughout a small storm (28 mm total rainfall) in mountainous terrain near Canberra, Australia. Similar results were also observed by Bonell and others (reported in Chapter 11) for tropical rainstorms near Cairns, Australia. Furthermore in these locations rainfall intensity is often correlated with isotopic composition, even over time scales of a few minutes. Figure 5.2 shows rainfall intensity and deuterium concentrations for a tropical storm in the Babinda catchment, Australia; transitions between periods of high and low intensity rainfall tend to be accompanied by marked isotopic changes also, with periods of most intense rainfall usually associated with low isotope concentrations, possibly due to differing altitudes and temperatures of the original condensation. Because infiltration into the upper soil zone is affected by local soil heterogeneity as well as by rainfall intensity (see Chapter 11), the initial isotope profile in catchment soils following a rainfall event may be far from spatially uniform. Spatial variations in the isotopic composition of precipitation are by comparison relatively unimportant on a catchment scale due to the generally much larger scale

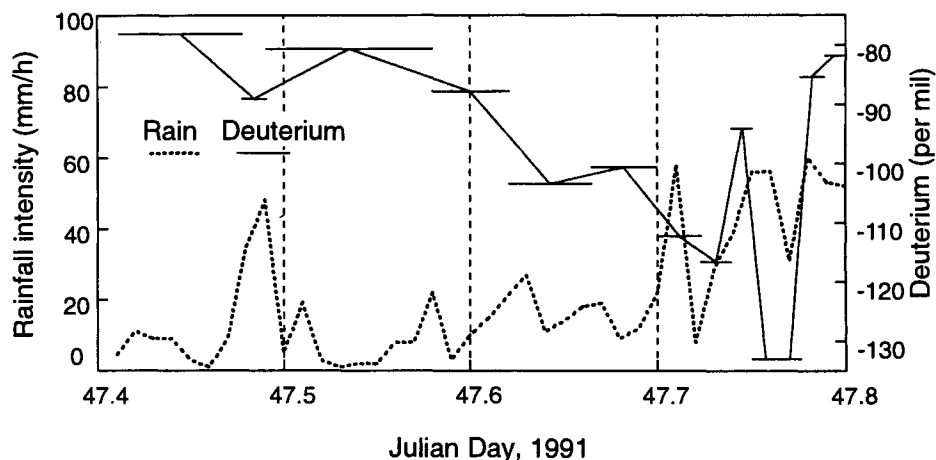


Figure 5.2. Rainfall intensity and deuterium concentrations for a tropical storm showing correlations between rainfall intensity and deuterium concentration variations.

of synoptic weather patterns (apart from orographic effects in catchments having significant relief, which lead to a significant and systematic isotopic difference in inputs to the soil profiles of the upper and lower parts of the catchment).

During precipitation on vegetated catchments, a significant proportion of rainfall is intercepted by the vegetation, and re-evaporated (this is usually referred to as "interception loss"); losses range up to an average of about 30% for well vegetated catchments in regions of normally low humidity. This evaporation potentially modifies the isotopic signature of the soil water, and in particular the relationship between oxygen-18 and deuterium may be expected to depart from the MWL observed for precipitation in general. However, although this effect is observable, its significance is reduced due to the high humidities prevailing during a storm (ensuring re-evaporation along a "line" in oxygen-18/deuterium space of slope 8), exchange with an atmosphere containing water vapor itself effectively in equilibrium with rainfall, and near complete re-evaporation of the canopy moisture store at the end of an event (see Chapter 2). It is possible, however, that this process can contribute to an identifiable soil water isotopic signature, distinct from either the groundwater store or current rainfall, and so yield information on the pathways of water movement through the catchment.

5.3 Processes Leading to Soil Water Concentration Variations: Evaporation

5.3.1 Introduction

Evaporation of catchment water is an important factor because of the distinct isotopic signature imparted to the remaining water, even though evaporative losses (as distinct from transpiration from plants) are often quite a small proportion of total rainfall. Only in arid catchments or catchments with a high proportion of the surface area covered with permanently near-saturated zones (such as swamps or seeps) and long residence times is evaporation from the soil a significant term in the water budget. In catchments where the runoff coefficient (ratio of

average annual runoff to average annual precipitation) is small, the strong enrichment of stable isotopes in soil water near the soil surface can have a big effect on both runoff and groundwater isotope concentrations. In humid catchments, where runoff ratios are comparatively high, modifications of isotopic signatures due to evaporation are usually small, and processes involving mixing and dispersion usually dominate the modification of the isotope signature of precipitation.

The development of profiles of deuterium and oxygen-18 in soils is discussed in terms of a simple physical model for water movement in soils, as discussed in Chapter 1. In essence, in the liquid phase water is considered to *move in response to potential gradients* according to Darcy's law, and the heavier molecular weight isotopic species of water are modeled as *simple solutes undergoing convection, dispersion and molecular diffusion*. In the vapor phase, all isotopic species of water diffuse as *ideal gases in response to concentration gradients*, according to Fick's law. Fractionation results from *small differences in diffusivities* (particularly in the vapor phase), and also from *differences in the saturated vapor pressure* between different isotopic species.

In this section, we will take a detailed look at the way in which exchange processes within the catchment modify the isotopic composition of water, and the dependence of these processes on the physical parameters of the catchment and the atmosphere. We show how the above simple conceptual model is sufficient to explain a wide range of experimental data, and to develop a general theory of isotope movement in unsaturated soils. We begin with the steady exchange process at a simple liquid-air interface in the absence of mixing, such as may approximate evaporation from a saturated soil, and then progress to consider more complicated and realistic physical configurations.

5.3.2 Saturated soils

The isotope profile

Experiments on the distribution of stable isotopes in the porewaters of saturated soil columns were initially reported by Zimmerman et al. (1967). They showed that, in contrast to previous work on evaporation from open water bodies, the presence of the soil effectively prevented turbulent vertical mixing, and the resulting steady-state isotope profile could be explained in terms of a balance between an upwards convective flux and a downwards diffusive flux of isotopes. Given a concentration gradient of isotopes due to evaporation from a soil column (see Figure 5.3 with $z_{ef} = 0$), the net upwards flux of isotopes at depth z is simply:

$$\rho E(R - R_\infty) \quad (5.1)$$

while the opposing diffusive flux due to the concentration gradient is:

$$\rho D \cdot dR/dz \quad (5.2)$$

where R and R_∞ are the isotope ratios or concentrations at depth z , and in the bulk soil water below the surface, respectively, and ρ is the bulk density of liquid water. Equating these alternative expressions for the flux results in a stable isotope profile in the soil-water boundary layer of the form:

$$R = R_{\infty} + (R_0 - R_{\infty}) \exp(-z/z_l) \quad (5.3)$$

where R_0 is the isotope ratio or concentration at the soil surface; and the soil-water isotopic boundary layer thickness z_l is given by:

$$z_l = D^* / E \quad (5.4)$$

Here E is the steady evaporation rate, and D^* is the effective liquid phase diffusivity of isotopes in the pore water. In the conceptual model which lies behind Equation 5.3, it is assumed implicitly that the evaporation rate is so low that temperature differences (due to latent heat effects) and hydraulic resistances are negligible, and the water table is maintained at the soil surface; while evaporation is controlled by the resistance of the atmospheric boundary layer immediately above the soil surface. The effect of varying soil properties with depth is simply to "stretch" the length scale of Equation 5.3 (see Barnes and Allison, 1983, Equation 5.21).

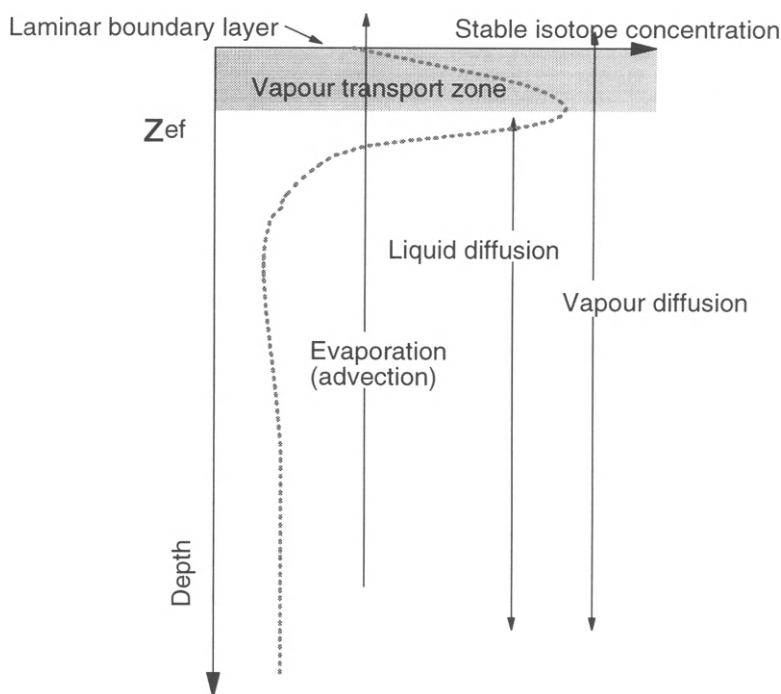


Figure 5.3. Schematic view of an evaporating soil column.

The derivation of Equation 5.3 applies to virtually any solute which may be present in the water, and which is evaporatively concentrated at the surface, provided that the effective diffusivity D^* of Equation 5.4 is appropriate to that particular solute. In the case of deuterium and oxygen-18, the diffusivities differ by only a few percent, and the respective values of z_l are effectively identical. Then Equation 5.5 implies that the concentrations of deuterium and

oxygen-18 will be linearly related. As an example of the application of this theory, Figure 5.4 shows experimental profiles of deuterium and oxygen-18 concentrations (measured in "δ-units"; see Chapter 2) in a laboratory column uniformly packed with a medium sand. Linear regression of the two sets of concentration data gives:

$$\delta_2 = 4.2 \delta_{18} - 3.6 \quad (5.5)$$

with coefficient of determination, $r^2 = 0.995$, and Equation 5.5 has been used to scale the oxygen-18 results in Figure 5.4. A value of z_i of 34.2 mm was used in Equation 5.3, producing the fitted (solid) line in Figure 5.4, which then gives an excellent fit to both sets of data.

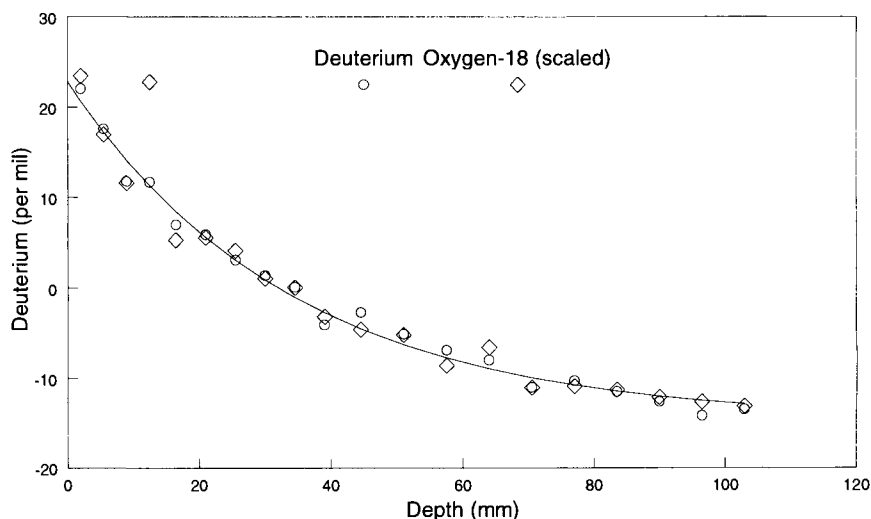


Figure 5.4. Isotope profiles in a saturated soil column.

The effective liquid state diffusivity

The effective diffusivity, D^* is proportional to the self diffusion coefficient of water, which takes the value of $2.3 \times 10^{-9} \text{ m}^2/\text{s}$ at 20°C (Mills, 1973), but is reduced by a factor which takes into account the reduced cross-sectional area (or porosity) available for diffusion in soil and the tortuosity factor of the pore space in the soil. For saturated sand, the available porosity is simply the water content θ , while for the tortuosity factor, a value of 0.66 measured by Penman (1940) appears to be adequate. For clays, much lower tortuosities (down to 0.1) have been found (see discussion and references in Barnes and Allison, 1988); and for unsaturated soils, the effective liquid phase diffusivity is further reduced by the reduction in available pore space and increased tortuosity (lower tortuosity factor).

Origin of enhanced surface concentrations

The precise mechanism by which the enhanced surface concentrations of deuterium or oxygen-18 are produced now needs to be discussed. In contrast to non-volatile solutes such as chloride or bromide salts, water molecules containing deuterium or oxygen-18 molecules are free to evaporate along with the molecularly lighter water molecules which make up the bulk of the

water, and the liquid water surface is not an effective barrier for these tracers. However, as discussed in Chapter 2, slight differences in chemical potential between the different molecular species of water lead to differences in isotope ratios in liquid water and in water vapor in equilibrium with it (equilibrium fractionation); similarly small differences in vapor phase molecular diffusivities due to the greater mobility of the lighter species leads to differential rates of escape for the different molecular species during non-equilibrium processes such as evaporation (kinetic fractionation).

Our model is one of evaporation from a planar air-water interface by diffusion through an atmospheric boundary layer of thickness Δz , according to Fick's Law. Immediately above the air-water interface (see Figure 5.3) the isotopic composition of the water vapor is determined by that of the liquid water R_0 , and so the isotope ratio in the vapor phase is:

$$R_0^v = \alpha^* R_0 \quad (5.6)$$

where α^* is the equilibrium fractionation constant (subscripts "0" refer to surface values of the parameters). Evaporation may then be considered as a dynamic process where, at a particular temperature, the tendency of water molecules to escape from the surface is proportional to the relative humidity immediately above the surface, while the probability of atmospheric water molecules ultimately condensing on the surface is proportional to the relative humidity h_a at the upper edge of the diffusive boundary layer (i.e. that point in the atmospheric boundary layer where resistance due to molecular diffusion gives way to turbulent resistance; usually a few mm at most). The net evaporation rate E is then given by:

$$E\rho = D^{v*} N^{sat}(1-h_a)/\Delta z \quad (5.7)$$

where N^{sat} is the saturated absolute humidity at the given temperature, and D^{v*} is the effective diffusivity of water vapor in air. Similarly, the relative tendency of the minor isotopic species to escape from or be captured by the surface is proportional to $\alpha^* R_0$ and $h_a R_a$, respectively, so that the net evaporation rate E_i of isotopes is:

$$E_i \rho = D_i^{v*} N^{sat} (\alpha^* R_0 - h_a R_a) = E\rho R_\infty \quad (5.8)$$

where the second equality follows from the assumption of steady-state evaporation, and D_i^{v*} is the effective vapor diffusivity of isotopes. Elimination of the evaporation rate between Equations 5.7 and 5.8 lead to an expression for the surface concentration in terms of the external concentrations:

$$R_0^v = \alpha^* R_0 = h_a R_a + (D^{v*}/D_i^{v*})(1-h_a) R_\infty \quad (5.9)$$

Another way of looking at this result is that the surface isotope concentration in the vapor phase is given by an average of the isotope ratios of the incoming water and the atmospheric water vapor, weighted according to the relative humidity, which is a direct consequence of the application of Fick's law.

Because the thickness of atmospheric boundary layer or laminar layer above the soil surface is subject to fluctuations due to turbulence in the air above it, the effective vapor diffusivities

are not simply the molecular diffusivities of the isotopic species of water vapor in air. Brutsaert (1975) has suggested that under turbulent conditions where the laminar layer is continually disturbed, the effective diffusivity can be modeled as proportional to the molecular diffusivity, raised to some power n , where $0.5 \leq n \leq 1$; with $n = 0.5$ appropriate to fully turbulent conditions, and $n = 1$ to laminar flow. Then:

$$D^{v*}/D_i^{v*} = (D^v/D_i^v)^n = 1 + \eta \quad (5.10)$$

where the ratio of molecular diffusivities, D^v/D_i^v , is effectively independent of temperature, and according to Merlivat (1978) has the value 1.0249 for deuterium, and 1.0285 for oxygen-18. The result is that fractionation effects (equilibrium and kinetic) are approximately additive, and in δ -value notation (Chapter 2) Equation 5.9 can be approximately rewritten:

$$\delta_0 = \delta_\infty + h_a(\delta_a - \delta_\infty) + \epsilon^* + \eta(1 - h_a) \quad (5.11)$$

In this form, the additive nature of equilibrium fractionation (represented by $\epsilon^* = 1 - \alpha^*$), and kinetic fractionation (represented by $\eta(1 - h_a)$, where $\eta = (D^v/D_i^v)^n - 1$), is clear. This fractionation is primarily responsible for the origin of the concentration gradient in the liquid phase.

Using Equation 5.9 we find that in order to match the measured isotope concentrations at the soil surface for both oxygen-18 and deuterium, and hence the slope of the oxygen-18/deuterium relationship in Equation 5.5, it is necessary to choose a value of $n = 0.63$, rather than $n = 0.5$ which would be appropriate to fully turbulent conditions. We notice that, although the molecular diffusivities of isotopic species differ significantly in both the vapor phase and the liquid phase, it is only the vapor phase diffusivities which cause kinetic fractionation, according to this model. The reason is that in the vapor phase each species diffuses independently, according to the ideal gas law, while in the liquid phase diffusion is dominated by convection, so that the differential effects of diffusion are not evident.

From Equations 5.3, 5.4 and 5.9 we now can predict steady state isotope profiles in saturated soils, given the evaporation rate and atmospheric relative humidity, and isotope ratios in the deep soil water and atmospheric water vapor.

Effects due to salinity

In saline soils, pore waters may reach saturation in various salts, most commonly gypsum or sodium chloride. Potentially this has an effect on evaporation isotope profiles in two ways. Firstly, at these high salinities it is possible that the equilibrium fractionation factor, α^* , may be affected by differential changes in chemical potentials or activities of the isotopic species. Sofer and Gat (1972, 1975) give experimental evidence for a number of inorganic salts, which suggests that concentrated solutions of these salts generally act to reduce the equilibrium fractionation for deuterium, while for oxygen-18 different salts may enhance or inhibit fractionation. Secondly, the saturation vapor pressure over a saline solution is reduced compared to that over pure water, as water molecules are increasingly inhibited from leaving the water surface. In terms of the above formulation, this reduction in the saturation vapor pressure is equivalent to replacing the assumption of unity for the relative humidity of water vapor in contact with liquid water (and under negligible tension) by some lesser value. For example, above a saturated solution of sodium chloride, the relative humidity is effectively reduced by about 30% relative to pure water at the same temperature; while other salts may

give even greater reductions. This has the effect of lowering the evaporation rate, and also affects the kinetic fractionation term in Equation 5.11.

By inserting the relevant equilibrium fractionation for saline solutions at the surface concentration, replacing the factor $(1-h_a)$ in Equations 5.7, 5.9 and 5.11 by (h_o-h_a) , and replacing R_o^v by $h_o R_o^v$ in Equation 5.8 (where h_o is the effective relative humidity immediately above the evaporating surface), the previous equations will also serve to predict isotope profiles in the presence of salinity. The net effect of salinity is to decrease isotopic exchange and hence fractionation.

5.3.3 Unsaturated soils

Exchange processes which determine isotope profiles in unsaturated soils differ only in detail from what has already been discussed for saturated soils, with the same basic physical processes remaining relevant. Instead of all fluxes within the soils being in the liquid phase, there is now the possibility of water and isotope movement in the vapor phase, and isotopic exchange between the two phases must be allowed for throughout this zone. One consequence is that there is now no sharply defined surface of evaporation; the resistance of the surface soils to vapor movement, rather than the atmospheric resistance, rapidly becomes the determinant of the evaporation rate in drier soils, and the zone in which evaporation occurs becomes progressively broader and deeper. In addition, the ability of isotopes to diffuse in both the liquid and vapor phases has an effect similar to increasing the length-scale z_i defined in Equation 5.4, so that the gradient of the isotope profile is much broader than it would be in the absence of vapor phase diffusion.

The theory of water movement in the unsaturated zone due to gradients in the matric potential ψ has a long history in soil science and is outlined in some detail in Chapter 1. The work of Philip and co-workers (see, for example, Philip, 1969) has been particularly influential, and it is this approach which we follow here. For simplicity, and because we are concerned here mainly with largely vertical exchange processes, we restrict the analysis to a one-dimensional vertical model (Figure 5.3), and ignore lateral fluxes; and we continue to maintain the fiction of isothermal conditions.

According to this approach, the liquid flux of water in the unsaturated zone, q_l , is proportional to the gradient in the total potential, which is the sum of the gravitational and matric potentials (this is called Darcy's Law). The proportionality "constant" is the hydraulic conductivity, which depends strongly on the matric potential, but not on the gradient. Although an analog of Darcy's Law will also apply theoretically to transport of the heavier isotopic species of water in the liquid phase, their concentration is always sufficiently dilute so that their movement can be considered only in terms of convection and diffusion relative to the bulk water, as in the previous section:

$$q_i^l = q^l R - \rho D^* dR/dz \quad (5.12)$$

The only difference is that the effective diffusivity D^* is lower than for saturated soils due to a lower available pore space, characterised by the unsaturated water content θ , and decreased tortuosity factor (increased tortuosity).

In the vapor phase we assume that water vapor acts as an ideal gas, so that the flux of isotopes is independent of that of the bulk water. Then the vapor phase flux of isotopes in unsaturated soils, q_i^v , is determined by Fick's law of diffusion (cf. Equation 5.2):

$$q_i^v = -D_i^{v*} \frac{d}{dz}(R^v h N^{sat}) \quad (5.13)$$

where h is the relative humidity within the air filled pore space of the soil, and the effective diffusivity D_i^{v*} has a slightly different interpretation to its previous definition, Equation 5.8. A similar expression holds for the water vapor flux q^v :

$$q^v = -D^{v*} \frac{d}{dz}(h N^{sat}) \quad (5.14)$$

The significant difference between Equations 5.13 and 5.14 is that under isothermal conditions and in the absence of a relative humidity gradient, Equation 5.14 predicts no bulk flux of water in the vapor phase; it is still possible to have significant fluxes of isotopes, if there is a concentration gradient (similar considerations apply to any volatile tracer, such as tritium, for instance).

Under unsaturated steady-state conditions, although the total water flux through the soil column must still be constant, individual contributions from the liquid and vapor components are constantly varying, determined mainly by the dependence of the hydraulic conductivity on the matric potential. The relative humidity is determined by the thermodynamic relationship:

$$h = \exp(\psi/\bar{\psi}) \quad (5.15)$$

where at 20°C, $\psi = 135$ MPa, compared to a value of $\psi = 1.5$ MPa at wilting point ($h = 0.989$). Consequently, except in very dry soils where liquid flow is negligible, or close to the soil surface, the relative humidity throughout a soil column will be close to unity. Near the surface, where the soil is in equilibrium with an atmosphere with relative humidity less than unity, liquid phase movement of water will be negligible, and the work of Barnes and Allison (1984, Equation 5.16) implies that isotope concentrations must increase rapidly beneath the surface. Consequently the transition region, where evaporation is taking place and in which water fluxes in the liquid and vapor phases are of similar magnitude, will be narrow (except in very dry soils). If we denote the depth of this region, which we call the evaporation front, by z_{ef} , where the isotope ratio is R_{ef} , then a similar profile to that given in Equation 5.3 results:

$$R = R_\infty + (R_{ef} - R_\infty) \exp - [(z - z_{ef})/\bar{z}] \quad (5.16)$$

where $\bar{z} = z_l + z_v$, z_l is given by Equation 5.3, and the length scale z_v which is characteristic for diffusion in the vapor phase, is given by the expression:

$$z_v = \frac{D^{v*} N^{sat}}{\rho E} \quad (5.17)$$

Where variations in water content are appreciable, neither z_l nor z_v are constant, and it is necessary to modify the length scale (see Barnes and Allison, 1988, Equation 5.6). Note that the form of Equation 5.16 predicts an approximately linear relationship between measured oxygen-18 and deuterium concentrations, as before.

Figure 5.5, reproduced from Allison and Barnes (1983), shows steady-state isotope and water content profiles from a column packed with an aggregated form of the clay mineral attapulgite. The solid curve shows the results of fitting an equation of the form of Equation 5.16, but allowing for variations in water content (resulting in a slight distortion of the length scale). The length scale $\bar{z} = z_l + z_v$ is 69 mm, corresponding to an evaporation rate of 1.1 mm/day. Figure 5.5 clearly indicates the rapid increase in isotope concentration near the surface, above the evaporation front at depth $z_{ef} = 35$ mm. As in Figure 5.4, oxygen-18 data has been scaled onto the same curve as the deuterium data, using the regression relationship:

$$\delta_2 = 2.64 \delta_{18} - 12.5 \quad (5.18)$$

(cf. Equation 5.5).

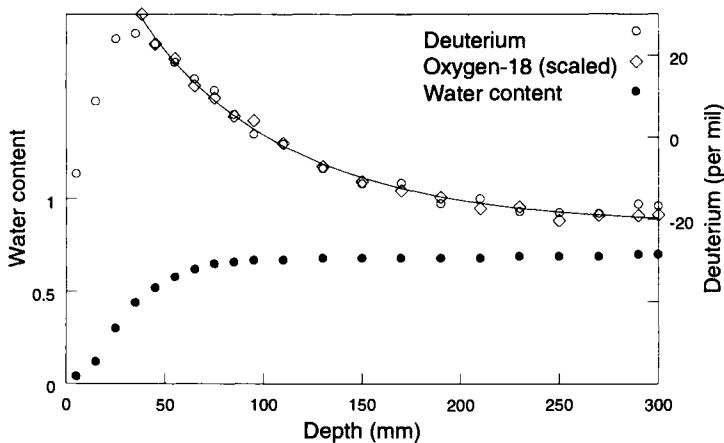


Figure 5.5. Deuterium and oxygen-18 profiles in an unsaturated soil column.

The same arguments used to obtain Equation 5.11 are also valid for calculating the peak height, with δ_{ef} replacing δ_0 , and regarding the upper 35 mm (above z_{ef}) of the soil column as part of the atmospheric laminar layer. The measured peak heights can be matched by assuming a value for the exponent n (see previous section) of 0.95. This high value of n (leading to a relatively low slope in the oxygen-18/deuterium relationship) results from the relatively thick layer of soil through which the water vapor must diffuse, dominating the overall diffusive resistance of the atmospheric boundary layer.

In summary, the main effect of unsaturated soils on isotope profiles relative to saturated soil profiles is to increase the ability of the isotopes to diffuse, by providing alternative pathways for diffusion, particularly in dry soils. This is in contrast to the behavior of non-volatile solutes, such as chloride or bromide salts, which become virtually immobile in dry soils. Barnes and Allison (1984) calculated that diffusion in the liquid and vapor phases were equally effective at a saturation fraction (water content divided by porosity) of about 0.2; at water contents lower than this vapor phase diffusion dominates, but may still be appreciable at higher water contents. Another effect due to water vapor movement in unsaturated soils is to modify the slope of the linear relationship between oxygen-18 and deuterium concentrations. This is due to

modification of the balance between kinetic and equilibrium fractionation, with kinetic fractionation effects increasing as the effects of atmospheric boundary layer turbulence become less significant for evaporation (see discussion preceding Equation 5.10).

5.3.4 Unsteady evaporation

The previous sections have concentrated on developing a theory of isotopic exchange in soils under steady-state evaporative conditions. Under natural conditions, steady-state evaporation is the exception rather than the rule, so that it is necessary now to consider the additional complication of time-varying fluxes. Soil scientists distinguish several stages of evaporation from an initially wet soil column. At the beginning, soil resistance to water supply to the surface is negligible, and evaporation is limited by the available energy and atmospheric resistance. As the surface dries out, soil hydraulic resistance rapidly becomes more important, and a drying front moves down through the soil (second stage drying). Finally, the soil profile may reach some steady-state if it is in contact with a water table, or evaporation may become limited by the presence of an impervious layer (e.g. rock), after which the evaporation rate decreases rapidly. Unsteady evaporation during the second stage of drying is the process which we consider mainly in this section.

In addition to the equations for fluxes in the liquid and vapor phases which we have introduced above (cf. Equations 5.12 - 5.14), under unsteady evaporation it is necessary to introduce equations representing the local conservation of mass for water and isotopes. The one dimensional forms of these equations can be written as:

$$\rho \partial \theta / \partial t = - \partial q / \partial z \quad (5.19)$$

and

$$\rho \partial (\theta R) / \partial t = \partial q_i / \partial z \quad (5.20)$$

where q and q_i are the total fluxes in both liquid and vapor phases for water and isotopes, respectively (we have implicitly ignored storage in the vapor phase). Because fluxes and other quantities can now vary both in space and time, it is necessary to introduce partial derivatives in Equations 5.19 and 5.20, and a formal mathematical treatment necessarily becomes more complicated. However, under certain conditions which are often approximated in natural soils (i.e. uniform initial profile, and constant atmospheric isotope concentration at the soil surface), it turns out that variations in space and time are simply connected, and a simple one dimensional analysis is possible. The penalty is that it is necessary to introduce a variable which is neither time-like nor space-like, but is a combination of both. Although it is necessary to impose quite specific assumptions in order to use this analysis, it is possible to use the understanding gained in this way to obtain efficient estimates of hydraulic parameters, and to understand the special features of unsteady flow in more complicated situations. In particular, it is possible to check the validity of assumptions and the adequacy of equations such as Equation 5.20, so that if necessary numerical schemes based on these equations can be used with confidence in more general models.

During the second stage of drying of a soil column, it is found that the evaporation rate usually decreases approximately as the inverse of the square root of time. In order to gain an understanding of this, we consider a soil profile at water content θ_0 which begins to dry out.

Assume also that there is a sharp drying front at $z = z_{ef}$, with the water content $\theta = \theta_0$ in the region above this depth, where water moves by vapor transport alone (see Figure 5.3). Then ignoring diffusive resistance of the atmospheric boundary layer, the flux of water vapor through the "dry" soil in response to the relative humidity gradient is:

$$q^v = D^{v*} N^{sat} \frac{1-h_a}{z_{ef}} \quad (5.21)$$

But mass conservation requires that this flux is matched by the rate at which water is removed from the profile:

$$q^v = \rho(\theta_\infty - \theta_0) \frac{dz_{ef}}{dt} \quad (5.22)$$

Equating these two expressions for the flux, and solving the simple differential equation for z_{ef} , gives the result:

$$z_{ef} = \lambda_{ef} t^{1/2} \quad (5.23)$$

where:

$$\lambda_{ef}^2 = \frac{2D^{v*} N^{sat}(1-h_a)}{\rho(\theta_\infty - \theta_0)} \quad (5.24)$$

Equations 5.21 and 5.22 show that, for this simple example, as evaporation progresses the depth to the evaporating front increases as the square root of time, and the evaporation rate decreases as the inverse of this.

Under the same assumptions, stable isotope profiles can also be calculated. In the region above the plane of evaporation, application of Fick's law implies that the isotope profile is approximately linear, whereas below this, diffusion of isotopes in the absence of convection gives a more extended error-function profile than the exponential form previously encountered. Specifically,

$$\begin{aligned} hR &= h_a R_a + (R_{ef} - h_a R_a) \lambda / \lambda_{ef}, & \lambda < \lambda_{ef} \\ R &= R_\infty + (R_{ef} - R_\infty) \frac{\text{erfc}(k\lambda)}{\text{erfc}(k\lambda_{ef})}, & \lambda > \lambda_{ef} \end{aligned} \quad (5.25)$$

where:

$$\begin{aligned} h &= h_a + (1-h_a) \lambda / \lambda_{ef} \\ k^2 &= 4(D^* + \frac{D^{v*} N^{sat}}{\rho \theta_\infty}) \end{aligned} \quad (5.26)$$

and $\lambda = z t^{1/2}$ scales both distance and time. The peak isotope concentration, R_{ef} is given by Equation 5.11 (with R_{ef} replacing R_0 as before), but the role of the length scale $\bar{z}$ (cf. Equation

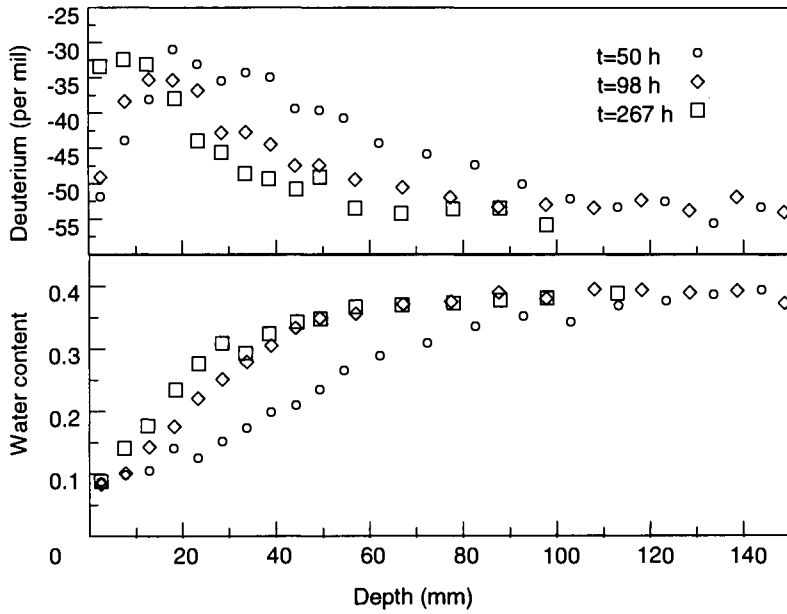


Figure 5.6. Water content and deuterium profiles for unsteady evaporation from a soil column, as a function of depth.

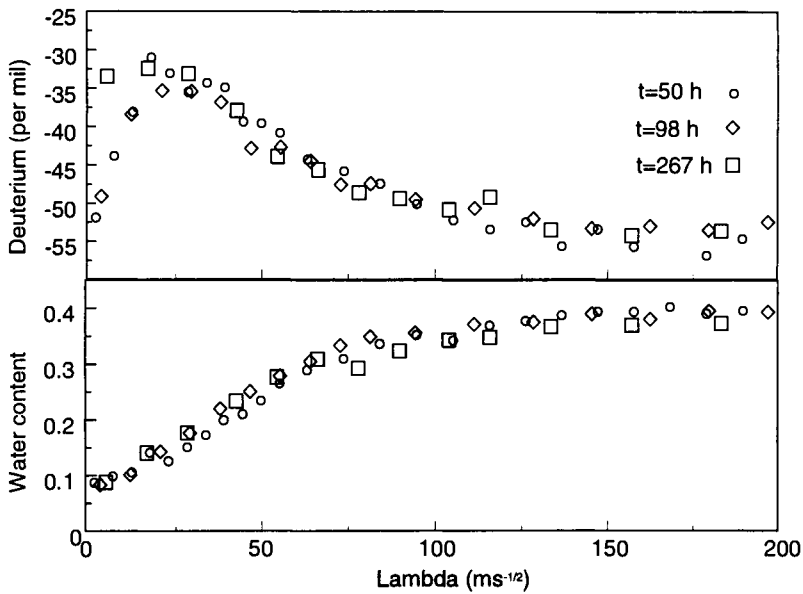


Figure 5.7. Water content and deuterium profiles for unsteady evaporation from a soil column, as a function of the reduced variable λ .

5.16), combining diffusion in both liquid and vapor phases, in the absence of a constant evaporation rate is now taken by the parameter k^2 . (For saline solutions, the factor $(1-h_0)$ in Equations 5.24 and 5.26 are replaced by $(h_{ef} - h_0)$ as before. Similarly, the factor $(R_{ef} - h_0 R_0)$ in Equation 5.25 is replaced by $(h_{ef} R_{ef} - h_0 R_0)$). In this example, the surface enrichment is constant, and water content and stable isotope profiles during evaporation progress downwards at a rate proportional to the square root of time.

Although this example appears exceedingly simplistic, involving unrealistic assumptions, it illustrates many features which are observed in experiments during evaporation from real soils. Following infiltration into a soil column, after drainage due to gravity ceases to be significant, the water content of a uniform soil will often be approximately constant with depth. Soil physicists have pointed out that under these conditions the subsequent soil moisture distributions due to infiltration or evaporation at the surface are "similar", with profiles at different times being scaled by the parameter λ . Similarly, stable isotope profiles scale in the same way (Barnes and Walker, 1989). The parameters λ_{ef} and k also give good indications of the appropriate length and time scales in the more general case, when appropriate generalizations are made (e.g. $(\theta_s - \theta_0)/(1-h_0)$ in the expression for λ_{ef} (Equation 5.24) is replaced by the surface value of $d\theta/dh$, which is proportional to the slope of the adsorption isotherm for water). These considerations imply that both cumulative evaporation and total isotopic enrichment increase proportional to $t^{1/2}$, with total enrichment also proportional to $(R_{ef} - R_\infty)$.

Figure 5.6 shows deuterium and water content profiles from a series of evaporating soil column experiments, with experiments terminated at different times. When plotted as a function of the combined parameter λ , the sets of experimental data are collapsed onto the one curve (Figure 5.7). A detailed examination of cumulative evaporation during the experiments (Figure 5.8) shows close agreement with the expected $t^{1/2}$ behavior, except for the first hour or so. (By ignoring atmospheric resistance, the above theory predicts an infinite evaporation rate at $t = 0$, whereas the conditions of the theory are only met when sufficient time has elapsed, so that atmospheric resistance is negligible compared to that of the soil).

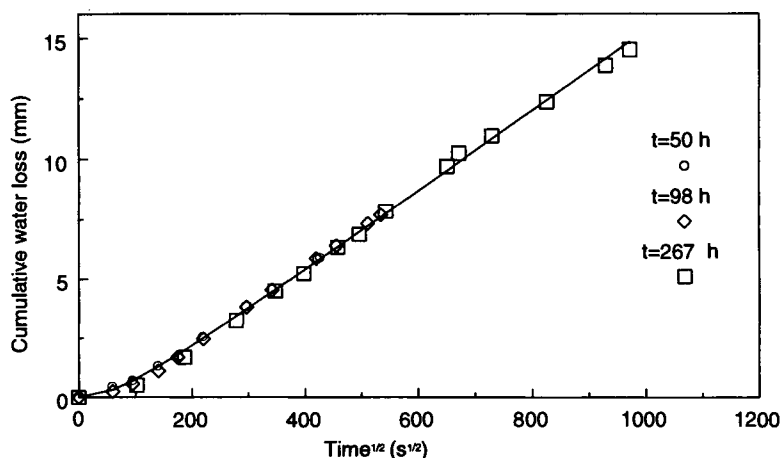


Figure 5.8. Cumulative evaporation during unsteady evaporation from a soil column.

The solid line, fitted to the experimental data by assuming that total evaporative resistance is due to the sum of diffusive resistances in the soil and the atmospheric boundary layer, suggests that atmospheric resistance is dominated by the soil resistance after only 2 hours. But this requirement of negligible atmospheric resistance is precisely that which we required above for the parameter η (Equation 5.10) to have its maximum value (for $n = 1$), and we may expect that stable isotope profiles will scale according to λ precisely under the same conditions as the water content profiles.

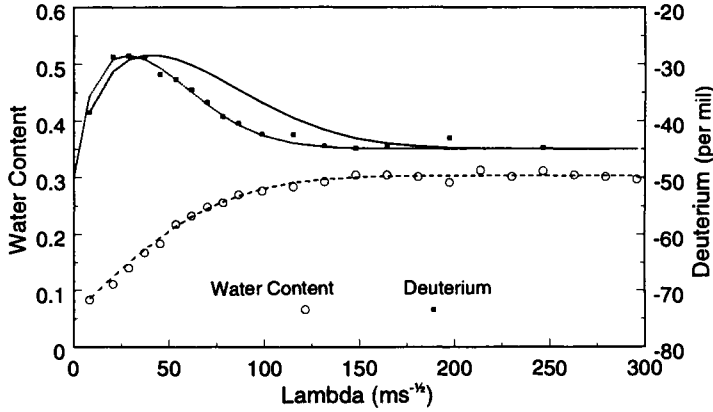


Figure 5.9. Water content and deuterium profiles during evaporation from a very dry soil.

Using this theory enables detailed investigations of water behavior which would be otherwise very difficult. Figure 5.9 shows water content and deuterium profiles for one of a series of experiments involving soil columns packed with small (500μ) aggregates of the clay mineral attapulgite. The very high microporosity of this mineral allows it to hold significant amounts of water at very low matric potentials; at the highest water content used, $\theta = 0.4$, the corresponding matric potential was 1.5 MPa. Consequently, water movement was expected to be predominately in the vapor phase. The solid curve fitted to the water content data is obtained from a solution of Equations 5.14 and 5.20, assuming that $d\theta/dh$ is constant. [Although this assumption is unrealistic, a detailed mathematical analysis without this assumption indicates that the full solution is approximated by assuming a constant value (the surface value) for this derivative]. It has the form:

$$\frac{\theta_{\infty} - \theta}{\theta_{\infty} - \theta_a} = \operatorname{erfc}(\lambda/\lambda_{ef}) \quad (5.27)$$

(cf. Equation 5.25 above), where $(\theta_{\infty} - \theta_0)/(1 - h_a)$ is replaced by $d\theta/dh$ in the expression for λ_{ef} , Equation 5.24. Deuterium profiles for the same experiments (Figure 5.9) show far greater discrepancies with curves calculated under the same assumptions of vapor movement only, and having the form:

$$\frac{\theta_{\infty} R_{\infty} - \theta R}{\theta_{\infty} R_{\infty} - \theta_0 R_0} = \operatorname{erfc}(\lambda/\lambda_{ief}) \quad (5.28)$$

where $\lambda_{ief} = \gamma \lambda_{ef}$, and:

$$\gamma^2 = \frac{D_i^v}{D^v} \frac{d(\theta R)/d(hR)}{d\theta/dh} \quad (5.29)$$

(cf Equation 5.10). The fitted curves gave good agreement with the observed isotope data at the lowest water content, but values of γ chosen to match the height of the observed isotope peak could not match the observed length scale of the deuterium profiles at the higher water contents. Further analysis indicates that isotope profiles in very dry soils are extremely sensitive to small amounts of liquid water movement, and that only a few percent of liquid water movement is sufficient to account for the discrepancy (dotted curve in Figure 5.9).

In summary, in this Section (5.3.4) we have shown that the theory previously developed for unsteady evaporation from soils can be naturally extended to describe stable isotope profiles under the same conditions. The principle assumptions are the validity of the unsaturated form of Darcy's law for liquid phase flow, and ideal gas kinetics in the vapor phase. Using a well known simplifying set of boundary conditions allows parameter determination, and at the same time, exploration of a physically plausible scenario which approximates evaporative behavior in real soils. The close correspondence between theoretical and experimental profiles suggests confidence in the wider application of Equation 5.20, at least for isothermal soil profiles.

5.3.5 Temperature effects

So far in this chapter we have chosen to ignore effects on isotopic exchange processes due to temperature gradients. Most of the coefficients which we have introduced, such as effective diffusivities, the hydraulic conductivity and the equilibrium fractionation factor, are temperature dependent, but the dependence is usually no more than a few percent per degree, and can be accommodated by assuming an appropriate mean value for the coefficient. It is only when considering isotope profiles near the soil surface, particularly in moderately dry soils where diurnal temperature gradients of more than 100°C per meter are possible in the surficial few cm, that these temperature dependences become important. Although during evaporation there is an interaction between water and heat transport, due to convection and latent heat effects, for the purposes of explaining the relevant processes we choose to consider an imposed temperature profile, $T(z)$. For evaporation in moderately dry soils where the effects are most pronounced this is a reasonable approximation. Then the main effect is on water transport in the vapor phase, where now N^{sat} of Equations 5.13 and 5.14 is a function of temperature, and hence position. Depending on the sign of the temperature gradient, the temperature gradient can either enhance evaporation (temperatures increasing with depth) or inhibit it (temperatures decreasing with depth).

It can be shown (e.g. Rose, 1966) that assuming a constant specific heat for soil, the response of the soil temperature to an imposed sinusoidal surface temperature $T_s = T_\infty + \Delta T \cos(2\pi t/\tau)$ (appropriate to either the diurnal or annual cycle) is:

$$T = T_\infty + \Delta T \cos(2\pi t/\tau - z/z_T) \exp(-z/z_T) \quad (5.30)$$

where the temperature length scale z_T , which depends on the thermal diffusivity and specific heat of the soil and is proportional to the square root of the period τ , is typically about 0.2 m

for the diurnal cycle, and 4 m for the annual cycle, for moderately dry soils. ΔT and T_{∞} are the temperature amplitude and mean surface temperature, respectively.

Figure 5.10 gives an example of field isotope profiles which have been significantly affected by soil temperature gradients. Figure 5.10a shows four temperature profiles measured at three monthly intervals in a sand dune in central Australia in 1984-85. The solid lines are versions of Equation 5.30 appropriate for the given sampling dates, and with $T_{\infty} = 27^{\circ}\text{C}$, $\Delta T = 10^{\circ}\text{C}$ and $z_T = 3.5$ m, and times are relative to January 9. Equation 5.30 fits the measured data well beneath the upper 0.5 m where the diurnal cycle effects the temperature measurements, except for the second profile between 1 - 4 m, where measured temperatures appear to be depressed by several degrees C. This corresponds to an increase in water content at these soil depths, due to infiltration of (presumably cold) rainwater from an event of nearly 40 mm, several weeks prior to this sampling. Measured gravimetric water content profiles between 8 m and 9 m depths over the four sampling times were constant to within 0.0003, and the mean water content of 0.0065 corresponds to a matric potential of 5 - 10 MPa, suggesting that no drainage is occurring past this depth. Cumulative soil water stored above 8 m are shown in Figure 5.11, and indicate significant transport of water in both directions to at least 6 m. (A comparison with the water content profiles of Figure 5.10c indicates the usefulness of integrated water content profiles in smoothing out variations due to small scale heterogeneities, etc.). Calculations based on Equation 5.14 indicate that apart from the first 1m, this is almost entirely due to water movement in the vapor phase in response to the measured temperature gradients.

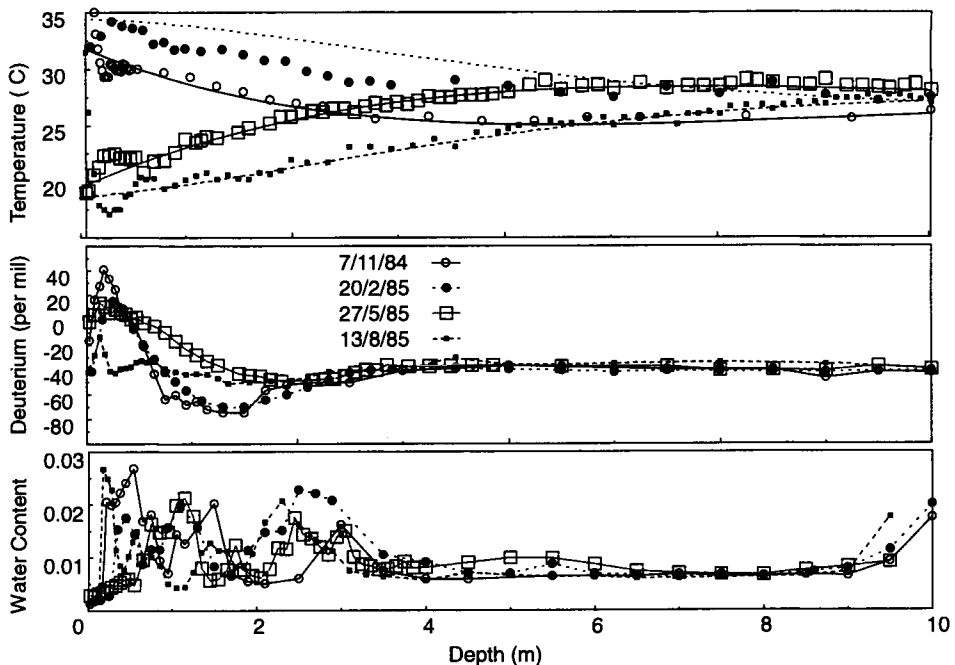


Figure 5.10. Temperature, deuterium and water content profiles from a sand dune.

Figures 5.10b and 5.10c show corresponding deuterium and water content profiles. Two features of the isotope profiles deserve attention. The first is that each of these profiles is significantly smoother than the corresponding water content profile, especially below the surface layers, despite the low water contents which themselves suggest minimal liquid phase diffusion. The second is the presence of a “trough” of lower isotope concentrations at a depth of 1-1.5 m observed during the first sampling, which persisted during the following samplings but became progressively less pronounced and moved to greater depths. This behavior is not at all correlated with changes in water content, but seems to be associated with a change in sign of the temperature gradient. It therefore appears that under conditions of low water contents and high air-filled porosity, vapor phase fluxes induced by temperature gradients may have significant effects on the distribution of deuterium concentrations in soil profiles.

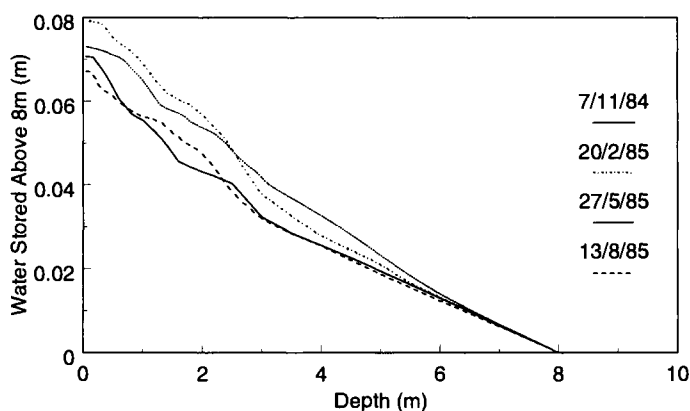


Figure 5.11. Cumulative water stored above 8m depth in sand dune.

The effect of temperature gradients on water movement in unsaturated soils is due primarily to the temperature dependence of the saturated water vapor density, which increases sharply with temperature (the relative increase $N^{sat} \cdot dN^{sat}/dT$ at 20°C is approximately 0.06°C⁻¹). The molecular diffusivity of water vapor in air also increases with temperature, but this effect is much more modest (the relative increase at 20°C is approximately only 0.006°C⁻¹). [Note: Hydraulic conductivity also depends directly on temperature, due to the viscosity of liquid water decreasing by a factor of two between 10°C and 40°C, but there is little effect on water flow due to temperature *gradients*; see Philip and de Vries, 1957; Sophocleous, 1979]. This effect can be accounted for directly using the same model as before, Equation 5.14, but where now N^{sat} is regarded as a function of temperature, and hence position. From Equation 5.14, we see that, even when there is no gradient in relative humidity, a temperature gradient will result in a water vapor from the warmer to the colder parts of the soil, subject to availability of water. Under approximately steady-state conditions, Barnes et al. (1989b) showed that for an exponentially decreasing temperature profile (i.e., of the form of Equation 5.18, but setting the cosine function to one), isotope profiles showing a pronounced isotopic minimum could be adequately predicted using the model we have developed here. Under the conditions of the experiment, the form of the isotope profile was modified from the simple exponential form of Equation 5.16 to the double exponential form:

$$R = R_{\infty} + (R_{ef} - R_{\infty} - v) \exp[-(z - z_{ef})/\bar{z}] - v \exp[-(z - z_{ef})/z_T] \quad (5.31)$$

where

$$v = \frac{\beta(\epsilon + \eta)\Gamma(T_{ef} - T_{\infty})}{(z_T/\bar{z} - 1)}; \quad \Gamma = d/dT[\ln(N^{sat}(\epsilon + \eta))] \quad (5.32)$$

T_{ef} is the temperature at $z = z_{ef}$, and $\beta = z_v/(z_l + z_v)$ is a measure of the effectiveness of diffusion in the vapor phase relative to that in the liquid phase. These equations show that this depression of stable isotope concentrations within the profiles becomes more pronounced as the diffusion length scales approach that of the temperature profile.

By also considering profiles in sealed columns, Barnes et al. (1989b) showed that in the region of the isotope minimum, it was possible for water movement in the liquid phase in response to gradients in matric potential to be balanced by vapor movement in response to a temperature gradient, so that a small net evaporative flux could result from much larger opposing fluxes in the separate phases, which non-volatile solutes such as chlorides were not able to follow.

Following this same sort of analysis it is possible to analyse the data of Figure 5.10. In this case liquid phase transport appears negligible for the majority of the soil profile, and the isotopic minimum is produced as the result of Raleigh-type fractionation between the hotter and cooler areas of the profile. With no liquid transport to offset the vapor flux, large fractionation effects (more than 30‰ for deuterium) are encountered when the temperature gradient is favorable. During winter, when the temperature gradients reverse, the isotopic minimum gradually decays as fluxes in both phases are towards the surface.

Apart from choosing appropriate values for the temperature dependent coefficients (such as diffusivities etc.), major new features of soil isotope profiles due to temperature gradients (such as secondary isotopic minima are unlikely to be encountered in other than very dry soils, where water contents are low, and the effect on streamflow composition is minimal. The main effect of temperature gradients is to enhance or diminish evaporation through changes to the humidity gradient.

5.3.6 Oxygen-18/Deuterium Relationship

A common feature of the theoretical isotope profiles derived above in Equations 5.3, 5.16 and 5.25, but *not* 5.27 or 5.31 is that in each case the dependence on depth for both oxygen and deuterium is approximately the same, so that variations in deuterium are linearly related to those in oxygen-18. For Equation 5.27, the relationship is also approximately linear below the maximum. The exception of Equation 5.31 arises because in this case, although length scales are the same for both isotopes, the depth of the secondary minimum in the profile does not scale in the same way as the primary maximum. The slope of the oxygen-18/deuterium relationship in each case (excluding Equation 5.31) is approximately

$$d\delta_2/d\delta_{18} = \frac{\delta_{2ef} - \delta_{2\infty}}{\delta_{18ef} - \delta_{18\infty}} \quad (5.33)$$

where δ_{ef} is given by the right hand side of Equation 5.11. In practice, so-called evaporation lines from soil water profiles may have slopes varying from about 2 to 5 or greater. The higher values are typical of saturated soil profiles, and also for oxygen-18 and deuterium values from evaporation of free water bodies, such as lakes or evaporation pans, while very low values tend to be found in soil profiles with low water contents.

Allison et al. (1983) showed that the principal factor which determines the value of the slope (Equation 5.32) is the kinetic fractionation terms in Equation 5.10. This result may be understood as follows. Figure 5.1 shows the results of isotopic analyses of oxygen-18 and deuterium for rainfall and water vapor collected over a period of several years at one location (Heidelberg, Germany). Results for both rainfall and water vapor fall close to the MWL. In fact, it is often the case that on average, water vapor isotope concentrations appear to be in approximate equilibrium with (i.e. derived from) water of the same isotopic composition as local rainfall; in this case the mean water vapor and rainfall isotopic compositions correspond approximately to an equilibrium at a temperature of about 12°C (see Figure 5.1). Furthermore, the ratio of the equilibrium fractionation factors, ϵ^* , for deuterium and oxygen-18 lies between 9 and 7 for temperatures between 0 and 45°C (i.e. it decreases slightly with temperature). On the other hand, kinetic fractionation is of approximately equal magnitude for both oxygen-18 and deuterium and is independent of temperature. Any significant reduction in slope below 8 must then be due to the influence of kinetic fractionation, which is approximately twice as great for dry soils as for free water. As an example, consider evaporation into an atmosphere of relative humidity 50% and isotopic composition in equilibrium with the deep soil water ($\delta_a = \delta_s + \epsilon^*$). Then for saturated soil, with $n = 0.5$ in Equation 5.10, the predicted slope has value 3.8, while for a "dry" soil with $n = 1$, the predicted slope decreases to 2.7.

The observed dependence of the slope of the deuterium/oxygen-18 relationship on evaporation is significant because it is virtually the only catchment process by which meteoric waters are modified such that the relationship provided by the MWL is substantially altered (see Chapter 2 for details). It can be shown that, on an oxygen-18/deuterium diagram, a mixture of two waters of distinct isotopic composition will itself have composition which lies on the line joining the compositions of the two parent waters (the so-called "mixing line"); the distance along the line away from a parent varies inversely with the relative contribution of the parent to the mixture. This means that mixtures of any two waters on the MWL will remain on the MWL, and waters which plot off (below) this line are clearly indicated as having been influenced by kinetic fractionation, and hence evaporation. Isotope analyses of water samples from an evaporated soil profile will then plot to the right of the MWL, intercepting it approximately at the composition of the precipitation which originally wet the soil profile. Where a significant quantity of evaporatively modified soil water is present before infiltration, mixing of meteoric water and this soil water will result in initial compositions somewhat displaced from the MWL. Figure 5.12 shows isotopic compositions of soil waters from an arid zone soil profile, showing such a displacement from the MWL, and a low slope for the upper, evaporated part of the profile.

Care must be taken in interpreting oxygen-18/deuterium plots, because of the risk of confusion due to the several possible influences on the slope. Firstly, it is possible for light rainfalls in low humidity conditions to exhibit compositions which are shifted from the meteoric water line due to partial evaporation during precipitation; however, these events are seldom hydrologically significant in catchments. Secondly, although kinetic fractionation is the single most important

determinant of low slopes, the slope of the oxygen-18/deuterium relationship depends also on relative humidity, and the isotopic composition of the source of the evaporating water and the atmosphere. In the example given above, for instance, if the atmospheric humidity was 30% rather than 50% as assumed, the slope of the relationship for a saturated soil column is predicted as 2.5 (and 1.8 for the "dry" column). In fact, by artificially varying the composition of the original soil water, it is possible to produce large negative slopes, or slopes much greater than 8, but not for waters of meteoric origin. Low slopes are therefore not necessarily indicative of evaporation from "dry" soil, and this sort of interpretation requires careful choice of the appropriate value for the atmospheric relative humidity. A third possible source of confusion is where isotopic compositions of soils from several locations are plotted together, without other evidence that the source water for each measurement is related. Whereas this sort of analysis based on many data points is capable of providing significant evidence for such a relationship, spurious "slopes" may be determined due to disparate origins of the original waters. This is particularly true in catchment studies where landscape heterogeneity results in very different residence times for soil water from different parts of the catchment, and hence different isotopic compositions.

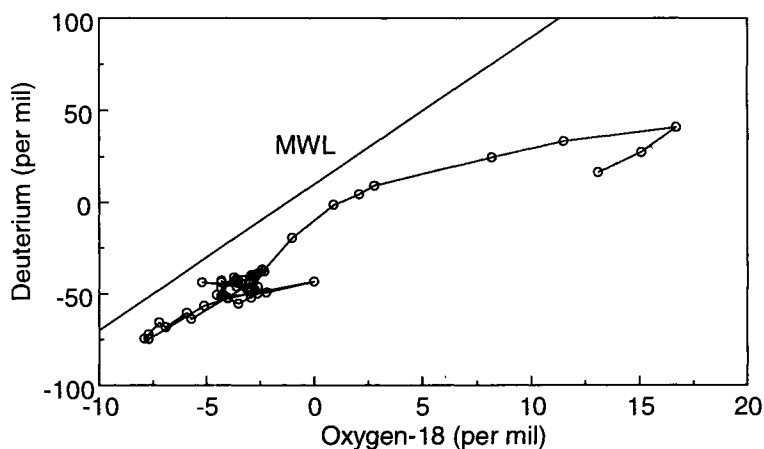


Figure 5.12. Plot of oxygen-18 vs deuterium for sand dune profile.

Alternatively, using the analytically determined relationship between oxygen-18 and deuterium, it is sometimes possible to determine, not only that the water has undergone a significant degree of evaporation, but also what the original isotopic composition of the water was. In soil isotope profiles, by following the trajectory on the oxygen-18/deuterium plot as the profile is descended, it is possible to observe the point at which evaporated water which has originally infiltrated the upper part of the profile has mixed with the displaced prior water, and hence determine the quantity of infiltration from an event which is stored in the soil. The characteristic isotopic signature imparted by the evaporation process can be a powerful tool in unravelling the pathways which water takes through a catchment where evaporation is significant, particularly when used in conjunction with other tracers such as chlorides to distinguish between evaporation, transpiration and various mixing processes.

5.3.7 Further modifications due to salinity and transpiration

The processes of transpiration, and mixing of groundwater bodies, are dealt with in more detail in Chapters 6 and 21, but for completeness are mentioned briefly here specifically because of their ability to influence observed soil water isotope profiles.

The remainder of this chapter has been concerned with evaporation from unvegetated soil surfaces, where extraction of soil water does not play a part. Because transpiration is non-fractionating, it effectively removes water and isotopes at depth from the soil profile. The precise effect on the form of the isotope profile depends on the amount of extraction as a function of depth, but, apart from drying out the soil, it will generally result in an isotope profile which is more compact than would be expected from the bare soil evaporation rate, because diffusion of isotopes in the liquid phase is opposed by both the evaporation and transpiration fluxes.

Perhaps the more significant effect due to the presence of salt is due to enhanced mixing which occurs when saline groundwaters emerge at a seep, where the salinity is increased by evaporation (or transpiration). In the same way as indicated above for stable isotopes, a concentration gradient develops near the surface, and solutes will diffuse downward in the liquid phase against the evaporative flux. Provided the evaporation rate remains sufficiently high, an approximately exponential profile of both salinity and stable isotopes results and salt accumulates at the surface, ultimately leading to efflorescence of solid salt. Alternatively, should the evaporation rate be insufficient to support this dense boundary layer of saline water, eventually the surface brine density may exceed a critical value, and unstable fingers of salt water develop, effectively destroying the surface profile, and mixing the high surface concentrations of salt and isotopes deep within the profile. The critical density difference between the surface water and deeper upwelling water which can be sustained by a given evaporation rate is given by:

$$\Delta\rho = \rho_{\infty}\theta E\lambda_{crit}/K \quad (5.34)$$

where ρ_{∞} is the density of the upwelling water, K the hydraulic conductivity at water content θ , and λ_{crit} is a critical Raleigh number, of value approximately 10. If the evaporation rate is low enough so that this density difference is exceeded, a discernible plume fed by the salt fingers may eventually form, transporting both salt and stable isotopes away from the surface. Resulting isotope profiles can show unusual features, such as secondary maxima and minima at depth. Under saturated conditions, if the groundwater system is sufficiently deep, it is possible for the accumulation of salt in the surface layers to induce large-scale circulation of the brines. Then this mechanism may lead to the progressive isotopic enrichment of the whole groundwater body, the amount of enrichment depending on the degree of exchange and mixing with other groundwater bodies. Herczeg et al. (1992) appealed to this mechanism to explain measurements of isotope concentrations in a surface transect of a salt lake, and used it to obtain estimates of evaporation rates from the lake surface and the degree of mixing.

5.4 New Research Directions

Most of the important aspects of evaporation and isotopic exchange in soil water have been comparatively well studied at the laboratory scale. The pressing problems in catchment isotope

hydrology have to do with obtaining an understanding of how these individual processes are integrated at the catchment level. The unrevealed, and perhaps unobtainable, character of catchment heterogeneity coupled with the dominant role it provides in determining catchment response implies that attention must now be directed to the study of isotopic exchange processes on a catchment, rather than plot, scale. From the point of view of this chapter, the outstanding problem is to develop techniques to obtain accurate estimates of residence times for water and solutes, and the dependence of the residence times on catchment characteristics, climatic conditions, land use, etc. These estimates are not possible from isotopic data alone, any more than they could be inferred from hydrometric data alone, but will require intelligent use of data from different sources. Available evidence from isotopic tracers points to a wider range of residence times than had previously been suggested by traditional hydrometric data, but also indicates that isotopic techniques are appropriate for investigating such issues.

Rather than pay attention to details obtained from individual measurements, future progress will require an understanding of the information content of a series of such measurements, with experimental design attempting to obtain the maximum information for the minimum expenditure. This will require a more coordinated approach than has sometimes been evident, with isotopic sampling frequencies more closely related to the frequencies of other forms of data collection.

Further emphasis on the temporal and spatial distribution of isotopes in rainfall is necessary in order to obtain greater resolution of the isotopic signal input to catchments. Similarly, a better characterization of transpiration losses is necessary in order to extend the usefulness of isotopic data to longer term studies where such losses are significant.

Given the experimentally demonstrated sufficiency of the above formulation for stable isotope movement in soil water under evaporation and infiltration, it is now possible to proceed with confidence to formally develop computer based models of coupled water and stable isotope movement in soils (e.g. Shurbaji and Phillips, 1995).

5.5 Summary

We have presented here a consistent theory of isotopic exchange processes in catchment soils. The theory is an extension of soil physical theory of water and solute movement in soils. Liquid water movement is assumed to be proportional to the hydraulic potential (Darcy's law), with liquid phase movement of isotopes by simple convection and diffusion. Water and isotope fluxes in the vapor phase are assumed to follow Fick's law of diffusion for ideal gases. Fractionation occurs on change of state, because small differences in chemical potential between isotopic species result in a slightly higher affinity for the vapor phase for the lighter species; and slightly higher molecular diffusivities of these lighter species in the vapor phase also contribute to fractionation during diffusive transport of water vapor. Detailed experimental evidence has been presented to justify the development and use of the above model during evaporative exchange of oxygen-18 and deuterium in soil water with the atmosphere.

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Plants, Isotopes and Water Use: A Catchment-Scale Perspective

Todd E. Dawson and James R. Ehleringer

6.1 Introduction

6.1.1 *Plants and catchment-level processes*

Beginning with one of the very first well-documented catchment experiments in 1909 at Wagon Wheel Gap, Colorado, in the United States, hydrologists began to acknowledge that plants influence the *patterns* of water movement at the catchment scale (see Bates and Henry, 1928). Since that time, water resource and forest management practices have been closely coupled, based on the premise that forests do influence water yield and quality at the catchment scale (Bosch and Hewlett, 1982). Closer scrutiny of over 100 catchment studies (Bosch and Hewlett, 1982) that acknowledge the importance of trees and forests in hydrologic processes reveals, however, that little or no consideration is given to the regulatory role, through changes in *rates* of transpiration, that plants can play in water movement. In fact, commonly evaporation, a physical process, and transpiration, a biophysical process, are lumped into a single variable in estimating water balance -- evapotranspiration (E_t), as discussed in Chapter 1. This view is a gross oversimplification of the processes of evaporation and transpiration, and is very likely to be a primary reason for why the vapor-phase water-flux component of the hydrologic cycle is poorly understood and parameterized in many hydrologic models (Rind et al., 1992).

It is estimated that sixty-five percent of all rainfall that occurs over the land surface is effectively removed from those surfaces by the recycling force of evaporative processes (Chahine, 1992). It has also been estimated that plants cover approximately 70% of this surface (Whittaker, 1975) and are a primary route by which 80% of the water in surface and sub-surface soils re-enters the hydrologic cycle over land (Chahine, 1992; Gleick, 1993; Dawson, 1993a; Newson, 1994). However, just as streams do not behave as single geological conduits for water flux over the land because of various internal characteristics and processes (Likens, 1985), neither are plants passive meteorological conduits for water flux off of the land. Plants possess small pores on their leaf surfaces - stomata - that can finely regulate the quantities and rates of water loss. As such, when considering both the *patterns* and *rates* of water flux from a given piece of land, a catchment, or from a riparian zone, the regulatory influence of plants must not be ignored. With the notable exception of research with forested *Eucalyptus* catchments in Australia, India, and South Africa (reviewed in Calder et al., 1992a), rarely are plants considered explicitly in hydrologic research at the catchment level (Newson, 1994). The data which are commonly presented are biased towards a perspective which views plants as simply intercepting or evaporating water from their surfaces with no consideration for how well they can regulate water flux.

This chapter expands upon this perspective and considers, in some detail, the role of plants and vegetated surfaces in water movement patterns and their abilities to influence these patterns and rates of water movement at the catchment level. The analysis of stable isotopes of hydrogen and oxygen in plant- and source-waters has, in recent years, substantially improved our ability to better understand the soil-plant and plant-atmosphere interface so that we might better understand catchment level processes. We suspect that a major reason for why plants have not been considered more explicitly in catchment hydrology is because of (a) a lack of an easily applied method at the catchment scale, and (b) poor communication among hydrologists and forest tree biologists interested in hydrologic processes at the catchment level. Isotope tracer studies, especially with naturally occurring stable isotopes, provides a powerful method as well as a common arena for drawing these two groups of scientists together.

Our discussion begins with the plants themselves and builds toward a landscape- or catchment-scale perspective (after Burt, 1992) but does not reduce the plants growing in and on these catchments to simple evaporative surfaces or passive conduits for water movement. Rather, we view plants as "regulators" of water flux in the hydrosphere. To accomplish this, we first present existing information on plants, water, and stable isotope analyses and then expand upon this data base to provide a catchment-level perspective (for recent reviews focused on the botanical perspective see Ehleringer and Dawson, 1992 and Dawson, 1993b). We first discuss water transport processes as influenced by plants, how plants use and modify soil and ground water, and how they regulate water movement at the individual and stand levels. We present a number of examples of how stable isotope analyses of plant- and source-waters are providing new insights into the patterns of water movement, uptake and use for a diversity of ecosystems. We end by presenting a number of examples where we believe the isotope approach to studying plant-modified water movement may provide important insights into catchment-level processes on both a short-term and long-term basis.

6.1.2 Working premise concerning plants, isotopes and water use

The basis of what we present derives from the fundamental observation that there is no fractionation of either oxygen (^{16}O , ^{18}O) or hydrogen (H, D) isotopes in water during the uptake process by plant roots (Figure 6.1; Wershaw et al., 1966; Allison et al., 1984; White et al., 1985; Dawson and Ehleringer, 1991; Thorburn et al., 1993; but see Lin and Sternberg, 1993 for an unusual exception). Variation in the stable isotopic composition of water in catchment sources (soils, streams, and ground water) are largely produced by two phenomena: (1) evaporative isotopic enrichment from the surface layers (Allison et al., 1983; Allison and Hughes, 1983; Barnes and Allison, 1983, 1988), and (2) seasonal and storm-related changes in the isotope composition of precipitation inputs (Chapter 3; Friedman et al., 1964; Gat, 1980; Yurtsever and Gat, 1980; Ferronsky and Polyakov, 1982; Ingraham and Taylor, 1991). A third process, thermal and chemical modification along gradients that develop between the bulk soil and aquifers (Chapter 2; Fontes, 1980; Gat, 1982; Barnes and Allison, 1989), can also effect the composition of deep aquifers or in geothermal areas (Hoefs, 1997).

When water is transported between the roots and the shoots within a plant, its isotopic composition (the D/H or $^{18}\text{O}/^{16}\text{O}$ of xylem-sap) remains unaltered until it reaches tissues or organs such as leaves (Dongmann et al., 1974; Flanagan and Ehleringer, 1991; Flanagan et al., 1991) or young, unsuberized stems (Dawson and Ehleringer, 1993; Thorburn and Mensforth,

1993), that are losing water to the external atmosphere. Evaporative processes cause significant enrichment of the heavier isotopes (D or ^{18}O) within the xylem-sap. The magnitude of isotopic enrichment is a function of the leaf transpiration rate (E_p), the humidity gradient between the site of water loss and the atmosphere as well as the δD or $\delta^{18}\text{O}$ (see below) of the atmospheric water (Dongmann et al., 1974; Zundel et al., 1978; Leaney et al., 1985; Farquhar et al., 1993; Flanagan et al., 1991, 1994). In order to understand and document patterns of water use, uptake and transport by plants, it is essential to collect and analyze the xylem-sap before it is exposed to evaporative enrichment. If this is done, the analysis of this sap and of the source water δD and/or $\delta^{18}\text{O}$ can provide a powerful tool for tracing the spatial and temporal patterns of water uptake and use and the effect of these patterns on hydrologic processes.

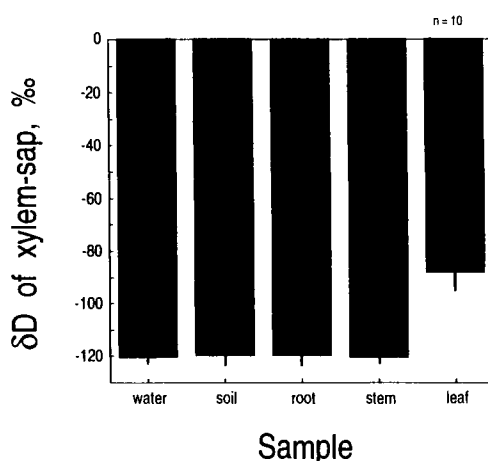


Figure 6.1. The stable hydrogen isotopic composition (δD) of water in the soil, the roots, and the suberized stems of *Acer negundo* (summer time; Utah, USA). The data show that there is no isotopic fractionation during water uptake (data taken from Dawson and Ehleringer, 1991, 1993b).

6.2 Water Uptake and Water Transport in Plants

6.2.1 Background

In order to understand the role of plants in catchment-level hydrologic processes, one must be able to accurately quantify the components of the catchment balance (Chapter 1). Some inaccuracies may result when parameters are estimated by difference. Accurate measures of each water balance parameter (Equation 6.1) permits us to achieve "closure" for forested catchment studies (see Kaufmann and Kelliher, 1991; Kaufmann and Landsberg, 1991). A catchment provides a convenient unit of study for advancing towards closure because inputs and outflows for an area where the boundaries are known can be directly measured (see for example chapters in Swank and Crossley, 1988). However, our task does not stop here. In addition to outflows, we must know the magnitude of water losses from the catchment via evaporation and plant transpiration. Spittlehouse and Black (1981) present a simple hydrologic mass balance model for a catchment:

$$\theta_{i-1} - \theta_i + (P - E_t - D - R) \Delta t / z = 0 \quad (6.1)$$

where the quantity $(\theta_{i-1} - \theta_i)$ is the change in the volumetric water content (θ ; m^3/m^3 ; see Topp and Davis, 1985) in the rooting zone over the time period Δt and $i-1$ and i are the beginning and end, respectively, of this time period. P , E , D , and R are the rates of precipitation, evapotranspiration, drainage (percolation) into the soil volume, and runoff during Δt (mm/time) respectively. Δ is equal to $i - (i-1)$ and z is the depth of the rooting zone. Rearranging Equation 6.1 as:

$$z(\theta_{i-1} - \theta_i) = ([E + D + R] - P)\Delta t \quad (6.2)$$

we can more easily relate the change in the volumetric water content of the zone in which a plant extracts its water ($z(\theta_{i-1} - \theta_i)$) to outputs ($[E + D + R]$) and inputs (P) to the catchment over time (Δt). P and R can be accurately measured if a catchment is appropriately gauged (see Swank and Crossley, 1988). D is more difficult to determine so it is often assumed to be zero for catchments underlain by bedrock (for example see Likens et al., 1970). Because assuming D is zero can be an important source of error in catchment water balance studies (Tanner, 1968; Calder, 1992b), some estimate of D must be obtained to gather sound water balance information for a catchment. Another important source of error comes with determining evapotranspiration (E), which must be broken into its component parts, evaporation (E_w) and plant transpiration (E_p) where:

$$E_w = g_a(e_s - e_a) \quad (6.3)$$

where g_a is the bulk aerodynamic conductance from any surface to a known reference height, e_s is the saturation vapor pressure at the surface -- including the soil surface (e_{st}), leaf surfaces of understory plants (e_{sp}), and canopy tree leaf surfaces (e_{st}). All three of these parameters must be determined at their unique surface temperature. The all-inclusive term, e_s , includes water which is intercepted by a plant canopy and then re-evaporated back to the atmosphere. The actual vapor pressure in the atmosphere normalized to the conditions at the evaporating surface is e_a . Following Whitehead and Hinckley (1991), transpiration (E_p) from a dry canopy can be expressed as:

$$E_p = \Omega E_{eq} + (1 - \Omega)E_{imp} \quad (6.4)$$

where the coupling factor, Ω (Equation 6.9 below), determines the relative importance of the terms E_{eq} and E_{imp} where E_{eq} is the equilibrium rate of transpiration, expressed as:

$$E_{eq} = \epsilon A / [(\epsilon + 1)\lambda] \quad (6.5)$$

where A is the energy available as a driving force for transpiration, ϵ is the change in latent heat content relative to the change in sensible heat content of saturated air (equal to s/γ , where s is the slope of the relation between saturation vapor pressure and temperature, and γ is the psychrometric constant) with l being the latent heat of vaporization. The imposed rate of transpiration, E_{imp} , is:

$$E_{\text{imp}} = g_c D_m / P \quad (6.6)$$

where g_c is canopy conductance to water vapor, D_m is the saturation vapor pressure difference between the atmosphere measured at a known height in the mixed layer well above the surface of the canopy and the surfaces of the leaves where water is leaving, and P is atmospheric pressure. For simplicity, the term g_c incorporates both conductance of water vapor from inside of leaves into the boundary layer around a leaf (g_i) as well as the conductance from the boundary layer into the external atmosphere (g_{hl}). In practice, these two processes are usually separated and either measured or estimated independently. For catchment level studies this may be impractical; however, we combine them here. The air saturation deficit measured above plant canopy height, but still within the plant's canopy boundary layer, D , is related to D_m by the relation:

$$D = \Omega D_{\text{eq}} + (1 - \Omega) D_m \quad (6.7)$$

where D_{eq} , the equilibrium air saturation deficit, is expressed as:

$$D_{\text{eq}} = \gamma \epsilon A / [(\epsilon + 1) C_p g_c] \quad (6.8)$$

and the coupling factor, Ω , is expressed as:

$$\Omega = (\epsilon + 1) / (\epsilon + 1 + [g_a / g_c]) \quad (6.9)$$

where C_p is the volumetric (specific) heat capacity of air at a constant and known pressure and temperature. Often, tall, aerodynamically rough forest canopies commonly cause values of Ω to be small (0.1 - 0.3) because g_a is greater than g_c and E_p is largely driven by D_m (Whitehead and Hinckley, 1991; Meinzer, 1993). This is not always true, however, and the degree of coupling between the bulk atmosphere and a plant canopy will be significantly influenced by the species (Jarvis and McNaughton, 1986), the prevailing climatic conditions (e.g. wind velocity), and stand characteristics within the catchment (e.g. tree size and density; Dawson, 1996). Modification of the transpiration equation (6.4) for a partially dry canopy can be found in Whitehead and Hinckley (1991). Further details of Equations 6.3 - 6.9, the assumptions behind using them, and how they are obtained can be found in Jones (1992), Monteith and Unsworth (1990) and references therein.

6.2.2 Measurements of water uptake and transport by plants

It should be apparent from the very brief discussion presented above that vegetated lands cannot be treated as freely evaporating surfaces. Plants do exert a significant degree of control over the patterns and rates of evaporative water loss. In order to relate the leaf-level measurements to entire plant canopies and eventually to catchment studies, it is important that we understand how plants modify the patterns and rates of water movement at that scale. Tools and techniques for measuring or estimating water vapor flux through individual plants include

lysimeters (Rutter, 1968; Newson, 1994) or sap flow gauges (Swanson and Whitfield, 1981; Baker and van Bavel, 1987; Jones et al., 1988; Hinckley et al., 1994; Dawson, 1996). Techniques for entire forest stands include Bowen ratio-energy balance and eddy correlation (McNaughton and Jarvis, 1983; Kaufmann and Kelliher, 1991; Hollinger et al., 1994; Herbst, 1995; Dawson, 1996). Early studies using isotopes employed radioactive tracers to obtain estimates of E_p and E_t (Kline et al., 1970; Luvall and Murphy, 1982; Waring and Roberts, 1979; Waring et al., 1980) and these types of studies continue today, in both plantations (summarized in Calder et al., 1992a, b) and in natural stands (Bishop and Dambrine, 1995). While these studies are informative, radioactive tracer methods are impractical, especially in natural catchments because they not only "pollute" the basin for subsequent investigators but are prohibited in many areas because the catchment may be used for other purposes (e.g. public water supply).

In recent years, the use of stable isotopes of hydrogen and oxygen in water have provided not only a new and easily applied, non-radioactive method, but many new insights into how plants modify soil water and/or take up water from different regions in the soil or times of the year (reviewed in Ehleringer and Dawson, 1992; Dawson, 1993b). It has now been well documented (Walker and Richardson, 1991) that marked isotopic gradients exist in both δD and $\delta^{18}O$ within the soil profile (see Chapter 1 for a full explanation of isotopic fractionation in water). The upper soil layers are commonly enriched in the heavier isotopes in water (D and ^{18}O) due to evaporative fractionation which is the preferential loss of the lighter isotopes in the vapor phase as water evaporates from the upper soil surface (Figure 6.2).

The isotopic composition of water changes markedly with depth, often converging upon a relatively stable value at depths below an isotopically unstable zone (UZ) present in some soils (see Figure 6.2). This stable value most often reflects "stored" soil water or ground water. The isotopically unstable zone observed in some (but not all) soils is sometimes a result of old water that has remained in this zone from past rainfall or percolation events. However, more commonly it is caused by phase changes, such as condensation events when water vapor in the soil airspace/matrix reaches its dew-point as the soil becomes cooler with depth (Mazor, 1991). Chapters 5 and 7 provide detailed discussions of water in soils and ground water.

When plants are growing in the soils, further modification of soil-water isotopic composition can result from patterns of water uptake and water loss from plants rooted at different depths. In the simplest case, we might expect the magnitude of change in the isotopic composition of soil water to be different between a tilled and fully planted crop field, or between a forested and deforested catchment. The presence of plants, which can take water up from many different layers in the soil, should modify not only the soil volumetric water content, but also the isotopic soil water profile. It is well known that plants have a marked influence on the water yield of a catchment (Likens et al., 1970; McMinin and Hewlett, 1975; Bosch and Hewlett, 1982; Swank and Crossley, 1988) as well as on the transpiration rate (Figure 6.3; Lemon, 1966, Kramer and Boyer, 1995). Furthermore, on sites where plants are deeply rooted and take up deep soil water or ground water, the water within the profile will be depleted more quickly, resulting in a different soil moisture profile than on soils lacking plant cover (Figure 6.4).

Recent studies with crop plants (Croak et al., 1987, Baker and van Bavel, 1986), shrubs (Richards and Caldwell, 1987; J. Richards. pers. comm.), a desert treelet (Mooney et al., 1980a) and canopy trees (Dawson, 1993c, 1996; unpublished data) have all shown that water can be transferred within plant root systems from wet to dry regions of the soil and then released. This

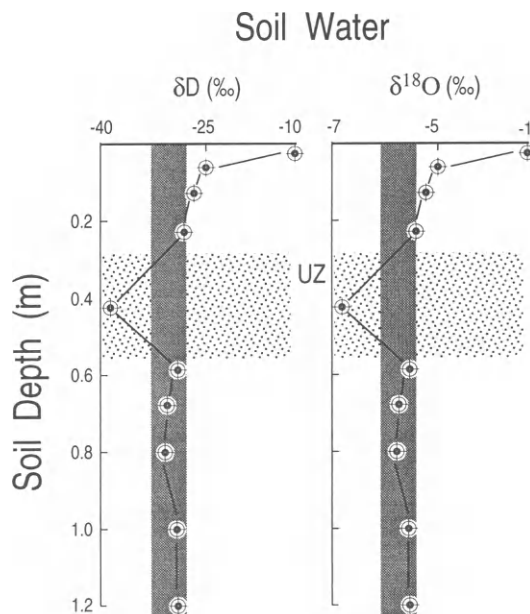


Figure 6.2. The δD and $\delta^{18}O$ of soil water as a function of depth in the Australian soil profile (modified from Walker and Richardson, 1991). Note a marked isotopic depletion zone depicted as a lightly stippled area at approximately 40 cm deep (UZ; unstable zone - see text for explanation). Such a zone can cause problems in studies of water uptake by plants if it is assumed that only surface soil water, which is enriched in the heavier isotopes, and deeper source water (ground water), which is depleted in the heavier isotopes, are the only two sources. Vertical shaded areas depict the range of isotopic values for the deep source water.

process (hydraulic lift) not only changes the volumetric water content of the soil, but also the isotopic profile. For example, Dawson (1993c) has recently demonstrated that large sugar maple trees (*Acer saccharum*) redistribute ground water into the upper soil layers by the process of hydraulic lift. Using δD , he demonstrated that the isotopic composition of soil water near large trees was indistinguishable from ground water and very different than the δD of the bulk soil sampled away from the trees (Figure 6.5). Additional studies using sap flow and energy balance methods showed that this additional "pool" of water created by hydraulic lift could be as much as 100 L every night (Emerman and Dawson, 1996). This process enhanced total water discharge from the forest by 2-fold (Dawson, 1996), and demonstrates how the presence of plants can have a marked effect on not only soil moisture and thus the hydrologic balance but on the isotopic composition of that moisture (Dawson, 1993c).

If we hope to use isotopic tracers in catchment-level studies, it will then be essential that we understand how the plants that grow in these catchments are influencing the isotopic composition of water in the soil profile, as well as the rates of water use from different water sources in the catchment. Below, we present a number of case studies which demonstrate the use of stable isotopes in plant water uptake and water source research (see Section 6.4). Our goal is to show how this kind of information can be used at the catchment scale. However, before the case studies we will briefly discuss water movement within plants.

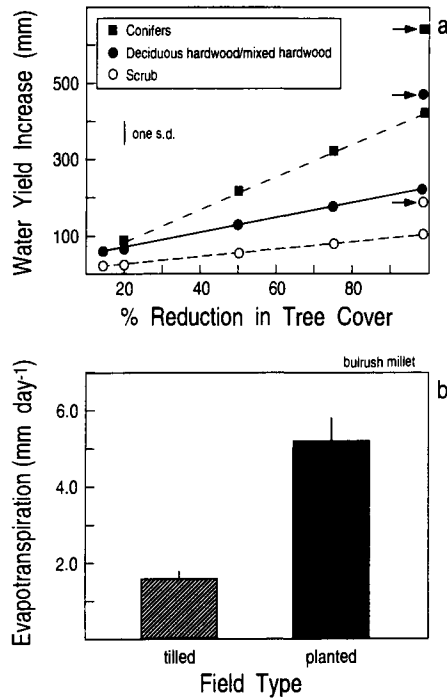


Figure 6.3. (a) Water yield as a function of percent reduction in tree cover for catchments of different forest types (USA). Lines are drawn through averages. Symbols with arrows at right show the extremes for each 'forest' type (redrawn from Bosch and Hewlett, 1982). (b) Evapotranspiration for tilled and planted plots (redrawn from data from in Lemon, 1966) in the northeastern (upstate New York) United States.

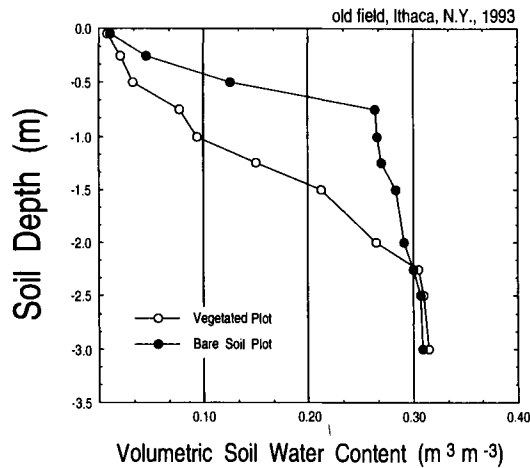


Figure 6.4. Volumetric soil moisture content (2) as a function of depth for paired, 20 m², plots with and without plants growing on them. The vegetated plots support plant taxa composed primarily of grasses, perennial clonal herbs, and a few small trees and shrubs rooted to a maximum depth of 2.25 m. (2) was determined by time domain reflectometry (TDR) for a clay-loam soil (Dawson, unpublished data).

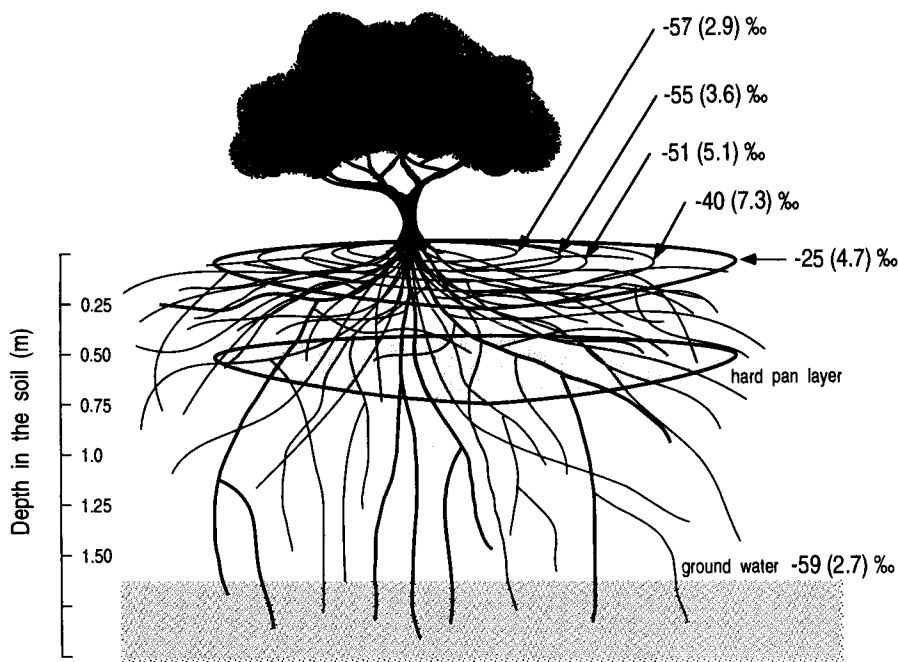


Figure 6.5. The δD of soil water ($\pm$ s.d.) within the principle rooting depth of plants as a function of distance away from sugar maple trees (*Acer saccharum*) conducting hydraulic lift (HL) near Ithaca, New York, USA (HL is water transport from ground water through the root system to above the impermeable hard pan layer and loss to soil water below the trees - modified from Dawson, 1993c).

6.3 Stomatal Regulation of Water Movement in the Soil-Plant-Atmosphere Continuum

6.3.1 Water movement and the regulatory role of plants: the leaf-level

Water loss from plant leaves or canopies is governed by minute pores on their surface - stomata. The aperture of these stomata, and thus the rates of water loss, are markedly changed by a variety of environmental factors which include the plant and soil water status and atmospheric humidity (Ziegler et al., 1987), two factors which also influence the catchment water balance (Equations 6.1 and 6.2). Exposure of plant leaves to dry air (low humidity or high evaporative demand for water) can cause a direct change in leaf and canopy transpiration rates or an indirect change which is mediated through changes in the plant and soil water status (Figure 6.6; see Gollan et al., 1985, Schultze et al., 1987 for reviews). Leaf stomata also respond to changes in soil water potential and the soil-to-plant water potential gradient (Kramer and Boyer, 1995; Kozlowski, 1964-1983). As soils dry and the water potential gradient steepens, it becomes more difficult for a plant to extract enough soil water to meet its transpirational demands as well as its needs for growth and other metabolic functions. A consequence of a steeper water potential gradient between the soil and leaves is stomatal closure and a reduction in leaf and canopy transpiration (Figure 6.7).

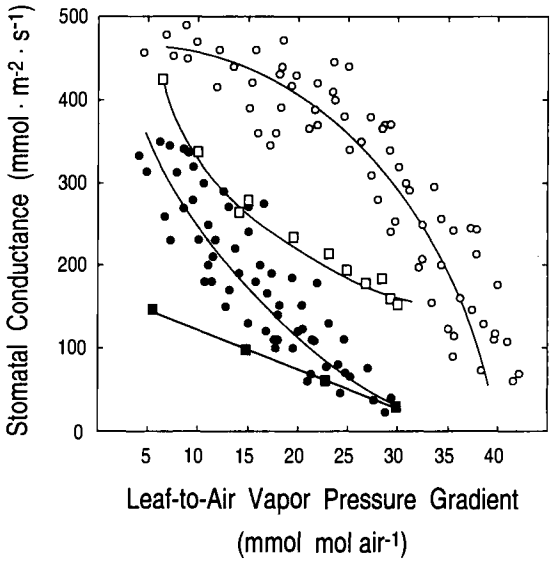


Figure 6.6. Stomatal conductance for water vapor (g_s) as a function of the leaf-to-air vapor pressure gradient for *Acer negundo* female (open circles) and male (closed circles) trees, *Sesamum indicum* (open squares), and *Corylus avellana* (closed squares). As the evaporative gradient from the leaf to the air increases (and relative humidity decreases) water loss rates decline because leaf stomata close (from Schultze and Hall, 1982; Schultze, 1986; Dawson and Ehleringer, 1993).

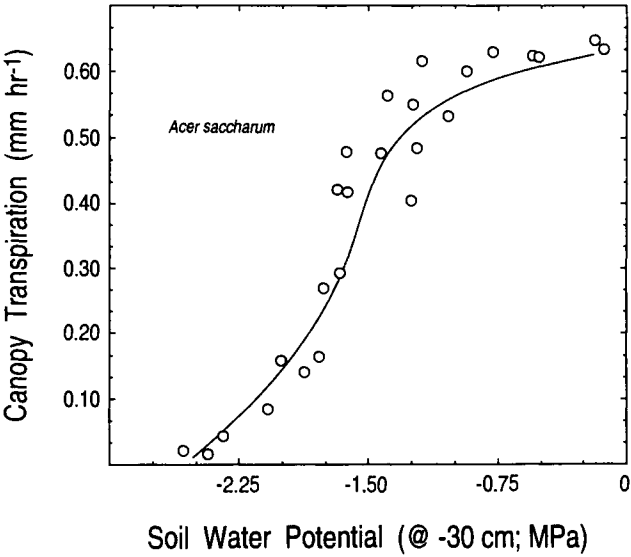


Figure 6.7. Mid-summer canopy transpiration based on sap flow from sugar maple (*Acer saccharum*, $n = 5$) trees as a function of soil water potential (closed symbols) near Ithaca, New York, USA. Soil water potential by psychrometry (modified after Dawson, 1993c and 1996).

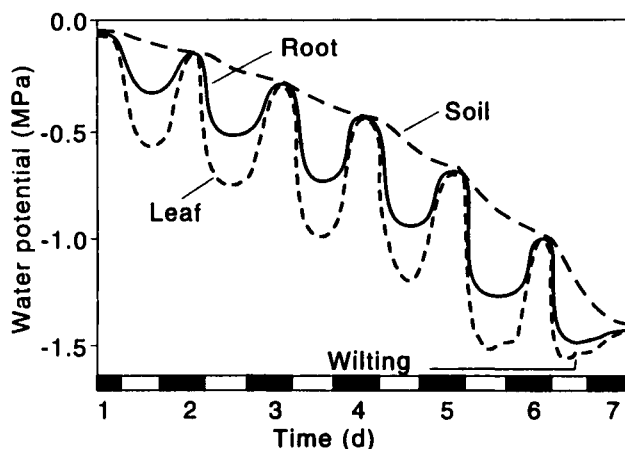


Figure 6.8. Schematic diagram of the changes in leaf, root, and soil water potential during the course of the day-night (shaded blocks) period and over a seven day drought. The greatest daily fluctuations occur in the plant leaves which are exposed to high evaporative demand from the environment at the same time soil water becomes progressively more limited. The gradual decline in maximum daily water potential is caused by plants using up stored soil water to the point at day 7 where permanent wilting occurs (after Slatyer, 1967 - taken from Larcher, 1995).

Soil and plant-water content (or water potential) also changes during the course of a day, or a growing season (Figure 6.8), or with changes in physiographic features such as slope exposure, soil type, and degree of vegetation cover (Figure 6.9). These changes will in turn influence the rates and patterns of water loss from individual plants as well as from plant stands.

6.3.2 Water movement and the regulatory role of plants: the stand-level

Water deficit or stress measured at the leaf level, induced by either low atmospheric humidity or soil moisture content, is manifest as a reduction in total canopy transpiration (E_p ; Equation 6.4) and thus a lowered total evapotranspiration (E_t) at the entire stand (or catchment) level. For example, using a simulation model, Lynn and Carlson (1990) show that plant water stress has an important influence on transpiration on remotely sensed plant canopies. The model is built around the correlation that when plant temperature (determined radiometrically) rises and leaf water potential declines, stomatal resistance to water loss increases. In their model, plants with a low critical leaf water potential (i.e. low tolerance to water stress-induced stomatal closure), have lower overall transpirational water loss due to a combination of soil, plant and atmospheric influences (e.g. soil water content, critical leaf water potential, vapor pressure gradient from the leaf to the air; Carlson, 1991). They conclude that the transpiration component of stand level water balance is a function of *both* soil water content and plant physiology. Therefore, understanding stand- (or catchment-) level water balance cannot occur if evaporation and transpiration are lumped into a single water balance term. Instead, separate attention must be given to the regulatory role of plants in land surface water flux and the interaction between water availability, water stress, and plant transpiration. Recent modeling work by Running and Hunt (1993) makes an important step towards making these types of linkages and has enhanced our understanding of forest water (and carbon) balance.

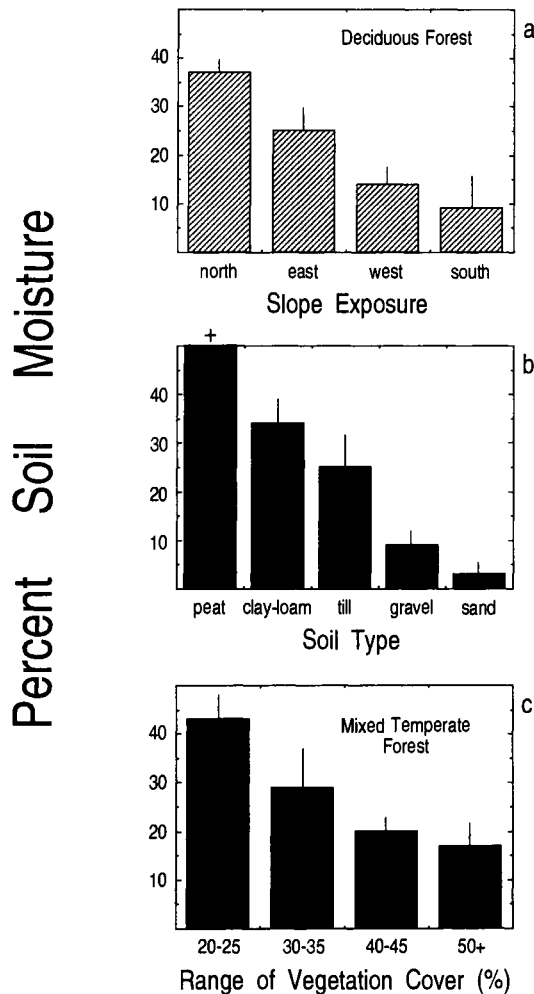


Figure 6.9. Percent soil moisture content as a function of (a) slope exposure, (b) soil type, and (c) percent vegetation cover (from data in Kramer and Boyer, 1995).

The amount of water consumed by a plant stand is a function of the area (and/or mass) of transpiring leaves. On a continental scale, as chronic water stress develops and water availability declines, it is manifest at the plant level as a significant decline in the amount of leaf area displayed per unit of land surface area -- the so-called, leaf area index (LAI; m^2/m^2). Data extracted from various sources (in Larcher, 1995) on the relationship between LAI and the average growing season soil water potential (the botanical index of plant water stress; more negative water potential values indicate greater water stress and/or lower water availability) shows that LAI increases as water availability increases (Figure 6.10). The slope of this relationship is shallow and linear when average soil water potential is relatively low (-1.25 to -3.20 MPa), indicating very small changes in LAI over a broad range of soil water potentials (and corresponding plant water stress). Interestingly, at higher soil water potentials (considered

mild plant water stress; -1.0 to -0.4 MPa), LAI increases exponentially with less water stress (high water potentials; Figure 6.10). This implies that in regions of higher average soil moisture content (higher water potentials), E_t would be predicted to increase exponentially with increased water availability (or progressively less plant water stress). This relationship would be predicted to have a marked influence on stand- or catchment-level water balance. For example, several recent studies, for a variety of vegetation types, using both empirical data and models, show that rates of E_p and/or E_t are reduced with declining soil water content (or water potential) and that the magnitude of the change is very often related to the LAI (notable examples are: Dolman et al., 1991; Hunt et al., 1991; McNaughton and Jarvis, 1991; and Kelliher et al., 1993).

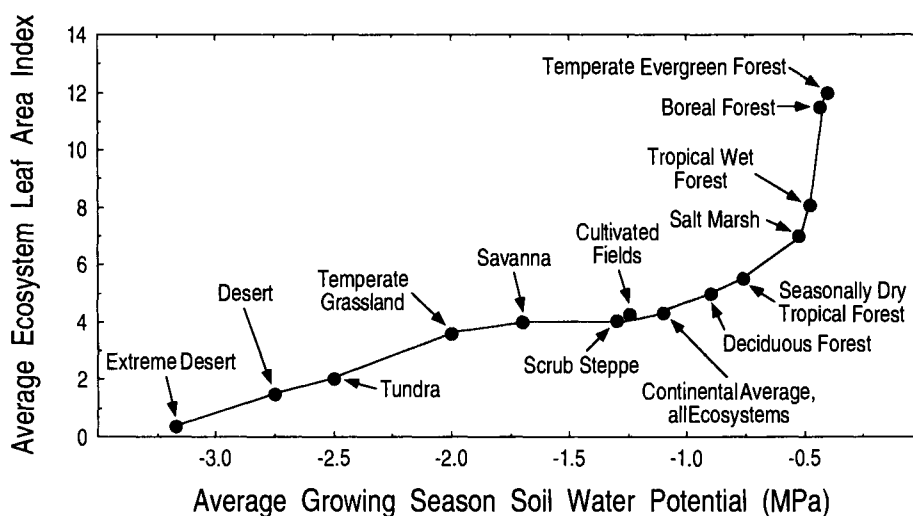


Figure 6.10. Average ecosystem leaf area index (LAI; m^2 leaves m^{-2} ground) as a function of the average seasonal soil water potential for major ecosystems of the world (drawn from data in Larcher, 1995).

6.4 Water Sources and Water Use by Plants: Case Studies Using Stable Isotopes

Understanding the patterns of water uptake by plants requires that the methods we employ provide a dynamic, rather than a static, picture of below ground water movement. The traditional methods used to study root systems (excavation, rhizatron, or even minirhizatron methods; Böhm, 1979; Caldwell and Virginia, 1988) have been largely inadequate for such purposes. The application of stable isotope analyses of water at natural abundance levels in the environment and in the plant are now providing new insights on the dynamics of root functioning including the utilization of water by plants across a broad range of taxa, inhabiting a variety of natural communities (see Dawson, 1993b; Ehleringer and Dawson, 1992). Although few of these studies have explicitly addressed how the patterns of water uptake, measured on individual plants may influence the dynamics of water movement at the catchment level, we believe that several of the examples we show here can be naturally and easily extended to this level.

Plants may utilize many potential water sources depending first upon the plant and secondly upon the spatial and temporal properties of the soils and climate in a particular region. Water sources include precipitation, soil water, ground water, runoff, fog and even salt water (see Dawson, 1993b). In order to know which one of these potential sources a plant may be using, it is necessary to collect these waters and determine their stable isotopic composition (δD and $\delta^{18}O$). These values are then compared with those of the water extracted from the xylem (water transport) tissues of plants growing in the same environment. This information also provides an indirect method for determining the rooting depth of a plant when clear differences in source water δD and $\delta^{18}O$ can be identified, such as between shallow-rooted plants which use soil water and deeply rooted plants which use groundwater. Detailed descriptions on water collection methods are given by Dawson (1993b,c), Dawson and Ehleringer (1993), Thorburn et al. (1993), Thorburn and Mensforth (1993), and Lajtha and Marshall (1994). The following case studies demonstrate the power of utilizing stable isotope analyses in plant and environmental waters as an avenue for improving our understanding of water uptake patterns in plants.

6.4.1 Riparian forest communities

An important component of most catchments are the forests that grow in variable source areas (Chapter 1) adjacent to streams. These riparian forests are important because they sit at the interface between the terrestrial and aquatic portions of the catchment and thus influence the surface and subsurface fluxes of water and other substances linked to water (e.g. nutrients and dissolved organic carbon). It is often assumed that the plants (trees in particular) that inhabit these streamside communities utilize the surface stream waters. However, in an investigation in the Intermountain west of the United States, Dawson and Ehleringer (1991) demonstrated that it was only the smaller trees which used the stream water, while mature trees growing in very close proximity to the stream used little or none of this water source (Figure 6.11). An analysis of the δD in source waters and the water extracted from the xylem sap of young and mature riparian trees revealed that the larger, mature trees, were using ground water, regardless of how close they were growing to the surface water source (Dawson and Ehleringer, 1991). In reviewing the long term stream flow data for this area, it became clear that although this stream was characterized as a "perennial" water course, for some years streamflow and thus tree water supply was extremely low during the long, dry summers of this semi-arid region. Hence, mature trees which use ground water are using the most reliable water source from a long-term perspective. By investing in deeper roots, plants inhabiting these riparian forest communities ensure that during drought periods they will have ample water to meet their requirements for growth and reproduction.

At least three other studies from riparian communities in both the United States and Australia have confirmed the findings of Dawson and Ehleringer (1991), that stream side trees do not necessarily use surface stream water. For example, Thorburn and Walker (1993) and Mensforth et al. (1994) have studied the water use patterns of *Eucalyptus camaldulensis* inhabiting the semi-arid flood plains along the River Murray in south eastern Australia and found that these riparian trees use ground water and not the surface stream water, especially if they were growing at distances greater than 15 m from the stream. Trees growing closer to the stream used stream water in the summer season and soil water in the winter. However, even the streamside trees, with roots growing directly in the water were only using, on average, 50% of this water source (Thorburn and Walker, 1993). These findings were similar to those reported

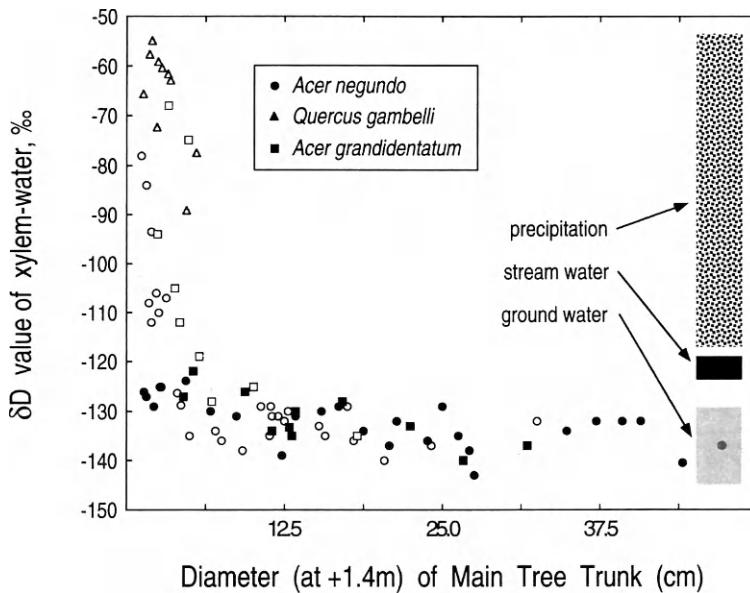


Figure 6.11. The hydrogen isotope ratio of water extracted from the xylem of three dominant tree species as a function of their size and distribution; trees growing nearest the stream are shown with open symbols and away from the stream with closed symbols. The bars along the right-hand side of the figure show the long term range of isotopic values for all of the water sources; local precipitation, stream water, and ground water (modified from Dawson and Ehleringer, 1991).

by Smith et al. (1991), who also demonstrated that riparian trees switch water sources, using water in the surface layers early in the growing season and then switching to the deeper ground water during drought periods. Another study conducted along the Colorado River in the western United States (Busch et al., 1992) has also demonstrated that the dominant riparian trees all used ground water rather than the river water (see examples reviewed in Figures 6.20 and 6.21 below). In summary, all of the studies conducted on riparian trees demonstrate that they can be very opportunistic in their water use patterns, either in time or in space. Although these also demonstrate some of the difficulty in predicting how riparian trees may behave with respect to water uptake and use, they do point out that these taxa can and do exploit several different water sources. Knowledge of this sort should make a difference in understanding how riparian trees influence catchment water balance.

6.4.2 Arid and semi-arid plant communities

Woodlands, shrub lands, savannas and deserts cover approximately 44% of the Earth's land surface (Whittaker, 1975). The plants that characterize these arid and semi-arid communities are often exposed to strong bimodal rainfall patterns (see Chapter 13 for examples). In summer, precipitation is derived from warmer climatic regions, and the isotopic composition reflects this (precipitation is more enriched in the heavy isotopes D and ^{18}O ; see Dawson 1993b). These summer rains are often very brief and thus do not penetrate very deeply into the soil layers

(Ehleringer et al., 1991). In contrast, water in the deep soil layers or in aquifers is derived primarily from winter recharge storms. These storms arrive from cooler regions that have precipitation that is significantly more depleted in the heavy isotopes D and ^{18}O (more negative) and often saturate the soil.

These bimodal rainfall patterns with different isotopic composition provide an ideal opportunity to study water uptake patterns by the diverse plant growth forms that characterize these communities. For example, Ehleringer et al. (1991) investigated differential utilization of summer rains by an array of plants living in the desert along the Utah-Arizona border in the United States. They showed that nearly half of the annual precipitation in this region is derived from summer rain. The annual plants and a shallow-rooted desert succulent relied on these summer rains, where the more deeply rooted perennial plants used a mixture of summer and winter rains or ground water (Figure 6.12). In an adjacent Pinyon-Juniper woodland, Flanagan and Ehleringer (1991) also observed that the dominant trees and shrubs used either only ground water (e.g. Utah juniper [*Juniperus osteosperma*] and rabbitbush [*Chrysothamnus nauseosus*]) or some proportion of summer precipitation and ground water (e.g. pinyon pine [*Pinus edulis*] and big sage [*Artemisia tridentata*]). Flanagan et al. (1992) extended this work and showed that pinyon pine and big sage which derived a large proportion of their water from summer precipitation also had lower predawn water potentials (greater water stress; Figure 6.13). This observation was also made by Valentini et al. (1992) for the evergreen shrubs and trees growing in the Mediterranean 'macchia' in northern-central Italy and Dawson (unpublished data) for temperate deciduous forests inhabiting central New York State in the United States (Figure 6.13). These studies showed that the species which utilize ground water also transpire more water for a given amount of carbon fixed in photosynthesis (poor water-use efficiency; see Farquhar et al., 1989). Working on Utah juniper along a gradient of summer precipitation, Gregg (1991) demonstrated that trees utilized a greater and greater proportion of deep ground water as summer precipitation became more unreliable (shown in Ehleringer and Dawson, 1992).

All of these studies demonstrate, that regardless of whether a plant inhabits arid, semi-arid, or mesic regions, there can be a strong relationship between water source and water use patterns. In cases where plants have access to deeper water sources they may not experience significant seasonal water stress and, in the end, may transpire more than plants which utilize shallow soil water (Figure 6.13). This was recently demonstrated by Dawson (1996) when he compared the water use patterns and water sources utilized by small, shallow-rooted and large, deeply-rooted sugar maple [*Acer saccharum*] trees (see below). Understanding the primary source of water for species inhabiting any region where water can become limiting should provide important insights for estimating and modeling regional-scale water balance.

6.4.3 Temperate forest communities

The very first studies which used stable isotopes in water from the xylem sap of plants were done in temperate forest communities. Temperate regions have also been the focus of some of the most extensive catchment hydrology studies (Likens et al., 1977; Bosch and Hewlett, 1982; Swank and Crossley, 1988). Oddly, no single study has merged the study of water uptake and water use by trees using stable isotopes with a hydrologic analysis of water movement at the catchment scale.

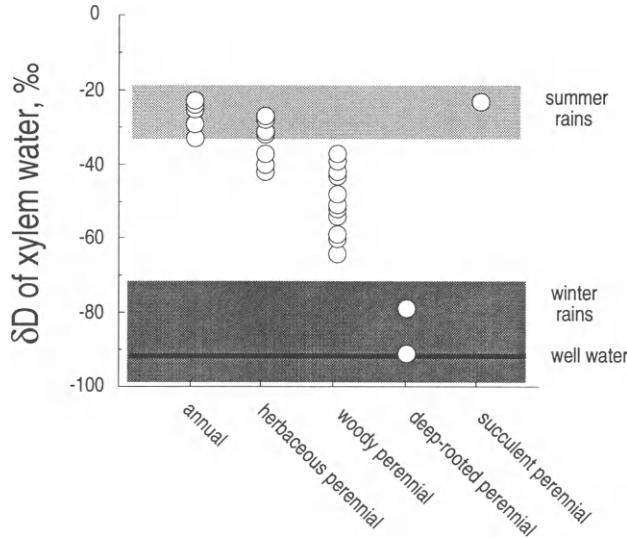


Figure 6.12. The hydrogen isotope ratio (δD) of water extracted from the xylem of several different desert plants species, grouped by life form, growing near the Utah-Arizona border, USA. The gray areas represent the range of δD values obtained for summer and winter rains which fell at the site. The solid line is the δD of well water (ground water) at this site. Based on a figure and data in Ehleringer et al. (1991).

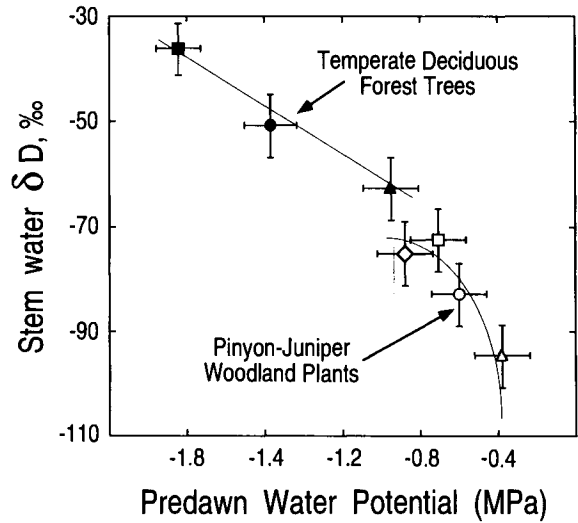


Figure 6.13. The hydrogen isotope ratio (δD) of water extracted from the xylem of a variety different trees and shrubs as a function of their predawn water potential. Open symbols are for plants growing in the semi-arid pinyon-juniper woodland in southern Utah, USA. Closed symbols are for plants growing in the temperate deciduous forests of central New York, USA. Plants noted with triangular symbols use ground water ($\delta D = -95$ and -64 ‰ for Utah and New York, respectively). Plants noted with square or diamond symbols use mostly rain water ($\delta D = -67$ and -34 ‰ for Utah and New York, respectively). Plants noted with circular symbols use some mixture of the two water sources (after data in Flanagan et al., 1992 and Dawson et al., in prep). See text for species names.

White et al. (1985) were among the first to analyze of stable isotopic variation in source waters and xylem sap extracted from tree cores. They showed that the eastern white pine, *Pinus strobus*, which inhabits a good portion of the northeastern United States, responds very quickly to summer precipitation events. Immediately after rain had fallen, trees growing in both wet and dry sites would take up water from upper soil layers (Figure 6.14). As the soils dried out, these same trees would show a shift towards using ground water or a mixture of rain water and deeper soil water (closed symbols in Figure 6.14). Interestingly, when rain water was not available, dry site trees could be shown to draw upon their heartwood water reserves, a pattern also seen in both red maple [*Acer rubrum*] and sugar maple [*A. saccharum*] inhabiting many of the same forest communities as white pine (Figure 6.15; White et al., 1985; Dawson, unpublished data). The ability of these trees to draw on both sapwood water which carries water from recent rain fall events and heartwood water which stores water from past water uptake events should be an important mechanism for buffering them against water stress and permitting them to meet their transpirational demands when soil water is limited.

Sugar maple has an additional mechanism for meeting its transpirational demands - the ability to take up water at night from deeper soil layers, transport it through its root system, and then release it into the upper soil layers where it is used the following day by both the tree itself as well as shallow-rooted neighbors growing in close proximity to these trees (Dawson, 1993c, 1996). This process is termed "hydraulic lift" (after Richards and Caldwell, 1987) and has been shown to occur now in both shrubs and trees. Utilizing stable isotope analysis of water, and standard water relations measurements, Dawson (1993c) was able to show that ground water that moved by the process of hydraulic lift into the upper soil layers by maple trees was used to some extent by all neighboring plants and that plants which were using this water source demonstrated less water stress (higher, or less negative leaf water potentials) and greater rates of stomatal conductance from their leaves (Figure 6.16). These data indicate that during drought periods water can not only move from deeper soil layers but that it can also be lost back to the atmosphere by both the trees and the adjoining plant community.

At the catchment scale this information has a number of potentially important implications. First, it means that more water moves through the soil-plant(s)-atmospheric continuum than would be expected (shown in Dawson, 1996). Secondly, a hydraulically lifted water source could have a strong influence on the distribution and abundance of *all* plant species and in turn of the amount of water movement within a catchment or forest stand. Third, estimates of E_p (from sap flow methods) and E_t (from Bowen ratio data) are 1.5 to 3-fold higher for large trees "mining" deep water sources, allowing them to maintain a more favorable water status and thus greater rates of transpiration over the course of a day and the growing season (Dawson, 1996).

A common feature of the two studies cited above was the application of a mixing model as a way to determine the proportion of each water source with a unique stable isotopic signature used by a plant or plants within a particular ecological/hydrological setting. White et al. (1985, also see White, 1988) applied a model that estimated both the proportion of different water sources used by white pine trees at a particular point in time (e.g. after rain fall) as well as the proportions of surface soil water and ground water used by trees at different sites over the course of a growing season. Dawson (1993c) developed a simple two end-member mixing model to calculate the proportion of the end-members found in any xylem sap sample. The model was applied to the δD data gathered from environmental and plant-water sources. The isotopic composition of the two end-members used in the model were soil-water (SW), derived

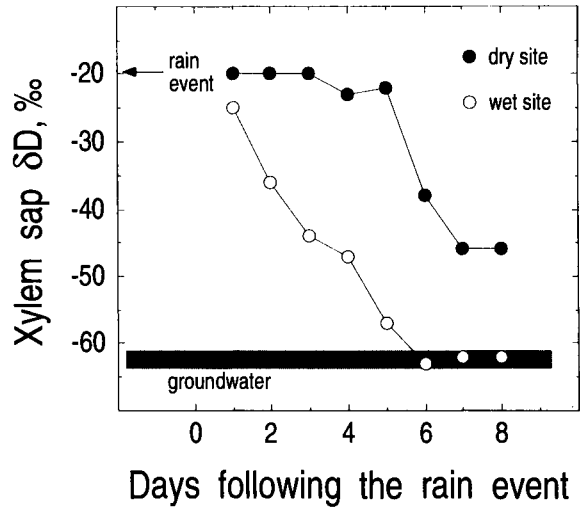


Figure 6.14. Changes in the hydrogen isotope ratio (δD) of water extracted from the sapwood of eastern white pine, *Pinus strobus*, growing in New York State, USA, following a summer rainfall event. Note that trees growing at the dry site did not have access to ground water while trees growing at the wet site did. Heartwood δD values from trees growing at the dry site were -47‰ (redrawn from data in White et al., 1985 shown in Ehleringer and Dawson, 1992).

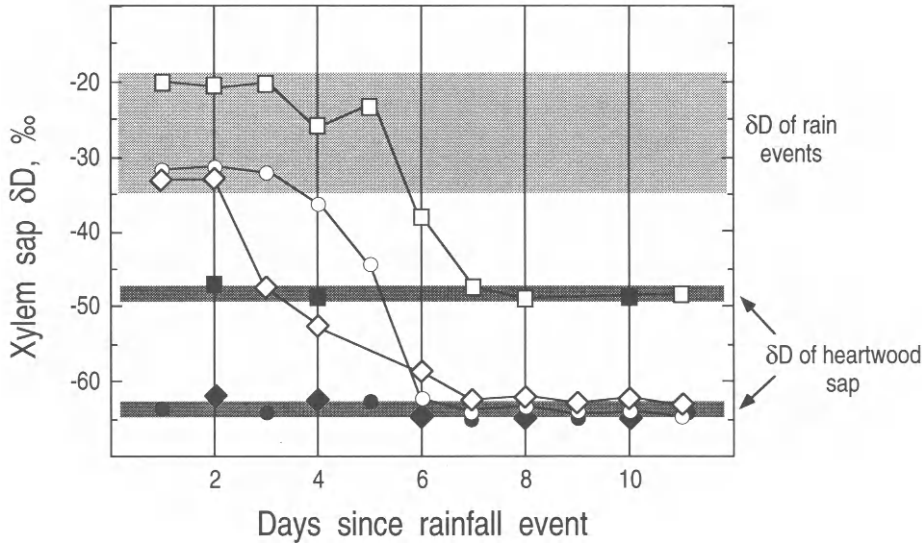


Figure 6.15. The changes in the hydrogen isotope ratio (δD) of water extracted from the sapwood (open symbols) and heartwood (closed symbols) of eastern white pine, *Pinus strobus* (squares), red maple, *Acer rubrum* (circles), and sugar maple, *A. saccharum* (diamonds), following a summer rainfall event. The trees were growing near Ithaca, New York, USA. Stippled areas show of range of δD values for rains (upper) and the lower two the δD of heartwood sap (data from White et al., 1985 and Dawson et al., in preparation).

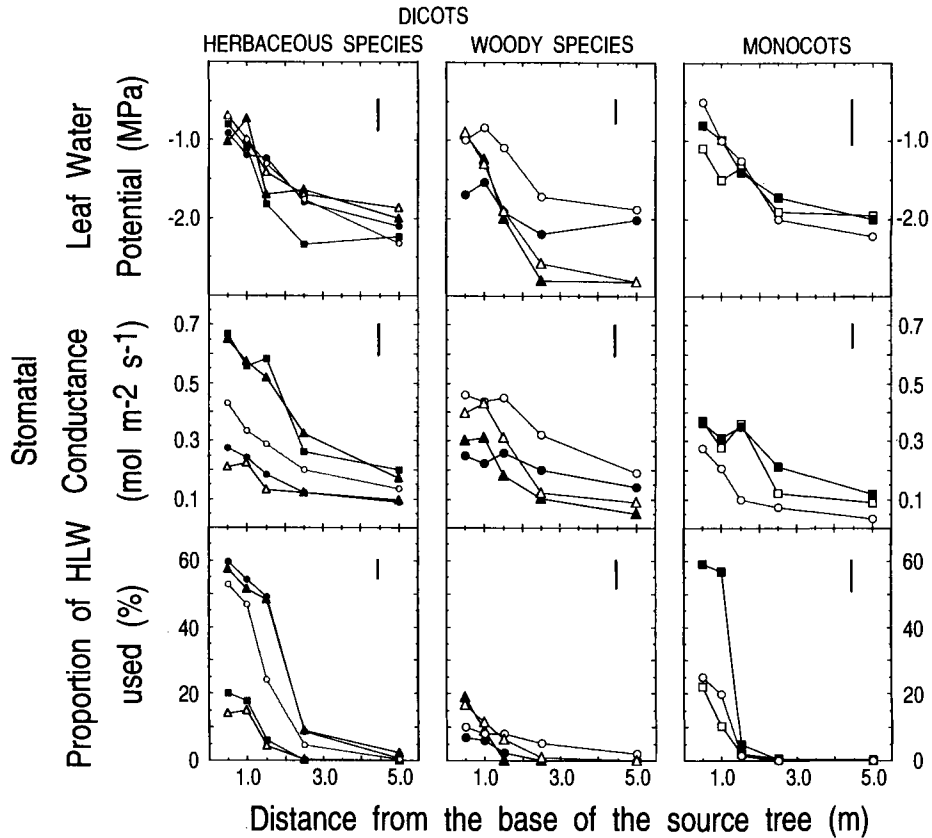


Figure 6.16. Midday leaf water potential (upper panel), maximal rates stomatal conductance to water vapor (middle panel), and the proportion of hydraulically-lifted water (*HLW*; lower panel) used by co-occurring plant taxa with mature *Acer saccharum* trees as a function of distance (m) from the tree base. The proportion of *HLW* used by these species was determined with a mixing model (Equations 6.10 - 6.12). Values are means ($n = 5$ per species at each distance). Bars in the upper right hand corner of each panel represent the standard deviation of the values which appear in that panel. For the purposes of being able to see the individual responses, plant taxa were grouped into dicot and monocot categories, and herbaceous and woody classes within the dicots. Symbols are as follows: dicots; herbaceous species, *Asarum canadense* (open triangle), *Fragaria virginiana* (closed triangle), *Thalictrum dioicum* (open circle), *Podophyllum peltatum* (closed circle), and *Solidago flexicaulis* (closed square). For dicots; woody species (central set of panels), *Vaccinium vacillans* (open triangle), *Lindera benzoin* (closed triangle), *Fagus grandifolia* (open circle), *Tilia heterophylla* (closed circle). For monocots; *Holcus lanatus* (open square), *Smilacina racemosa* (closed squares), and *Trillium grandiflorum* (open circle). Based on data taken from Dawson (1993c) and modified after Dawson, 1995. The study was conducted near Ithaca, New York, USA.

from the spring precipitation, and hydraulically-lifted water (*HLW*), derived from ground water and transported into the upper soil layers by sugar maple trees. The proportion of *HLW* in the xylem-water of a plant utilizing it is the ratio of difference along the mixing line between xylem-water (*XW*) and soil-water to the difference between *HLW* and *SW*. The difference (β) between *XW* and *SW* (β_{SW-XW}) is:

$$\beta_{SW-XW} = (\delta D_{SW} - \delta D_{XW}) \quad (6.10)$$

where δD_{SW} is the δD of the soil-water collected in a zone not influenced by hydraulic lift but at the principle rooting depth of that species, and δD_{xw} is the δD of the xylem-water extracted from each species. Further, the difference between *HLW* and *SW* (β_{SW-HLW}) can be given as:

$$\beta_{SW-HLW} = (\delta D_{SW} - \delta D_{HLW}) \quad (6.11)$$

where δD_{HLW} is the δD of hydraulically lifted water (from ground water) used during the growth period of interest. The proportion of *HLW* (P_{HLW}) in the xylem-water can then be given as:

$$P_{HLW} = \beta_{SW-xw} / \beta_{SW-HLW} \quad (6.12)$$

Dawson (1993c) points out that δD_{SW} will vary in the final calculation of P_{HLW} depending upon the unique rooting depth of each species such that plants with shallow roots will have a δD_{SW} that is less negative due to evaporative enrichment within the upper soil layers.

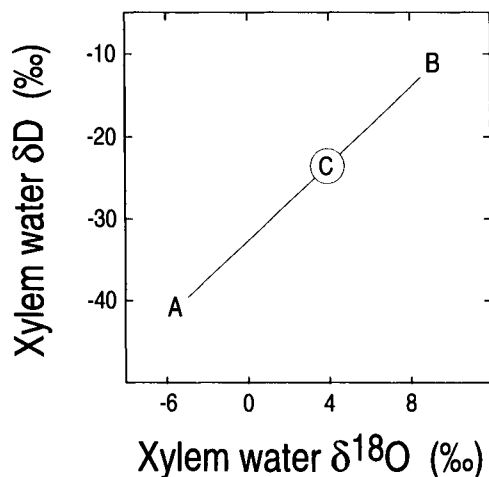


Figure 6.17. A hypothetical relationship between the stable hydrogen (δD) and stable oxygen ($\delta^{18}O$) isotopic composition of different water sources. The line connecting the points "A" and "B" is the "mixing" line. Assuming a linear relationship between A and B, this line can be used to determine the proportion of these two water sources ("end members") within the xylem sap of trees with a isotopic composition of "C" (modified from Thorburn et al., 1993).

Thorburn and Walker (1993) use a similar type of model that used both δD and $\delta^{18}O$ in the environment and the plant's xylem sap to determine the proportion of different waters that were transpired by *Eucalyptus camaldulensis* inhabiting riparian habitats exposed to soil water, ground water, or stream water (Figure 6.17). This model provided these researchers with an extremely powerful tool for demonstrating that trees of *E.camaldulensis* growing in creek-side habitats use between 0 and 45% of the creek water, and yet also used between 0 and 60% of the ground water depending upon the time of the year they sampled. Furthermore, inland trees

seemed to always use more ground water (40 - 63 %) than creek-side trees (Thorburn and Walker, 1993). All of these mixing models provide powerful ways to extend the isotope information obtained from source and plant samples towards a catchment perspective. That is, understanding not only which water sources plants are using, but the relative proportions of each provides a way to more accurately determine the water balance for plants inhabiting different community types and catchment with different physiographic characteristics (see below). The method employed by Thorburn and Walker (1993) is perhaps the most powerful since using both δD and $\delta^{18}O$ increases the precision of water budget estimates.

6.4.4 Coastal plant communities

Coastal plant communities are some of the most productive communities in the world and part of this productivity is due to the fact that water and perhaps nutrients move very rapidly through them (E_p can be as high as 1600 mm/yr of water or between 160 - 190 % of the rainfall that passes through these communities on an annual basis; Larcher, 1995). Much of the water in these communities is saline, however, and can have a marked influence on the vegetation type and thus patterns and rates of E_p . A series of studies conducted by Sternberg and coworkers (Sternberg and Swart, 1987; Sternberg et al., 1991; Ish-Shalom et al., 1992; Lin and Sternberg, 1993) have shown that along marked salinity gradients, plants demonstrate a clear partitioning of the different water sources (Figure 6.18). For example, marked transitions can be observed in the dominant plant community which grows along hydrogen isotope/salinity gradients of coastal Florida within the United States (Sternberg and Swart, 1987; Sternberg et al., 1991). At the high salinity end of the gradient which supports mangrove vegetation, the δD of source and plant waters shows direct uptake of sea water. Sea water is more enriched in the heavier isotopes D and ^{18}O . It has been shown that plant species which can take up sea water while also excluding the sea salts actually can isotopically fractionate the δD (but not $\delta^{18}O$) in water during the uptake process (an exception of the rule that no fractionation occurs during water uptake by plants; see Lin and Sternberg, 1993). Moreover, the red mangrove (*Rhizophora mangle*) grew many of its roots in an area where it had access to a water source that was less saline (near the surface; Lin and Sternberg, 1994). At the fresh water end of the gradient where the isotopic composition becomes more negative relative to sea water, hardwood hammock vegetation predominates (Figure 6.18). The use of either fresh water or sea water (and in a few cases a mixture of the two sources) coupled with different physiological tolerances among the array of coastal plant taxa leads to a diverse vegetation mosaic which are recycling all water sources through these coastal ecosystems.

Many coastal regions of the world are inundated by fog which is depleted in the heavier isotopes relative to the water source from which it was formed (Aravena et al., 1989; Ingraham and Matthews, 1988, 1990; see Chapter 3). Mooney et al. (1980b) and Rundel et al. (1991) have suggested that fog is likely an important source of water for plants, especially in coastal desert regions that receive very little or no precipitation input on annual basis (the Atacama or "fog-loma" coastal deserts of Peru and northern Chile; Aravena et al., 1989; Armesto and Vidiella, 1993). Hydrological studies within many coastal regions have shown that 25 - 75 % of all the moisture input comes from fog (Oberlander, 1956; Ornduff, 1974; Dawson, 1993b; Byers, 1953). For the Redwood (*Sequoia sempervirens*) inhabiting the coastal regions of northern California and southern Oregon in the United States, it has been estimated that between 25 - 45 % (an in some years more) of the soil moisture is fog-derived (250 mm/year;

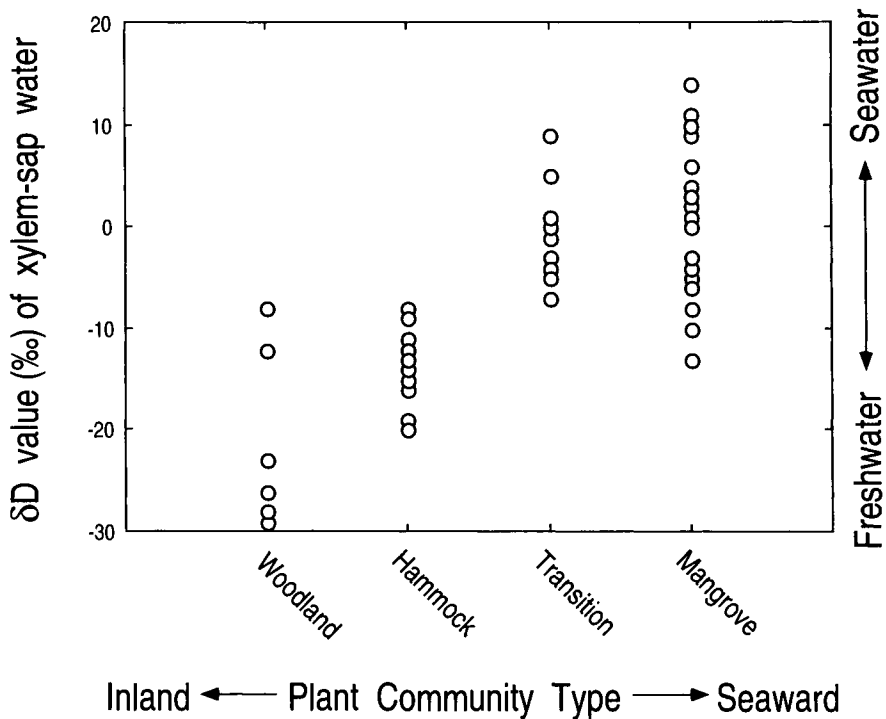


Figure 6.18. The δD of water extracted from the xylem of plants from four different coastal communities in southern Florida (USA) as a function of their position along an inland (freshwater) to seaward (seawater) gradient. Modified after Dawson (1993b); based on data in Sternberg and Swart (1987) and Sternberg et al. (1991).

Azevedo and Morgan, 1974; Harris, 1987). Much of this hydrologic input comes directly from fog-drip off of the tree foliage (Dawson, 1996 and in press). Water samples collected over the course of three years (1992 - 1994) in the redwood forests along the coast north of Arcata, California demonstrate that the plants inhabiting this region are using fog-precipitation (Figure 6.19; Dawson, 1996 and in press). Interestingly, during the summer, when fog in this region is heaviest, this water source can comprise 65% or more of the water used by many of the herbaceous and woody understory plants. In contrast, the dominant tree, *Sequoia sempervirens*, derived, on average, about 30% of its water from fog-precipitation. Ground water and deep soil water from winter rains comprised the primary water source for this tree (Figure 6.19). A similar type of process also should occur in cloud forests found in many tropical regions of the world (for example see Cavelier and Goldstein, 1989).

All of the studies cited above provide compelling evidence that the use of the stable isotopic compositions of water sources and the plants that use these sources can be a powerful tool for exploring water movement through the soil-plant-atmosphere continuum. Such studies are now forming the cornerstone for addressing current issues related to the management of water resources and have provided a solid foundation for scaling up to the entire catchment. In order to successfully accomplish this scaling effort, it is important to account for the magnitude of water flux in the soil, in surface flows and through plants inhabiting these catchments.

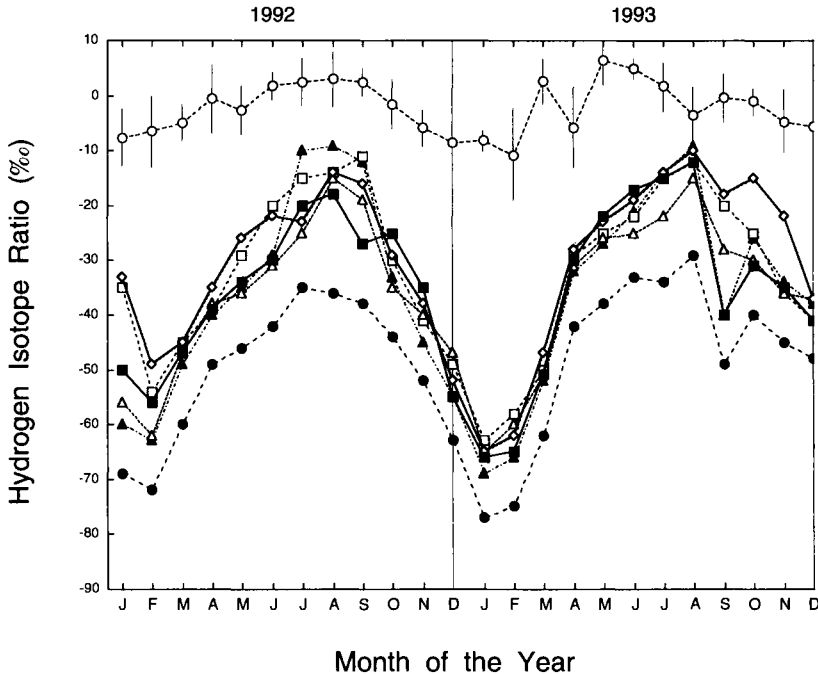


Figure 6.19. The average stable hydrogen isotope ratio (δD) of rainfall (filled circles), fog (open circles) and water extracted from the xylem of plants ($n = 15/\text{species}$) from a coastal site north of Arcata, California (USA) during the period from January 1992 through December 1993. The plant species are the coastal Redwood (*Sequoia sempervirens*; filled squares), Redwood sorrel (*Oxalis oregana*; open diamonds), California rose-bay (*Rhododendron macrophyllum*; open triangles), sword fern (*Polystichum munitum*; open squares), and salal (*Gaultheria shallon*; filled triangles). Fog was obtained from fog-collectors ($n = 10$) and from fog-drip off *S. sempervirens* foliage ($n = 7$) and pooled to obtain the mean value. Error bars on the fog data are standard deviations ($n = 17/\text{month}$). Error bars for the rainfall and plant data are not shown because they made it difficult to see the trends for each line. Variation about the mean δD values for the rainfall are $\pm 7.1\text{‰}$ in 1992, and $\pm 5.9\text{‰}$ in 1993, and $\pm 6.4\text{‰}$ and $\pm 7.4\text{‰}$ in 1992 and $\pm 8.6\text{‰}$ in 1993 for the xylem-water δD values from all of the plant species (adapted from Dawson, in press).

6.5 Current Issues Involving Plants and Catchment-Scale Hydrologic Processes

6.5.1 Invasive plants and site water balance

Increasingly, plant communities, and especially those characterized by some type of disturbance regime, are becoming dominated by invasive, highly competitive species (Heywood, 1989). Many of these species are deeply rooted (phreatophytic; literally, "well" plants), such as salt cedar (*Tamarix* spp.), that have high water requirements (Campbell and Dick-Peddie, 1964) and thus have a clear impact on many ecosystem processes, especially hydrologic processes (Vitousek, 1990). To the extent that these species continue to invade, dominate, and pre-empt water from the native vegetation, we should expect marked changes in hydrologic processes for the catchments in which they grow. In situations where these types of invaders may occur, the stable isotope analysis of source and plant waters may provide an important way for determining the potential impacts they may have on water resources and surface-subsurface

interactions at the catchment level. For example, in a recent investigation on riparian phreatophytes of the southwestern United States, Busch et al. (1992) demonstrated a close hydrologic linkage between the river, ground and soil water during the early part of the growing season and that plants used water from all of these sources. However, as drought set in, poplar and willow (*Populus fremontii* and *Salix gooddingii*, respectively) were shown to only use deeper water sources while salt cedar (*Tamarix ramosissima*) appeared to use all water sources and despite suffering greater water stress, continued to transpire (Figure 6.20). This study points out the potential of using stable isotope analysis of source and plant water in hydrologic research where there traditionally has been a strong dependence on correlative data. In this case, understanding that *Tamarix ramosissima* is a facultative rather than an obligate phreatophyte may factor prominently in management decisions that involve this invasive species. Because it uses all potential water sources, as a species *T. ramosissima* will have a significantly greater impact on catchment water balance than will any of the native plants.

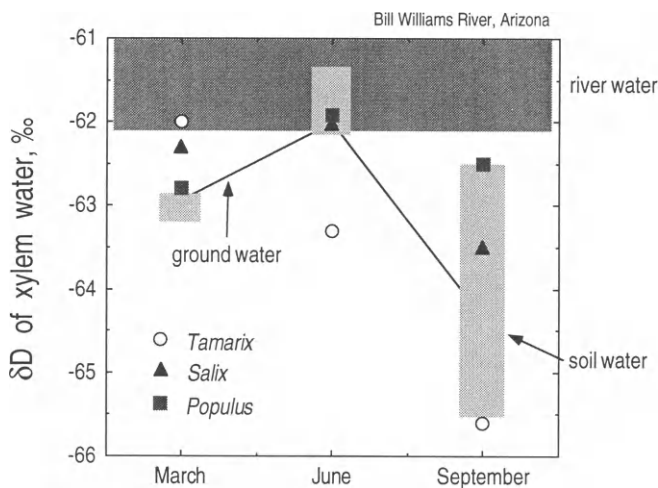


Figure 6.20. The time course of δD in the water extracted from the xylem of fremont poplar (*Populus fremontii*), willow (*Salix gooddingii*) and salt cedar (*Tamarix ramosissima*) - riparian phreatophytes - growing along the Bill Williams River (Arizona, USA; drawn from data in Busch et al., 1992). The shaded area at the top of the figure show the range of δD for river water. The stippled bars at each month is the range of δD seen for soil water at the same site. The δD of ground water is shown by the line.

6.5.2 Stream diversions and riparian manipulations

Stream diversions are an important way of providing water for human consumption and for generating hydroelectric power throughout much of the world. Work conducted by Smith et al. (1991) was designed to specifically address the effects of diverting stream water on the functional responses of riparian plants. Working at Bishop Creek along the eastern escarpment of the Sierra Nevada Mountains of California in the United States, Smith et al. (1991) evaluated the water sources used by several species over the course of the dry season and for plants growing along stream reaches where water had or had not been diverted. The δD values obtained for tree, soil, ground, and surface water suggested that early in the season trees used

water from the surface sources (soil or stream) but that as drought developed later in the season, ground water became the primary water source (Figure 6.21). In the short term, although adult trees may be able to utilize ground water if streams are diverted, juvenile trees cannot and will die. However, longer term stream diversions eventually lead to a decline in ground water levels because plants are transpiring this water source away and because the aquifer itself is not recharged annually. This will eventually lead to adult tree mortality, as well (Smith et al., 1991).

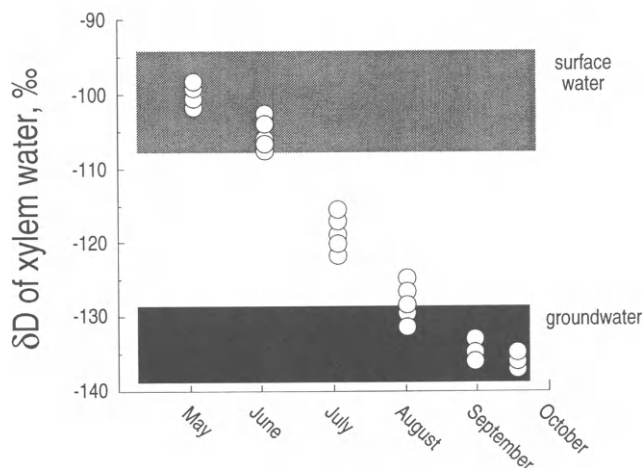


Figure 6.21. The time course of water uptake by a variety of plant species (open circles) growing along a diverted stream draining from the Sierra Nevada mountains, California (USA). The gray areas show the range of δD for surface (stream) waters and ground water (drawn from data in Smith et al., 1991).

Another example comes from the recent work along the River Murray in southeast Australia. The alteration of surface water flows and the rise of saline water tables (Jolly et al., 1993) has caused salt accumulation in the semi-arid floodplain soils in the Murray-Darling basin, Australia's largest hydrologic basin. The river red gum trees (*Eucalyptus camaldulensis*), one of the dominant trees on the floodplain, are now experiencing radical changes in water logging and salinity as a result of this altered hydrologic regime. Interestingly, isotopic evidence showed that these trees use a significant proportion of the highly saline ground water each year (Mensforth et al., 1994) and this is having a significant impact of the trees' water relations (Thorburn et al., 1994) as well as on the long-term health of the forests which live along this altered floodplain (Jolly et al., 1993). These types of investigations provide an excellent example of how powerful the stable isotope method can be for understanding how the manipulation of riparian hydrology can impact not only the water itself but also the vegetation that depends upon it.

6.5.3 Deforestation, reforestation and desertification

The loss of forest cover by either natural disturbance or human-induced deforestation causes radical changes in local and regional climatic conditions, and in the hydrology of an area once

forested (Bruijnzeel, 1991). Generally, when trees are removed from a parcel of land, the radiation and heat load increases markedly (e.g. 2.5 to 3.5EC over the Amazon Basin; Shukla et al., 1990) and, as a consequence, the water stress visited upon the remaining trees or on trees adjoining the deforested land increases dramatically (Covich, 1993). The removal of trees caused E_p on both a catchment and on a plot basis, to decline by 30% (Shukla et al., 1990) or more due to a loss of canopy leaf area. Furthermore, as water and heat stress increase on a deforested region, the remaining trees generally close their stomata and as such E_p declines (Johns, 1992). In addition, as pointed out above, runoff will increase in deforested catchments and thus the water that would normally reside in either the soils or the vegetation is lost from the catchment.

At the regional level it is known that plant transpiration can be responsible for recycling up to 80% of the precipitation that falls on a forested region (Gleick, 1993). As a result, loss of the forest trees results in a reduction of average rainfall by 25% or more, especially in the rain forest regions of the Amazon Basin (Shukla et al., 1990) and West Africa (Fearnside et al., 1990). Deforestation also leads to a net reduction in the primary productivity of a catchment and thus directly impacts both the hydrologic and carbon cycles and indirectly impacts the mineral cycles (Likens et al., 1977). In stands of trees that can be shown to use water from a variety of sources, particularly deeper sources like ground water, tree removal should have a marked influence on the magnitude of surface/subsurface hydrologic interactions as well as the strength of hydrological linkages between surface, soil, and ground water. For example, Dawson (1993c, 1996) has conjectured that if sugar maple trees, which conduct hydraulic lift, are removed from a catchment, the subsurface waters that were once linked by this process to surface layers are now disconnected and this should have a marked influence on the remaining plants in the community (see Figure 6.16 and Section 6.4.3). The absence of hydraulic lift might, in turn, cause a decline in the biogeochemical cycling driven by this subsurface-to-surface water movement. In fact, a comparison of individual tree leaf water potential and E_p for large sugar maple trees (conducting hydraulic lift) versus small trees where there was no lift (i.e. no access to ground water) demonstrates quite clearly how important trees that have access to deeper water sources can be on the speed and magnitude of water discharge from the forest stand (Figure 6.22).

One extreme ecological outcome of deforestation and the subsequent climate changes that come with it is *desertification*, or the conversion of once vegetated land to a vegetationless state by the activities of man. Nine million square kilometers of the arid and semi-arid regions of the world have been converted to deserts by the loss of vegetation and increased aridity, salinity, and/or loss of valuable soil (Dregne, 1983; Bruijnzeel, 1991). One third of this area is in the Sahel region of Africa. The process of desertification, like deforestation, leads to a decrease in average precipitation, increased wind-induced soil loss and erosion, and an overall loss of soil water holding capacity for both crops and any remaining native plants. Although we could find no study which has investigated plant water use, stable isotopes, and desertification *per se*, such an investigation could provide important insights as to which hydrologic processes lead to this extreme alteration in landscape level water balance.

The work of Jolly et al. (1993) comes close to making this linkage. They showed a link between tree death and increasing salinity and how the modified hydrologic regime might be manipulated to slow or even reverse the desertification process. Isotopic analyses of ground and soil water were an integral part of this study and their data raised a very important issue about

reforestation of arid lands. For example, it would be interesting to know if areas that have been essentially converted to desert could be rehabilitated and revegetated by reforestation practices with extremely drought tolerant or phreatophytic plants. An analysis of plants which use deep water sources (e.g. in Section 6.5.1) and how they deal with an altered hydrologic regime (e.g. in Section 6.5.2) may be one important step in developing rehabilitation procedures. Reforestation has clearly been shown to alter and improve catchment level water balance (Swank and Crossley, 1988). Studies which attempt to merge the philosophy of ecosystem rehabilitation with research on hydrologic and plant water use using stable isotopes may hold great promise in our attempts to understand how to slow and/or reverse the processes of deforestation and desertification.

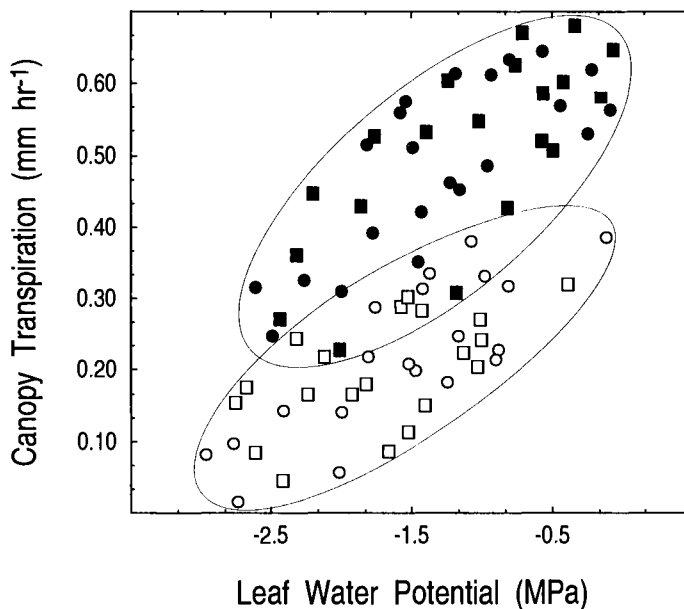


Figure 6.22. The canopy transpiration rate (E_p ; see Equation 6.4) for *Acer saccharum* (sugar maple) as a function of midday leaf water potential for large trees conducting hydraulic lift (closed symbols) or small trees which had no hydraulic lift (open symbols). The E_p data were collected from trees using sap flow, porometric and Bowen ratio methods. Circles around the points represent the ranges seen for both small and large trees (modified after Dawson, 1996).

6.6 Long-term Record of Water Use by Plants

We have shown how the application of stable isotopes can provide valuable information on the short-term dynamics of water uptake and water use by plants from a variety of different ecosystems. One of the greatest challenges, however, is understanding to what extent these short-term data can provide insights over greater lengths of time. The well established field of dendrochronology was founded on the premise that analysis of the information "recorded" in tree rings and the cellulose that composes them is a way to obtain this long-term perspective (Fritts, 1976).

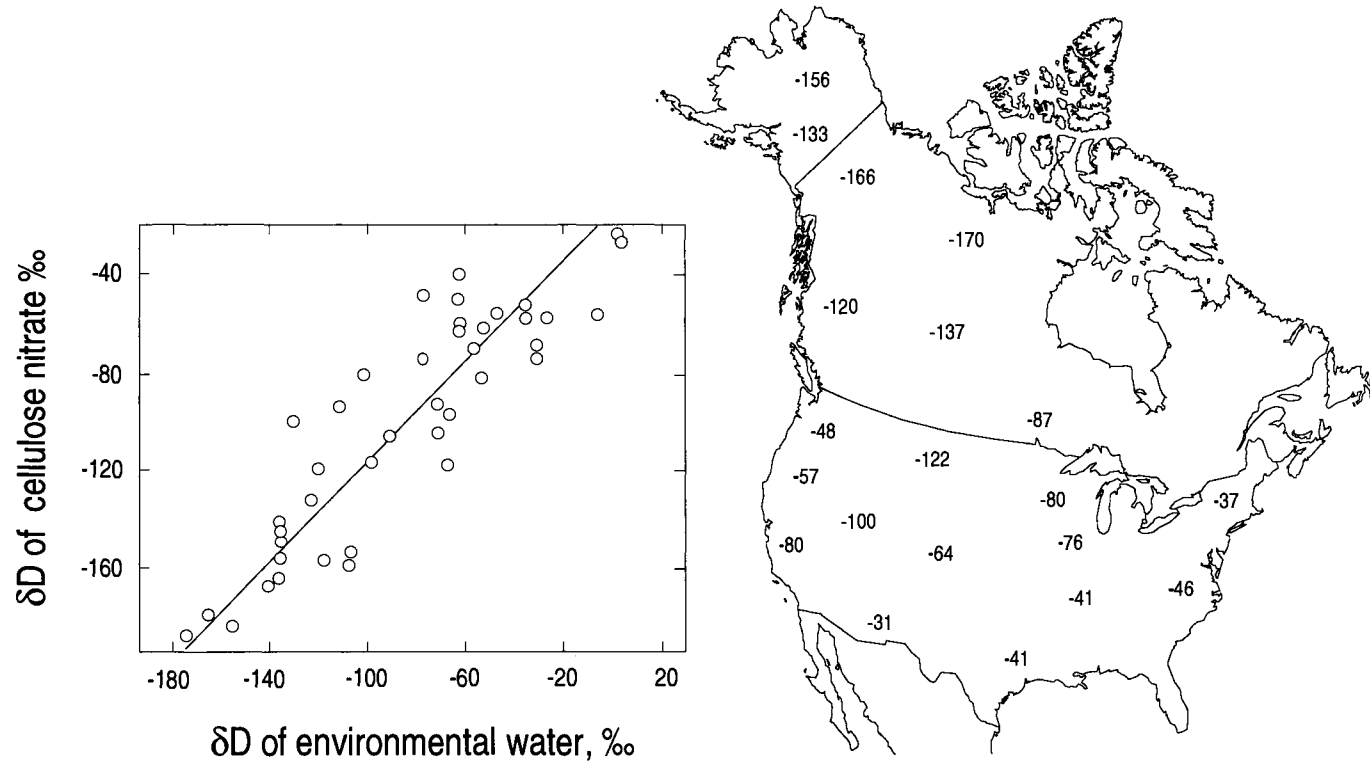


Figure 6.23. The correlation between δD of cellulose nitrate in tree rings of selected tree species inhabiting North America and the δD of the environmental water source they were using (based on a figure in Yapp and Epstein, 1982b - from Ehleringer and Dawson, 1992). The distribution of δD of cellulose nitrate in tree rings of selected tree species inhabiting North America (map at right; based on information in Yapp and Epstein, 1982a - modified from Ehleringer and Dawson, 1992).

Early investigations which used the analysis of the nonexchangeable hydrogen and oxygen isotopes in tree ring cellulose provided important information on past climates. For example, when the isotopic ratio of cellulose (which has been nitrated to remove the hydrogen isotopes that can exchange with water in the plant after the cellulose is synthesized) was determined, Yapp and Epstein (1976; 1982a, b) discovered that it was strongly correlated with the hydrogen isotopic ratio of local precipitation (or better, the meteoric water) present in the area where the trees were growing (Figure 6.23). Because there is also a significant correlation between the δD and $\delta^{18}O$ of precipitation and the temperature at the time when it fell (between 5.5 and 5.81 per $^{\circ}C$, they used tree-ring data to reconstruct past temperatures (Yapp and Epstein, 1982a,b; Gray and Song, 1984). Thus, the potential for reconstructing past climates from the isotopic composition of tree ring cellulose was established. Yakir et al. (1994) extended this work and showed that comparison of the $\delta^{13}C$ and $\delta^{18}O$ in tamarix wood from the Roman siege rampart with present-day tamarix growing in the Masada region of Israel, indicated that ancient trees lived in a less arid climate compared to extant trees.

These studies using oxygen isotopic analyses in wood cellulose were successful because there is constant isotopic fractionation (enrichment) of 27‰ between water in the leaf and that which ends up in the cellulose (Sternberg and DeNiro, 1983; Sternberg et al., 1986; Yakir and DeNiro, 1990). A similar single fractionation factor has not been found for hydrogen isotopes in wood cellulose. In fact, the data which do exist would initially suggest little or no fractionation (Yakir, 1992; Dawson, 1993c; White et al., 1994). Instead it is more likely that there are two large fractionation events that are opposite in direction (possibly one in the leaf and another in the stem) which offset each other giving the appearance of little isotopic fractionation between environmental water and non-exchangeable hydrogens in cellulose. Yakir and DeNiro (1990) and White et al. (1994) have developed competing models to explain the environmental and biochemical factors influencing hydrogen isotope ratios in tree-ring cellulose.

Whether the mechanism proposed by either group turns out to be correct or not, using the correlation shown in Figure 6.23 still provides a very powerful tool for reconstructing the water use histories of plants. They may also provide a way to examine long-term water use patterns in forested catchments (also see Dawson, 1993b). If changes in the hydrology of a catchment influence the sources of water the trees are using, then the analysis of the hydrogen and oxygen isotopic composition of tree rings may provide a method to gain a historical perspective on the catchment water balance. The method also provides a way to integrate information on plant water use in time, just as the water uptake studies cited above provide a greater spatial perspective. Many more applications of stable isotope tree-ring analyses are likely to contribute to our long-term understanding of annual fluctuations in catchment hydrology once we have a mechanistic understanding of what influences the hydrogen isotope ratios of cellulose.

6.7 Merging the Study of Stable Isotopes in Water with Studies of Water Uptake and Water Use in Plants and the Hydrology of Catchments

In this chapter we have tried to show (1) how an understanding of the process of water transport, as influenced by plants, may be important at the catchment scale, (2) how plants use and modify soil and ground water and how they regulate water movement at the individual and stand level, and (3) how stable isotope analysis of plant- and source-waters are providing new insights into the patterns of water movement, uptake and use for a variety of ecosystems and plant types on both a short-term and long-term basis.

We know of no single study that has drawn these three areas together into an integrated perspective on the role of plants in hydrologic processes at the catchment scale. Recently, there have been a number of studies that have used a variety of isotope, energy balance, and water relations methods to gain a greater understanding of water use (E_p) in trees and forests and how it is influenced by the either water sources available to the plants or the hydrologic properties of the area they inhabit (examples are: Walker and Richardson, 1991; Calder, 1992a and references therein; Dugas et al., 1993; Thorburn et al., 1993; Dawson, 1996). An isotope tracer approach advocated by Calder (1992) and Dugas et al. (1993) is an important step towards integrating isotope tracers, measures of plant transpiration, and hydrology together. One drawback of this approach, however, is that the isotope tracer method is invasive and may influence the hydraulic conductivity of the tree and thereby the transpiration estimates (e.g. the injection method will cause air embolisms to form in the water conducting tissues of a tree and thus significantly change estimates of transpiration since the "natural" flow path has been altered; see Tyree and Sperry, 1989). Furthermore, the tracers themselves are either radioactive or enriched in stable isotopic composition and thus cannot be used in natural plant stands or compared to isotope studies at natural abundance levels. Lastly, the majority of similar work that has been done is on single trees or young, even-aged, plantation grown trees. As such, it is not clear how these methods may apply to trees growing in natural stands and non-uniform catchment terrain.

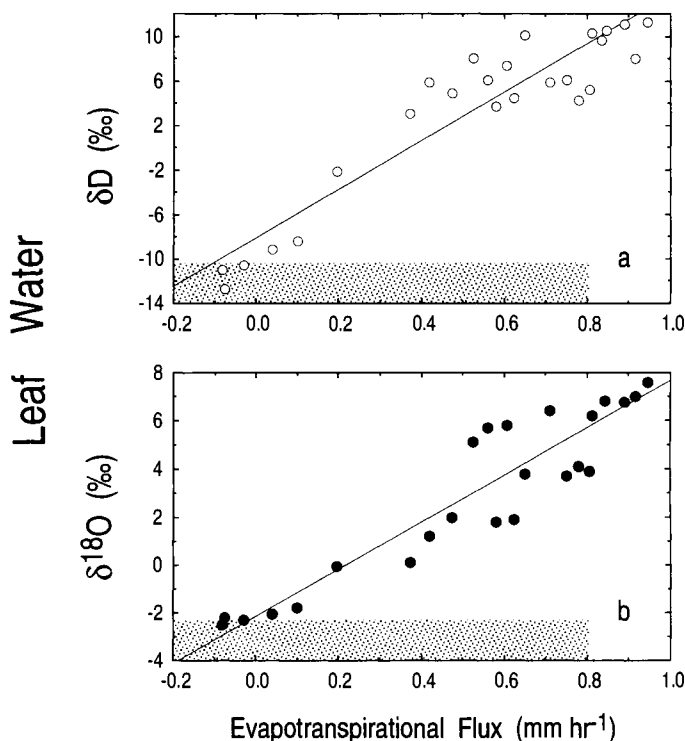


Figure 6.24. The relationship between "E_i flux" determined by aerodynamic-energy balance methods and (a) the δD and (b) the δ¹⁸O of leaf water extracted from alfalfa (redrawn from Bariac et al., 1989).

A recent study by Dawson (1996) has advocated a variation on the methods used by Calder, Dugas, and others for natural forested catchments. Here, the stable isotope methods and approaches presented above were coupled with detailed analyses of evaporation (Bowen ratio) and transpiration (sap flow) measured separately and on trees growing in a defined area. As shown above (Figure 6.22), this approach allowed Dawson to simultaneously measure water loss from the stand while identifying the sources of water used by different sized trees. Ideally, this approach could be extended to also measure the isotopic composition of the water leaving the canopy or forest stand as a way to combine an understanding of the rates and magnitudes of water movement through the stand to the water sources used by trees. Bariac et al. (1989) present part of such a research program with field-grown alfalfa. By evaluating water fluxes from stable isotope information at natural abundance levels, energy budget techniques, and plant physiological measurements, in a field where soil water inputs were well known, they were able to link the daily changes in plant transpiration to a) water uptake patterns, b) water storage capacity of the plant, and c) to the fluctuations in aerodynamic regime, stomatal opening and water supply in the soil (Figure 6.24). Brunel et al. (1992), Simpson et al. (1992), and Wang et al. (1995) have applied similar methods to other crops. Such an approach should also be feasible for trees growing in well-defined catchments or regions. In fact, it is now possible to merge eddy correlation techniques used to understand forest mass and energy exchanges (e.g. Hollinger et al., 1994) with stable isotope tracer methods so that ecosystem pools and fluxes can be partitioned. This approach, called relaxed eddy-accumulation (see Pattey et al., 1993), will help in providing realistic estimates of E_p and E_t as well as identifying the water sources from which they came so that their relative importance and contribution to the hydrologic balance of the catchment will be independently measured rather than estimated by difference.

Understanding what influences the hydrologic cycle has and will continue to be important for ecological, economic and social reasons (Gleick, 1993). We believe that there is much to be gained by applying the stable isotope techniques cited above towards elucidating the role that plants play in the hydrologic cycle; such a research agenda should be part of all future hydrologic research. For this goal to be realized, however, it will be important for plant biologists and hydrologists who are employing isotope tools and tracers in their research to collaborate.

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Chapter 7

Isotopes in Groundwater Hydrology

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7.1 Introduction

Catchment hydrologists commonly ignore the possibility that there is significant groundwater within the geologic framework of catchments. Instead, the bedrock is erroneously viewed as generally impermeable and of little relevance to surface water hydrology. Furthermore, deep groundwater flow systems often extend beyond the boundaries of small catchments, with consequent implications for hydrologic budgets. Hence, the linkages between deep groundwater and catchment hydrology need to be better understood. Aspects typically investigated in assessment of groundwater resources include the quantity of water available, its sustainable exploitation rate, and the water quality. Catchment hydrologists and hydrogeologists usually deal with the first two aspects. They estimate the dimensions and the hydrodynamic characteristics of the water bearing formations from detailed geological surveys, exploratory drillings and geophysical data. They also derive the aquifer water balance from precipitation and runoff measurements and evapotranspiration estimates, in order to achieve an estimate of the groundwater recharge rate. Knowledge of recharge rate is essential for rational and sustainable exploitation of the water resources.

Hydrochemists typically focus on water quality. Often their approach is limited to answering the question of whether the chemical and bacteriological characteristics of groundwater are suitable for domestic (drinking water), agricultural (irrigation), and industrial uses. Sometimes they also derive information on groundwater origin and geochemical history from the chemical data, including the interactions between water and the host rock minerals. The degree of interaction depends on the nature and texture of the host rock, on the nature and concentration of dissolved compounds (e.g. CO_2 affects pH and, consequently, the chemical reactivity of water), on the temperature (e.g. thermodynamics of geochemical processes control reaction equilibria and kinetics), and on the time of contact between water and rock (i.e. the mean residence time of water in the aquifer).

Isotope hydrologists deal with the isotopic compositions of groundwater and dissolved compounds, which are relevant to understanding the water's geochemical history and the hydrological conditions of the system. The concentration of stable isotopes (^{18}O and D) in groundwater depends mainly on the origin of the water, as will be seen later. Effects of water-rock interactions on water isotopic composition become important only at high temperature. For instance, high-enthalpy geothermal waters -- which are not discussed in detail in this book -- are often enriched in ^{18}O due to water-rock isotopic exchange. On the other hand, the isotopic composition of dissolved compounds, which are present in much smaller amounts than water,

may be significantly affected by isotopic exchange with the rock minerals. The extent of the isotopic exchange depends on the physico-chemical parameters listed above for water-rock interactions, and the proportions of reactants; exchange has the most effect on the least abundant reactant. However, the isotopic fractionation at the thermodynamic equilibrium depends only on temperature.

The concentration of radioactive isotopes and dissolved compounds in groundwater depends on the initial concentration and residence time of groundwater in the aquifer. These two factors determine the amount of radioactive isotope(s) decayed, removed or added during water-rock interaction processes. For instance, ^{14}C concentration in dissolved inorganic carbon (DIC) depends on the rate of radioactive decay and the extent of the isotopic exchange between DIC and the host rock. The exchange depends, among other things, on the time and size of rock surfaces in contact with water. Other effects important for radioactive isotope application in groundwater hydrology are introduced by the physical nature of the aquifer (unconfined, semi-confined or confined; porous or fractured/fissured), which controls the groundwater flow and dispersion.

As geochemical tools, stable and radioactive environmental isotopes provide information on the geochemical processes operating on groundwater, and on the hydrogeological characteristics of aquifers including origin, time and rate of recharge, and aquifer interconnections. This information, often not accessible by means other than isotope techniques, is valuable in the assessment and management of groundwater resources, especially in areas where long-term series of observation data are missing. Information provided by environmental isotopes is also useful in modeling groundwater systems. The following sections discuss the scientific background of applications of environmental isotope techniques to groundwater hydrology.

7.2 Isotopic Variations in Waters Recharging the Aquifers

7.2.1 *The isotopic composition of precipitation*

Stable isotopes

The stable isotope composition of groundwater reflects that of the precipitation in the recharge area that seeps through the soil and the unsaturated zone to reach the water table. The isotopic variations of precipitation (discussed in detail in Chapter 3) have recently been summarized by Rozanski et al. (1993), using the database existing at the International Atomic Energy Agency (IAEA). Statistical treatment of data on T, D and ^{18}O concentration in monthly precipitation in a global network of about 180 stations, have also been published (IAEA, 1992a).

Precipitation is formed by condensation of atmospheric vapor derived from evaporation from water and land surfaces. Isotopic fractionation takes place during evaporation of water -- first, when the isotopically lighter molecule of water, $^1\text{H}_2^16\text{O}$, evaporates preferentially; and later in the inverse process of vapor condensation, when the isotopically heavy molecules ($^1\text{H}^16\text{O}$ and $^1\text{H}_2^{18}\text{O}$) condense preferentially (see Chapter 2 for details). The extent of condensation is determined by the decrease of temperature, which thus becomes the main factor controlling the stable isotope composition of precipitation. As the temperature of condensation decreases, δD and $\delta^{18}\text{O}$ values of precipitation also decrease.

Because temperature of condensation is correlated with ground temperature, the isotopic composition of precipitation exhibits the following relative variations in the concentration of heavy isotopes:

- a) seasonal variations in the temperate and polar zones: winter precipitation is depleted and summer precipitation is enriched;
- b) variations correlated with the precipitation amount in the tropical zones: heavy rains are depleted and light rains are enriched;
- c) variations correlated with the altitude: precipitation at high altitude is depleted and at low altitude is enriched;
- d) heavy isotope enrichment due to partial evaporation of raindrops during fall; this effect is particularly noticeable for light rains in arid zones.

Other effects of temperature on the isotopic composition of precipitation, such as “continental” and “latitude” effects, are only of marginal interest for the study of the isotopic composition of groundwater. Spatial variations of isotopic composition of rain are usually neglected, although they may sometimes be significant, depending on the size and features of the area under investigation and the type and origin of precipitation. Numerous examples of this effect are reported by Blavoux (1978) and in Chapter 3.

Climatic changes that occurred during the Quaternary were accompanied by variations of the isotopic composition of precipitation. This has been repeatedly observed in ice cores from Greenland and Antarctica, showing that the ice-cap accumulated during the Pleistocene glaciations is depleted in heavy isotopes with respect to modern precipitation. Also, shorter cold periods during the Holocene are recorded by the ice-cap isotopic composition.

Other materials that may preserve the isotopic record of past climatic changes are lacustrine deposits, speleothems, tree cellulose, and groundwater (see Chapter 22). In groundwater studies, it has been shown that water recharged during the late Pleistocene in Europe (Rozanski, 1985), and in the Sahara desert (Sonntag et al., 1976; Dray et al., 1983) is systematically depleted in heavy isotopes relative to modern precipitation. In the case of Sahara, the heavy isotope depletion was also observed for groundwaters recharged during the early Holocene and reflects humid periods, rather than colder ones. Humid periods occurred in the Sahara about 10,000 to 6,000 years ago, during which time groundwater recharge took place with sufficient regularity and efficiency.

Tritium concentration

The variations of tritium in precipitation are discussed in Chapter 3, and have been reviewed recently by Rozanski et al. (1991). The statistical treatment of monthly tritium data in precipitation in the IAEA global network has been published by IAEA (1992a). The largest variations of tritium concentration in precipitation occurred in the 1950's and 1960's as a consequence of atmospheric thermonuclear tests. Before these tests the tritium concentration in continental precipitation ranged between 5 and 15 TU on continents. After the tests started, the tritium concentration increased dramatically and reached a maximum in 1963, when spring rains in the northern hemisphere had values up to three orders of magnitude higher than pre-bomb levels.

Since 1963 in the northern hemisphere, and 1964 in the southern hemisphere, the tritium concentration in precipitation has decreased, and now it is back to the natural, pre-bomb level in most parts of the world. Only in regions where artificial tritium sources (e.g. heavy water nuclear reactors, industries using tritium for luminous devices) are present, the tritium levels may be higher than the natural ones.

Tritium is a relatively short-lived isotope, with a half-life of 12.43 years. Thus, it can be used only to study systems where the residence or transit time of groundwater is in the range between a few years and about 100 years. Like the oxygen and hydrogen stable isotopes, tritium is part of the water molecule and, therefore, is an almost ideal tracer of water.

7.2.2 *The isotopic composition of surface waters*

Rivers and lakes are also sources of groundwater recharge. The isotopic composition of river water reflects that of precipitation over the catchment basin. If the basin largely consists of mountains, where rains are often more abundant, the river water will be depleted in heavy isotopes as a consequence of the altitude effect. In this case, groundwaters will be depleted with respect to the local precipitation. This has been observed in an Andean foothill in western Argentina, which has an arid to semi-arid climate, and where groundwater is recharged by rivers descending from the high Andean Cordillera. The groundwater exhibits a dramatic depletion in heavy isotopes with respect to local rains: up to 13‰ in $\delta^{18}\text{O}$ and 100‰ in δD (Albero et al., 1987, 1989).

Seasonal isotopic variations in rivers are often correlated with discharge variations affected by seasonally variable contributions of different water sources. For instance, alpine rivers show a decrease of heavy isotope concentration in late spring and early summer, because of the increased contribution of water from snow melt (see examples of this in Chapters 4 and 12). Other isotopic variations in rivers are caused by heavy rains after a relatively dry period. In this case, the different isotopic and chemical compositions of rain and groundwater allows the direct contribution of rain water to river discharge to be distinguished from that of groundwater. This information is used to make the storm runoff hydrograph separations (Fritz et al., 1976; Fritz, 1981; Fritz and Stichler, 1983). Additionally, this information allows estimation of the groundwater renewal rate after intense rain events, a rate which isotopes have shown to be much higher than expected.

Lake water is often enriched in heavy isotopes as a consequence of evaporation. Therefore, the contribution of lake water to groundwater can be identified and, under favorable conditions, quantified (see Chapter 14). The degree of enrichment depends on the lake water balance. The maximum enrichment occurs in closed lakes, where all the inflowing water is removed by evaporation (Gonfiantini, 1986).

In arid regions, river water has also been found to be enriched in heavy isotopes with respect to adjacent groundwater. The most prominent example is the River Nile in Sudan and Egypt with a $\delta^{18}\text{O}$ value around 0‰ whereas the adjacent groundwater often is represented by paleowater with $\delta^{18}\text{O}$ close to -10‰. Any mixture between the two end members is reflected in the stable isotope composition which makes the stable isotope contents a powerful tool in studying surface-groundwater relationships (see Chapter 13).

7.3 Isotopic Effects in the Unsaturated Zone

7.3.1 Mechanisms of infiltration

The infiltration of precipitation water through soil and the unsaturated zone is, in principle, an isotopically non-fractionating process. There are, however, processes that have an indirect effect on the isotopic composition of the infiltrating water, as first indicated by Gat and Tzur (1967). The mechanisms for infiltration of snow precipitation are different than those of rain precipitation. Only the latter are discussed below.

Only rain falling above a certain threshold rate contributes to recharge. That threshold value depends on the climatic conditions and the vegetation type, both of which determine the evapotranspiration rate, and on the soil nature. For instance, rains over bare karst terrains will seep easily and rapidly through joints and fissures. The same applies for rains over surfaces covered by gravel and coarse sand. In these cases minor change in the isotopic composition of precipitation can be expected. On the other hand, a significant proportion of rainfall falling on vegetative catchments is intercepted by plants and re-evaporated. The throughfall that reaches the land surface will infiltrate slowly and in small proportions, with most of it removed by evapotranspiration. Thus, a certain enrichment in heavy isotopes of the infiltrating water may occur due to evaporation (plant transpiration does not fractionate soil water). The extent of this isotopic change, as well as the rain fraction lost by evapo-transpiration and plant interception, depends on the climate and the seasonal characteristics of plant cover (see Chapter 6).

Water ponding on the land surface becomes enriched in heavy isotopes due to evaporation, a process which is in competition with the concurrent infiltration. In these conditions, infiltration is usually very slow and limited because the land surface where ponding occurs has usually been modified by weathering and deposition of clay and fine silt reducing soil permeability. Similar infiltration mechanisms occur in the bottom of lakes, which rarely are a significant source of recharge for groundwater. Groundwater recharge can also occur from river banks and stream beds. Frequently these banks and beds consist of coarse materials well suited for water infiltration. This type of recharge can often be identified by tritium and stable isotopes (Carlin et al., 1975; Stichler et al., 1986; Stuyfzand, 1989).

7.3.2 Water movement in the unsaturated zone

In humid and semi-arid conditions the prevailing or net movement of water in the unsaturated zone is downwards to the water table. In arid conditions, the net movement of water can be upwards: water moves up in liquid and vapor phases in the unsaturated zone, eventually reaching the land surface to be lost in the atmosphere (Barnes and Allison, 1988). Although these evaporative losses exceed recharge, sporadic recharge can still take place after exceptional rain events. In all these cases isotopes can help to investigate water movements and estimate gains and losses of water in aquifers.

Groundwater recharge

The percolation of water through the unsaturated zone often resembles *piston flow*, i.e. any given water front would advance uniformly downwards to the aquifer, with the same velocity and negligible dispersion and mixing. Under these ideal conditions, the percolating recharge

water would preserve its isotopic and chemical characteristics (e.g. chloride concentration). Chapter 5 covers the physics of unsaturated soil water movement in considerable detail.

The piston flow model is a simplified way of representing the water movement. The downward velocity of the water usually is statistically distributed around a mean value. The dispersion of the velocity distribution depends on various factors: the heterogeneous soil grain-size distribution, which determines the tortuosity of the water molecule paths; the vertical permeability variation, which is more pronounced than the horizontal permeability variation; the occurrence of short cuts and preferential paths of percolation; the capacity of soil particles to fix water molecules, etc. Consequently, the isotopic stratification of water derived from cyclic events of short period and limited amplitude, such as seasonal variations of stable isotope and tritium values in precipitation, can only in rare cases be preserved for more than one year.

In the case of a tracer pulse injection, the peak of concentration can be preserved for many years in the vertical profile and the piston flow model can be usefully adopted. The peak will be less pronounced and more dispersed with increasing time and depth, but still will be recognizable, if not superimposed by another tracer injection peak. Early examples of this application were reported by Smith et al. (1970) in a chalk soil in England, and by Dinçer et al. (1974) and Sonntag et al. (1980a) in a sand dune in Saudi Arabia. It was still possible to identify the 1963 tritium peak 28 yrs later in a sand soil in semi-arid conditions in Senegal at a depth of about 12 m, and to estimate a recharge rate of 22 to 26 mm/yr (Aranyossy and Gaye, 1992; Tandia et al., 1993). Presently, the bomb-tritium peak can only be expected to be found in the unsaturated zone if the recharge rate is low (arid conditions) and the thickness of this zone is sufficiently high (e.g. sand dunes). Under humid or even semi-arid conditions, the 1963 tritium peak has already reached the water table, or is fully dispersed through the unsaturated soil column.

Evaporative discharge

In arid conditions, evaporative losses of groundwater may constitute an important component of the shallow aquifer water budget, comparable with or even greater than recharge. Groundwater is transported by capillary forces from the water table to the depth of the "evaporation front" (see Chapter 1 for details of soil water flow), from which it is removed as vapor and transported to land surface by diffusion, and eventually lost to the atmosphere.

Stable isotope variations in soil moisture are established in both liquid and gaseous phases along vertical profiles in the unsaturated zone, as a consequence of the isotopic fractionation accompanying phase changes and the different diffusion rates of isotopic molecules. From the form of an isotopic profile (Figure 7.1) it is possible to estimate the evaporative losses of groundwater, as first proposed by Barnes and Allison (1983), Allison and Barnes (1983) and Sonntag et al. (1985).

At the evaporation front, the liquid water exhibits the maximum enrichment in heavy isotopes. From the evaporation front downward, the isotopic composition of water tends towards that of groundwater, the gradual change being due to back-diffusion of heavy isotopes. From the evaporation front upward, the heavy isotope concentration of water rapidly decreases, but here the change is due to equilibration and mixing with atmospheric vapor.

The system approaches a steady state, in which the net vapor loss to the atmosphere occurs at a constant rate, and the vapor lost has the same isotopic composition as groundwater. The

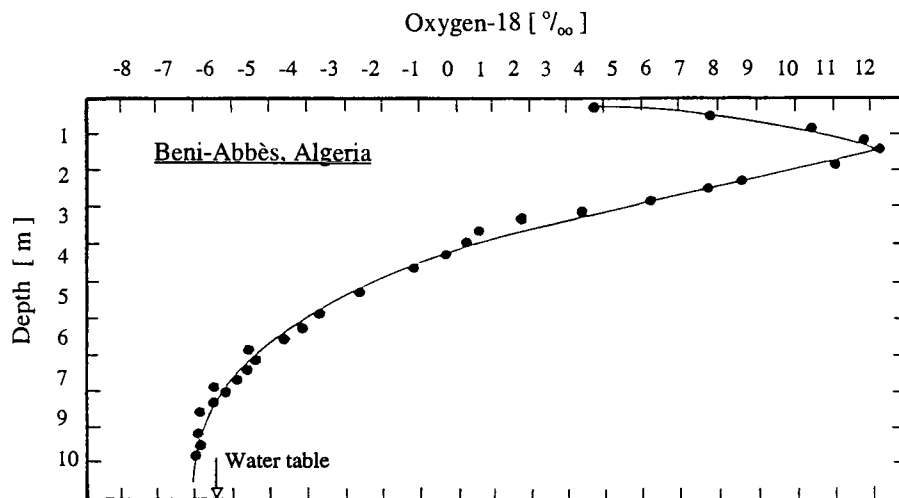


Figure 7.1. Oxygen-18 isotope profile in the unsaturated zone at Beni-Abbès, Algeria (Fontes and Edmunds, 1989, modified).

isotopic steady-state profile can be temporarily overshadowed by infiltrating precipitation, but soon thereafter is re-established. Due to depth and thermal inertia, the system is largely insensitive to short-term variations of external parameters.

7.3.3 Dissolution processes

Gas and solid compounds dissolve in water that percolates through the unsaturated zone. Some of the dissolved compounds are of major importance for groundwater investigations.

Noble gases as paleoclimatic tools

The noble gas dissolution in groundwater and its geochemical and climatological implications were first discussed by Mazor (1972), and more recently reviewed by Stute and Schlosser (1993). The solubility of atmospheric noble gases in water obeys Henry's law and therefore depends on temperature and their concentrations in air. When rain water reaches the land surface, it contains dissolved noble gases at concentrations equal or close to those corresponding to equilibrium with the atmosphere. When this water slowly percolates through the unsaturated zone, re-equilibration takes place at the mean annual temperature of the infiltration site. The concentrations of noble gases in soil air are the same as in the free atmosphere. Noble gas concentrations in groundwater (except helium) do not change significantly in water parcels that penetrate into deep aquifers and are cut off from contact with soil air. Therefore, the noble gas concentrations can provide an estimate of the temperature in the recharge area at the time of infiltration.

Noble gas solubilities in water increase with temperature. The rate of increase is greater for gases with high atomic mass, so that xenon has the highest gradient and neon the smallest.

Helium, which is also formed by radioactive decay and can migrate upward from deeper Earth crust layers, shows concentration variations in groundwater of several orders of magnitude and therefore is not suitable as a paleothermometer. The effects of non-atmospheric contributions to noble gas concentrations in groundwater are normally negligible for neon, argon, krypton, and xenon, and can be evaluated from the isotopic ratios.

Noble gas concentrations in groundwater can also be affected by dissolution of air bubbles which may occur during rapid infiltration. The concentration of neon, with a solubility that is almost independent of temperature, can be used to identify such "excess air" and to correct xenon and krypton concentrations. Xenon and krypton concentrations are temperature-sensitive and, after correction, can be used for paleothermometric determinations.

Noble gases in groundwater dating

Radioactive isotopes of noble gases in the terrestrial environment have been reviewed by Florkowski and Rozanski (1986). A number of papers dealing with their application in groundwater studies are included in a recent IAEA publication (1992b). Chapter 9 covers age-dating of young groundwaters with noble gases. An advantage of using noble gases for dating is the absence of chemical interactions with the matrix. Relating initial concentrations of noble gases with rates of radioactive decay provides groundwater age. In some cases, however, *in situ* production of noble gases may mask the initial concentrations.

In recent years, two radioactive isotopes of krypton, ^{81}Kr and ^{85}Kr , have been gaining credit as groundwater dating tools (Lehman et al., 1991; Smethie et al., 1992; Ekwurzel et al., 1994). In particular, ^{85}Kr , formed during the atmospheric nuclear tests and released by nuclear reactors and nuclear fuel reprocessing plants, with a half-life of 10.76 years, may become a good substitute for tritium as a dating tool for young groundwater. The history of ^{85}Kr concentration in air is well known (Figure 7.2) and therefore ^{85}Kr dating is already possible. Krypton-81, formed in the atmosphere from stable krypton isotopes by cosmic rays, has a half-life of 2.1×10^5 years and could be used for determination of groundwater ages ranging from 50,000 to 800,000 years. However, there are still unsolved problems related to the efficient detection of this radioisotope in groundwater.

Argon-39, formed in the atmosphere by neutrons of secondary cosmic radiation, has a half-life of 269 years. Its application as a groundwater dating tool is limited, however, because it is also formed *in situ* through the reaction $^{39}\text{K} \rightarrow (\text{n}, \text{p})^{39}\text{Ar}$. Such a process may not be negligible in potassium-rich aquifers (e.g. granitic rocks). Nevertheless, if the lowest ^{39}Ar content encountered in any groundwater sample from the aquifer under investigation is equal to or below the current detection limit (5% of the modern $^{39}\text{Ar} \approx 9 \times 10^{-5}$ Bq/l Ar), then the *in situ* production is probably negligible (Loosli, 1992).

Carbon dioxide dissolution

Carbon dioxide dissolution in water takes place mainly in the unsaturated zone, and especially at the plant rooting zone, where the CO_2 partial pressure in soil air is one to two orders of magnitude greater than in the surrounding atmosphere as a consequence of plant respiration. The CO_2 concentration is higher in summer than in winter as a consequence of increased biological activity due to higher temperature and longer daylight (Dörr and Münnich, 1987; Hinkle, 1994).

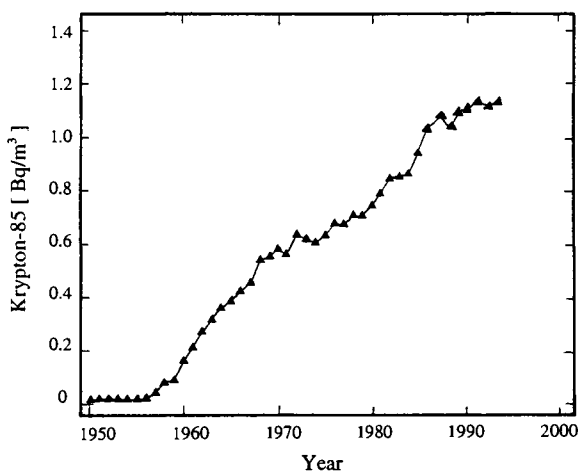


Figure 7.2. The yearly mean values of ^{85}Kr concentration in the lower troposphere of the Northern Hemisphere (data from Weise et al., 1992; Sartorius, 1994).

CO_2 dissolution lowers pH which in turn induces dissolution of soil minerals, especially carbonates. It may happen, however, that very little carbonate is available in the unsaturated zone, either because of the soil type, or because most of the carbonate has already been removed from the soil profile (Salomons and Mook, 1986). In this case the recharging water will be slightly acid when it reaches the water table, and it will eventually attain neutrality through geochemical processes occurring in the aquifer.

Carbon and oxygen isotopic fractionation occur during the CO_2 and carbonate dissolution process. The oxygen isotopes in CO_2 re-equilibrate rapidly with water, which, being by far more abundant, dictates the oxygen isotope composition of the carbonate system (H_2CO_3 - HCO_3^- - CO_3^{2-} - H_2O). In contrast, the carbon isotopes of dissolved species do not exchange with other carbon-bearing compounds. Therefore the carbon stable isotopes can be used to estimate the fractions of DIC deriving from different sources, and in particular those from soil CO_2 and from carbonate dissolution (see Chapter 18). The identification and estimation of the sources of dissolved carbon is of paramount importance for groundwater dating with ^{14}C , which is discussed in detail in Chapter 17.

7.4 Shallow Aquifers

The shallow aquifer can be recharged by precipitation and surface waters and, in discharge areas of groundwater systems, by water ascent from deeper aquifers. This last recharge mechanism will be presented in Section 7.5.3.

7.4.1 Recharge by precipitation

Groundwater recharge occurs when the water percolating through the unsaturated zone reaches the water table. The recharge rate, however, can be evaluated from the movement of water in

the unsaturated zone. In temperate climates, this movement often obeys a piston flow model, as demonstrated by the displacement of artificial tracers and environmental tritium (see Münnich, 1983). Under arid and semi-arid climatic conditions, the 1963 thermonuclear tritium peak can still be detectable three decades later (Aranyossy and Gaye, 1992; Tandia et al., 1993). However, since the tritium is part of the water molecule, the peak shape and position at shallow depth can be affected by evaporation. From this point of view, bomb ^{36}Cl is probably a more reliable environmental tracer. Thermonuclear ^{36}Cl was produced by neutron activation of ^{35}Cl in sea salt. The maximum of ^{36}Cl concentration occurred around 1955, almost 10 years prior to the tritium peak in precipitation. There have been several attempts to use bomb ^{36}Cl , along with tritium, to investigate mechanisms of recharge, particularly under arid and semi-arid conditions (Phillips et al., 1988; Walker et al., 1992; Cook et al., 1994; Liu et al., 1995).

In the saturated zone, water moves toward the discharge area as laminar flow in an ideal isotropic porous medium. Therefore, the water age stratification can be preserved in the upper region of a shallow aquifer, if recharge takes place only by vertical infiltration of precipitation. Thus, it is possible in principle to use the penetration depth H of thermonuclear tritium below the water table in order to estimate the average recharge rate R by using the simple equation:

$$R = \frac{n_f H}{t} \quad (7.1)$$

where n_f is the effective porosity and t is the time elapsed since 1954, i.e. since the year when the tritium concentration in precipitation sharply increased due to atmospheric thermonuclear tests (Brown, 1961). The applicability of the method is limited to the upper region of the shallow aquifer, at the top of a water table mound, where vertical movement of water is prevailing (Andres and Egger, 1985; Delcore, 1989). Equation 7.1 can also be used when the water samples are collected from supply wells tapping the whole aquifer thickness. In this case, H stands for the thickness of the unconfined aquifer and t for the mean residence time derived from the measured tritium content of the sample.

A more comprehensive approach was adopted by Robertson and Cherry (1989) to estimate recharge in an unconfined aquifer near Sturgeon Falls, Ontario, Canada. Several piezometers were established to collect groundwater samples from the water table down to a depth of 21 m. The maximum tritium concentration was observed at a depth of 6 to 10 m, whereas values below 1 TU were found at a depth greater than 16 m. A one-dimensional advection-dispersion model, with vertical velocity of 0.27 to 0.42 m/year and α_L (longitudinal dispersivity) equal to 0.02 m, was used to fit the tritium profiles. This model allowed an estimate of the recharge rate of approximately 150 mm/year equal to 16% of precipitation.

The rate of groundwater recharge also depends on the type of vegetation cover. For instance, Allison and Hughes (1972) were able to show that, in Southern Australia, there is little groundwater recharge in forest areas, where the tritium content of water in the top 20 cm of the shallow unconfined aquifer ranged from 0.4 to 3.5 TU (in 1970-71). These small tritium concentrations indicated that virtually all the rain water was recycled by evapotranspiration. In contrast, under pasture lands the tritium content of the shallow unconfined aquifer was 5 to 23 TU, with an average value of 12 TU, showing active recharge. Assuming a completely mixed reservoir model, the recharge under pasture land was estimated to be at least five times higher

than beneath forests; the difference was attributed to the evapo-transpiration in the forest environment.

The potential of the tritium method to estimate groundwater recharge is enhanced by carrying out a parallel determination of the ^3He produced by the tritium decay, which remains stored in groundwater (Schlosser et al., 1988, 1989). The tritiogenic ^3He concentration, $[^3\text{He}]^*$, in water is obtained by extracting the total dissolved ^3He concentration from the atmospheric and nucleogenic contributions through determination of the dissolved neon concentration. Neon in groundwater has no sources other than the atmosphere. Assuming that there is neither a ^3He loss nor a contribution from the deeper aquifer regions, the groundwater age is given by:

$$t = 17.93 \times \ln \left(\frac{[^3\text{He}]^*}{[^3\text{H}]} + 1 \right) \quad (7.2)$$

where 17.93 years is the mean life of tritium (which is different from the half-life).

Schlosser et al. (1988, 1989) report the $^3\text{H}/^3\text{He}$ age variation with depth (Figure 7.3) at a site in Germany. The model adopted is that of Vogel (1967), in which the vertical component of water velocity linearly decreases with depth, with advective-dispersive transport of the tracer. They found that helium-3 losses due to diffusion towards the water table become significant for vertical flow velocity below a critical limit of about 0.25-0.5 m/year (using the diffusion coefficient of ^3He in water). However, even in such a case, the identification of the $^3\text{H}+^3\text{He}$ peak remains possible and can be used for dating.

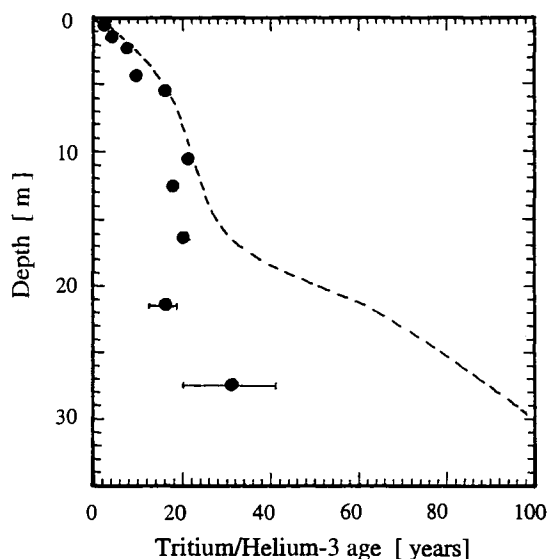


Figure 7.3. The observed (heavy dots) and modeled (broken line) tritium/ ^3He ages of water sampled from multi-level wells located in shallow groundwater system Liedern/Bocholt, Germany (Schlosser et al., 1989, modified). The deviation between the observed and calculated tritium/ ^3He ages most likely is caused by advection of younger water in the depth range below about 10-15 m.

The ^3H - ^3He method was further elaborated and validated by Solomon and Sudicky (1991) and Solomon et al. (1993), who studied again the Canadian site previously investigated by Robertson and Cherry (1989). Solomon et al. showed that when the diffusion coefficient of helium-3 in porous media is used (instead of the diffusion coefficient in water), the above cited critical limit for vertical flow velocity is reduced by a factor of about 10. The vertical velocities and the recharge rates derived from the ^3H - ^3He study (Ekwurzel et al., 1994) were in excellent agreement with those estimated independently from tritium profiles.

Natural chlorine-36 variations in groundwater were used to compare past recharge rates with the modern one (Stute et al., 1993). In the confined Carrizo sand aquifer, Texas, it was found that from 16,000 to 20,000 years ago (dating by ^{14}C) the recharge rate was twice that of 2,000 years ago (about 20 mm/year versus 10 mm/year), while from 25,000 to 35,000 years ago, the recharge rate was only half (about 5 mm/year). The estimates are corrected for cosmogenic production rate changes due to variations of the Earth's magnetic field.

Under special circumstances, stable isotopes also can provide information on groundwater residence time. The mean isotopic composition of precipitation is presently changing in many parts of the world as a consequence of fluctuating climate (Rozanski et al., 1992; see also Chapter 22). In Switzerland, at altitudes above 2000 m asl, a temperature increase of about 1.5°C during the late eighties has been accompanied by a parallel increase of 1.5‰ of the ^{18}O concentration in precipitation, which in turn has caused an increase of 1.2‰ of the ^{18}O concentration in the Grindelwald First Spring. The prompt response of spring water to the isotopic composition change of precipitation indicates that the residence time of water, previously estimated at three years from tritium data, has shortened as recharge has increased (Schotterer et al., 1993, 1995).

Also, the attenuation of seasonal ^{18}O and D variations in young groundwater of unconfined aquifers can be employed to estimate the mean residence time of groundwater (Maloszewski et al., 1983). A recent example of the application of this method for estimating the recharge rate of a small Alpine groundwater system in Austria was given by Ramsbacher et al. (1992); several others are shown in Chapter 21.

7.4.2 Recharge from surface waters

Stable isotopes are often used to identify groundwater recharge by rivers and lakes. These water bodies frequently have isotopic compositions different from that of precipitation over the study area. Rivers often carry water that is derived from precipitation at much higher altitude, and are therefore depleted in heavy isotopes. Sometimes, in arid climates, river water may be enriched in D and ^{18}O through evaporation. Significant heavy isotope enrichment by evaporation is a common feature of lakes and swamps, particularly in semi-arid and arid climates.

Applications of stable isotopes to determining surface water-groundwater interrelations are numerous, and only some of them will be cited here. Based on D and ^{18}O , Dinçer et al. (1979) were able to demonstrate significant recharge through the Okavango swamps in Botswana to the underlying groundwater system. Payne and Schroeter (1979) were able to estimate that the Chimbo River's (Ecuador) contribution to groundwater was about one third of that of local precipitation. The estimate was based on the fact that precipitation was enriched by 2.9‰ in

$\delta^{18}\text{O}$ and 23‰ in δD with respect to the river, which drains water from the higher elevations of the Andean Cordillera. In other regions in the Andean foothills, where local precipitation is scarce, groundwater recharge by rivers may approach 100% (Albero et al., 1987, 1989; Miró and Gonfiantini, 1981).

Stable isotopes were used by Stuyfzand (1989) to identify recharge in aquifers in the Netherlands by bank filtration from the Rhine River. The river water was depleted in heavy isotopes with respect to autochthonous groundwater because it is derived largely from the Alpine catchment basin. The groundwater age derived from the tritium content, together with the river water fraction given by the stable isotopes, was used to estimate the rate of physico-chemical processes that degrade contaminants originating from the Rhine.

In the case of the aquifers exploited to supply water to the city of Lima, Peru, it was possible to identify the sources of recharge (the Rímac and Chillón rivers and some artificial reservoirs) and to evaluate their respective contribution in groundwater (Ruiz and Rojas Molina, 1995). The two rivers have different average isotopic compositions: the mean values of the Rímac are -14‰ and -103‰ in $\delta^{18}\text{O}$ and δD , while those of the Chillón are less negative by 1.3 and 11‰, respectively. These negative values reflect the high altitudes of the rivers' catchment basins, which reach more than 4,000 m asl. The artificial reservoirs are considerably enriched in heavy isotopes by evaporation. There is no recharge by rains because the area is very dry (the average annual precipitation in Lima is 20 mm/yr).

When regular and well-marked stable isotope variations occur seasonally in rivers, these can be observed with some delay and reduced amplitude in wells near the river. The delay, as well as the possible shift in isotopic composition, gives the transit time of river water to groundwater and its fraction with respect to other recharge sources. Stichler et al. (1986) have reported an investigation on groundwater in the Passau Island in the Danube River, Germany, which indicates that on four sites monitored, the river water fraction ranged from 77% to 96% with a delay of 48 to 114 days. The seasonal stable isotope variations in the Danube River are due to Alpine snow melting, which produces a minimum of the heavy isotope concentrations in spring. This pulse of isotopically depleted water can be used to predict the minimum time required for river water and its dissolved pollutants to reach groundwater. A similar investigation near Heilbronn, Germany was undertaken to identify groundwater derived from bank infiltration from the River Neckar. In this case, the river water fraction ranged from 30 to 100%. The study also applied artificial tracers that complemented the stable isotope results (Hötzl et al., 1989). Stable isotopes are also useful to indicate artificial recharge by irrigation measures commonly used in arid and semi-arid regions. In a recent study of groundwater recharge sources in Sudan, Urbka et al. (1993) have identified recharge by irrigation water from the Blue Nile in the Gezira area near Khartoum.

Significant groundwater recharge by natural lakes is infrequent, because sedimentation tends to seal the lake bottoms (see detailed discussion of these processes in Chapter 14). There are areas, however, where important leakages from closed lakes to groundwater have been identified, by exploiting the fact that water of closed lakes is usually enriched in heavy isotopes by evaporation. In a limited area in the west of Lake Valencia, Venezuela, a lake water contribution of as much as 40% was observed in groundwater on the basis of its stable isotope composition. This indicates a small leakage flux sufficient to keep the lake salinity low (Alvarado et al., 1995). The same occurs in Lake Atitlán, Guatemala: springs in the Rio Madre

Vieja Valley, south of the lake, deliver water that derives in part from the lake, as indicated by the enrichment in heavy isotopes with respect to other groundwaters. The isotopic compositions indicate that the lake contribution to the total discharge in the springs (estimated to be around $7.2 \text{ m}^3/\text{s}$) is about $1.1 \text{ m}^3/\text{s}$, a figure which is in agreement with computations of the lake balance (Baldizón et al., 1995).

Lateral infiltration from river banks may create a horizontal gradient in tritium concentration, which can be used to delimit the area of influence of river recharge. In a study by Carlin et al. (1975), it is clearly shown that at the well fields of Borgo Panigale and Tiro a Segno (which supply drinking water to the city of Bologna, Italy), the high-tritium recharge waters of the Reno River can penetrate to distances of 600 m and 400 m, respectively, from the river (Figure 7.4). The intensive exploitation of the confined horizons of the multilayer alluvial aquifer has produced a piezometric depression, which in turn determines the recharge from the river. The information derived from tritium measurements is useful to delineate the area of potential groundwater contamination by the river water. In the example described above, the decrease of tritium content with distance from the river is accompanied by a parallel decrease of the ^{14}C content, and by a small but clear variation of the stable isotope composition. This pattern confirms that the inflow of river water into the aquifer confined horizons started only recently, in connection with the groundwater exploitation.

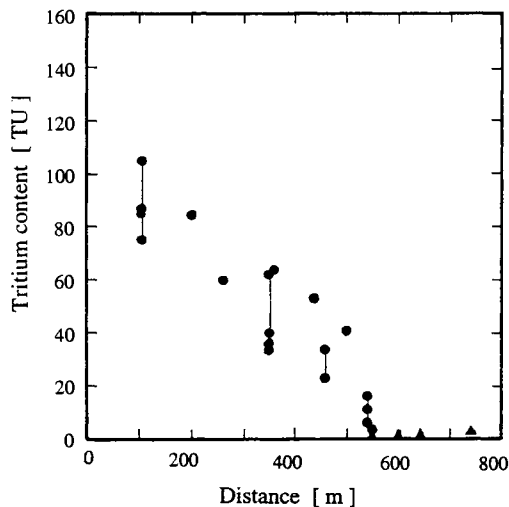


Figure 7.4. Tritium content of groundwater in 1973 versus distance from the Reno River, Italy (Carlin et al., 1975, modified).

Radon can also be used to identify bank filtration into groundwater and to estimate the horizontal water velocity (see Chapter 20). Hoehn and von Gunten (1989) observed that the radon concentration in groundwater increased regularly (4.7 to 17 Bq/l) with increasing distance (13.5 to 111 m) from the Glatt River, Switzerland. Assuming a piston-flow model for the horizontal movement of water, and assuming that ^{222}Rn (half-life 3.8 days) is produced at a constant rate by the parent ^{226}Ra (assumed to have a constant concentration in the aquifer

materials), the residence time of water (i.e. the time since infiltration from the river bank) can be deduced from the radon concentration up to a limit of about 20 days, after which secular equilibrium between ^{222}Rn and ^{226}Ra is attained. Other assumptions are that the radon content of the river water is negligible and that of groundwater beyond 111 m represents the equilibrium concentration. The linear regression between distance and residence time produces an average groundwater horizontal flow velocity of 4.6 m/day, which is in agreement with other estimates made with tracers. This velocity is an estimate for lateral flow from the river under the hydraulic conditions at the time of the measurement. Under different conditions, groundwater can flow towards the river, in which case the radon content in the transition zone becomes constant as the secular equilibrium is attained.

A more complex example of shallow aquifer recharge from surface waters has been reported by Payne et al. (1979). The salinity of shallow groundwater in the Mexicali Valley, an arid region in Mexico close to the border of California, has increased during the last two decades. The groundwater stable isotope composition and the chloride concentration range between the values of the old Colorado River and those of the Wellton-Mohawk canal, which receives irrigation waters from the Yuma region, Arizona (Figure 7.5). Chloride and stable isotope contents are correlated, indicating that the good quality groundwater recharged by the Colorado River in the past is being replaced by poor quality water from irrigation drains.

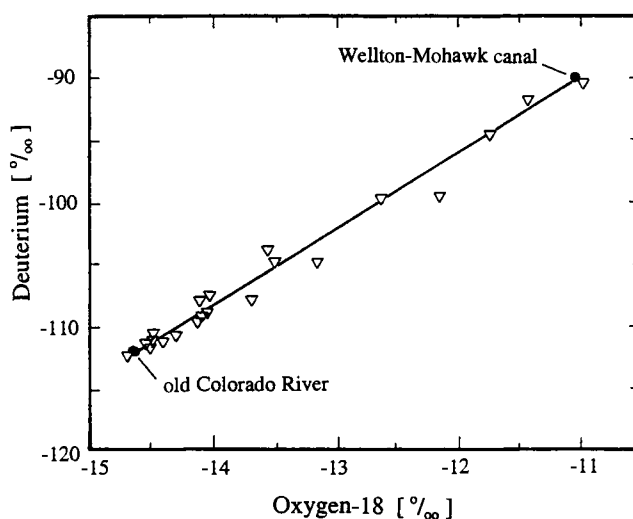


Figure 7.5. Stable isotope composition of groundwater in the Northeast and East Mexicali Valley, Mexico (Payne et al., 1979, modified).

7.4.3 Hydrodynamical models of shallow groundwater systems based on isotopic data

Tritium, when used as a tracer, is particularly suitable for hydrodynamic models of shallow groundwater systems, which usually contain recently recharged water. In some cases, ^{14}C can also be used, either when dealing with old groundwater in arid areas where modern recharge is negligible, or in humid areas where thermonuclear ^{14}C can be identified in groundwater.

To correctly interpret the tritium and/or ^{14}C data in shallow aquifers, the vertical age distribution of groundwater should be established. In a homogeneous aquifer of constant thickness and permeability, the variation of groundwater age with depth x below the water table is given by (Vogel, 1967, 1970):

$$t = \frac{nH}{W} \ln \left(\frac{H}{H-x} \right) \quad (7.3)$$

where H is the aquifer thickness (from the water table), W is the recharge rate by precipitation (water height per unit time), and n is the porosity. Assuming that the contribution of each depth is the same, the mean age of groundwater between depths x_1 and x_2 is:

$$t_M = \frac{\int_{x_1}^{x_2} \frac{nH}{W} \ln \left(\frac{H}{H-x} \right) dx}{x_2 - x_1} \quad (7.4)$$

Therefore, knowing the mean age of groundwater (e.g. by means of a radioactive isotope) at the depth x_1 to x_2 , it is possible to compute the recharge rate.

It should be noted, however, that the mean water age of a water mixture cannot be computed directly from a radioisotope content by simply applying the radioactive decay law. The mean water age of the mixture is given by:

$$t_M = \sum_{i=1}^n f_i t_i \quad (7.5)$$

where f_i is the fraction of the water having age t_i . The relative concentration of a given rare isotope of an element in the mixture is:

$$C_M = \frac{\sum_{i=1}^n f_i m_i C_i}{m_M} \quad (7.6)$$

where C_M and C_i are the ratios between the rare isotope and the most abundant one respectively in the mixture and in the component i , and m_M and m_i are the molar concentrations of the element. If $m_1 = m_2 = m_i = m_M$ (which is certainly true for tritium, and possible for ^{14}C), Equation 7.6 can be simplified to:

$$C_M = \sum_{i=1}^n f_i C_i \quad (7.7)$$

Accordingly, the apparent age computed from C_M with a piston-flow model is:

$$t_{PF} = \frac{1}{\lambda} \ln \frac{C_0}{C_M} \quad (7.8)$$

where C_0 is the so-called "initial" isotopic ratio, i.e. the isotopic ratio at the time $t = 0$ before the radioactive decay starts, corrected for other processes that may occur later. For ^{14}C , such processes are carbonate dissolution, isotopic exchange with matrix carbonate, inputs of inorganic carbon (DIC) species not derived from soil CO_2 , etc. C_0 is assumed to be the same for all the components of the mixture, which is true for ^{14}C if modern water containing bomb ^{14}C is not present.

The piston flow age should be compared with the mean age of water:

$$t_M = \sum_{i=1}^n f_i t_i = \frac{1}{\lambda} \sum_{i=1}^n f_i \ln \frac{C_0}{C_i} \quad (7.9)$$

where λ is the decay constant. It can be demonstrated that t_M is always greater than t_{PF} and that the difference depends on the age distribution and the age value. This problem will be further discussed in the section dealing with confined aquifers, for which the use of ^{14}C is more appropriate.

In the case of tritium, the initial concentration has been very variable over the last half century as a consequence of atmospheric thermonuclear tests. Therefore, for tritium Equation 7.9 should be written as:

$$t_M = \frac{1}{\lambda} \sum_{i=1}^n f_i \ln \frac{C_{0,i}}{C_i} \quad (7.10)$$

where $C_{0,i}$ is the initial isotopic ratio of component i rather than the initial isotopic ratio of the mixture C_0 .

Now the problem is how to establish the age distribution in water. By adopting the Vogel model and the age distribution given in Equation 7.3, one can compute the tritium content of water at a given observation time in each depth interval as a function of the recharge rate (provided that the tritium input, the tritium concentration in precipitation, is known). This is shown in Figure 7.6 for a hypothetical unconfined aquifer. In this computation, however, several assumptions have been made that considerably simplify the problem: (i) hydrodynamic dispersion was not considered; (ii) the aquifer was assumed to be completely isotropic in all directions; (iii) distortion of the flow lines, and therefore of the water age distribution due to pumping, was not considered. Ideally, the method can be applied in relatively undisturbed conditions (i.e. when the exploitation is negligible). The method requires sampling at different depth intervals; if the whole water column is sampled, the tritium content is relatively independent of recharge, except for low recharge rates.

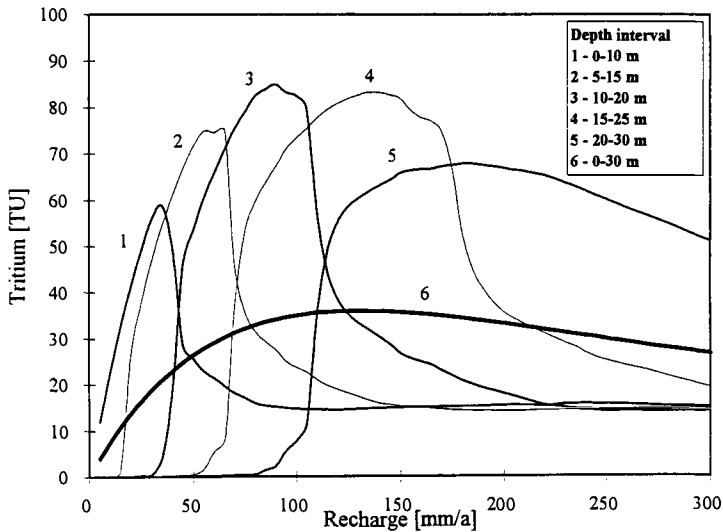


Figure 7.6. Tritium concentration at various depths in a hypothetical unconfined aquifer in 1994, as a function of recharge rate, computed according to Vogel model (Vogel, 1967; 1970). Tritium input function based on Vienna precipitation data.

The lumped-parameter models, often called black-box models, have been used for interpretation of environmental isotope data in groundwater systems since the early years of isotope hydrology. In a lumped-parameter model, spatial variations of physical characteristics of the given system (porosity, hydraulic conductivity, etc) are ignored and the system is described by one or several adjustable parameters, which are derived from the tracer input-output relationships. The methodology of lumped-parameter modeling is widely used (for overview see Zuber, 1986; Richter et al., 1993; and Chapter 5). Applications of lumped-parameter models to catchment studies are discussed in Chapter 21.

Compartmental models treat hydrological systems as a series of interconnected compartments or cells, in which water is fully mixed. Whenever possible, the cell size and distribution try to mimic the structure of the systems. Fluxes between cells are then adjusted by iterations to best fit the hydrological, chemical and isotopic data available. At the end, a value of the mean residence time T of water in the system is obtained. This provides an estimate of recharge R through the relation $T = V/R$, where V is the volume of the system.

Tritium, with levels being elevated during the three decades after the start of the atmospheric thermonuclear tests, was probably the best tool to use for these models. The recursive equation giving the tritium concentration C in a given cell of volume V at the time $(i+1)$ can be obtained from the tritium and water balance equations:

$$C_{i+1}V_{i+1} = C_iV_i + C_{Pi}P_i + C_{Ri}I_i - C_iE_i - \lambda V_iC_i \quad (7.11)$$

$$V_{i+1} = V_i + P_i + I_i - E_i \quad (7.12)$$

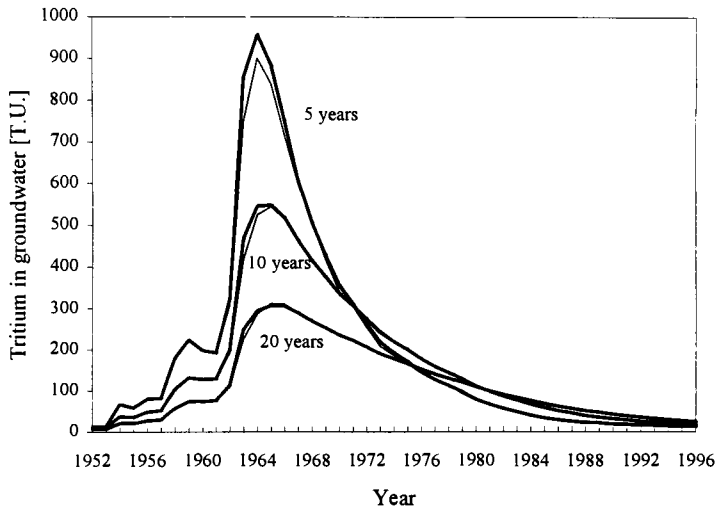


Figure 7.7. Response of one-cell (heavy line) and two-cell (light or dotted line) systems to the tritium input function based on Vienna precipitation data, for three different mean residence times of water in the system.

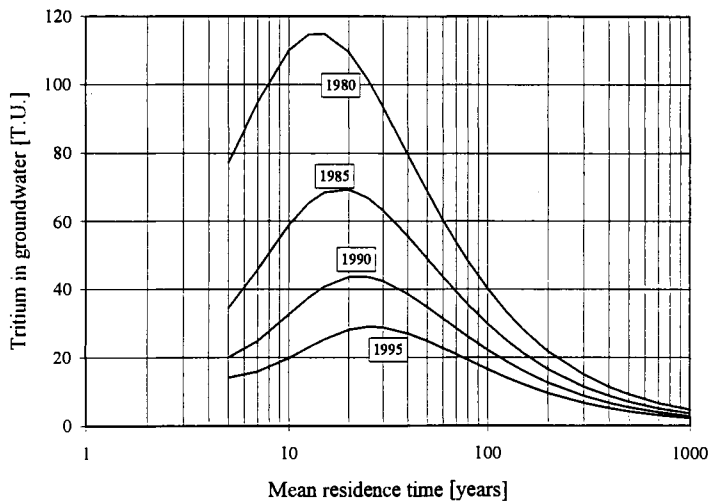


Figure 7.8. Tritium concentration in a well-mixed aquifer in different years and for different residence times. The tritium input function is based on Vienna precipitation data.

where P is the direct recharge by precipitation, I is the inflow from upstream cells, and C_p and C_i are the respective tritium concentrations; E , with a tritium concentration equal to that of the cell, is the outflow towards downstream cells. Figure 7.7 shows the variation of tritium content in a one-cell and a two-cell system with various turnover times, for the tritium input function based on Vienna precipitation data. Figure 7.8 shows the relationships between tritium content and turnover time in a one-cell, well-mixed system.

For simplification, in the examples shown in Figures 7.7 and 7.8, it has been assumed that cell volume, recharge, inflow and outflow are constant. It is possible, however, to let these parameters vary; for instance, recharge could be a function of precipitation amount in each time interval considered. It is necessary to include such variability in the models if the amount of precipitation, which is the main parameter governing recharge and the dynamics of ground-water systems, shows important variations in the selected time interval. This consideration applies in particular to the seasonal variations of precipitation amount if the time interval is a month, or the large interannual variations in arid zones if the interval is a year.

If the tritium content of precipitation can be assumed as constant (as it practically has been since 1988) a steady state will be reached in which the tritium content is given by:

$$C = \left(\frac{C_p}{T_p} + \frac{C_l}{T_l} \right) \frac{T}{1 + \lambda T} \quad (7.13)$$

where T_p and T_l are respectively the turnover time due to precipitation and that due to inflow from other cells. These times are related to the total turnover time by:

$$\frac{1}{T_p} + \frac{1}{T_l} = \frac{1}{T} \quad (7.14)$$

Probably, the steady state of Equation 7.13 has not yet been achieved in many catchment hydrological systems. A continuous monitoring of tritium concentration will indicate the rate at which the steady state is approached, from which the hydrodynamic characteristics of the system can be derived.

Some examples of applications of tritium data in field studies are given below and additional samples are provided in Chapter 21. Przewlocki and Yurtsever (1974) used a multi-compartment model to fit the tritium content variations from 1969 to 1973 in a spring in southern Austria. Compartments or cells are interconnected in series, as shown in Figure 7.9; it is believed that this is a reasonable representation of the hydrogeological situation in the spring catchment area. Recharge by precipitation takes place only in the first cell, from which it displaces an equivalent amount of water and pushes it down along the cell chain. Full mixing is achieved in each cell. Six cells produced the best fitting, with a mean residence time of 7.5 years for the whole system. A similar approach was adopted to describe the tritium variation in the Modry Dul basin, Czech Republic, for which the mean residence time was 5.25 years.

A multicompartment model was used also by Allison and Hughes (1975) to describe the tritium variations observed in a shallow aquifer in Southern Australia. At the time of the study, the groundwater had a tritium content ranging between 0.3 and 4.9 TU, with an average value of 2.2 TU. The aquifer is recharged by local precipitation and lateral inflow from a limestone aquifer whose water has a mean tritium content of 0.2 TU. The model predicts 24×10^6 m³/year or 120 mm/year for lateral recharge, and 27 mm/year for local precipitation. Conventional hydrological estimates give 18×10^6 m³/year and 70 mm/year, respectively. It is believed that the tritium-based estimate for local recharge is more likely.

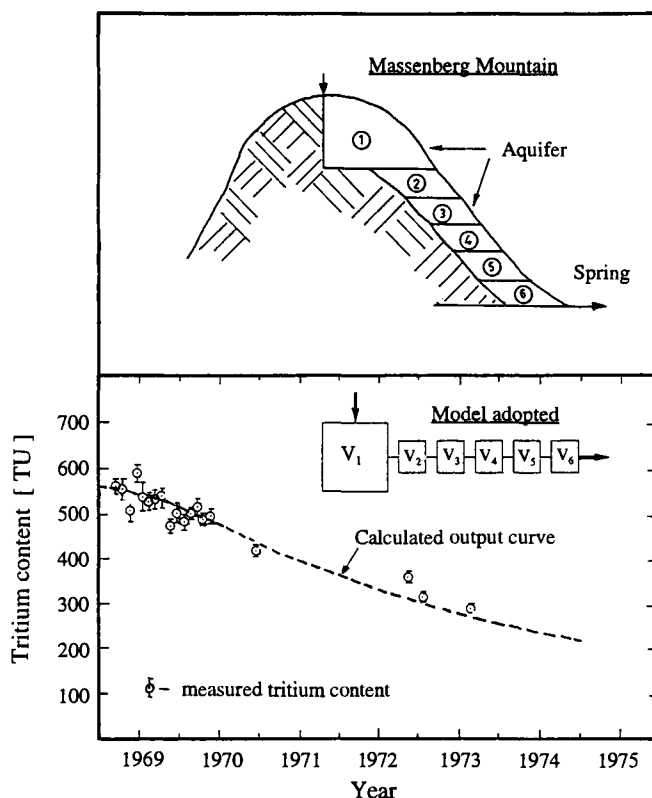


Figure 7.9. Calculated tritium output curve for the Grafendorf spring, southern Austria, using a multi-compartment (Przewlocki and Yurtsever, 1974, modified). The best fit of measured and calculated changes in concentrations of tritium in the spring water was obtained with the model consisting of seven compartments. The calculated turnover time of water in the system was 7.5 years.

The approach of Allison and Hughes was critically reviewed by Colville (1984), who drew attention to the effects on the model results produced by various factors, e.g. scatter of field tritium values, errors in deriving the tritium content of rains before 1966 from values at Kaitoke, New Zealand, variations of precipitation amount, irrigation returns, hydrodynamic dispersion, etc. Obviously, a disadvantage of applying tritium in modeling groundwater dynamics in the southern hemisphere and in the tropical belts is the relatively low tritium content of precipitation even during the period immediately after the peak of atmospheric thermonuclear tests (Gonfiantini et al., 1990; Rozanski et al., 1991).

A more complex multicompartment model was used by Yurtsever and Payne (1986) to interlink tritium and discharge variations observed in the period 1963 to 1980 in the Manavgat River, the outlet of a large karst system in southern Turkey. The model, which included nine compartments on three different depth levels, mimicked the hydrodynamic features of the system as they could be inferred from recession hydrographs. The hydraulic information of the system indicated the presence of three reservoirs: a shallow reservoir, having a characteristic residence time of 3 to 4 months; an intermediate depth source, with characteristic residence

time of 9 months to one year; a deep reservoir, with a much longer residence time of water, which was providing the base flow. A good match between modeled and observed values of cell residence times and fluxes between cells were established after 1000 iterations. Figure 7.10 shows the tritium and discharge values provided by the model in comparison with those observed in the Manavgat River.

A multi-cell, multi-tracer approach, combining isotope and geochemical data, has been used successfully in several recent case studies in Israel (Adar et al., 1992; Adar, 1994). In this approach the aquifer is divided into cells within which the isotopic tracers and dissolved constituents are assumed to undergo complete mixing. For each mixing cell, mass balance equations expressing the conservation of water isotopes and dissolved chemical species are formulated. These equations are then solved simultaneously for unknown rates of recharge.

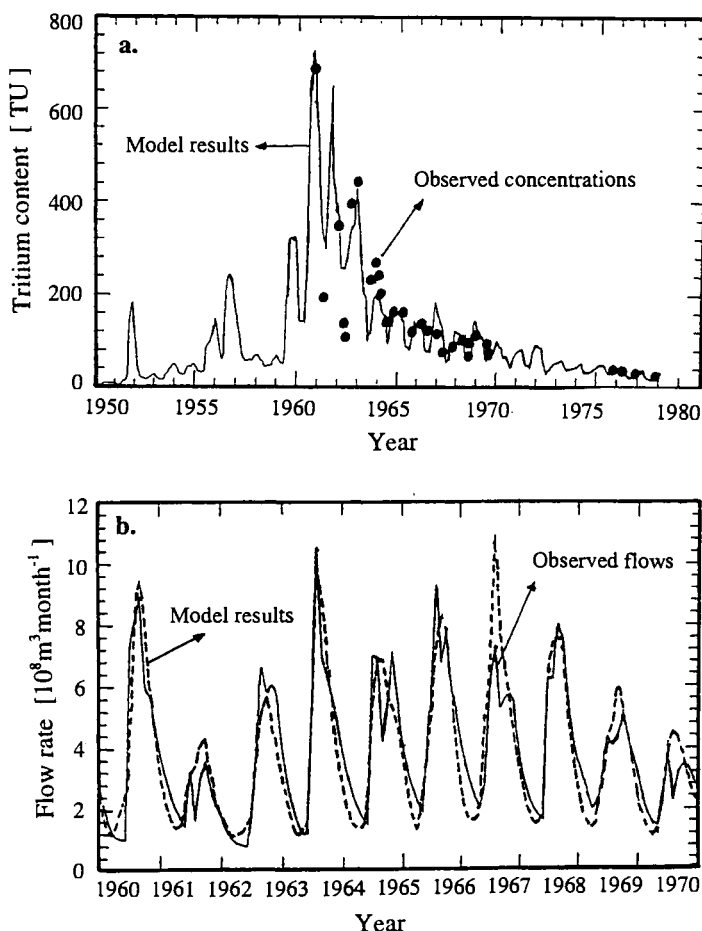


Figure 7.10. a) Comparison of model calculated tritium output concentrations with actual observed values in Manavgat river, southern Turkey. b) Comparison of model calculated flows with actual observed flows in Manavgat river. (Yurtsever and Payne, 1986, modified).

7.5 Deep Groundwater

7.5.1 Groundwater movement in confined aquifers

In catchments where groundwater flow through rock formations controls baseflow, deep groundwater flow must be considered. Isotopic tracers can be particularly useful for understanding residence times, groundwater age, and seasonal recharge processes. Groundwater flow in deep, confined aquifers is usually slow under natural conditions. In aquifers that pinch-out between two aquicludes and do not have a well-defined discharge area, the water flow may be very limited, just enough to compensate the diffuse leakage across the aquicludes (where aquicludes may be considered strata with a permeability coefficient lower than 10^{-8} m/s). In some cases, aquifer discharge occurs through faults that establish hydraulic connections with shallower aquifers or springs across the interbedded impermeable formations. In other cases, confined aquifers may eventually discharge into shallow unconfined groundwater bodies at lower altitude some distance from the recharge area.

Such slow water movement implies that in confined aquifers, groundwater may have a considerable age, and may have been recharged in climatic conditions quite different from today's. Such water is often referred to as *fossil water*; this expression does not mean simply old water, but rather water recharged in conditions not present today. Environmental isotopes can aid in identifying characteristics of fossil groundwater such as age, recharge conditions, interconnections with other water bodies, etc., which are useful for correct exploitation and paleoclimatological investigations. Intense exploitation causes an increase of discharge and at the same time induces new recharge. These changes in the natural flow conditions can induce inflow of water from other aquifers if a depression is created in the piezometric surface during pumping.

Environmental isotopes help in identifying and studying a number of processes that take place in confined aquifers, as will be illustrated by the examples reported below. The scientific literature on isotopes in deep groundwater is vast. The following are some examples pertaining to deep groundwater investigations in catchments.

7.5.2 Groundwater age

The knowledge of groundwater age and its distribution within a deep water-bearing formation is useful for assessing the dynamics of groundwater and planning its exploitation. Stable isotopes and noble gases are useful for identifying fossil groundwater, whereas radioactive isotopes play the most important role in providing a relative groundwater age.

Radioactive isotopes

The most useful environmental radioisotopes for determining groundwater age in confined aquifers are those with a half-life ranging from 10^3 to 10^6 yrs, while those with a half-life below 100 yrs have limited applicability in confined groundwater systems. Among the first category of isotopes, the most important one used is ^{14}C , which has a half-life of 5730 yrs. This isotope is present in soil CO_2 that dissolves in groundwater at the plant root level in the unsaturated zone. The carbonatic species formed are subject to interaction with the matrix carbonate, and this gives rise to a number of problems in ^{14}C age computation (Wigley et al., 1978; Fontes,

1983, 1992; Geyh, 1992), which are also discussed in Chapter 17. Other radioisotopes that have been applied include argon-39 (half-life 269 yrs; Loosli et al., 1992; Forster et al., 1992), silicon-32 (≈ 140 yrs; Fröhlich et al., 1988), uranium-234 (2.45×10^5 yrs; Fröhlich and Gellermann, 1987), chlorine-36 (3.01×10^5 yrs; Bentley et al., 1986; Fabryka-Martin et al., 1987; Andrews and Fontes, 1992), krypton-81 (2.1×10^5 yrs; Lehmann et al., 1991), and iodine-129 (1.57×10^7 yrs; Fabryka-Martin et al., 1985). Radiogenic helium isotopes have also been used (Weise and Moser, 1987; Torgersen, 1992; Mazor and Bosch, 1992) and methods reviewed (Ivanovich et al., 1992). The geochemical background of many of these methods however, is not well-developed. The following discussion on groundwater dating concentrates on aspects related to groundwater dynamics, which may have a bearing on age determinations. For the geochemical aspects the reader is referred to Chapters 8 and 16 of this book.

In isotropic, confined aquifers the water flow is laminar. If the aquifer is artesian, as often occurs, and inflow of younger water along the water path can be excluded, groundwater age increases more or less regularly from the recharge area in the direction of flow. Confined aquifers therefore provide a suitable environment for applying the already mentioned piston flow model. Well sampling allows, in principle, collection of water samples with limited age dispersion. The effect of hydrodynamic dispersion on groundwater age distribution and age determination by radioisotopes must be evaluated. Considering age as a "tracer" of water, the fraction of water with age ranging from t_1 to t_2 at a given distance from the recharge area can be computed numerically for a unidimensional advective-dispersive system from the equation for tracer dispersion in a unidirectional flow in a semi-infinite medium (De Marsily, 1981).

As an example, the age distribution for values of the dispersion coefficient from 10 to 500 m^2/year is shown in Figure 7.11. Figure 7.12 shows the difference in per cent between the age computed from ^{14}C by using the piston flow model and the mean age of groundwater, the latter always being greater than the first. It can be seen that for dispersion coefficients up to 100 m^2/year this difference is in general tolerable, unless the water velocity drops well below 0.05 m/year. Moreover, the difference between mean age and piston flow age decreases with decreasing porosity, as shown in Figure 7.12.

In the case of chlorine-36, which has a half-life two orders of magnitude greater than ^{14}C and is therefore suited to study confined aquifers of vast dimensions, dispersion reduces groundwater ^{36}Cl ages up to only 10 % at a distance of 1,000 km from the recharge area, assuming a Darcy velocity of 0.05 m/year (Figure 7.13). The hydrogeological characteristics of the system for which the computation has been made are comparable with those of the Great Artesian Basin in Australia (Bentley et al., 1986). In this case, a regular decrease of $^{36}\text{Cl}/\text{Cl}$ ratio with increasing distance from the recharge area in the flow direction was reported, which would indicate a mean water velocity of about 1 m/year. Nevertheless, it has been suggested that the observed chlorine isotope ratio trend was due to dilution by chloride dissolution rather than to decay. In fact, the ^{36}Cl concentration, expressed in ^{36}Cl atoms per unit volume of water, did not decrease along the water path in the aquifer (Andrews and Fontes, 1992). Recently, the concept of the Great Artesian Basin as one active hydraulic system has been challenged by Mazor (1995), who used geological, hydrological and isotope data to show that the Basin consists of stagnant aquifers hydraulically isolated from each other.

The effective typical detection limit of ^{14}C can be set at 1 PMC (Percent of Modern Carbon). This means that the ^{14}C dating method covers an age range of up to 20-30,000 years, if the

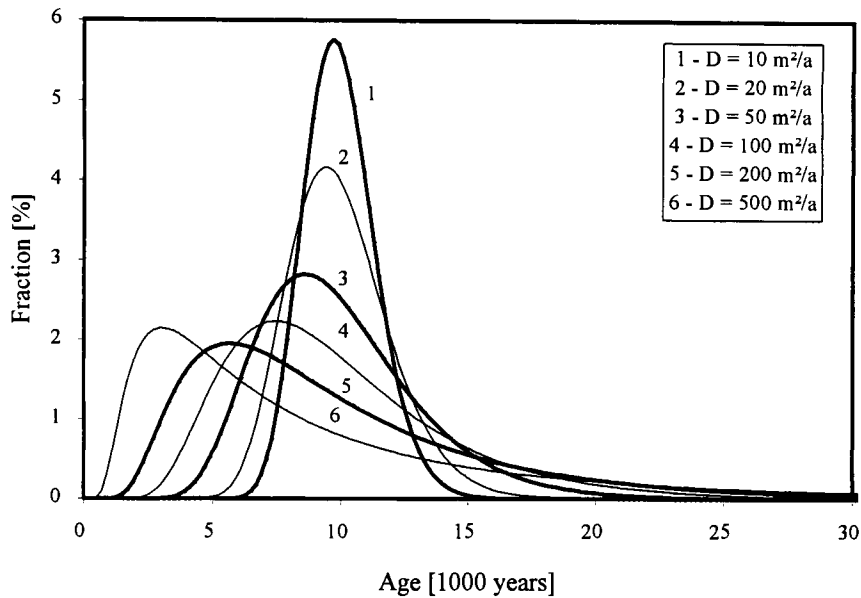


Figure 7.11. Groundwater age distribution at a distance of $X = 10,000$ m from the recharge area, flowing with Darcy velocity of 0.1 m/a in a porous aquifer with effective porosity of 10%. The age percent fractions are computed over a 200 years time interval. The retardation coefficient has been taken equal to 1 (no retardation).

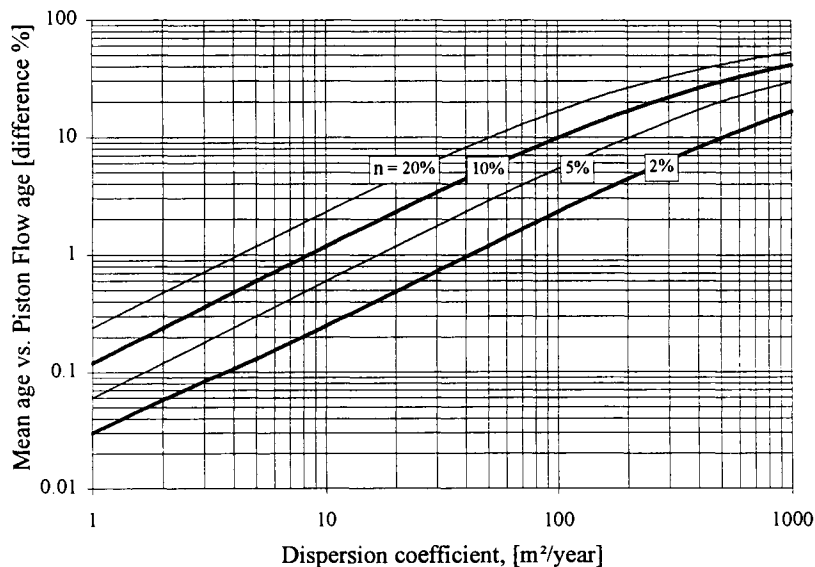


Figure 7.12. Effect of dispersion on the C-14 piston flow age of groundwater flowing with Darcy velocity of 0.1 m/yr . The difference between the mean age and the piston flow carbon-14 age of groundwater is plotted as a function of the dispersion coefficient, for selected effective porosities. In this computation the DIC concentration has been assumed constant, and the interaction with the matrix negligible.

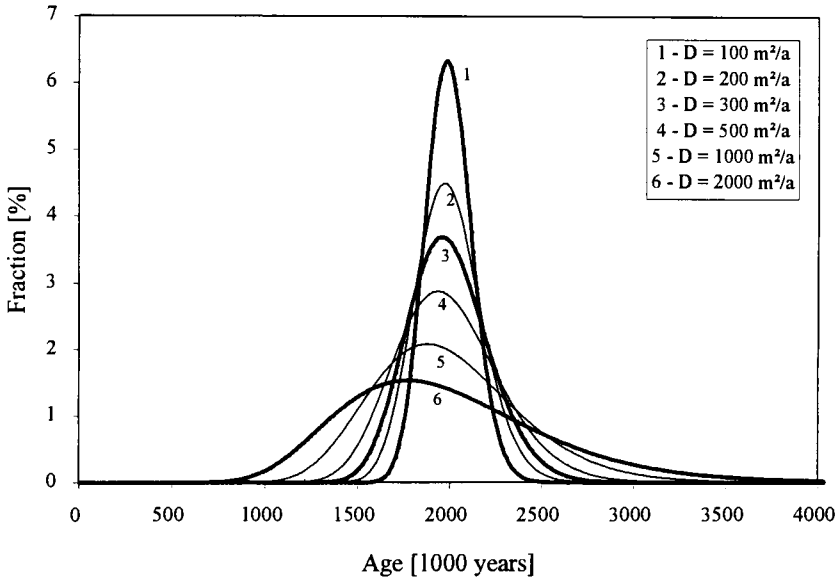


Figure 7.13. Distribution of water age at a distance of $X=1,000$ km from the recharge area, for different dispersion coefficients. Water is flowing with a Darcy velocity of 0.05 m/yr in a porous aquifer with effective porosity of 10% . The age percent fractions are computed over a $20,000$ years time interval. The retardation coefficient has been taken equal to 1 (no retardation).

piston flow model is applied. With a water velocity of about 1 m/year which is representative for many large aquifers in arid and semi-arid zones, the ^{14}C would drop below the detection limit $20\text{--}30$ km away from the recharge area. This distance can be further reduced by geochemical interactions between dissolved inorganic carbon and the aquifer matrix, particularly in double-porosity systems like fissured carbonate rocks (Maloszewski and Zuber, 1991). These interactions may give rise to a correlation between ^{13}C and dissolved carbonate species (Pearson and Hanshaw, 1970) and also between ^{13}C and ^{14}C concentrations (Figure 7.14; Gonfiantini, 1988). In fact, in many confined aquifers (especially in large aquifers in arid environments) the ^{14}C content of groundwater is frequently below the detection limit because of decay and geochemical processes.

The age range of ^{14}C may extend much further than $30,000$ years if flow models other than the piston flow are applied. For instance, if the full mixing model is used, the equation giving the mean residence time t_M , or mean age, of water in the well mixed reservoir is:

$$t_M = \frac{1}{\lambda} \left(\frac{C_0}{C} - 1 \right) \quad (7.15)$$

where C_0 is the initial ^{14}C content, C is the observed ^{14}C content of DIC, and $1/\lambda = 8267$ is the mean life of ^{14}C . If $C = 1$ PMC and $C_0 = 100$ PMC, t_M exceeds $800,000$ yrs. Considering that the mean age calculated by Equation 7.15 is connected with the (mean) recharge rate R of an unconfined aquifer according to:

$$t_M = \frac{nH}{R} \quad (7.16)$$

this result would correspond to a minimum measurable (mean) recharge rate R of about 0.1 mm/yr for an aquifer of a thickness $H = 1000$ m and a porosity $n = 10\%$. Such conditions can only be found in great sedimentary basins of arid and semi-arid zones and would most certainly be beyond the scope of most catchment studies.

In deriving the equations above, it is assumed that all the groundwater components have the same DIC concentration and initial ^{14}C content, irrespective of age. This last assumption is erroneous when groundwater has interacted with the aquifer matrix in a way that affects its ^{14}C content. Greater water mixing typically occurs in fractured and fissured aquifers than in porous aquifers. However, full mixing is never achieved in aquifers of sizeable dimensions and with a well-defined water flow direction. As for tritium, a multicompartmental model can be applied to take into account the increased hydrodynamic dispersion.

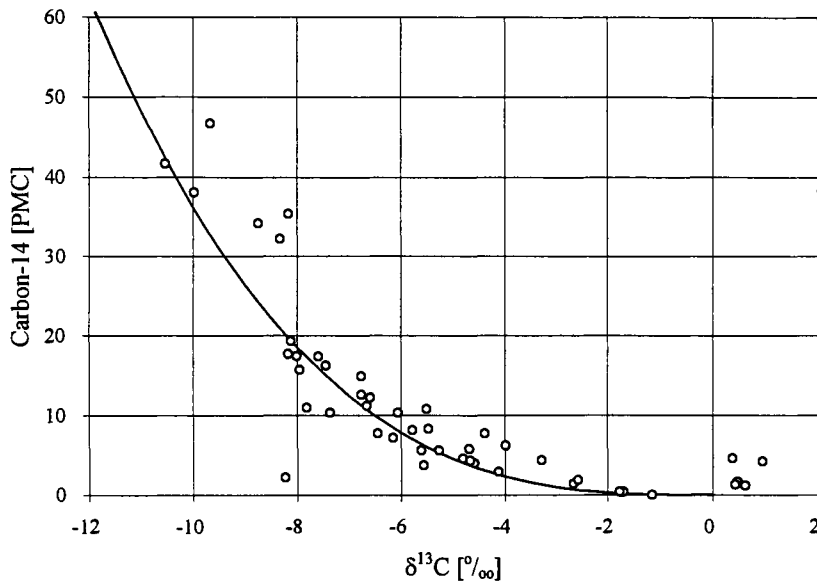


Figure 7.14. Carbon-14 versus carbon-13 content in bicarbonate dissolved in groundwater of Cyrenaica aquifer, northern Libya (Gonfiantini, 1988, modified).

Assuming a model with cells in cascade (where recharge occurs only in the first cell) and disregarding all processes other than decay that may affect the ^{14}C content of DIC along the groundwater path, the mean age t_M of groundwater in the n^{th} cell is given by:

$$t_M = \sum_{i=1}^n t_i = \frac{1}{\lambda} \left(\sum_{i=1}^n \frac{C_{i-1}}{C_i} - 1 \right) \quad (7.17)$$

Assuming now for simplicity that the mean residence time of water is the same in all the cells or compartments: $t_1 = t_2 \dots = t_n$, one can derive:

$$t_M = n t_1$$

$$C_1 = \frac{C_o}{1 + t_1 \lambda}$$

$$C_2 = \frac{C_1}{1 + t_2 \lambda} = \frac{C_o}{(1 + t_1 \lambda)^2}$$

$$C_n = \frac{C_o}{(1 + t_1 \lambda)^n}$$

Finally, we obtain:

$$\ln \frac{C_0}{C_n} = \frac{t_M}{t_1} \ln(1 + t_1 \lambda) \quad (7.18)$$

where t_1 is the mean residence time in each cell. In other words, the logarithm of the ^{14}C content in the n^{th} cell is a linear function of mean water age t_M , as for the piston flow model, but with a different slope. This can be seen in Figure 7.15, which shows the difference of ^{14}C content between the piston flow model and the model with equal cells in cascade. It appears that the deviation from the piston flow model increases with increasing mean residence time of water in cells, as should be expected, because longer residence time implies increased dispersivity.

In conclusion, one of the major problems in using radioactive isotopes for groundwater dating is the assessment of an age distribution function. If the age obtained (assuming the simple piston flow model) does not exceed one half-life, the difference with respect to the *true* mean age is negligible, whatever the age distribution -- provided it is a continuous function of age. Above the limit of one half-life, it is possible in principle to obtain an estimate of the mean age of water from the radioisotope content, if hypotheses can be formulated based on the form of such a function. If the age distribution is discontinuous (e.g. mixing of old deep groundwater with recent shallow groundwater) it is impossible to estimate the mean age of the mixture if the fraction of each component cannot be assessed independently. Also, the hydrogeological meaning of such an age estimate becomes questionable.

Among the radioisotopes available for groundwater dating, ^{14}C is considered the most important tool for deep groundwater, in spite of the serious problems connected with interactions of DIC species with the aquifer matrix. Carbon-14 also should be used with caution when there is the suspicion of a contribution of ^{14}C -free deep CO_2 , a quite common feature of geothermal waters, which may have a very low ^{14}C content despite containing tritium. In any case, the experience accumulated in using ^{14}C for groundwater dating is so vast, the hydrological systems studied so numerous and the data available so abundant, that the experienced isotope hydrologist should be able to make sound judgments on the value and use of ^{14}C data in any possible situation.

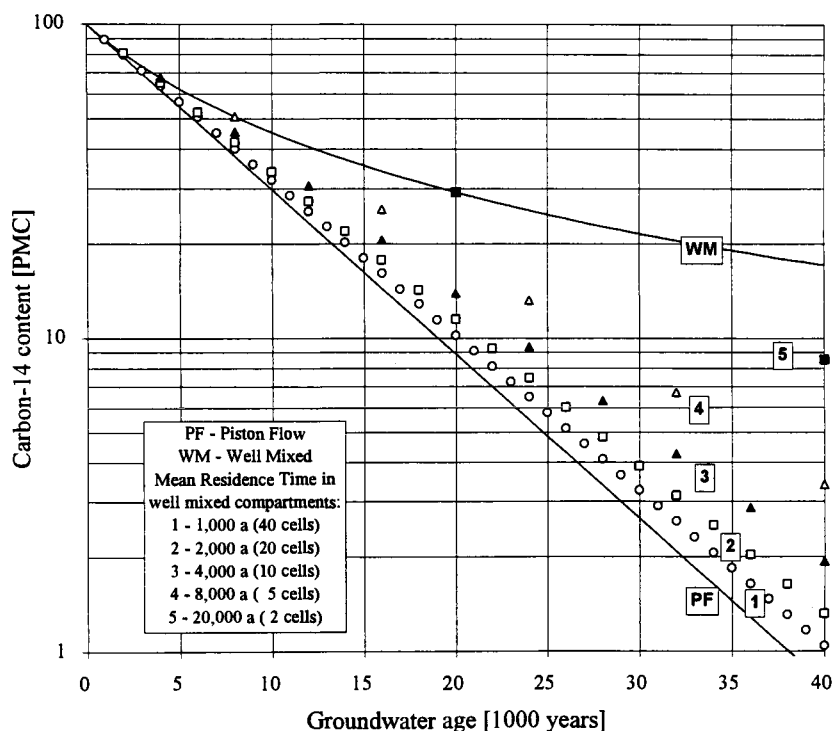


Figure 7.15. Difference between groundwater ages computed from the same carbon-14 content, with different models: piston flow, well mixed reservoir, and multicompartment models with different number of equal cells in cascade.

Among other radioisotopes, chlorine-36 has already found a firm place among the tools available for groundwater dating, despite limited experience. The usefulness of chlorine-36 lies in its long half-life and to the fact that dissolved chloride ions are relatively conservative. Chlorine-36 is therefore expected to play an increasing role in dating very old groundwaters, especially for studying water dynamics in large, regional aquifers and in impervious rock formations. This last application is required for the hydrogeological assessment of radioactive waste-disposal sites. All other radioisotopes require additional investigations and testing before becoming routine dating tools. Their geochemistry and applications are described in Chapters 8 and 9.

Stable isotopes and noble gases: the identification of paleowaters

Stable isotopes and noble gas concentrations (also discussed in Chapter 9) do not provide the age of groundwater, but indicate the climatic conditions under which groundwater was recharged. The stable isotope composition of precipitation depends mainly on the air temperature and/or amount of rainfall; therefore, it reflects, broadly speaking, the prevailing climatic conditions (Rozanski et al., 1992, 1993; also see Chapter 3). Considering that climate has shown strong variations during the major part of the Quaternary, with changes from colder to warmer and from dry to humid periods, one may expect that these variations are mirrored

by the isotopic composition of old groundwater. Long-term temperature variations can also be recorded by noble gas concentrations.

The long-term trend of $\delta^{18}\text{O}$ vs. temperature in precipitation at selected continental stations in the northern hemisphere has a slope of 0.4 ± 0.1 to 1.1 ± 0.1 ‰ °C⁻¹ (Rozanski et al., 1992). Smaller gradients are evident in tropical stations, where the temperature variations are usually smaller and precipitation occurs mostly during one season. Hence, in the tropics, the correlation between isotopic composition and the amount of precipitation is more important than the correlation with temperature. While the data available for tropical stations are inconclusive for the long-term correlation, they indicate a strong seasonal correlation between isotopic composition of precipitation and amount. For instance, monthly data for the three African stations of Bamako (Mali), N'Djamena (Chad) and Kano (Nigeria), all in similar semi-arid climatic conditions typical of the Sahel, show a marked seasonal gradient of -0.0146‰ per mm for the ^{18}O content vs. precipitation amount.

The lack of long-term correlation is possibly due to the fact that variations in the amount of yearly precipitation appear random (e.g. do not seem to follow any multiannual cycle or trend). There is no doubt, however, that in tropical stations a depletion of heavy isotope content in groundwater indicates the occurrence of more humid climatic conditions at the time of recharge. To quantify this climatic difference in terms of increased precipitation in the past is not possible, unless the seasonal correlation is used, a procedure which is questionable and perhaps incorrect.

The use of gradients (defined by modern isotopic compositions versus temperature and precipitation amount) to estimate climatic conditions in the past must also take into account the change of the sea water isotopic composition that occurred during glaciations, when 2 - 3 % of the present ocean water was stored on the continents as ice. At that time, sea water was enriched by about 1.3‰ in $\delta^{18}\text{O}$ (Shackleton, 1987). Such an enrichment will decrease the effects of lower temperature and/or higher rainfall amount on the isotopic composition of groundwater recharged more than 15,000 years ago. In special situations, such as in certain coastal regions where Quaternary climatic changes may have had a limited effect on the isotopic composition of precipitation, the signal deriving from heavy isotope enrichment of sea water can completely mask the heavy isotope depletion of rainfall caused by lower temperature. This effect may explain why in the Aveiro coastal aquifer (Portugal), the isotopic composition of groundwater shows a slight enrichment in heavy isotopes in the portion of the aquifer with confined groundwater and ^{14}C ages corresponding to the late Glacial period (Carreira et al., 1996). A similar enrichment was observed in an aquifer in South Africa (Vogel et al., 1982) and Florida, USA (Plummer, 1993). In the Florida aquifer, the enrichment was attributed to a different rain regime, but heavy isotope enrichment of sea water could also have played a role.

Noble gas concentrations also allow the identification of paleogroundwaters. Because noble gas solubility depends on temperature, the method works better at mid and high latitudes where the temperature increase from Pleistocene to Holocene has been greater. For example, in a deep Eocene aquifer in Aquitania (France) the noble gases indicated a recharge temperature 5 to 7 °C lower than the modern mean annual temperature (Blavoux et al., 1993). The deep groundwater was also depleted in heavy isotopes with respect to modern shallow groundwater by 2-3 ‰ in $\delta^{18}\text{O}$ and 20-30 ‰ in δD . Similar observations were made in a Jurassic limestone aquifer near Krakow, Poland (Osenbrück et al., 1993), where a noble gas temperature of 2-

3.5°C lower than the modern one was accompanied by a heavy isotope depletion of groundwater; and in Tertiary aquifers in the southern Germany alpine foreland (Bertleff et al., 1993). Interesting results have been obtained recently for several aquifers located in the tropics (Stute et al., 1992, 1995a,b). The "noble gas paleothermometer" showed a temperature difference between Holocene and the Late Glacial of about 5°C. These results challenge the widely adopted CLIMAP reconstructions for low-latitude regions (less than 2°C for the tropical ocean) and have important implications for the modeling of the global climate, as discussed further in Chapter 22.

It is important to identify the occurrence of "fossil" groundwater in aquifers on the basis of their isotopic imprint. Observations of fossil groundwaters are relatively more frequent in arid environments, where modern recharge is low and the occurrence of paleowaters is a quite common phenomenon (Degens, 1962; Sonntag et al., 1979, 1980a,b; Dray et al., 1983; Gonfiantini et al., 1974; Edmunds and Walton, 1980; Srdoc et al., 1980; Fontes et al., 1991; and many others). In humid climates, paleowaters occur mainly in large confined aquifers (Fritz et al., 1974; Bath, 1983). A discussion on paleowater occurrence and characteristics can be found in Fontes (1981).

7.5.3 Interconnections between aquifers

Environmental isotopes, and especially stable isotopes, can be used to identify hydraulic interconnections between aquifers. The obvious prerequisite is that the interconnected aquifers have different isotopic compositions. The stable isotope composition of groundwater in the confined part of the *Continental intercalaire*, a large Lower Cretaceous aquifer in north-western Africa, is relatively uniform (Gonfiantini et al., 1974). It is depleted in $\delta^{18}\text{O}$ and δD by about 3 and 20 ‰, respectively, compared to groundwater in the overlying aquifer called the *Complexe terminal*. In two areas, however, stable isotopes provide a clear indication that the *Continental intercalaire* is discharging into the overlying aquifer. Near El Hamma in Tunisia, a fault system connects the two aquifers. The occurrence of such an interconnection was already suggested by hydrogeologists on the basis of piezometry, and it has been confirmed by stable isotopes. In this area the groundwater in the *Complexe terminal* has the same isotopic composition of that in the *Continental intercalaire*. The heavy isotope depletion of groundwater decreases gradually in the flow direction, as water from the *Continental intercalaire* mixes with that from the *Complexe terminal*. At Ouargla, an oasis in the Sahara desert in Algeria, stable isotopes indicate that the *Continental intercalaire* is locally leaking into the less deep *Complexe terminal*, in spite of the fact that the two aquifers are separated by a clayey formation several hundreds of meters thick.

A case in which vertical leakage between two aquifers is induced by exploitation has been reported by Payne et al. (1980). At Hermosillo, in north-western Mexico, major exploitation of the alluvial aquifer has caused a vast cone of depression in the water table. The alluvial aquifer lies above a low-permeability clay formation about 100 m thick. Below this formation there is a deep confined aquifer with a piezometric surface up to 30 m higher than the water table in the alluvial aquifer. The two aquifers contain water with different stable isotope compositions, which were used to detect a contribution of up to 20 % of deep groundwater in the shallow aquifer.

Isotopes can also be used to prove the lack of hydraulic interconnections between aquifers. In southern Latium, Italy, the water balance considerations led to the conclusion that the limestone aquifer of Monti Simbruini discharges into the Monti Lepini limestone aquifer through a hypothetical interconnection between them. Stable isotopes demonstrated that the hypothesis was incorrect, and that the two aquifers were actually hydraulically independent (Celico et al., 1984).

7.5.4 Geothermal groundwaters

Geothermal groundwaters are defined as groundwaters that have a temperature higher than expected from the normal geothermal gradient. Geothermal waters from springs and drilled wells usually have temperatures well below the boiling temperature, and their apparent excess heat is due to deep underground circulation and subsequent uprising to surface or shallower horizons. Only these low-enthalpy geothermal waters will be discussed here.

Isotopically, low-enthalpy geothermal waters behave as cold groundwater. Their stable isotope composition reflects that of precipitation over the recharge area. In fact, the enhanced rate of rock-water interactions at the modestly higher temperature, which in most cases leads to enrichment in ^{18}O , is usually insufficient to cause a significant change of the water isotopic composition. For instance, recent investigations of thermal springs in Eastern Pyrenees, France (Krimissa et al., 1993), Central Vietnam (Nguyen Trac et al., 1994) and South-east China (Wang and Pang, 1994), have indicated that thermal waters have been recharged at an altitude much higher than that of emergence, because they are always significantly depleted in heavy isotopes with respect to cold springs and surface waters in the vicinity.

The tritium content of thermal waters is usually low, often below the detection limit, unless mixing with shallow groundwater does occur, because deep circulation implies very slow movement. ^{14}C should be used with caution, because of the increased rate of isotopic exchanges with the aquifer minerals (Thilo and Münnich, 1970); ^{14}C ages should therefore be considered as *maximum* ages. Finally, possible release of radiogenic rare gases from rocks may affect significantly their contents in thermal waters.

A recent isotopic and hydrochemical study of Sudeten thermal waters (Poland) allowed Ciezkowski et al. (1992) to identify the occurrence of two reservoirs. The smaller contains water with 10 years residence time as derived from tritium. The larger reservoir, whose water is depleted by about 0.8‰ in $\delta^{18}\text{O}$ and 7‰ in δD , appears to have been recharged either during a cooler period during the Pleistocene or the early Holocene, at an altitude about 1000 m higher than that of the study area.

7.6 Groundwater Studies in Catchments

7.6.1 Present situation and case study examples

Hydrological investigations of groundwaters in catchments with isotope techniques require identification and characterization of the components of the basin water balance (precipitation inputs, surface waters, shallow and deep groundwaters, etc.) and of their interrelations. In large

basins, these components may exhibit isotopic variations from one zone to another, according to the geographical and geological characteristics of the various sub-basins in the catchment area. Thus, the number of samples to be analyzed increases in proportion with the size and complexity of the catchment.

Isotopic variations with time may also occur within the catchment as a consequence of concentration variations in the input. Such concentration variations happened in tritium during the years after 1953 making this isotope very useful for studying water dynamics in hydrological systems. Models of water age distributions based on the tritium output response were formulated since the early applications (see, for instance, Eriksson, 1963; Nir, 1964; and Chapter 21).

One of the first isotopic studies of a large catchment was carried out by Brown (1961, 1970) in the Ottawa River Valley (Canada) using tritium introduced by thermonuclear tests. Although this study was based only on tritium monitoring in the Ottawa River and in other minor rivers in the period 1956-1969, it provided the first tritium output function of a complex hydrological system after repeated pulse injections of the same isotope. The tritium output was the result of mixing in unknown proportions of waters with different residence times (ages) and origins, occurring in the various sub-units of the catchment.

Since the Ottawa River Valley study, many other isotopic investigations have been conducted; some selected case studies are summarized below. It should be pointed out that these studies were planned mainly to clarify specific hydrogeological aspects of complex aquifer systems. They were not intended to be comprehensive investigations of the hydrological behavior and balance of catchment by a multidisciplinary approach including environmental isotopes.

The hydrological system of the Cul-de-Sac plain in the Haiti Republic was investigated by Gonfiantini and Simonot (1987). Most of the country's population is concentrated and most agricultural and economic activities take place in a 500 km² plain, situated within a graben between two Eocene karst anticlinoria. Isotopes helped in identifying groundwater origin and enabled delineation of major flow patterns in the Quaternary alluvial aquifer of the plain, which is the most important water-bearing formation. The stable isotope concentration map of the aquifer showed that the major sources of groundwater recharge are rivers flowing from the southern karst range into the plain. By contrast, the recharge originating from the rivers in the northern range is negligible. Saline groundwaters occur along the northern foothills. The conductivity of these waters was up to more than 10,000 $\mu\text{S}\cdot\text{cm}$; they were also significantly enriched in heavy isotopes, although without any significant deviation from the meteoric water line (Craig, 1961). These waters derive from modern recharge, but it was shown using stable isotopes that they have been impacted by sea water intrusion. Such intrusion, a consequence of intense exploitation, is the major cause of groundwater salinization in the Port-au-Prince area.

The Tulum Valley in Argentina was studied by Alberio et al. (1987). This valley, about 200 km east of the Andean Cordillera, extends over 440 km². The isotopic investigation indicated that groundwater recharge derives from two main sources; the San Juan River (which is fed mainly by precipitation over the high Cordillera and therefore is depleted in heavy isotopes ($\delta^{18}\text{O} = -16.0\text{‰}$), and by streams fed by rains on the hills surrounding the valley which are less depleted in heavy isotopes: $\delta^{18}\text{O}$ about -6 to -8 ‰). Areas where one or the other source prevails can be

identified, but the San Juan River appears to be by far the major source of groundwater recharge. Precipitation over the valley is less than 100 mm/yr and does not contribute to the recharge of the aquifer.

An interesting example of hydraulic interconnection between different regions of a karst watershed has been investigated by Flora and Longinelli (1989) using stable isotopes. Many large karst springs along the northeastern Adriatic coast (near Trieste, Italy) exhibit lower heavy isotopes concentrations in summer than in winter. This apparent six-month phase shift of the isotopic composition variations with respect to those of precipitation cannot result from a simple delay due to water retention in the basin. Since summer precipitation is rare in Mediterranean climate, its contribution to the spring discharge is only minor. Therefore, one explanation of the "phase shift" is that the contribution of the more elevated inland part of the watershed dominates during the summer. In the winter, the coastal part of the watershed contributes more to spring discharge. This seasonal change of the predominant recharge area is in agreement with the different rain regimes of the two regions.

Taylor et al. (1989) investigated the water dynamics of the Canterbury Plains, South Island, New Zealand (catchment size approximately 150 km long and 50 km wide) using stable isotopes and tritium. The tritium data extend over 27 years, a period that encompasses the peak and decline of thermonuclear tritium in precipitation. Most of the groundwater systems of the plains are recharged by rivers, but there are some areas where recharge by local precipitation is significant. Precipitation is enriched in heavy isotopes relative to rivers. However, the contribution of precipitation to groundwater recharge appears significantly lower than previous estimates. The confined water-bearing formation, which is exploited to supply the coastal city of Christchurch, is recharged mainly by deeper aquifers, from which tritium-free groundwater ascends into the shallowest horizons through gaps in the confining layers. Groundwater exploitation appears to induce river recharge in the plains.

Long term tritium records (1961-1983) in river waters were used by Michel (1992) to estimate residence times of groundwater in the catchments in the U.S.A. ranging from 4,500 to 75,000 km². His model splits the river discharge into two components: recent rain water and delayed groundwater (with an exponential age distribution). Mixing ratios and mean age of the groundwater component were adjusted to produce the best correlation between computed and observed tritium concentrations. The results obtained are shown in Table 7.1. The fraction of groundwater ranges from more than 50% for the Sacramento, Colorado and Potomac Rivers, to less than 10% for the Kissimmee River, which has also the smallest basin. The residence time of groundwater in the Potomac catchment was 20 years, 14 years for the Colorado catchment, and only 2.5 years for Kissimmee catchment. Both mixing ratio and residence time of water depend on the geological nature of the basin and aquifers. For instance, the Kissimmee watershed consists mainly of karst terrains which promotes a large degree of interaction between surface water and groundwater. On the other hand, when the residence time is short, the tritium content of groundwater is close to that of precipitation, and the mixing proportions obtained from the model will be affected by large uncertainties.

Taylor et al. (1992) investigated the Wairau Plain, South Island, New Zealand. The plain has an area of 170 km² within the 3825 km² watershed. Again, the major sources of recharge to the shallow gravel aquifer are the rivers, while the contribution of precipitation is at most a few percent, as indicated by stable isotopes. Tritium concentrations indicate that the groundwater

Table 7.1. Contribution of groundwater to the total outflow from several river basins in the U.S.A. on the basis of the long-term tritium observations (adapted from Michel, 1992).

River Basin	Surface area, km ²	Groundwater fraction, %	Groundwater age, years
Colorado R. at Cisco, Utah	75.000	60	14
Kissimmee R. before Lake Okeechobee	4.500	6	2,5
Mississippi R. at Anoka, Minnesota	53.000	36	10
Neuse R. at Vanceboro, N.C.	11.000	27	11
Potomac R. at Point of Rocks, Maryland	27.000	54	20
Sacramento R. at Sacramento, CA	77.000	65	10
Susquehanna R. at Harrisburg, PA	70.000	20	10

moves rapidly in the upper gravel aquifer and much more slowly in the less permeable underlying formation. In the latter, the mean transit time of water to reach the confined zone of the aquifer was estimated to be about 10 years. The confined aquifer seems to leak into the shallow aquifer. Tritium data for the period 1968-1989 was used to model the discharge of the Wairau River. In a manner similar to the study of Michel (1992), river water was treated as a two-component system that included recent rain water (age equal to zero) and delayed groundwater with exponential age distribution and a mean age of 8 years.

The meaning of mean residence times, derived from tritium values, for groundwater in large catchments is debatable. Such mean residence times are the result of mixing waters from different aquifers, possibly with largely different mean ages and tritium contents. In theory, there are an infinite set of mixing proportions and groundwater age values that can produce the same tritium content at the outlet of the catchment. The hydrogeological features of the basins, the geochemical characteristics of groundwaters, the application of other isotopes, etc., may help in understanding the true meaning of the apparent groundwater residence times derived from tritium.

More elaborate models have been developed using environmental isotopes and other more conventional data (piezometric levels, chemical composition, river discharge variations, etc.), that better represent the complex aspects of groundwater systems. In the study of the Managvat River by Yurtsever and Payne (1986), already presented in Section 7.4.3 of this chapter, the compartment model tried to differentiate among the various types of groundwater contributing to the river. However, long term tritium data -- particularly those of the sixties and early

seventies when the decrease of thermonuclear tritium was more marked -- are available only in a few cases.

Attempts have been made to use stable isotopes to evaluate the mean residence time of groundwater in small catchments by exploiting the damping of seasonal isotopic variations in streams with respect to those in precipitation (Fritz, 1981). For example, Leopoldo et al. (1992) derived groundwater mean residence times of 4 to 5 months for two small watersheds of 1.6 and 3.3 km² in the State of São Paulo, Brazil. This technique appears applicable only in very small basins that have a uniform distribution and uniform isotopic composition of rains. For large rivers, the damping of seasonal variations is practically complete, unless the relative contribution of the different regions of the basin to the river discharge change with a season.

A compartmental model has been used by Yurtsever and Buapeng (1992) to describe the confined multi-aquifer system of the Bangkok basin (Thailand) located in the Chao-Phraya river drainage. The system includes a shallow aquifer and several confined, hydraulically independent aquifer units. The first three of these units are intensively exploited, and are those that were modeled. The model was calibrated with stable isotopes and ¹⁴C data, using data from wells which exploit only one aquifer. Little use was made of tritium, because it was below or close to the detection limit in all groundwater samples, and only 3 - 5 TU in river water (in 1988-1989). The model provided quantitative estimates of the relative contribution of different sources to aquifer replenishment. The estimates are based on the fact that precipitation (mean $\delta^{18}\text{O} = -6.6\text{‰}$) is generally depleted in heavy isotopes with respect to groundwater ($\delta^{18}\text{O}$ from -6.8 to -4.1 ‰), whereas rivers are enriched ($\delta^{18}\text{O}$ from -4.1 to -1.0 ‰). River water infiltration contributes significantly to recharge only in areas adjacent to the river. Information on flow dynamics and residence-time distribution within each aquifer unit was provided by ¹⁴C, the content of which ranges from 16 to 0 PMC.

7.6.2 Research trends and needs

Most of the catchment studies conducted have used isotope techniques to identify sources of recharge and to estimate water fluxes, within the framework of a multidisciplinary hydrological study. In some cases the isotopic investigations yielded only qualitative results. In other cases, quantitative information was derived (e.g., fraction of water of a given origin in an aquifer or estimates of groundwater fluxes). These research avenues must be pursued to refine and improve the application of isotope techniques in groundwater hydrology. First, research should be addressed towards the refinement of analytical techniques to achieve better precision and lower detection limits of the isotopic species being measured. Second, research should be carried out to further develop the basic geochemistry of those "new" environmental isotopes that have shown promising results in hydrology, but have not yet found wide application. Third, efforts should be made to develop and refine methods of data analysis and interpretation.

Improvement of analytical techniques

Specific attention should be devoted to the measurement of tritium. At present, natural water levels are usually below 20 TU, and most frequently below 10 TU. This low concentration makes it difficult to fully exploit the information which in principle tritium can provide. Use of tritium must be continued in cases that involve young groundwaters because tritium is part of the water molecule, and therefore is an optimal tracer of water.

The minimum detection limit that can be obtained with low level counting techniques is in the range of 0.1-0.2 TU, and efforts should be made by each laboratory to reach this limit. In the future, the ideal solution for tritium analysis is the application of the tritium/helium-3 method (Clarke et al., 1976; Torgersen et al., 1979), allowing a detection limit of at least one order of magnitude lower (see Chapter 9). For instance, Jean-Baptiste et al. (1992) quote a detection limit of 0.003 TU! Unfortunately this method is only recently gaining some popularity in hydrological applications, probably because of the high cost required for the purchase of the mass spectrometer and specific requirements with respect to the sampling technique. As the thermonuclear tritium disappears, the tritium concentration in hydrological systems tends to reach a steady value somewhere between 2 and 10 TU depending on the latitude. This steady-state natural labeling of precipitation with tritium can still be used in hydrological applications provided that sufficiently low detection limits of this isotope in routine analysis are reached.

Stable isotope determinations can also be improved. The errors currently quoted by most laboratories are 0.1 ‰ for the $^{18}\text{O}/^{16}\text{O}$ ratio and 1‰ for the D/H ratio, but they can be reduced respectively to 0.02 and 0.2‰, as quoted by laboratories working in isotope oceanography. Modern mass spectrometers can reach these limits, but refinements are necessary in sample preparation methods. With the analytical errors quoted above, it will be possible to better define the isotopic signature of groundwater bodies, to determine small differences in the isotopic compositions among them, and to obtain a more detailed picture of their interrelations.

Automation of stable isotope determinations in water samples is now common for the $^{18}\text{O}/^{16}\text{O}$ ratio, and becoming a routine technique for the D/H ratio (Horita, 1988; Coplen et al., 1991). Automation is needed to obtain a high throughput of stable isotope measurements. In fact, stable isotopes are and most probably will remain the main isotopic tool in hydrology, and the possibility of analyzing a large number of samples is essential especially in catchment investigations. An enhanced analytical precision for tritium and stable isotopes, coupled with a high analytical throughput, implies a different sampling strategy with respect to that usually adopted, with a much better coverage of the area under study, and a selection of the sampling points that takes into account the possibility of determining small but hydrologically significant isotopic differences. There are already examples in literature of this approach (Davisson and Criss, 1996).

The application of the accelerator mass spectrometry method (AMS) in the determination of ^{14}C concentration does not yet improve the analytical precision with respect to the usual low level counting technique. Nevertheless, sampling for AMS ^{14}C analysis is simpler so more samples could be collected. It is doubtful that an increased precision of ^{14}C measurements, although desirable, would be really beneficial in groundwater studies. In fact, the limitations of the method are due mainly to the geochemical interactions of dissolved carbonate species with the aquifer matrix, the interpretation of which remains complex. For this reason, the ^{14}C determination on dissolved organic carbon (DOC) in groundwater, which appear free from geochemical interactions, may be the most promising development of ^{14}C application (Wassenaar et al., 1992).

Less commonly used environmental isotopes

Environmental isotopes other than those mainly discussed in this chapter (hydrogen and oxygen stable isotopes, tritium, ^{14}C and carbon-13), and sulfur (Chapter 15) and nitrogen isotopes (Chapter 16), are used less in groundwater hydrology. "New" isotopic tools that appear

particularly promising in groundwater studies include the stable isotope ratios $^{11}\text{B}/^{10}\text{B}$, $^{37}\text{Cl}/^{35}\text{Cl}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and the radioactive isotopes for groundwater dating: ^{36}Cl and ^{129}I . The geochemistry of these and other less-used isotopes in catchments is discussed in Chapters 8, 9, 18, and 20.

Development and refinement of data interpretation methods

The most fruitful and useful investigations are those in which quantitative results are achieved. Therefore the quantitative aspects of isotopic investigations need to be strengthened, and the most efficient tools to attain this goal are models of catchments based on hydrodynamical, hydrogeological and geochemical data, in addition to isotopic data. Some examples of hydrological model formulation at the watershed scale were given in this chapter; continuous and rapid progress in this field is expected.

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Chapter 8

Lithogenic and Cosmogenic Tracers in Catchment Hydrology

Gregory J. Nimz

8.1 Introduction

A variety of physical processes affect solute concentrations within catchment waters. The isotopic compositions of the solutes can indicate which processes have determined the observed concentrations. These processes together constitute the physical history of the water. Many solutes in natural waters are derived from the interaction between the water and the rock and/or soil within the system -- these are termed "lithogenic" solutes. The isotopic compositions of these solutes provide information regarding rock-water interactions. Many other solutes have their isotopic compositions determined both *within* and *outside* of the catchment - i.e., in addition to being derived from catchment rock and soil, they are solutes that are also transported into the catchment. Important members of this group include solutes that have isotopic compositions produced by atomic particle interactions with other nuclides. The source of the atomic particles can be cosmic radiation (producing "cosmogenic" nuclides in the atmosphere and land surface), anthropogenic nuclear reactions (producing "thermonuclear" nuclides), or radioactive and fission decay of naturally-occurring elements, principally ^{238}U (producing "in-situ" lithogenic nuclides in the deep subsurface). Current language usage often combines all of the atomic particle-produced nuclides under the heading "cosmogenic nuclides"; for simplicity we will often follow that usage here, although always indicating which variety is being discussed. This chapter addresses the processes that affect the lithogenic and cosmogenic solute concentrations in catchment waters, and how the isotopic compositions of the solutes can be used in integrative ways to identify these processes, thereby revealing the physical history of the water within a catchment system.

The concept of a "system" is important in catchment hydrology (Chapter 1). A catchment is the smallest landscape unit that can both participate in all of the aspects of the hydrologic cycle and also be treated as a mostly closed *system* for mass balance considerations. It is the near closure of the system that permits well-constrained chemical mass balance calculations to be made. These calculations generally focus on lithogenic solutes, and therefore in our discussions of lithogenic nuclides in the chapter, the concept of chemical mass balance in a nearly closed system will play an important role. Examination of the isotopic compositions of solutes provides a better understanding of the variety of processes controlling mass balance. It is with this approach that we examine the variety of processes occurring within the catchment system, such as weathering and soil production, generation of stormflow and streamflow (hydrograph separation), movement of soil pore water, groundwater flow, and the overall processes involved with basinal water balance.

In this chapter, the term "nuclide" will be used when referring to a nuclear species that contains a particular number of protons and neutrons. The term is not specific to any element. The term "isotope" will be used to distinguish nuclear species of a given element (atoms with the same number of protons). That is to say, there are many *nuclides* in nature - for example, ^{36}Cl , ^{87}Sr , ^{238}U ; the element Sr has four naturally-occurring *isotopes* - ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr .

This chapter will first discuss the general principles that underlie the study of lithogenic and cosmogenic nuclides in hydrology, and provide references to some of the more important studies applying these principles and nuclides. We then turn to a discussion of their specific applications in catchment-scale systems. The final section of this chapter discusses new directions in the application of lithogenic and cosmogenic nuclides to catchment hydrology, with some thoughts concerning possible applications that are currently unexplored.

8.2 Processes that Affect Lithogenic and Cosmogenic Isotopic Compositions in Hydrologic Systems

8.2.1 *Lithogenic and cosmogenic solutes used in hydrologic analysis*

Lithogenic solutes that have isotopic compositions useful in hydrology include: 1) those that have varying isotopic ratios due to radioactive decay of other nuclides: Sr, Pb, Nd, and U-decay series elements; 2) those that have varying isotopic ratios due to fractionation by natural processes: Li, B, C, S, Cl (^{35}Cl , ^{37}Cl), and perhaps Fe (hydrogen and oxygen are also in this group, although they are not "solute"); and 3) those that have varying isotopic ratios due to particle-induced changes in the nucleus of the atom: Cl, Ca, Ar, and I. Cosmogenic solutes available for hydrologic studies include ^7Be , ^{10}Be , ^{14}C , ^{22}Na , ^{24}Na , ^{36}Cl , ^{39}Ar , ^{41}Ca , and ^{129}I . Many of these also have a lithogenic origin ("in-situ" production), and so are also listed with the lithogenic solutes. In this chapter we will discuss the isotopes of Li, Be, B, Na, Cl, Ca, Sr, I, Nd, Pb, as well as the lithogenic aspects of the U-decay series (the $^{234}\text{U}/^{238}\text{U}$ ratios). Because the isotopes of Li, Be, B, Na, Ca, stable Cl, and Nd have only recently been used in hydrology, they will be discussed under the heading "New Directions" in catchment hydrologic studies.

8.2.2 *Origin of lithogenic nuclides in natural waters: mineral reactions*

Catchment water originating as precipitation is dilute to the extent that it is undersaturated with respect to the minerals that make up the rock and soil. Under these unsaturated conditions, the minerals begin to react with the water until saturation is reached. Often, when several minerals are simultaneously reacting, the water will become saturated in minerals other than those dissolving. The saturated phases will likely precipitate from the water, leading to decreased saturation of those phases originally reacting and thereby continuing the dissolution process.

Two approaches are commonly used to assess mineral-water reactions: the "mass-balance" approach, and the "thermodynamic" or "reaction-path" approach. The mass balance approach models the reactions in the system on the basis of observed minerals and measured water solute concentrations. Garrels and MacKenzie (1967) were the first to make rigorous use of this approach, and it has been used often since that time (Cleaves et al., 1970; Miller and Drever,

1977a; Plummer and Back, 1980; Paces, 1983; Drever and Hurcomb, 1986). Garrels and MacKenzie were able to quantitatively demonstrate that solutes in groundwater within granitic rocks in the Sierra Nevada mountains were derived from reactions involving the major mineral phases of the granitic rocks, plagioclase, biotite, and alkali feldspar. Kaolinite and smectite, commonly observed "weathering" minerals, were products in the reactions.

The reaction-path approach models observed differences in solute concentrations within groundwaters on the basis of thermodynamic stabilities (Helgeson et al., 1969; Plummer et al., 1983). When the water passes from one lithology to another along a flow path, the reaction-path approach provides a means of calculating the water-solute-rock reactions that should occur (i.e., that are thermodynamically favored). The mass-balance approach alone cannot make predictions concerning these reactions. In the reaction-path approach, the inferred minerals may not be known to exist in the system (due to, for example, the inability to obtain rock samples from depth), and water samples containing inferred intermediate solute concentrations may not have been collected. This is the typical situation in regional groundwater studies and often makes the reaction-path approach the more useful of the two. However, the two approaches are complementary: the mass-balance approach cannot violate thermodynamic considerations, and the reaction-path approach cannot violate system mass-balance considerations. Further, the mass-balance approach can suggest the reaction equations to be used in ("tested" by) thermodynamic calculations. Whether thermodynamically favored reactions actually occur in a groundwater system can be tested by mass balance calculations involving measured solute concentrations. The most thorough studies combine the two approaches to model the chemical evolution of a groundwater system (e.g., Plummer et al., 1991b).

8.2.3 *Origin of lithogenic nuclides in natural waters: trace element exchange*

Most of the nuclides of interest in catchment hydrology are isotopes of elements that occur in trace concentrations in the minerals within the system, and consequently within the waters of the system as well. Neither the mass-balance nor the reaction-path approaches are able to completely characterize the solute concentrations of trace elements. This is primarily because both approaches focus on stoichiometric mineral reactions, while trace element concentrations are not primarily controlled by the stoichiometry of the minerals within the system. Trace elements can be considered to be in "solution" within the crystal lattice, and therefore to exhibit Henry's Law behavior. They often reside within the crystal lattice in sites where "Pauling's Rules" are violated (Pauling, 1960), leading to local charge imbalances or to local structural defects in the crystal lattice. This permits them to be easily replaced by other ions. The behavior of trace elements in hydrologic systems must therefore be treated differently from the behavior of elements that are stoichiometric constituents of the common minerals.

There are five predominant mechanisms by which trace element concentrations can vary within a mineral-water system: 1) co-precipitation, in which the trace element is incorporated into a precipitating mineral (as Sr is incorporated into calcite); 2) dissolution (or "co-dissolution", a term rarely used), in which a trace element is dissolved into water during the dissolution of a mineral phase (the reverse process to co-precipitation); 3) incongruent solution, in which a mineral reaction is occurring whereby one mineral type is altered to produce another mineral type (e.g., kaolinite altering to gibbsite, or calcite altering to dolomite); 4) mineral diffusion, in which the difference in chemical potential between a mineral and a surrounding fluid causes

the trace element to diffuse into or out of the mineral phase (Henry's Law equilibrium), 5) ion exchange, in which ions of one type are replaced by ions of a second type creating greater thermodynamic stability. Ion exchange can occur within the crystal lattice, as when sodium ions replace calcium ions in plagioclase during albitization, or within the ionic layers adsorbed onto mineral surfaces (e.g., in the Stern and Gouy layers in clay minerals). The commonly used term "leaching", when used to describe the removal of trace elements from the mineral phase, is generally referring to one or more of the final three mechanisms.

Each of the five mechanisms can be described using distribution coefficients, which define the relative concentrations of the trace elements in the mineral as compared to the fluid. Theoretically, each trace element would have a distribution coefficient relative to a given mineral phase and fluid composition that would define its equilibrium concentrations during any of the above five processes. For example, during the precipitation of calcite, Sr will substitute for Ca in its crystallographic site at a fixed rate, producing a quantitative distribution of Sr between the calcite and the fluid. Knowing the concentration of Sr within the fluid, one could calculate the equilibrium concentration within the calcite. In actuality, water-rock systems are rarely in equilibrium in nature, and the distribution coefficient can be used only as a guide to the relative concentrations. However, equilibrium is usually closely enough approached that distribution coefficients have been used very productively to model trace element behavior in hydrologic systems (Banner et al., 1989; Banner et al., 1990; Musgrove and Banner, 1993).

While neither the mass-balance nor the reaction-path approaches are directly capable of modeling trace element behavior, both approaches can be useful when considering either co-precipitation, dissolution, or incongruent solution. If it is assumed that a given trace element behaves in a manner similar to a certain key stoichiometric element during these chemical reactions (e.g., Sr behaving like Ca during feldspar weathering), the effect of the reaction on the trace element concentrations within the system can be assessed by examining the behavior of the stoichiometric element. The distribution of the trace element in the system is monitored by the changes in concentration of the stoichiometric element in the fluid. The resulting trace element isotopic compositions can then be estimated based on the redistribution of the trace element in the system. Recent additions to the mass-balance and reaction-path approaches have used similar methods to model isotopic behavior of non-stoichiometric elements in the water-rock reactions (e.g., the mass-balance computer code NETPATH; Plummer et al., 1991a, 1992).

Models for the isotopic evolution of groundwater systems have also been developed that focus specifically on trace element Henry's Law behavior during mineral reactions. Nabelek (1987) developed equations for calculating the changes in trace element concentrations in rock due to infiltration of a fluid. The equations permit the calculation of the concentration of trace elements in the coexisting fluid at any point in the reaction process, provided that the initial and final concentrations in the rock, the initial and final bulk distribution coefficients, and the fluid/rock ratio are known. The approach is similar to that developed by Taylor (1977) for stable isotopes, allowing the Nabelek equations to be extended to stable isotopes. The Nabelek approach is most useful for calculating the fluid/rock ratio in the system. The equations do not explicitly define the associated changes in radiogenic isotopic compositions that occur in conjunction with the changes in elemental concentrations. Instead, these changes would have to be calculated separately based on the elemental exchange between the fluid and rock.

Banner and Hanson (1990) developed equations for calculating simultaneous trace element and isotopic variations (including radiogenic isotopic compositions) during the interaction between minerals and groundwater. These equations incorporate mineral-water distribution coefficients and fractionation factors for stable isotopes. They rely on mass balance in the sense that concentrations within, and masses of, minerals must balance concentrations within, and masses of, groundwater. However, like the Nabelek equations, they are not based on dissolution or reaction equilibria, but on the distribution of trace elements within the system. The methods have been demonstrated to be particularly valuable when used in conjunction with either the mass-balance or reaction-path approaches (Banner et al., 1990; Musgrove and Banner, 1993).

Approaches based primarily on distribution coefficients within the system have the advantage that they can model ion exchange and mineral chemical diffusion reactions as well as mineral precipitation/dissolution reactions. Ion exchange, in particular, can be an important mechanism controlling the behavior of nuclides within groundwater systems. For example, groundwater passing through a clay-rich zone where Ca is exchanged for Na will also lose a significant proportion of its Sr, according to the prevailing distribution coefficient. Subsequently emerging into a zone where Sr is available for solution into the water (by any of the five mechanisms discussed above), the dissolved Sr will now have the isotopic composition of Sr in the new zone. The observed Sr isotopic compositions before the water passed through the clay layer may be very different from those observed after the clay layer. Numerical approaches employing distribution coefficients could model this change in Sr isotopic composition, whereas approaches employing traditional mass balance and reaction path equilibria could not.

8.2.4 Origin of isotopic variations: radiogenic nuclides

Many elements have isotopes that are produced in nature through the radioactive decay of parent nuclides. The daughter nuclides are termed "radiogenic". Although we speak of "parent" and "daughter" nuclides, there is really only one atom involved in the decay: the daughter atom is the same atom as the parent, only after decay it has a different number of neutrons in its nucleus. The change in the number of neutrons can occur in a variety of ways. First, a neutron can "release" an electron, thereby becoming positive in charge, a proton. The number of protons in the nucleus is therefore increased by one. This is called beta decay (an electron is a "beta" particle). Second, a neutron can be formed in the nucleus by the "capture" of an electron by a proton, thereby becoming neutral in charge. The number of protons in the nucleus is therefore decreased by one. This is called beta capture, or electron capture. Third, a nucleus can discharge an alpha particle, which is composed of two neutrons and two protons. This is called alpha decay. These three forms of radioactive decay are by far the most common. Although there are several other forms of decay, none of them produce the nuclides that we will discuss in this chapter. Table 8.1 provides the production mechanism, the half-lives, and the isotopic abundances for the nuclides discussed in this chapter.

Parent nuclides can be fractionated from the isotopes of the daughter element by natural processes at or near the Earth's surface, leading over time to a wide range in daughter isotopic compositions. For example, Rb (^{87}Rb) can be separated from Sr by a number of processes, including crystal formation (magmatic as well as aqueous precipitation), differential mobility during the weathering reactions, and differential adsorption of Sr and Rb cations to solids. This leads to a wide range of Rb/Sr ratios in nature, producing a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Table 8.1: Lithogenic and Cosmogenic Nuclides Useful for Catchment Hydrology

Nuclide	Reported As	Half-life (yrs)	Primary Production Mechanisms	Primary Location of Production for Hydrologic Applications	Typical Values
^3H	(^3H) activity or Tritium Units (TU)	12.3	① $^{14}\text{N} + n \rightarrow ^3\text{H} + ^{12}\text{C}$ ② $^6\text{Li}(n, \alpha)^3\text{H}$ ③ Thermonuclear: various mechanisms	Atmosphere Thermonuclear weapons testing 1950's to 1960's	0-100 TU
$^6,7\text{Li}$	$\delta^6\text{Li}$	Stable	Primordial	Lithosphere (primordial)	-35 to +15
^7Be	(^7Be) activity, or [^7Be]	1.46×10^{-1}	Spallation of O and N	Atmosphere	$\sim 10^4$ atoms/g H_2O
^{10}Be	$^{10}\text{Be}/^9\text{Be}$ or [^{10}Be]	1.5×10^6	① Spallation of O and N in atmosphere ② Spallation of O in lithosphere	Atmosphere Shallow lithosphere (rock outcrop and soils)	$^{10}\text{Be}/^9\text{Be} \sim 10^{-7}$
$^{10,11}\text{B}$	$\delta^{11}\text{B}$	Stable	Primordial	Lithosphere (primordial)	-20 to +50
^{22}Na	(^{22}Na) activity	2 605	Spallation of ^{40}Ar	Atmosphere	~ 0.1 dpm/L H_2O
^{24}Na	(^{24}Na) activity	1.71×10^{-3}	Spallation of ^{40}Ar	Atmosphere	~ 0.3 dpm/L H_2O
$^{35,37}\text{Cl}$	$\delta^{37}\text{Cl}$	Stable	Primordial	Lithosphere (primordial)	-1.5 to +1.0
^{36}Cl	$^{36}\text{Cl}/\text{Cl}$	3.01×10^5	① $^{40}\text{Ar} + p \rightarrow ^{36}\text{Cl} + \alpha$ ② $^{35}\text{Cl}(n, \gamma)^{36}\text{Cl}$	Atmosphere Thermonuclear weapons testing 1950's to 1960's Lithosphere	10^{-15} to 10^{-11}
^{41}Ca	$^{41}\text{Ca}/\text{Ca}$	1.03×10^5	$^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}$	Shallow lithosphere (rock outcrop and soils)	10^{-18} to 10^{-13}
^{87}Sr	$\delta^{87}\text{Sr}$ or $^{87}\text{Sr}/^{86}\text{Sr}$	Stable	β -decay from ^{87}Rb	Lithosphere	$\delta^{87}\text{Sr} = -10$ to $+130$
^{129}I	$^{129}\text{I}/\text{I}$	1.6×10^7	① Spallation from Xe ② Induced (anthropogenic) and natural spontaneous fission of U	Atmosphere Thermonuclear weapons testing 1950's to 1960's Lithosphere	10^{-14} to 10^{-10}
^{143}Nd	ϵ_{Nd}	Stable	α -decay from ^{147}Sm	Lithosphere	-10 to +10
^{206}Pb	$^{206}\text{Pb}/^{204}\text{Pb}$	Stable	^{238}U -series decay chain endproduct	Lithosphere	18 to 20
^{207}Pb	$^{207}\text{Pb}/^{204}\text{Pb}$	Stable	^{235}U -series decay chain endproduct	Lithosphere	14.5 to 16
^{208}Pb	$^{208}\text{Pb}/^{204}\text{Pb}$	Stable	^{232}Th -series decay chain endproduct	Lithosphere	37 to 39
^{230}Th	($^{230}\text{Th}/^{232}\text{Th}$) _{AR}	7.54×10^4	α -decay from ^{234}U	Lithosphere	1 to 1.4
^{234}U	($^{234}\text{U}/^{238}\text{U}$) _{AR}	2.45×10^5	α - and β -decay: $^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234}\text{Pa} \rightarrow ^{234}\text{U}$	Lithosphere	0.8 to 5.0
^{238}U	($^{234}\text{U}/^{238}\text{U}$) _{AR}	4.468×10^9	Primordial	Lithosphere (primordial)	0.8 to 5.0

Notation and definitions:

- 1) Concentration [X]: The abundance of the nuclide per unit substrate, expressed in mass (e.g., $\mu\text{g/g}$) or atoms (e.g., atoms/gram substrate).
- 2) Activity Ratio (X/Y)_{AR}: The ratio of the radioactivity, expressed in units such as disintegrations per minute (dpm), of the numerator nuclide to that of the denominator nuclide.
- 3) Tritium Unit (TU): 1 TU = 1 atom of ^3H per 10^{18} atoms of hydrogen = 7.1 disintegrations per minute (dpm) = 3.2 pCi = 0.12 Bq
- 4) Delta (δ) notation: $\delta = \{ [(a/b)_{\text{sample}} / (a/b)_{\text{standard}}] - 1 \} \times 1000$
 where: for Li: $a = ^6\text{Li}$, $b = ^7\text{Li}$; and the reference standard is NBS L-SVEC
 for B: $a = ^{11}\text{B}$, $b = ^{10}\text{B}$; and the reference standard is NBS SRM951
 for Cl: $a = ^{37}\text{Cl}$, $b = ^{35}\text{Cl}$; and the reference standard is SMOC (standard mean ocean chloride)
 for Sr: $a = ^{87}\text{Sr}$, $b = ^{86}\text{Sr}$, and the reference standard NIST Sr standard NBS987, $^{87}\text{Sr}/^{86}\text{Sr} = 0.71025$
- 5) $\epsilon_{\text{Nd}} = \{ [(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}] - 1 \} \times 10000$
 CHUR = Chondritic Uniform Reservoir = 0.512636

In systems with high Rb/Sr ratios, time-integrated decay of ^{87}Rb to ^{87}Sr will produce high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (^{86}Sr is not radiogenic). Systems with low Rb/Sr ratios will produce low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In the same way, systems with high Sm/Nd ratios produce high $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, systems with high U/Pb ratios produce high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, and systems with high Th/Pb ratios produce high $^{208}\text{Pb}/^{204}\text{Pb}$ ratios. Such radiogenic isotopic variations are ubiquitous in nature and can be used to great advantage in hydrologic studies.

Water masses originating in different lithologies will likely have different Sr, Nd, and Pb isotopic compositions due to isotopic differences in the lithologies themselves. The isotopic compositions of dissolved Sr have been used to distinguish hydrostratigraphic units (Stueber et al., 1987; 1993), to delineate groundwater flow paths and recharge locations (Collerson et al., 1988; Peterman et al., 1992; Bullen et al., 1996), to recognize instances of groundwater mixing and distinguish the mixing endmembers (Stueber et al., 1987; Lowry et al., 1988; Lyons et al., 1995; Katz and Bullen, 1996; Negrel et al., 1997), to recognize paleohydrologic flow systems (Stueber et al., 1993), to track groundwater chemical evolution (McNutt, 1987; Connolly et al., 1990; Bullen et al., 1996; Clow et al., 1997), to determine the genesis of crude oils and oil-field brines (Starinsky et al., 1983a; Nakano et al., 1989), to assess petroleum reservoir connectivity (Smalley et al., 1992), and to identify groundwater contributions in surficial runoff (Aberg, 1995; Blum and Erel, 1995; Clow et al., 1997; Ben Othman et al., 1997). Allegre et al. (1996) combined the use of Sr, Nd, and Pb isotopic compositions to identify the sources of solutes in portions of the Amazon and Congo river basins. Although most of these studies are regional in scope, the principles upon which they are based can also be useful on the catchment scale, as will be discussed below.

8.2.5 Origin of isotopic variations: the mineral weathering sequence

Although many of the uses of lithogenic nuclides in hydrology, such as those just mentioned, are based on differences in whole-rock isotopic compositions, perhaps the most useful characteristic of lithogenic nuclides is that there are significant differences in isotopic compositions between different mineral types within the *same* rock or soil. This is because the ratios between the parent element (e.g., Rb) and the daughter element (e.g., Sr) vary between the mineral phases within the rock or soil. Through geologic time the relative abundances of the daughter nuclides will be different in each mineral phase.

Figure 8.1 demonstrates variations within a granitic rock in strontium isotopic values resulting from inter-mineralic variations in parent/daughter ratios. Biotite will have a Rb/Sr ratio of about 83, alkali feldspar about 1.25, hornblende about 0.30; and plagioclase about 0.03. When the granite formed, the Sr isotopic compositions would be the same in all of the mineral phases because Sr isotopes do not fractionate by magmatic processes and would be homogenized within the magma. After formation of the rock, the Sr isotopic compositions of the mineral phases would begin to change at a rate dependent on the Rb/Sr ratio of the mineral. For a granite that formed 50 Ma ago (Eocene) and began with a $\delta^{87}\text{Sr}$ value of -8.1 throughout the rock, the $\delta^{87}\text{Sr}$ values in the mineral today would be: +232.43 (biotite), -4.48 (alkali feldspar), -7.23 (hornblende), and -8.02 (plagioclase). See Table 8.1, note 2, for an explanation of the " $\delta^{87}\text{Sr}$ " terminology; Sr isotopic compositions have been normalized to the composition of the NIST Sr standard NBS987. Had this same granite instead formed 500 Ma ago (Ordovician), the $\delta^{87}\text{Sr}$ values today would be: +2406 (biotite), +28.12 (alkali feldspar), +0.60 (hornblende),

and -7.28 (plagioclase). The $\delta^{87}\text{Sr}$ value present in ground water associated with these granites could be very different depending on the mineral source of the Sr in solution. The utility of this for hydrology is that not all mineral phases within any rock or soil type weather at the same rate. Some mineral phases contribute solutes early in the weathering process while others persist and contribute solutes very late in the process.

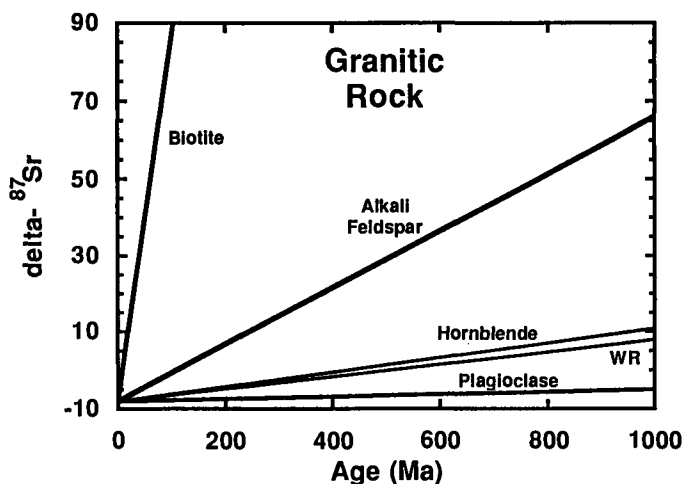


Figure 8.1. The change in Sr isotopic composition with time in minerals of a typical granitic rock. For all minerals and the whole rock (WR), initial (t_0) $\delta^{87}\text{Sr} = -8.1$. The Rb/Sr ratios depicted in this figure are: 83 (biotite), 1.25 (alkali feldspar), 0.30 (hornblende), 0.25 (WR), and 0.08 (plagioclase).

It has long been noted that the susceptibility of a mineral phase to weathering is related to its position in Bowen's Reaction Series (Goldich, 1938). The Reaction Series was devised by Bowen (1928) to represent the approximate crystallization sequence of minerals forming from an evolving magma, beginning with a high-temperature basic magma and resulting in a low-temperature silicic magma (Figure 8.2). Two crystallization series are actually present: the continuous series composed of the plagioclase compositions (anorthite to albite), and the discontinuous series composed of mafic minerals that have increasingly more complex crystal structures (olivine, a nesosilicate, to biotite, a phyllosilicate). The final steps of the Reaction Series involve alkali feldspar and quartz. During the weathering process, those mineral phases that form early in the Reaction Series, (e.g., olivine and anorthite) weather more readily than those phases that form late in the Series (e.g., quartz). In general, the discontinuous series weathers more readily than the continuous series (feldspars). It is commonly observed that during the weathering of feldspars, the plagioclase feldspars are much less resistant than the alkali feldspars. For relatively pure sandstones that lack easily weathered minerals, the number of weathering cycles experienced by the minerals, the "maturity" of the rock, is commonly judged first by the amount of (lack of) plagioclase, and then by the ratio of alkali feldspar to quartz (Pettijohn, 1975, p. 212). Thus, Bowen's Reaction Series can also be regarded as a weathering reaction series. A more elegant treatment of the weathering sequence as it relates to Bowen's Reaction Series is given by Curtis (1976), where it is demonstrated that the free-energy changes of the weathering reactions are more negative (more thermodynamically favored) for the mineral phases early in the Series as opposed to those late in the Series.

For the granitic rock depicted in Figure 8.1, the initial mineral phases that react during weathering will be those of the discontinuous series, hornblende and biotite. For a rock older than a few tens of millions of years, the hornblende $\delta^{87}\text{Sr}$ value will be similar to the whole rock value, but the biotite values will be extremely high (Figure 8.1). The initial Sr isotopic compositions released during weathering will be dominated by biotite compositions. As weathering proceeds, the amount of biotite remaining will decrease and the weathering of plagioclase will begin to dominate the Sr budget (and the Sr isotopic composition). Higher degrees of weathering will deplete plagioclase, with the result that the Sr budget becomes dominated by alkali feldspar. This sequence would characterize the evolution of a regolith soil derived from the granite. Through the weathering cycle the isotopic composition of the released Sr will change from high values (from biotite) to low values (from plagioclase) to moderate values (from alkali feldspar). This progression can be regarded not only as a temporal sequence, but also as a sequence occurring within the soil column. The isotopic compositions found in the upper, most weathered portion of the column will be different from those found in lower portions of the column. Potential uses of this isotope "stratigraphy" in catchment hydrology, as well as notable unexpected variations from it (Bullen et al., 1996; 1997) will be discussed later in this chapter.

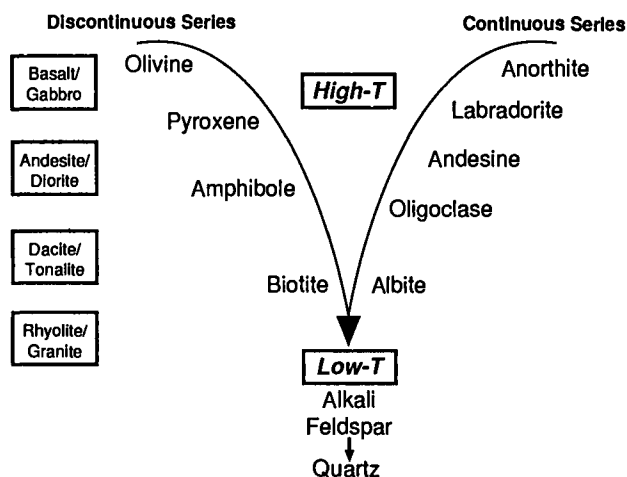


Figure 8.2. Bowen's Reaction Series. Crystallization of minerals in an evolving magma generally follows two simultaneous paths, represented by the Continuous Series (plagioclase feldspars) and the Discontinuous Series (olivine through biotite). Crystallization of alkali feldspars and quartz occurs at low-temperatures in more evolved, silicic, magmas. Magma types resulting from crystallization at each interval are represented in the small boxes on the left portion of the figure. The minerals highest in the Reaction Series (e.g., olivine and anorthite) are more susceptible to weathering than those lower in the Reaction Series (e.g., quartz).

8.2.6 Origin of isotopic variations: uranium isotopes and alpha recoil

Uranium-238 undergoes radioactive decay to produce ^{234}U through two very short-lived intermediate decays (^{234}Th with a half-life of about 24 days, and ^{234}Pa with a half-life of about one minute). Uranium-234 is also radioactive and decays to ^{230}Th (the half-life of ^{234}U is about

245,000 years). Over geologic time, an equilibrium, termed "secular equilibrium", is established between the production of ^{234}U from ^{238}U and the decay of ^{234}U . The uranium isotopes in any closed system will be in secular equilibrium after about five half-lives of ^{234}U (about 1.25 million years). The equilibrium is generally discussed in terms of the activity ratio between the isotopes. The "activity" of a radionuclide is the average number of atoms undergoing radioactive decay per unit time (for example, 10 decays/minute). For two nuclides to be in secular equilibrium, the ratio of their activities must equal one; that is, for a given amount of time, as many atoms are being produced as are decaying.

It has long been observed that the two uranium isotopes are seldom in secular equilibrium in natural waters (Cherdyntsev et al., 1955). The activity ratio of ^{234}U to ^{238}U is generally greater than one, often substantially greater. The cause of this is not entirely clear, although it is very likely a function of the alpha decay process that produces ^{234}Th . The alpha particle is ejected from the nucleus with sufficient energy that the recoil of the atom (72 MeV recoil energy) causes damage to the crystal lattice, leaving a path or track along its trajectory. The length of the typical track will vary with the density of the enclosing material, but has been estimated in geological materials to be between 10 nm (Huang et al., 1967) and 55 nm (Kigoshi, 1971), perhaps typically about 30 nm (Andrews et al., 1982). The damage to the crystal provides an area of weakness from which the atom can be more easily leached by water (Fleischer, 1988). This may account for some of the increase in ^{234}U relative to ^{238}U in the water, particularly in newly-recharged water with low uranium concentrations (Andrews and Kay, 1978). Another important mechanism for increasing the activity ratio is the recoil ejection of ^{234}Th from the crystal directly into the water. Although this would require the decaying ^{238}U atom to be within 10-55 nm of the edge of the crystal, it can be easily demonstrated that typical uranium concentrations in rocks would provide sufficient ^{238}U atoms at this depth to lead to the observed disequilibrium values (Fleischer, 1982; 1983; Andrews et al., 1982).

Another important consideration for $^{234}\text{U}/^{238}\text{U}$ disequilibrium is the redox condition of the groundwater. Uranium is moderately soluble under oxidizing conditions, existing in the UO_2^{+2} state (Langmuir, 1978). Under reducing conditions uranium is highly insoluble, and will tend not to enter into groundwater through leaching or dissolution processes. Enhanced leaching of ^{234}U from damaged sites will not be a mechanism for increasing the $^{234}\text{U}/^{238}\text{U}$ ratio in the water. Uranium-234 may still enter by direct recoil ejection; however, most of the ejected atoms will sorb onto mineral surfaces and not continue in solution (Andrews et al., 1982). This process is facilitated by the fact that the ejected atom is actually ^{234}Th rather than ^{234}U - thorium being even more insoluble than uranium - so that the ejected atom is quickly sited onto the mineral surface. Unless the concentration of uranium in the mineral phase (or sorbed on mineral surfaces in contact with the water) is extremely high in comparison with the concentration in the water, the dissolved ^{234}U undergoing radioactive decay is not replenished through recoil (Kronfeld and Adams, 1974; Andrews et al., 1982). The $^{234}\text{U}/^{238}\text{U}$ ratio will gradually decrease as a function of time. Under oxidizing conditions, therefore, the $^{234}\text{U}/^{238}\text{U}$ ratios in groundwater would be expected to increase with time, whereas under reducing conditions the ratio would be expected to decrease with time. The dependence of this decrease on the half-life of ^{234}U has made the uranium system attractive for groundwater dating purposes. While the many geochemical complications in the behavior of uranium has often led to unsatisfactory results (Latham and Schwarcz, 1989), it nonetheless appears that if the local hydrogeology and the behavior of uranium within the system are well enough characterized, uranium activity ratios can be used to place constraints on the age of the groundwater (Andrews and Kay, 1983; Fröhlich and Gellerman, 1987; Ivanovich et al., 1991).

The observed variations in uranium activity ratios have been used for many purposes in hydrology. They have been used to differentiate groundwater bodies and identify locations of interconnectivity (Guttman and Kronfeld, 1982; Ivanovich and Alexander, 1987), to place constraints on groundwater flow paths and flow rates (Kronfeld et al., 1979; Ivanovich et al., 1991), to assess groundwater mixing, endmember compositions, and mixing volumes (Ivanovich and Alexander, 1987; Banner et al., 1990), to identify instances of pore-water mixing (Andrews and Kay, 1982; Cuttall et al., 1986), to quantitatively assess water-rock chemical interaction (Andrews and Kay, 1983; Banner et al., 1990), to examine variations in mobility of actinides in natural environments (Krishnaswami et al., 1982; Latham and Schwarcz, 1989; Guthrie, 1991), to determine the geochemistry of uranium in particular hydrogeologic environments (Kraemer and Kharaka, 1986), and to aid in prospecting for uranium mineral deposits (Osmond et al., 1983).

8.2.7 Origin of isotopic variations: cosmogenic nuclides

In addition to changing the configuration of the nucleus by means of radioactive decay, atoms can undergo similar changes due to bombardment by nuclear particles (protons, neutrons, alpha particles). The bombardment causes a change in the nuclear and electronic configuration of the atom, producing a nuclide of another variety. There are three primary sources for the nuclear particles: cosmic radiation, U and Th within the Earth (neutron radiation due to both alpha decay and the spontaneous fission of uranium), and radiation released by nuclear weapons detonation. Nuclides produced from radiation from all three sources have important applications within hydrology.

Cosmic radiation source

Most of the cosmic radiation on Earth originates in the sun, although a significant amount also comes from outside of the solar system. The radiation particles are primarily protons and alpha particles, but their interactions with atoms in the Earth's atmosphere produce neutrons which also are capable of bombarding other atoms and producing new nuclides. The nuclides produced from cosmic radiation are termed "cosmogenic" nuclides, and are created either within the Earth's atmosphere or within minerals on the Earth's surface. Atmospheric interactions produce ^3H , ^7Be , ^{10}Be and ^{14}C (produced primarily from oxygen and nitrogen), ^{32}Si and ^{36}Cl (primarily from argon), ^{41}Ca and ^{81}Kr (primarily from stable krypton) and ^{129}I (primarily from xenon). Surface interactions produce ^3H , ^{10}Be , and ^{14}C (from oxygen), as well as ^{36}Cl (from ^{35}Cl) and ^{41}Ca (from ^{40}Ca). For all of these nuclides, surface production is very minor compared to atmospheric production, and it is the atmospheric component that is important in hydrology.

U and Th source

There are two mechanisms by which U and Th become sources for neutron radiation: ejection of alpha particles during radioactive decay, and ejection of neutrons during spontaneous fission of uranium. The alpha particle mechanism is indirect. The neutron radiation is produced when the alpha particles bombard lighter elements, such as aluminum and sodium. This causes a release of secondary neutrons through (α, n) reactions. Although silicon and oxygen are not highly susceptible to (α, n) reactions, their great abundance within the lithosphere makes them the most significant sources of neutron radiation by this mechanism.

Spontaneous fission is the natural process whereby an atom splits into two atoms of smaller mass, each about half the mass of the original atom. It is this process that, when artificially induced, produces the release of energy in atomic weapons. When fission occurs, neutrons are freed from the nucleus. These bombard other elements in rock or water, such as oxygen and silicon, producing even more free neutrons. In the natural environment, most of the effects of spontaneous fission are due to the most abundant uranium isotope, ^{238}U . The half-life for natural spontaneous fission decay of ^{238}U is ~6 orders of magnitude longer than the half-life for its radioactive decay. For typical rock matrices in the lithosphere, the rate of neutron production due to spontaneous fission of ^{238}U is about 5 or 6 times less than that due to alpha decay.

The neutrons produced by alpha decay or spontaneous fission are then capable of being incorporated into the nucleus of yet other atoms, creating atoms of increased mass (by one unit), i.e., creating a different isotope of that element. This process is termed "neutron activation". In rock and water, ^{36}Cl is produced from ^{35}Cl by this process. Alternatively, the incorporated neutron can "displace" a proton in the nucleus, creating an atom of the same atomic mass, but one unit lower in atomic number - i.e., an element one position lower on the periodic table. In rock and water, ^{39}Ar is produced from ^{39}K by this process. Nuclides produced by these processes are termed "in-situ" lithogenic nuclides.

Anthropogenic thermonuclear source

The third setting for nuclear particle bombardment is a thermonuclear event. The most significant of these for modern hydrologic studies are the atmospheric nuclear weapons tests of the 1950's and 1960's. The "bomb-pulse" hydrologic nuclides produced by particle bombardment include ^3H and ^{14}C (both produced from nitrogen and oxygen in the atmosphere), and ^{36}Cl (produced from ^{35}Cl in seawater). These nuclides were dispersed worldwide and although they are present in very small quantities, are detectable in all modern environments such as young groundwater. The atmospheric concentrations of ^3H , ^{14}C , and ^{36}Cl returned to pre-1950's levels during the 1980's. Groundwater currently being recharged is no longer fingerprinted by these bomb-pulse nuclides.

Commonly, the above three groups of nuclides (true cosmogenic, in-situ lithogenic, and bomb-pulse nuclides) are lumped together and jointly referred to as "cosmogenic nuclides". For simplicity, we will follow that usage as well. Table 8.1 provides the production mechanisms, the half-lives, and typical isotopic abundances for the cosmogenic nuclides of current importance in hydrology.

8.2.8 Origin of isotopic variations: fission products

The atoms of smaller mass resulting from the splitting of the atom during nuclear fission, either natural spontaneous fission of uranium or man-induced thermonuclear events, are another source of isotopic variation in nature today. Most of these "fission products" are nuclides with very short half-lives, but those with long half-lives have become important hydrologic tracers. The fission products resulting from spontaneous fission are termed "in-situ" lithogenic nuclides, just like the nuclides discussed above that result from neutron radiation flux. The fission products of anthropogenic origin are commonly called "bomb-pulse" nuclides, or "thermonuclear" nuclides, again just like those produced by thermonuclear particle bombardment. For hydrologic purposes, the most important fission products are ^{85}Kr and ^{129}I .

Importantly, unlike the bomb-pulse nuclides created by particle bombardment (^3H , ^{14}C , and ^{36}Cl), ^{85}Kr and ^{129}I abundances have not today returned to pre-1950's levels, but rather are still increasing in the environment due to the reprocessing of spent nuclear fuel (Smethie et al., 1992; Ekwurzel et al., 1994; Raisbeck et al., 1995; Wagner et al., 1996).

8.2.9 Hydrologic application of cosmogenic nuclides

Chlorine

The attractiveness of chlorine in hydrologic studies is that it is highly soluble, exists in nature as a conservative non-sorbing anion, does not participate in redox reactions, and has some quickly identifiable sources (e.g., seawater). The abundance of ^{36}Cl is usually reported as the atomic ratio of ^{36}Cl to total chloride in the sample. The ratio is always quite small in natural waters, typical values ranging from 10^{-15} to 10^{-11} . The four orders of magnitude range of $^{36}\text{Cl}/\text{Cl}$ ratios is due to several factors. In-situ lithogenic production will lead to ratios generally between about 10^{-15} and 10^{-13} . Over geologic time an equilibrium will be established between the subsurface in-situ production of ^{36}Cl and its decay (similar to the secular equilibrium of U isotopes discussed above; Andrews et al., 1986). The equilibrium $^{36}\text{Cl}/\text{Cl}$ value will depend on the rate of production of ^{36}Cl , which is a function of the U and Th concentrations in the aquifer. As Table 8.2 indicates, basalts, sandstones, and limestones typically have very low U contents, while silicic granitic rocks and shales have higher concentrations. Equilibrium $^{36}\text{Cl}/\text{Cl}$ values in sandstones and limestones should be on the order of $10\text{-}20 \times 10^{-15}$, whereas granitic rocks and shales will have values from about $30\text{-}100 \times 10^{-15}$ (Lehmann and Loosli, 1991). Precipitation input of cosmogenic ^{36}Cl to natural waters will lead to $^{36}\text{Cl}/\text{Cl}$ ratios as high as 10^{-12} . The ratio will vary as a function of distance from the oceans. The added chloride input from the ocean, which has a very low $^{36}\text{Cl}/\text{Cl}$ ratio, leads to low ratios along the coasts ($20\text{-}80 \times 10^{-15}$), while North American mid-continent values will exceed 500×10^{-15} (Bentley et al., 1986a). Ratios higher than 10^{-12} in natural waters are generally believed to indicate the presence of thermonuclear ^{36}Cl , where peak global values during the era of sea-level atmospheric nuclear weapons detonation were on the order of 10^{-11} .

However, ratios as high as $\sim 1500 \times 10^{-15}$ have been measured in material taken from several fossil rat middens believed to range between 10-30Ka based on radiocarbon dating (Phillips et al., 1997). These values are 2-3 times the expected atmospheric $^{36}\text{Cl}/\text{Cl}$ value based on Bentley et al. (1986a), and are interpreted by Phillips et al. to indicate increased cosmogenic production of ^{36}Cl (i.e., greater radiation flux) during that time period. Other indications of increased radiation flux, for example elevated ^{14}C or ^{10}Be concentrations, have not been observed in the geologic record for this time period. Thus, the reason for the observed higher $^{36}\text{Cl}/\text{Cl}$ ratios in the middens is still unresolved.

The half-life of ^{36}Cl is approximately 301,000 years. Attempts have been made to date old groundwater in confined aquifers through an interpretation of the affect of radioactive decay on the observed $^{36}\text{Cl}/\text{Cl}$ ratios (Bentley et al., 1986b; Phillips et al., 1986; Nolte et al., 1991). There are several obstacles to overcome. An assessment must be made of the subsurface addition of stable Cl isotopes to the water by either chemical reactions with rock, ion filtration (Phillips et al., 1986), or mixing with higher chloride waters; such additions can substantially change the $^{36}\text{Cl}/\text{Cl}$ ratio. An age interpretation also requires knowledge of the initial (t_0) $^{36}\text{Cl}/\text{Cl}$ ratio. The wide range in possible precipitation input values ($20\text{-}500 \times 10^{-15}$) makes t_0 estimates

Table 8.2: Typical Abundances of Elements Having Lithogenic or Cosmogenic Isotopes

Element	Upper Continental Crust	Silicic Granitoid	Basalt/ Gabbro	Shale	Terrestrial Sandstone	Marine Limestone	Seawater	River Water	Rain	Ground Water	Brines
Li	20	30	17	46	15	5.2	0.17	0.003	very low	<0.5	194
Be	3	3	1	2.1	0.26	0.18	6.0E-07	1.0E-05	1.0E-13	<0.05	--
B	15	10	5	194	90	16	4.5	0.01	--	<3	257
Al	80400	78326	95000	80100	32100	8970	0.001	0.05	0.01	<1.5	--
Cl	150	160	150	170	15	305	19000	7.8	<8	<380	151000
Ca	30000	27516	76000	22500	22400	272000	410	15	<1.4	<140	27400
Rb	112	150	130	243	197	46	0.12	0.001	--	<0.1	--
Sr	350	250	465	290	28	617	8	0.07	<0.005	<200	400 to 3480
I	1	0.5	0.5	3.8	4.4	1.6	0.06	0.007	<0.003	<0.3	48
Nd	26	23	25	18	24	8	2.3E-06	3.8E-05	very low	<0.05	--
Pb	20	17	6	20	14	16	3.0E-05	0.001	<0.035	<0.1	--
Th	10.7	14	1	13	3.9	0.2	5.0E-07	<1.0E-10	very low	<1.0E-4	--
U	2.8	3	2.7	4.1	1	2.2	0.003	4.0E-05	--	<10	--
Sources:	[1]	[1] [2]	[2] [3]	[2] [4]	[4]	[4]	[4] [5]	[1]	[2] [4]	[4] [7]	[4] [6]

Data sources: [1] Taylor and McClennan (1985); [2] Drever (1988); [3] Wedepohl (1969); [4] Hem (1989); [5] Turekian (1968); [6] Williams and McKibben (1989); [7] Various, from references in the text of this chapter

All values in $\mu\text{g/g}$ (ppm)

very problematic (Andrews and Fontes, 1993). In-situ production of ^{36}Cl must also be taken into account for the age interpretation, and requires an adequate assessment of the U and Th concentrations in the aquifer. Because t_p (precipitation) values are in the $20\text{--}500 \times 10^{15}$ range, in-situ production values in the 50×10^{15} range can have a significant affect on the observed $^{36}\text{Cl}/\text{Cl}$ ratios. Each of these obstacles can be quantified: addition of Cl can be monitored by directly measuring the Cl and other ionic concentrations in the water, in-situ production can be estimated after a measurement of aquifer U and Th concentrations, and t_p values can be estimated based on measured present-day precipitation values for the region. For cases where the attempt is to determine the water transit time between two sampling locations, rather than the absolute age of the water, the t_p value is simply the value measured at the upgradient location.

At the other end of the age spectrum, the presence of thermonuclear ^{36}Cl in groundwaters clearly indicates a young age for the water or, in a case of groundwater mixing, at least some significant portion of that water (Fabryka-Martin et al., 1991; Caffee et al., 1992; Hudson et al., 1993; Nimz et al., 1993). Thermonuclear ^{36}Cl will become increasingly important as an indicator of young water, as the thermonuclear ^3H which is present today in groundwater decays to background levels (by about 5 ^3H half-lives of the peak in atmospheric nuclear testing of the 1960's, or about the year 2025).

Cosmogenic, thermonuclear, and in-situ lithogenic ^{36}Cl have been used in a variety of hydrologic studies since the early 1980's. Chlorine-36 has been used to discriminate groundwater bodies and assess degrees of mixing (Phillips et al., 1984; Andrews et al., 1986; Dowgiallo et al., 1990; Torgersen et al., 1991), to determine groundwater flow paths (Andrews et al., 1986; Bentley et al., 1986a; Nolte et al., 1991; Beasley et al., 1993), to place constraints on groundwater age (Bentley et al., 1986b; Phillips et al., 1986; Fabryka-Martin et al., 1991; Nolte et al., 1991; Torgersen et al., 1991; Fehn et al., 1992; Purdy et al., 1996; Nimz et al., 1997), to identify very young - bomb-pulse - groundwater (Bentley et al., 1982; Habersack et al., 1986; Purdy et al., 1987), to determine instances of vertical recharge along a flow path (Purdy et al., 1987), to identify sources of chlorinity and salinity (Andrews et al., 1986; 1989; Paul et al., 1986; Phillips et al., 1986; Hedenquist et al., 1990; Yechieli et al., 1996; Balderer and Synal, 1997; Nimz et al., 1997), to identify sources of salt deposits (Magaritz et al., 1986; Paul et al., 1986), to estimate infiltration amounts and depths in arid regions (Norris et al., 1987; Phillips et al., 1988; Cecil et al., 1992; Cook et al., 1994), to make quantitative estimates of evaporation and evapotranspiration (Paul et al., 1986; Magaritz et al., 1990), and to investigate paleohydrologic conditions (Jannik et al., 1991; Torgersen et al., 1991; Andrews et al., 1994; Purdy et al., 1996).

Iodine

Iodine-129 is in many ways similar to ^{36}Cl . It is a soluble halogen that is fairly non-reactive, generally exists as a non-sorbing anion in natural waters, and is produced by cosmogenic, thermonuclear, and in-situ reactions. It is usually reported in hydrologic studies as the atomic ratio of ^{129}I to total I (which is virtually all ^{127}I). As is the case with $^{36}\text{Cl}/\text{Cl}$, $^{129}\text{I}/\text{I}$ ratios in nature are quite small, 10^{-14} to 10^{-10} (peak thermonuclear ^{129}I during the 1960's and 1970's reached $\sim 10^{-7}$; Fabryka-Martin et al., 1989). Iodine-129 differs from ^{36}Cl in that its half-life is very long (16 million years), it is highly biophilic, occurs in multiple ionic forms (commonly, I^- and iodate) which have differing chemical behaviors, and presents more problems analytically than ^{36}Cl (Roman and Fabryka-Martin, 1988; Fehn et al., 1987). The latter problem, perhaps more than anything, has led to far fewer ^{129}I studies than ^{36}Cl studies.

Groundwater age dating with ^{129}I faces most of the same obstacles faced by the ^{36}Cl method. A possible exception to this is the determination of t_0 values, since the $^{129}\text{I}/\text{I}$ ratio in the oceans and atmosphere is quite homogeneous due to the long half-life of ^{129}I (Fabryka-Martin et al., 1985). Thermonuclear ^{129}I has disrupted this homogeneity somewhat, particularly near nuclear power plants and production facilities, but for Earth-surface hydrogeological processes (such as recharge) that are older than or geographically removed from this activity, the t_0 input ratio will be approximately 10^{-12} (Fabryka-Martin et al., 1989). In-situ ^{129}I production can be very significant in a number of geologic environments with values that may exceed precipitation input values (for example, $^{129}\text{I}/\text{I}$ equilibrium values in granites will be $\sim 5 \times 10^{-12}$; Fabryka-Martin et al., 1985). Therefore, a careful understanding of the hydrogeology of the system will always be necessary. The subsurface addition of stable iodine (^{127}I) to groundwater is always possible, but since iodine is not an abundant element in most geologic settings, this presents less of a problem than does the addition of stable Cl to ^{36}Cl dating. A more substantial problem is that the long ^{129}I half-life makes it appropriate for dating old systems only. Old groundwaters have experienced a wider variety of hydrogeologic environments and phenomenon than have younger waters. Each of these can add complications to the interpretation of $^{129}\text{I}/\text{I}$ ratios.

Several hydrologic studies have made use of ^{129}I , and these demonstrate that if one is cautious concerning potential complications, $^{129}\text{I}/\text{I}$ ratios can be very useful. Iodine-129 has been shown to have value in placing constraints on groundwater age (Fabryka-Martin et al., 1985; 1989; Fehn et al., 1992; Moran et al., 1993), determining groundwater migration paths (Fabryka-Martin et al., 1988), identifying sources of salinity in groundwater and sources of salts in evaporite deposits (Fabryka-Martin et al., 1985; Fabryka-Martin et al., 1991; Fehn et al., 1992), estimating weathering rates and the behavior of iodine and uranium during weathering (Fabryka-Martin et al., 1988), and identifying the source geologic formation for hydrocarbons (Fabryka-Martin et al., 1985). Despite analytical difficulty and care required for interpretation of data, the promise demonstrated by these studies, along with the constancy in the atmospheric input ratio, the significant isotopic differences in existing in-situ reservoirs, and the hydrophilic and biophilic behaviors of iodine, the hydrologic uses of ^{129}I appear to be largely untapped.

8.3 The Application of Lithogenic and Cosmogenic Nuclides to Catchment Hydrology

Relatively few catchment-scale hydrologic studies have been published that employ lithogenic or cosmogenic nuclides (other than ^3H and ^{14}C). Those that have been published show interesting and valuable results, and many of these will be reviewed in the following sections. The intent of this section is not merely to provide a literature review. Instead, this section is focused on ways in which lithogenic and cosmogenic nuclides can be useful for understanding catchments. The processes occurring in a catchment system have traditionally been divided into a number of discrete sub-processes, each of which have measurable parameters that can be used to characterize catchment hydrology (Figure 8.3). The sub-processes together represent the possible paths of water and solutes as they are input into the system (precipitation, dry deposition, throughfall, stemflow), make their way through the system (overland flow, interflow, throughflow, subsurface flow), and ultimately leave the system (evaporation, transpiration, leakage, streamflow). This sub-division of processes will be used in the following discussion of lithogenic and cosmogenic nuclides in catchment hydrology.

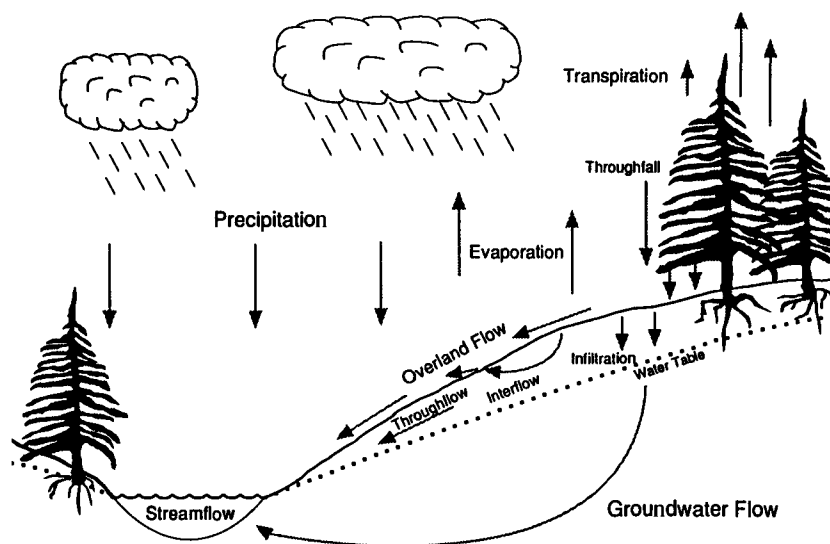


Figure 8.3. Catchment hydrologic processes composing a local hydrologic cycle. Each of these processes can be assessed by lithogenic and cosmogenic nuclides.

8.3.1 Input: precipitation, dry deposition, and throughfall

A significant quantity of solutes are imported into a catchment basin through aerosols, rain, and snow. The amount imported can be a surprisingly high amount of the total elemental budget for catchment waters. For example, Aberg et al. (1989) reported rainfall Sr concentrations of $1.8 \mu\text{g/L}$ in an area that received 900 mm of rain per year. This totals 16.2 g/ha of Sr per year. If the chemical denudation rate of this area is the estimated average rate for North America, $3.3 \times 10^5 \text{ g/ha/yr}$ (Garrels and MacKenzie, 1971), and the Sr concentration of the removed rock is the average for granitic rocks, $250 \mu\text{g/g}$ (Table 8.2), then the amount of Sr denuded from the basin would be 82.5 g/ha/yr . The incoming Sr from precipitation makes up 16.4% of all of the "free" Sr within the drainage area per year. Strontium added to the basin by aerosols (dry deposition) would increase the input amounts, possibly substantially. Clow et al. (1997) estimated that 26% ($\pm 7\%$) of the Ca in stream water within an alpine watershed in Colorado was derived from the atmosphere. The estimate was based on mixing calculations using Sr isotopic ratios, assuming Sr as an analogue to Ca. These studies make it obvious that the use of Sr isotopes for assessing hydrologic processes must take into account the amount of Sr input into the system under investigation, and the isotopic composition of that Sr. This would be the case for any solute present in meaningful quantities in precipitation and dry deposition, which excludes very few lithogenic nuclides. Notably, there would be very little Th input into the system relative to other lithogenic elements (Table 8.2); this suggests that the rainfall fractionation of Th from other lithogenic elements might be useful in elucidating processes that are closely tied with new rainfall, such as stormflow hydrograph separation.

The importance of aerosol components was demonstrated by Starinsky et al. (1983b). They sampled groundwater from wells and springs in a western coastal area of the Sinai peninsula. The Ca/Sr ratio of the water was much too low for the Sr to have been derived from the alluvial aquifer material. The isotopic composition of the Sr ($\delta^{87}\text{Sr} \approx -1.76$) was too dissimilar to the bedrock in the region ($\delta^{87}\text{Sr} \approx +13.7$) for it to have been the Sr source. The closest appropriate sources for the Sr were aragonite beach sands and sabkha deposits of the Sinai coastal plain, about 30 kilometers away. These deposits have the isotopic composition of the ocean ($\delta^{87}\text{Sr} = -1.48$), which is similar to the Sr in the groundwater samples. Starinsky et al. (1983b) concluded that the Sr in the groundwater reflected deposition of aerosols from the coast.

The isotopic composition of Sr has also been used to determine the origin of pedogenic carbonates in desert soils (caliche). There has long been a question of whether the Ca in caliche is derived from in-situ weathering or aeolian input. Because of the close similarity in geochemical behavior between Ca and Sr, the behavior of Sr can be used as an analog for Ca. Capo and Chadwick (1993) examined the Sr isotopic composition of rain, dust, and acetic acid leachates from the A, B and pedogenic carbonate horizons from a desert soil in New Mexico. The weak acid leach would dissolve carbonate material but leave silicate minerals as a "residue". The soil acetic acid leachate had $\delta^{87}\text{Sr}$ values of about -1.76, which is very similar to the local rain and dust values of about -1.90. The silicate fraction on the other hand had $\delta^{87}\text{Sr}$ values that ranged from +4.15 to +9.92. This strongly indicates that the Sr originated outside of the system and was input through rain and dust. It is not unreasonable, therefore, to conclude that by analogy much of the Ca in the caliche is also from external sources.

In a study combining elements from both of the above studies, Quade et al. (1995) observed regional variations in $\delta^{87}\text{Sr}$ in soil carbonates in coastal area of southern Australia. Near the ocean, the $\delta^{87}\text{Sr}$ values of the carbonates ranged from -1.20 to -0.63, similar to oceanic $\delta^{87}\text{Sr}$. The values gradually increase inland to a high of +6.97, which reflects increasing aeolian input from radiogenic continental material. In an area where the soil is strongly influenced by the volcanic ash of Mt. Gambier, the soil carbonate $\delta^{87}\text{Sr}$ values (~ -4.57) indicate a mixing of oceanic Sr ($\sim 60\%$) and Sr from the ash (40% ; $\delta^{87}\text{Sr} \approx -8.66$). This study is one of the clearest examples of the value of Sr isotopes in tracing atmospheric input into hydrologic systems.

Aberg et al. (1989) conducted an interesting study in Sweden on the solute relationships of rainfall, throughfall, and surface flow using Sr isotopic compositions. Rainfall compositions during a two year span of their study ranged from $\delta^{87}\text{Sr} = +1.34$ to +11.68. Water collected directly from throughfall ranged from $\delta^{87}\text{Sr} = +25.27$ to +39.21, while "surface runoff" (presumably overland flow) had a value of +34.29. A peat sample on the ground surface had $\delta^{87}\text{Sr} = +15.17$. All of these values are in sharp contrast to bedrock $\delta^{87}\text{Sr}$, which was +294.9 (whole rock value). The Sr isotopic composition of the rainwater from this drainage was changed significantly through interaction with the foliage (birch and spruce trees). The concentration of Sr changed from less than 3.5 $\mu\text{g/L}$ (rain) to 46-77 $\mu\text{g/L}$ (throughfall). The throughfall concentrations are significantly high relative to groundwater within the drainage. A sample of deep groundwater from the bedrock contained 161 $\mu\text{g/L}$, suggesting that the isotopic contribution from throughfall could be as much as 48% ($^{87}\text{Sr}/_{161}$) of the Sr isotope budget.

Similar findings have been reported for a forest basin in the Sangre de Cristo mountains of New Mexico by Graustein and Armstrong (1980). They were able to separate the throughfall from the broadleaf trees (aspen) from the fir trees (spruce) and found the aspen throughfall to have

higher $\delta^{87}\text{Sr}$ (+0.49 for spruce and +9.37 for aspen; rainfall was measured $\delta^{87}\text{Sr} = -0.35$ to +0.21). Analyses from fiber material from the trees themselves produced a similar difference: spruce bole had a $\delta^{87}\text{Sr}$ value of +5.42, aspen bole had a value of +13.31. Graustein and Armstrong felt that the difference between broadleaf and fir trees implied that the isotopic difference between rainwater and throughfall was largely due to aeolian input. Dust could cling to the aspen leaves better than the spruce needles, and eventually became part of the plant fiber.

In contrast, Bailey et al. (1996) suggest that most of the Sr in throughfall in their study area in New Hampshire results from canopy leaching rather than wash-off of dry deposition. The forest is composed of about 85% fir and 15% broadleaf trees, with wood from each having very similar $\delta^{87}\text{Sr}$ values ($\sim +14$ to $+15$). Bulk precipitation $\delta^{87}\text{Sr}$ values measured over the course of a year average +0.50. Throughfall $\delta^{87}\text{Sr}$ values measured during the same time average $\sim +12$ (through fir trees) and $\sim +14$ (through broadleaf trees). Bulk soils $\delta^{87}\text{Sr}$ values range from +16 to +25 (plagioclase separates $\delta^{87}\text{Sr} = +2.8$), and bedrock values range from +40 to +340. Dry deposition was not directly measured, and it was assumed by Bailey et al. that the Sr within wood and needles (broad leaves were not analyzed) is derived from the soil or rock. However, the similarity between $\delta^{87}\text{Sr}$ in soils, wood, and needles suggests that no external source of Sr is required to account for the observed $\delta^{87}\text{Sr}$ values. The difference in $\delta^{87}\text{Sr}$ between bulk precipitation and throughfall clearly indicates the importance in the solute hydrologic cycle of the Sr (and presumably other solutes) associated with the trees. While the importance of dry deposition is minimized in this study, the importance of the $\delta^{87}\text{Sr}$ value of throughfall discovered by the Aberg (1989) and Graustein and Armstrong (1980) studies is given strong support. When assessing the solute hydrologic cycle in catchments, the role of throughfall cannot be ignored.

Although atmospheric input of lithogenic nuclides into a hydrologic system is often ignored in isotopic studies, it should not be overlooked in catchment hydrology where surface water becomes an important consideration. The solute input is a significant percentage of the total solute budget for surface and near-surface waters, and the isotopic compositions of the incoming material are likely to be very different from those present in the catchment.

It is apparent that the use of cosmogenic nuclides in catchment hydrology relies on the external input of solutes into the system. Chlorine in North American rainwater has been measured to vary from about 8 mg/L along the coasts to about 0.1 mg/L inland (Junge and Werby, 1958). Like rainfall Sr, this is a significant input of Cl per year. However, while the atmospheric input of ^{36}Cl can be used as a groundwater tracer and for age dating old groundwater in large regional systems, the use of atmospheric ^{36}Cl on the smaller catchment scale with young water is limited. Thermonuclear ^{36}Cl on the other hand can be very useful on the catchment scale to discriminate water recharged during the 1950's and 1960's from older and younger water.

Thermonuclear ^{36}Cl has been detected in young water from many different localities (Phillips et al., 1988). In the $\sim 2 \text{ km}^2$ Wawona catchment in Yosemite National Park, thermonuclear $^{36}\text{Cl}/\text{Cl}$ values range up to $\sim 8500 \times 10^{-15}$ (Figure 8.4). Most of the water samples collected at depths less than ~ 100 meters contain $^{36}\text{Cl}/\text{Cl}$ ratios far in excess of the measured recent precipitation value of 134×10^{-15} (Caffee et al., 1992; Nimz et al., 1993). Because the opportunity for significant downward vertical mixing of the water is not present at this site, the thermonuclear ^{36}Cl signature indicates that virtually all of this young water has been recharged since the 1950's.

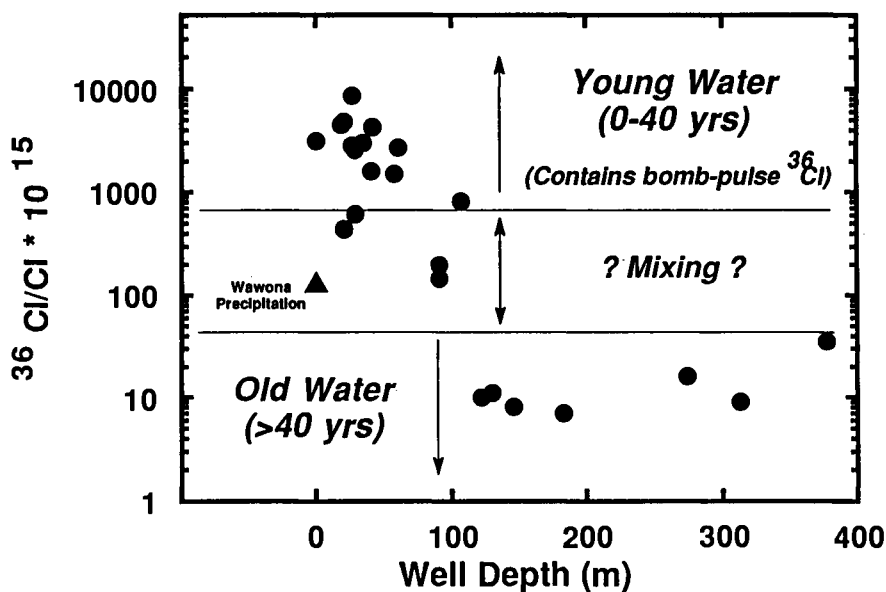


Figure 8.4. $^{36}\text{Cl}/\text{Cl}$ ratios in water from wells in the Wawona catchment of Yosemite National Park, California. Two distinct water types are present, one containing thermonuclear ^{36}Cl , and one containing exceptionally low values of $^{36}\text{Cl}/\text{Cl}$. A few intermediate samples may represent mixing of the water masses, or may represent pre-1950's water. The $^{36}\text{Cl}/\text{Cl}$ value from a rain sample collected from Wawona in 1993 is shown. This represents post-bomb-pulse precipitation, and should be similar to pre-1950's precipitation in the region.

8.3.2 The shallow system: hydrograph separation, weathering, and arid-region infiltration

Hydrograph Separation

The isotopic composition of the oxygen and hydrogen of water have been very useful in shaping modern perspectives of hydrograph separation (both streamflow and stormflow generation; Pearce et al., 1986; Sklash et al., 1986). Many other studies have successfully used solute mass balance to better understand the components of a stream hydrograph (Miller and Drever, 1977b; DeWalle et al., 1988; Robson and Neal, 1990; Wels et al., 1991). This suggests that solute isotopic compositions may be useful in hydrologic studies as well (see Chapter 18).

The studies discussed above by Aberg et al. (1989) and Graustein and Armstrong (1980) indicate that there can be significant isotopic differences between rain, surface flow, and groundwater flow. Aberg et al. examined the Sr isotopic compositions of exchangeable Sr within the soil column (from weak-acid leachates) and soil water (from lysimeters). The leachate/water $\delta^{87}\text{Sr}$ values (+37.8 to +44.4; decreasing downward in the soil column) were considerably higher than either the precipitation values (< +11.68), or the value obtained for surface flow (+34.29). Groundwater sampled from a depth of one meter had a $\delta^{87}\text{Sr}$ value of +34.49, and deeper groundwater (depth unspecified) had a value of +101.88. The differences in these isotopic compositions are more than sufficient to lend themselves to hydrograph separation analysis.

However, the isotopic composition of a solute species can change due to the addition of leachable solutes as water migrates. This is different from the case of oxygen and hydrogen isotopes which will not change as a result of migration in low temperature systems. The use of solute isotopic compositions for hydrograph analysis must take into account potential sources within the system for the solutes and the isotopic compositions of those sources. This is not to say that solute isotopic compositions can not be useful in identifying the origin of water in, for example, streamflow or stormflow. In the catchment analyzed by the Aberg et al. (1989) study, very high $\delta^{87}\text{Sr}$ values that might be observed in streamflow would certainly indicate a component of water from depth. Determining the *amount* of deep water present, however, would require an assessment of Sr mass balance. Conversely, low $\delta^{87}\text{Sr}$ values would not necessarily indicate that none of the streamflow was derived from depth, if the deep water dissolved substantial quantities of Sr with low $\delta^{87}\text{Sr}$ values as it migrated to the surface. Again, an assessment of potential sources of Sr and of mass balance would be required. The important observation, though, is that once the potential sources and mass balance have been determined, the measured isotopic compositions of the solute species must confirm the origins of the solutes and the degrees of mixing and/or dissolution.

Anthropogenic influences on lithogenic solute concentrations may in certain cases be detected by isotopic ratios (Flegel et al., 1989, 1993; Whitehead et al., 1997). Erel et al. (1991) used the Pb isotopic compositions of stream water, snow-fed lake water (the lake is at the source of the stream), local bedrock, and soil leachates to examine the Pb systematics in a remote mountain stream. The ratio of $^{206}\text{Pb}/^{207}\text{Pb}$ in the lake (1.183) is substantially lower than local bedrock and soil values (1.215-1.326), and closer to anthropogenic values measured in aerosols (analytical error is about ± 0.001). The anthropogenic Pb is likely deposited onto the snow that feeds the lake, and is directly transported to the lake by surface or near-surface flow. In a related study, Erel et al. (1990) demonstrated that atmospheric (anthropogenic) Pb is retained in the upper portions of the soil column and is not transported to shallow groundwater. Measurements of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.218) made in early spring on stream water collected 15 km downstream from the lake indicate that while some of the Pb is derived from weathering of bedrock, much of it is derived from anthropogenic sources as observed in the lake (much of the stream water in early spring likely originates in the lake itself). Measurements of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.247-1.297) made on stream water samples collected in autumn indicate that Pb concentrations are dominated by the weathering of bedrock. The observed $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are slightly higher than the bedrock whole-rock values (1.215-1.224), but lower than rock leachate values (1.326); this is likely the result of preferential weathering of high U/Pb minerals such as biotite, magnetite, and apatite. The autumn Pb isotopic measurements show the ratios progressively increasing downstream. With the assumption that some of the Pb in the stream originates in the headwater lake while the rest of it is derived from mobile (leachate) Pb derived from bedrock, mixing curves were developed which indicate that at about 5 km from the headwaters approximately 55% of the Pb in the stream is anthropogenic, while at 15 km about 20% is anthropogenic.

Weathering reactions

Another use of dissolved or leachable lithogenic nuclides is the assessment of weathering reactions. The variations in isotopic compositions within a soil column are due to variations in the weathering-residual mineralogy within the column. For example, in a follow-up study to that of Aberg et al. (1989), Wickman and Jacks (1992) determined that the higher $\delta^{87}\text{Sr}$ values observed in the upper 10 cm of the soil column, as opposed to those observed from 10

to 45 cm, were due to the predominance of alkali feldspar weathering. Plagioclase had been depleted through previous weathering in the most shallow zones, and only occurred in abundance below 10 cm. This is consistent with the expected isotopic ratios in each mineral (cf. Figure 8.1).

Analogous changes in exchangeable Sr isotopic composition were observed in a sequence of soils with variable ages (3–3000 Ka age range) developed on granitoid alluvium in the Central Valley of California (White et al., 1992; Bullen et al., 1997). Variations in soil mineralogy with age were documented (White et al., 1996) and samples from each age group were leached with an ammonium acetate solution to extract the exchangeable Sr. The youngest soils (< 10 Ka) had exchangeable Sr $\delta^{87}\text{Sr}$ values (~ -2.5) higher than the parental granitoid rocks (~ -4.6), showing an influence from a relatively radiogenic mineral (hydrobiotite and/or alkali feldspar).

Model calculations, as well as the even distribution of hydrobiotite throughout the soils, suggest that the incipient weathering of the granitoid at this site is dominated by Sr derived from alkali feldspar rather than hydrobiotite (Bullen et al., 1997). This is significantly different from the conventional expectation that early feldspar weathering will be dominated by plagioclase, and that observed elevated $\delta^{87}\text{Sr}$ values in younger soils must therefore be due to weathering of biotite. An important influence of biotite on $\delta^{87}\text{Sr}$ has been documented in very young glacial tills (Blum and Erel, 1997), but even in this very fresh, un-reworked material the influence of biotite on the $\delta^{87}\text{Sr}$ value of exchangeable Sr was negligible in tills older than about 10 Ka. Exchangeable Sr from the intermediate-aged soils (10–600 Ka) in the California Central Valley showed the progressive influence of plagioclase (lowering $\delta^{87}\text{Sr}$ values eventually to ~ -4.9). Exchangeable Sr from the oldest soils (3000 Ka) showed a slight increase in $\delta^{87}\text{Sr}$ relative to the intermediate-aged soils, which was attributed to residual alkali feldspar weathering. Even though the exchangeable Sr in this oldest soil is apparently still dominated by unradiogenic Sr from plagioclase, all of the plagioclase has completely weathered away. In order to numerically model this result successfully, Bullen et al. found it necessary for Sr exchange in the older clay-rich soils to be a relatively inefficient process. This is in opposition to models of Sr behavior in water-rock systems that assume or require Sr exchange to be an extremely rapid process (e.g., Johnson and DePaolo, 1997; Katz and Bullen, 1996).

Blum et al. (1994) report $\delta^{87}\text{Sr}$ measurements of stream waters draining two portions of a granitic batholith, one recently glaciated (~ 10 Ka) and the other glaciated at about 100 Ka ago. They observed consistently higher $\delta^{87}\text{Sr}$ values in water from the recently glaciated portion, and attribute this to weathering of biotite from the fresher surfaces scoured by the younger glaciation. The older surfaces showed less influence from biotite, which presumably had weathered away, and greater influence from plagioclase. Bullen et al. (1997) suggest that this study may be providing evidence that biotite relinquishes its Sr so quickly upon weathering that it no longer has an affect on the $\delta^{87}\text{Sr}$ budget of a deposited soil. That is, the radiogenic Sr is lost to surficial runoff prior to or during soil deposition. Blum et al. pointed out that an interesting implication of their observations is that glaciation of a granitic terrane may lead to a short-term increase in $\delta^{87}\text{Sr}$ values in streams draining the region (see also Blum and Erel, 1995). This could be the cause of correlations that have been noted in seawater $\delta^{87}\text{Sr}$ values and global climate cycles (Clemens et al., 1993).

Further complications to the behavior of Sr in water-soil (and potentially to water-rock) systems was demonstrated by Bullen et al. (1996) in a series of laboratory column experiments

conducted in an attempt to replicate a sequence of high-quality field measurements. They found that the rate at which water was passed through a 15 cm long column (4 cm diameter) filled with alluvial soil from the study area influenced the $\delta^{87}\text{Sr}$ value of the Sr dissolved in the water. Rapidly moving water contained radiogenic Sr characteristic of alkali feldspar. Slow moving water contained much less radiogenic Sr, characteristic of the plagioclase in the soil. This replicated closely the field measurements, wherein radiogenic Sr was measured in water being recharged through unsaturated soil, while less radiogenic Sr ($\delta^{87}\text{Sr}$ similar to the plagioclase) was measured in water flowing more rapidly through saturated soils at depth. Bullen et al. suggest that plagioclase in the unsaturated zone may develop surficial alteration deposits limiting dissolution and Sr removal. Rapidly moving water inhibits this coating, allowing the unradiogenic Sr from plagioclase to dominate the Sr budget. The dependence of $\delta^{87}\text{Sr}$ on flow rate is a very unexpected result. It may explain the apparent strong influence of alkali feldspar, relative to plagioclase, on the $\delta^{87}\text{Sr}$ values observed in young slow moving fracture-fill waters within the Wawona catchment of the Sierra Nevada reported by Nimz et al. (1992).

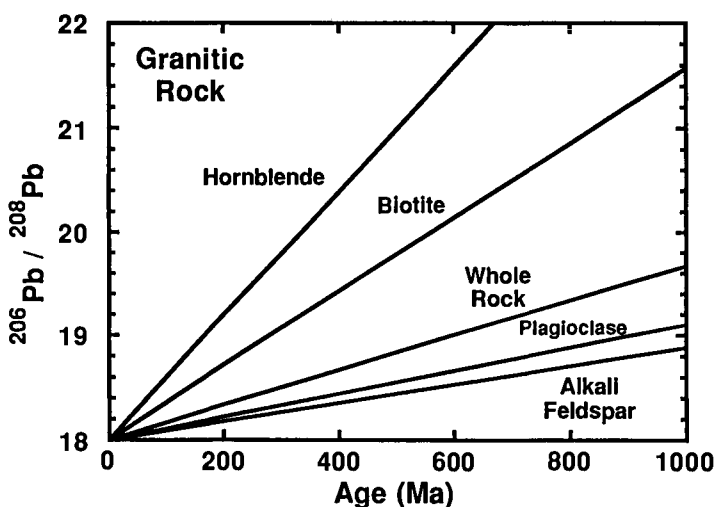


Figure 8.5. The change in Pb isotopic composition with time in minerals of a typical granitic rock. For all minerals and the whole rock (WR), initial (t_0) $^{206}\text{Pb}/^{204}\text{Pb} = 18$. The U/Pb ratios depicted in this figure are: 0.08 (alkali feldspar), 0.11 (plagioclase), 0.16 (WR), 0.34 (biotite), and 0.58 (hornblende).

Although most isotopic weathering studies have employed Sr, Figure 8.5 indicates that in some instances, particularly for older rocks, Pb isotopes may be useful in tracking the weathering sequence. There would be very significant differences expected in $^{206}\text{Pb}/^{204}\text{Pb}$ ratios within the minerals of granites older than about 200 Ma. While the weathering of hornblende cannot be readily distinguished from that of plagioclase using Sr isotopes, hornblende and plagioclase will likely have very distinctive Pb isotopic compositions. As was the case with Sr, plagioclase and biotite will also have very distinctive Pb isotopic compositions (Figure 8.5). Weathering occurring in hornblende and biotite at an earlier time, or at a more rapid rate, than plagioclase should be detectable in the Pb isotopic composition of leachable Pb in the soil, or the Pb in water draining the bedrock.

There are some potential complications to the use of Pb isotopes to elucidate hydrologic processes, including the strong possibility of anthropogenic contamination, the relative lack of mobility for Pb in groundwater, and the possibility for highly radiogenic Pb to exist in accessory minerals (e.g., apatite). But, in turn, each of these can also be used to an advantage: anthropogenic Pb is easily identifiable by its isotopic composition (Flegal et al., 1993; Veron et al., 1994), the differential mobility of Pb and Sr will produce covariation in concentrations in microenvironments, and the presence of accessory-phase Pb may allow unusually distinctive fingerprinting of both groundwater and weathering processes.

Arid region infiltration

Cosmogenic nuclides have been useful in studies focused on the shallow hydrologic system, particularly in studies assessing infiltration of water through the unsaturated zone in arid and semi-arid regions. Infiltration is a concern in both weathering studies and hydrograph separation analyses, and is also important to both recharge and solute transport studies. The peak in atmospheric input of ^{36}Cl from above-ground nuclear weapons testing in the 1950's and 1960's produced a corresponding peak in the soil column which migrates downward with infiltration. In principle, infiltration flux should be calculable based on the depth of the peak and the capacity of the infiltrating water to transport Cl. Several studies have used this approach, or variations of it, to assess downward water movement.

Cecil et al. (1992) measured ^{36}Cl in soil cores from the semi-arid Snake River Plain and found a sharp and well-defined peak in the $^{36}\text{Cl}/\text{Cl}$ ratio at one meter depth (total soil depth was six meters). The infiltration rate calculated from this was 0.71 cm/year. This is about twice the rate derived from Darcian flux calculations based on neutron log data collected from the site over a four year period. Given the magnitude and sharp definition of the ^{36}Cl peak, it is difficult to accept the lower calculated Darcian flux infiltration estimate, which would indicate a shallower depth for ^{36}Cl migration.

Similar infiltration studies have been conducted in New Mexico by Phillips et al. (1988) and in Nevada by Norris et al. (1987). Each of these studies demonstrated that it is possible to have more than one ^{36}Cl peak within the upper few meters of a soil column. Phillips et al. found clearly defined double peaks in their soil profiles, the cause of split peak (or the double ^{36}Cl pulse) was undetermined. The Norris et al. study found a single, but very broad and jagged, peak in the upper 1.5 meters at one location. However, at a second location a few kilometers away they found better defined peaks, but there apparently were three of them within the upper 1.5 meters of the soil column. At the first site the maximum of the peak coincides with a change in soil texture, whereas no such change occurs at the second location. Norris et al. suggest that the chloride systematics of the second site are indicative of a shallow hydrologically active zone overlying a hydrologically stagnant zone within the top 1.5 meters. The large fluctuations in $^{36}\text{Cl}/\text{Cl}$ ratios at this site are thought to be reflective of both the two hydrologic zones and possibly of lateral water flow between 0.5 and 1.0 meters depth.

Chlorine-36 and chloride mass-balance has been used to investigate soil water movement in southern Arizona (Liu et al., 1995). Here again a double ^{36}Cl peak was found. Because infiltration rates (Cl residence time in the soil) calculated on the basis of chloride mass balance were in good agreement with infiltration rates calculated using the lower ^{36}Cl peak, Liu et al. concluded that the lower ^{36}Cl peak represented true downward water flux. The upper peak was interpreted to represent upward water flux in response to the capillary pressure gradient during the dry season.

Cook et al. (1994) examined ^{36}Cl , ^3H , and chloride profiles for a semi-arid region of southern Australia including areas covered by eucalyptus forest and areas recently cleared for agriculture. Seven profiles were examined for ^{36}Cl and chloride (only one of these for ^3H), and all showed a sharp single peak in ^{36}Cl concentration within the top few meters of the soil column. The position at which chloride concentration reached a maximum was generally at a deeper level, often several meters deeper. Recharge fluxes calculated from chloride concentration and ^{36}Cl differed substantially, while fluxes based on chloride concentration and ^3H mass balance were in closer agreement. The apparent reason for this was that the ^{36}Cl peak was found in or near the root zone, while the chloride maximum was well below the root zone. The chloride maximum was therefore a closer indication of time-averaged fluxes through the zone below that affected by plant roots. Although the root zone apparently does not prevent a single ^{36}Cl peak from being observed, macropore flow and lateral flow due to root intake disrupt chloride migration (flux) and prevent the use of ^{36}Cl for recharge flux estimates. The ^{36}Cl peaks were instead providing an indication of mean soil water flux through the root zone.

Scanlon (1992) examined the ^{36}Cl and ^3H profile in the arid Heuco Bolson of west Texas, within the Chihuahuan desert. Chlorine-36 formed a single peak within the top meter of the soil column, and provides a calculated moisture flux estimate of 1.4 mm/year. Tritium occurred in three peaks within the top 2 meters, and provides a mass balance calculated moisture flux estimate of 7 mm/year. The higher ^3H moisture flux is attributed to vapor phase movement of ^3H . The vapor flux model was tested by comparing the fluxes calculated from the profiles with fluxes derived by numerical advective-dispersive simulations, both diurnal and seasonal. The simulated downward vapor flux was significantly higher than the simulated downward liquid flux, in qualitative agreement with the observed differences in ^{36}Cl and ^3H behavior. Because chemical diffusion alone cannot account for the ^{36}Cl profile, significant advection must also be occurring. The soil physics data would suggest that diffusion alone was occurring, which demonstrates the potential for error in using only soil physics data, which of practical necessity is collected over a short time interval. The ^{36}Cl profile is therefore a better indicator of long-term average moisture flux.

Allison et al. (1994) reviewed physical and chemical methods, including ^{36}Cl , for estimating infiltration in arid and semi-arid regions. In agreement with the Scanlon (1992) study, they concluded that the chemical methods are more successful in estimating groundwater recharge than physical methods such as water balance and Darcian flux measurements (based on soil physics data). However, they caution that ^{36}Cl may not be suitable in areas of very low recharge (< 50 mm/yr) or in areas of changing land use.

Relatively little use has been made of bomb-pulse ^{36}Cl to investigate infiltration processes and rates in non-arid climates. It would have proven very useful in hydrograph separation analysis during the period of high atmospheric concentrations (1960's-1970's). Several studies in non-arid climates have indicated that bomb-pulse ^{36}Cl is still present at shallow depths, and could be used for solute tracing and water infiltration (Bentley et al., 1982; Caffee et al., 1992; Andrews et al., 1994; Phillips et al., 1995). However, two related studies in the Canadian Great Lakes region have provided strong evidence that uptake and recycling of ^{36}Cl by vegetation may delay its deeper infiltration (Milton et al., 1997; Cornett et al., 1997). This suggests that chloride may not be a perfectly non-reactive hydrologic tracer in shallow hydrologic systems. On the positive side, it suggests that bomb-pulse ^{36}Cl may be useful as a tracer of modern solute input and cycling through the biosphere within vegetated catchments.

8.3.3 *Evaporation / transpiration*

Two studies in the Jordan River-Dead Sea region compared groundwater chloride concentration and $^{36}\text{Cl}/\text{Cl}$ ratio to the values measured in rainwater to determine the amount of water loss due to evapotranspiration before soil water reaches the water table (Paul et al., 1986; Magaritz et al., 1990). The method is based on the increasing solute concentrations in infiltrating water. This increase is due to both evapotranspiration and Cl gained through rock leaching. The ratio of ^{36}Cl to total chloride is used to differentiate between these two processes. There is a significant difference in $^{36}\text{Cl}/\text{Cl}$ ratios between the chloride leaching from the rock and the chloride within the incoming precipitation. Evapotranspiration will increase chloride concentration, but will not affect the $^{36}\text{Cl}/\text{Cl}$ ratio. Leaching of rock will both increase chloride concentration and alter the $^{36}\text{Cl}/\text{Cl}$ ratio. By using the $^{36}\text{Cl}/\text{Cl}$ ratios to factor out the chloride within groundwater or soil water introduced through rock leaching, the increase in chloride concentration due to evapotranspiration can be calculated. Magaritz et al. (1990) determined that the amount of water lost varied widely over the Jordan River basin, and ranged from 40 to 90 percent of the incoming precipitation.

8.3.4 *The deep system: groundwater flow*

Two important issues in catchment hydrology are the flow paths and flow rates of groundwater within confined or unconfined aquifers. Compared to surface water, groundwater is within the system for a long period of time, and significant chemical interactions with the rock or soil of the aquifer can occur. Physically separated groundwater masses can be differentiated by marked differences in chemical compositions. Reaction path modeling of observed changes in the groundwater chemistry can indicate flow paths. These compositional differences and modeled chemical reactions are usually accompanied by isotopic changes in the lithogenic elements within the water.

In the Wawona catchment within Yosemite National Park, two distinct stratified water masses are present. The Sr isotopic compositions of the two water bodies indicate that they have very different flow path histories (Figure 8.6). The high $\delta^{87}\text{Sr}$ values for the youngest, shallowest waters are due to the early dominant contribution of biotite (Nimz et al., 1992). Older, deeper waters progressively reflect interaction with other minerals in the granitic rocks, where the deepest samples ($\delta^{87}\text{Sr} \approx -4.0$) approach isotopic equilibrium with the aquifer rock (rock $\delta^{87}\text{Sr} = -4.6$ to -3.9). Water with $\delta^{87}\text{Sr}$ values most like those of the rock has migrated on longer flow paths and had more time to interact with the rock. The sharp distinction between the two water masses is important. It suggests that the shallow water infiltrates locally and reaches depths less than 100 meters before leaving the catchment (ultimately as outflow to the South Fork Merced River which drains the catchment). This cycling through the catchment occurs in time spans less than those required for Sr isotopic equilibration. The deeper waters apparently are recharged regionally rather than within the catchment, follow different flow paths than the shallow waters, and take considerably longer to reach their present locations - long enough to more fully equilibrate with the local lithology. The realization that two water masses occur and have a shallow interface (~100 meters depth) has important implications for water resource management of the local domestic water supply which is used by several hundred residents, public lodges and hotels, and a golf course.

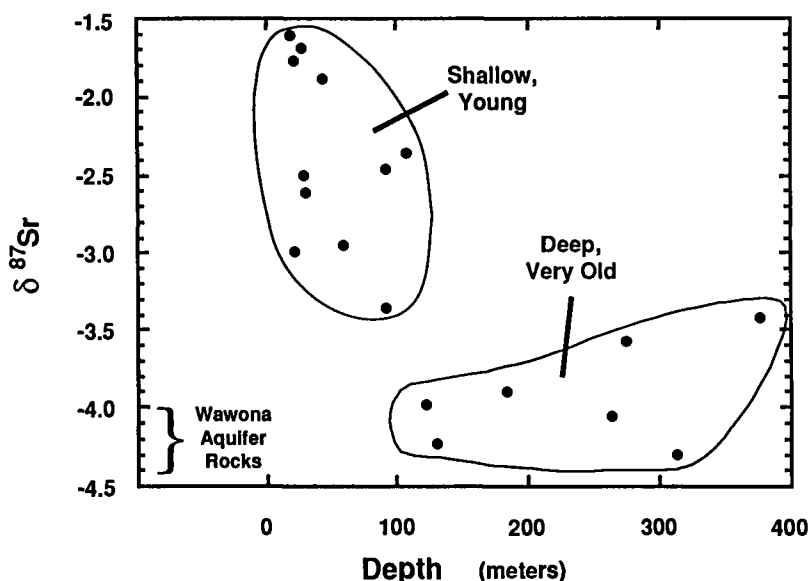


Figure 8.6. Delta- ^{87}Sr in water from wells in the Wawona catchment of Yosemite National Park, California. Low $\delta^{87}\text{Sr}$ values reflect Sr isotopic equilibrium with the host rocks ($\delta^{87}\text{Sr} = -3.0$ to -4.5), whereas the higher values indicate incomplete equilibration and the influence of biotite ($\delta^{87}\text{Sr} > +200$). The biotite-influenced water is younger and has not yet had time to completely react with the host rock. The deeper, unradiogenic waters are also known to be older, compare Figure 8.4.

Similar behavior of Sr isotopes is observed in waters from granitic rocks in the Aberg et al. (1989) study discussed previously. Here, the progressive changes in $\delta^{87}\text{Sr}$ values of leached exchangeable Sr and lysimeter water ($\sim +44$ to $\sim +38$) are observed to parallel changes in $\delta^{87}\text{Sr}$ within the soil itself ($\sim +124$ to $\sim +84$). In a deep water sample, the $\delta^{87}\text{Sr}$ value was much higher ($+100.9$), but still not yet in isotopic equilibrium with the host rock ($\delta^{87}\text{Sr} = +294.9$). It appears that on the catchment scale, complete isotopic equilibration of groundwater with granitic rocks requires considerable time. The Sr isotopic composition of water samples may therefore be useful as a qualitative indicator of relative age between the samples.

There have been several studies that have deduced flow patterns on the basis of U isotopic compositions in moderate sized drainage systems. Kronfeld et al. (1979) found U isotopic variation to be quite systematic within the $\sim 1000 \text{ km}^2$ Cenomanian carbonate aquifer system in the Beersheva region of Israel. In general, U activity values ranged from near secular equilibrium, 1.03, to values of nearly 2. The systematic changes allowed Kronfeld et al. to propose flow paths that curved around the major axes of buried geologic structures in the study area. Andrews and Kay (1982) were able to discern regional flow paths along a zone approximately 150 km in length by the use of $^{234}\text{U}/^{238}\text{U}$ activity ratio isopleths. Three distinct zones were identified where uranium leaching, uranium deposition, and interstitial fluid mixing occurred. Activity ratios in the system ranged from less than one to greater than three.

Variations in flow rates have also been observed using U isotopic compositions. Kronfeld and Rosenthal (1981) collected water samples from Bet Shean and Harod valleys in Israel, which comprise a single large drainage basin. The samples showed very small variations in U concentrations ($\sim 1\text{--}4\text{ }\mu\text{g/L}$), but large variations in $^{234}\text{U}/^{238}\text{U}$ activity ratios (<1.5 to >3.0). Three distinct water masses were identified, two of which occurred in rocks with very similar lithologies (carbonates). Initial preferential leaching of ^{234}U created the highest activity ratios observed in the system; as the water further reacted with the rock, the activity ratios became lower as the result of ^{238}U dissolution from areas previously leached of ^{234}U . For one of the carbonate units, the lowering of the activity ratio did not occur until the water was quite remote from the recharge area. In the other carbonate unit the lowering of the activity ratios occurred near the recharge areas. This difference was interpreted to be the result of lower permeability in the second carbonate unit. The relative flow rates between the units were very different, leading in one case to relatively old water near the recharge areas whereas in the other case water of the same age was able to flow much farther from the recharge area. The total distance along this flow path was about 10 kilometers. Significant differences in activity ratios between the two water masses were detectable within about one kilometer of the recharge areas.

Cosmogenic and thermonuclear ^{36}Cl may in certain instances be valuable on a catchment scale to provide information about differences in flow paths and flow rates. Water samples from the shallow wells (<100 meters) within the Wawona catchment contain $^{36}\text{Cl}/\text{Cl}$ ratios that are of thermonuclear origin, indicating that this water mass is less than about 40 years old (Figure 8.4). Flow rates must be sufficient to carry this water to the ~ 100 meter depth within these forty years. Water samples from the deepest wells, those which penetrate the lower and more evolved water mass, contain no thermonuclear ^{36}Cl and, in fact, have $^{36}\text{Cl}/\text{Cl}$ ratios that are far below that of recent local precipitation (Figure 8.4). The recent precipitation value (134×10^{-15}) is similar to the expected cosmogenic, non-thermonuclear, precipitation value for this region ($\sim 150 \times 10^{-15}$; Bentley et al., 1986a), and probably indicates what the pre-bomb $^{36}\text{Cl}/\text{Cl}$ value was for the Yosemite area. The extremely low $^{36}\text{Cl}/\text{Cl}$ values in the deeper waters therefore indicate that the chlorine in the water, or at least a large component of it, is very old (>1 Ma old). This is consistent with the observation made on the basis of Sr isotopic compositions that the deeper waters have different and longer flow paths than the shallow waters. Determining the absolute age of the deeper water is complicated by in-situ ^{36}Cl production and other problems involving Cl migration (Nimz et al., 1993), but the $^{36}\text{Cl}/\text{Cl}$ values clearly indicate that the water deeper than ~ 100 meters is of a distinctly different age than the shallower water, and must move along very different flow paths and probably at significantly slower flow rates.

8.3.5 System (basin) closure: mixing of water masses

The degree to which a catchment operates as a closed system is important when assessing hydrograph separation, water resource potential, and mass balance of both water and solutes. Solute concentrations are often used to assess the mixing of groundwater originating outside of a hydrologic system with water originating within the system (Christopherson and Hooper, 1992). Lithogenic and cosmogenic nuclides have been used to assess mixing, but have received much less attention on the catchment scale than on the regional scale. These nuclides have the advantage that while elemental concentrations can vary due to mineral formation (precipitation) reactions, lithogenic and cosmogenic isotopic ratios will not. Precipitation reactions can obscure mixing relationships if only elemental concentrations are considered.

Several studies have demonstrated the value of lithogenic nuclides in assessing groundwater mixing. Smalley et al. (1988) were able to identify mixing between meteoric ("fresh") water and more evolved saline water on the basis of the Sr isotopic compositions of the endmembers. The intermediate, moderately saline waters were not less chemically evolved (younger) counterparts of the saline waters, but rather were mixtures of the older saline and young meteoric waters. Lowry et al. (1988) were able to use Sr isotopic compositions of groundwater samples to distinguish between three endmembers, one of which was meteoric. Having recognized the meteoric component as a "dilution" effect, they were then able to use a Sr-isotope/Sr-concentration mixing curve to model the variations in chemical composition observed in the water samples. McNutt et al. (1984) were able to identify a *lack* of mixing in waters on the basis of Sr isotopes; this allowed them to realize the system consisted of what they termed "pockets" of water, each of which behaved as a closed system.

The isotopic composition of uranium has been used to assess mixing in much the same way as that of strontium. Three studies are of particular interest to catchment hydrology. Cuttall et al. (1988) were able on the basis of $^{234}\text{U}/^{238}\text{U}$ ratios to distinguish three groundwater types in the Lower Mercy Basin of western England, as well as zones of mixing between them. Ivanovich and Alexander (1987) found systematic variations in $^{234}\text{U}/^{238}\text{U}$ ratios between confined and unconfined groundwaters underlying Harwell, England. They were able to detect specific locations of leakage of the confined unit. Points of interconnection between groundwater masses were also identified in central Israel by Guttman and Kronfeld (1982). At these locations, ^{234}U -enriched water was able to migrate downward into the underlying formation. These interconnections could be generally correlated with geologic structures in the basin. Each of these three studies were conducted within individual catchment areas, sampling shallow waters over areas less than a few hundred square kilometers in size.

The cosmogenic isotopes ^3H and ^{14}C have been widely used to assess groundwater mixing. The use of ^{36}Cl for this purpose is increasing for a number of reasons. The order of magnitude or greater difference between atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios and rock equilibrium ratios can make mixing between recharge water and older water easy to identify. The very large difference between natural ^{36}Cl levels and thermonuclear ^{36}Cl levels lends itself easily to groundwater mixing studies. Dowgiallo et al. (1990) examined the $^{36}\text{Cl}/\text{Cl}$ ratios in water of the Mazowsze artesian basin of central Poland. Here, mixing of water containing atmospheric ^{36}Cl with older water containing low $^{36}\text{Cl}/\text{Cl}$ ratios was identified as the primary mechanism for observed decreases in $^{36}\text{Cl}/\text{Cl}$ along the flow path. However, certain samples in intermediate locations along the flow path had $^{36}\text{Cl}/\text{Cl}$ ratios that were too high for the modeled dilution curves. The higher values could not be explained by in-situ production of ^{36}Cl because the aquifer rocks contained low U and Th concentrations. Since the basin is artesian, downward leakage (recharge) of water with an atmospheric or thermonuclear ^{36}Cl component was improbable. Consequently, Dowgiallo et al. interpreted the increases to points of *upward* leakage of water from a formation underlying the confined aquifer that was known to contain high concentrations of U and Th.

Bentley et al. (1986a) discuss a preliminary ^{36}Cl study that was conducted in a large enclosed basin in Brazil (the Drought Polygon) in which water quality was a problem due to high Cl contents. The high-Cl water was meteoric, as could be determined by its atmospheric $^{36}\text{Cl}/\text{Cl}$ ratios. However, on the basis of a mixing array observed in the $^{36}\text{Cl}/\text{Cl}$ values, a second water was inferred to exist at depth in the basin. Component mixing diagrams indicated that the second water contained low concentrations of Cl. Although the study was preliminary, it was

suggested that a solution to the water quality problems in the basin might be to bypass the shallow high-Cl water and tap the deeper low-Cl water.

Carlson et al. (1990) were able to identify contributions to the chloride in three lakes in Antarctica on the basis of $^{36}\text{Cl}/\text{Cl}$ ratios. Chloride from a river source (atmospheric $^{36}\text{Cl}/\text{Cl}$) was distinguished from chloride from deep groundwater (low $^{36}\text{Cl}/\text{Cl}$) on the basis of mixing curves. A third component in one of the lakes could be identified as a seawater source, and the possibility of a seawater incursion was suggested. Although the role of lithogenic or cosmogenic nuclides in catchment lakes has not been discussed, the Carlson et al. study clearly indicates the potential for their use.

In a study of groundwater basins of western Nevada and eastern California, Phillips et al. (1995) used Cl concentrations and $^{36}\text{Cl}/\text{Cl}$ ratios in an attempt to identify the sources of chlorine in deep groundwaters, lakes, and streams. With the use of a numerical mass balance model and extensive Monte Carlo simulations, they derived accumulation times for both Cl and ^{36}Cl in subsurface waters and Mono Lake. The results suggest that a very significant subsurface input of chloride has occurred (or, is still occurring), with an accumulation time of 100-450 Ka before the present. The observed low $^{36}\text{Cl}/\text{Cl}$ ratios, and implied high chloride concentrations of the input, suggests a magmatic source for the chloride. Although the input pathways are not specified, mixing of geothermal fluids and meteoric waters would produce the range of $^{36}\text{Cl}/\text{Cl}$ values measured within the Mono groundwater basin.

8.3.6 *Streamflow: mass balance within the catchment*

For a catchment where all water fluxes can be quantified, mass balance within the system can be assessed through chemical analysis of input (precipitation and dry deposition), and output (stream water) (Cleaves et al., 1970; Hooper et al., 1990; Mast et al., 1990; Stauffer and Wittchen, 1991; Wilson et al., 1991a; 1991b). Lithogenic and cosmogenic isotopic compositions can be useful in these studies not only by identifying the sources for the solutes (as much of this chapter discusses), but also by being able to place constraints on the acceptable volumes of each solute from identified sources. For example, if it is thought that 20% of the Sr in a stream during stormflow comes from surface or near-surface (interflow) sources, then 20% of the isotopic composition of the Sr in the stream must reflect these sources. Further, the streamwater should be expected to have a component of ^{36}Cl commensurate with the 20% surface/near-surface Sr contribution. The magnitude of the ^{36}Cl contribution, and resulting $^{36}\text{Cl}/\text{Cl}$ ratio, will depend on the source(s) of ^{36}Cl , the Sr/Cl ratio of the various source compartments, and variations in mobility of Sr and Cl. However, taking these factors into account, the ^{36}Cl data must support a surficial source for twenty percent of the Sr in the system. The isotopic compositions of the solutes serve as a check on the solute mass balance assumptions. This approach has been used by several of the studies discussed in this section (Aberg et al., 1989; White et al., 1992; Blum et al., 1994).

8.3.7 *Lithogenic and cosmogenic nuclides: summary*

The preceding sections have attempted to summarize the processes that affect lithogenic and cosmogenic nuclides in hydrologic systems, and to discuss how knowledge of these processes

can be used to better understand catchment hydrology. The important consideration for both lithogenic and cosmogenic nuclides is the chemical behavior of the solute within the system. One must consider various sources of the solute, where sources are located within the system, and to what degree each source will likely contribute to the overall isotopic budget of the water within the catchment. Unlike considerations based only on solute concentrations, isotopic considerations permit the source of the solute to be identified. It is this identification of sources that can be used to examine mass input into the system, hydrograph separation, weathering reactions, infiltration paths and rates, evapotranspiration losses, groundwater flow paths and flow rates, groundwater mixing within the system, and general mass balance of the system.

There are as yet very few published studies employing lithogenic or cosmogenic nuclides that focus specifically on catchment hydrology. Despite the fact that the lack of such studies makes the entire subject a "new direction" in *catchment* hydrology, there are areas that can be considered truly new directions because their applications in hydrology *on any scale* are today almost completely unexplored. The following concluding section of this chapter discusses potential applications for catchment hydrology.

8.4 New Directions in Lithogenic and Cosmogenic Nuclides

8.4.1 *The other geologic giant: neodymium*

Besides Sr and Pb, the other lithogenic element having received widespread use in geology is Nd (Table 8.1). Important elemental fractionations occur in nature between ^{143}Nd and its parent ^{147}Sm , creating varying Nd isotopic compositions ($^{143}\text{Nd}/^{144}\text{Nd}$) through radiodecay. This has made Nd useful for age dating as well as many other geologic applications (DePaolo, 1988). Because the natural abundance of Nd is very small, and Nd is a very non-hydrophilic element in low temperature environments, the concentration of Nd in natural waters is extremely low (Table 8.2). Nonetheless, Nd isotopic composition can still be measured in natural waters (Goldstein and Jacobsen, 1987; Bullen and Kharaka, 1992). In most geological environments, the isotopic composition of Nd varies systematically, though inversely, with the isotopic composition of Sr (DePaolo, 1988). Therefore, as a hydrologic tracer, Sr would be the analyte of preference due to its higher concentration in natural waters. This is provided, of course, that the Sr and Nd originated from the same geologic source (e.g., the same aquifer rock). However, Sr and Nd do not have the same chemical behavior in all environments and in some groundwater samples may not be derived from the same geologic source. For example, Piegras and Wasserberg (1985) noted that in geothermal environments Nd can have a high affinity for water. An isotopic composition of Nd developed in geothermal environments would be unlikely to change if the water migrated away from the thermal area. A "fossil" Nd isotopic signature would remain in the water. The Sr isotopic composition obtained in the thermal area would likely not be retained, because Sr from the non-thermal zone would dissolve into the water, mixing or exchanging with the thermal Sr. In this case, Nd could serve as a useful hydrologic tracer. As is always the case with lithogenic nuclides, one must consider the geochemical behavior of the element of interest.

Except in very specific environments, Nd will not be as useful as Sr in the interpretation of the weathering process in rocks and minerals. Because of their similar geochemical behavior, Sm and Nd are not fractionated from one another as severely as Rb and Sr. This fact, combined

with the very long half-life of ^{147}Sm (1.53×10^{11} years), make inter-mineralic variations in Nd isotopes fairly small unless the system is quite old. Figure 8.7 shows Nd isotopic variations with time in a hypothetical garnet gneiss with similar mineralogy to the granite used in the Sr and Pb examples of Figures 8.1 and 8.5. Garnet is one of the few common, non-accessory, minerals to significantly fractionate Sm from Nd during its formation. In the example, Nd derived through weathering of garnet would be analytically resolvable from Nd derived from the rest of the rock, even at a fairly young rock age. Because analytical precision for Nd is generally about 1 unit on the epsilon scale (see Table 8.1 for the definition of the epsilon scale), the Nd from the other minerals would be difficult to distinguish unless the rock was several hundred million years old.

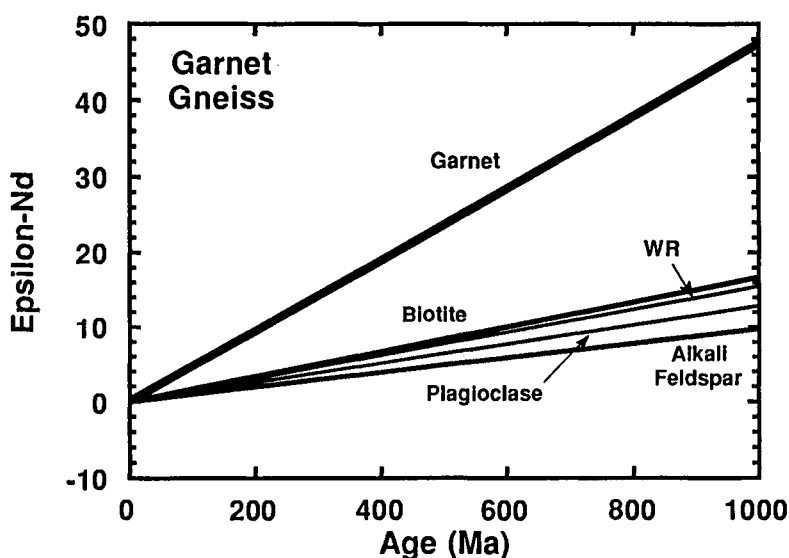


Figure 8.7. The change in Nd isotopic composition with time in minerals of a typical silicic garnet gneiss with a chemical composition similar to the granitic rocks depicted in Figures 8.1 and 8.5. For all minerals and the whole rock (WR), initial (t_0) $\epsilon_{\text{Nd}} = 0.0$. The Sm/Nd ratios depicted in this figure are: 0.61 (garnet), 0.22 (biotite), 0.13 (alkali feldspar), 0.16 (WR), and 0.17 (plagioclase).

8.4.2 Lithogenic elements with fractionating isotopes

Several elements derived through water-rock interactions have stable isotopes that are fractionated from one another by common natural processes. Three will be discussed briefly here: Li, B, and Cl.

Lithium is sufficiently abundant in the earth's crust and in natural waters (Table 8.2) that it will undoubtedly be useful in hydrologic assessments. The two naturally-occurring isotopes of Li, ^6Li and ^7Li , fractionate substantially during a wide variety of natural processes, including mineral formation (chemical precipitation), metabolism, ion exchange (Li substitutes for Mg and Fe in octahedral sites in clay minerals, where ^6Li is preferential over ^7Li), hyperfiltration, and rock alteration (Morozova and Alferovskiy, 1974; Chan and Edmond, 1988; Fritz and

Whitworth, 1994). The use of Li isotopic compositions in catchment waters to recognize the occurrence of one of these processes, or to trace water affected by the processes, should produce valuable results. Unfortunately, the ease with which Li fractionates has made laboratory isotopic analysis very difficult in the past. The Li isotopic fractionation during mass spectrometric analysis could not be controlled or sufficiently characterized. Recently, however, techniques have been developed that appear very promising (Chan, 1987; Xiao and Beary, 1989). Using these techniques, Bullen and Kharaka (1992) examined the Li isotopic compositions from thermal waters of Yellowstone National Park. Because the isotopes will fractionate during hydrothermal processes, it is not surprising that significant variations in the $^7\text{Li}/^6\text{Li}$ ratios were observed. The variations permitted Bullen and Kharaka to distinguish between water derived from marine sedimentary rocks and water derived from hydrothermally altered igneous rocks, thereby providing valuable information regarding regional groundwater flow paths.

Like lithium, boron shows a high degree of mobility in nature, and has two stable isotopes that are easily fractionated by a variety of natural processes (^{10}B and ^{11}B). The B isotopes are fractionated during H_2O phase changes in hydrothermal systems (Spivack et al., 1990; Leeman et al., 1992), during hydrothermal alteration of rock (Spivack, 1985), during mineral crystallization (Oi et al., 1989), during biological activity (Vengosh et al., 1994a; Eisenhut et al., 1996) and during the adsorption of dissolved B onto clay minerals (Schwarcz et al., 1969). The latter effect may be responsible for the large ^{11}B enrichment in seawater relative to both oceanic crust (Spivack and Edmond, 1987) and continental crust (Spivack et al., 1987). All of these effects combine to produce B isotopic variations in hydrologic systems that can be very useful. They have been used to trace the origin of water masses (Palmer and Sturchio, 1990; Xiao et al., 1992; Vengosh et al., 1995), to track the evolution of brines (Vengosh et al., 1991a; 1991b; Moldovanyi et al., 1993), to identify the origin of solutes within thermal springs (Vengosh et al., 1994b), to determine the origin of evaporites (Swihart et al., 1986; Vengosh et al., 1992), to examine hydrothermal flow systems (Leeman et al., 1992), and to trace groundwater contamination from microbiologically-treated sewage (Vengosh et al., 1994a). These studies suggest that under the appropriate circumstances, and for appropriate questions, boron could have applications in catchment hydrology. There are many aspects of B isotopic systematics in natural waters that remain poorly understood (see discussions in Vengosh et al., 1992; and Bassett, 1990). It may be fruitful to begin looking at boron isotopic ratios in "simple" catchment systems where high temperature boron isotopic fractionation is not presently occurring. Catchments systems in which the role of clay minerals can be clearly identified may provide particularly valuable information.

Like Li and B, Cl has two stable isotopes (^{35}Cl and ^{37}Cl) and is highly mobile in the hydrosphere. Unlike the isotopes of those two elements, however, Cl isotopes are not easily fractionated in nature. Small variations in $^{37}\text{Cl}/^{35}\text{Cl}$ values ($\delta^{37}\text{Cl} < 2.1\text{‰}$; for the definition of $\delta^{37}\text{Cl}$, see Table 8.1, note 2) were reported by Kaufman et al. (1984) in a number of different water types. In a single deep groundwater system in Texas, variations in $\delta^{37}\text{Cl}$ ranged from -1.29 to +0.53 ‰. Smaller, though still significant differences were reported for formation waters from the Michigan Basin (Kaufman et al., 1993). Desaulniers et al. (1986) reported evidence suggesting Cl isotope fractionation during diffusion-controlled processes in groundwater from Quaternary glacial deposits. Fractionation also can occur during high-temperature water-rock interactions (Eastoe et al., 1989). The ratio may also be affected by temperature variation in the ocean reservoir through time (Kaufman et al., 1993). Therefore, although there are no low-temperature fast-kinetic fractionation mechanisms for Cl isotopes,

there are sufficient isotopic variations in nature to make $\delta^{37}\text{Cl}$ useful as a hydrologic tracer. Depending on catchment lithology, the Cl isotopes might be useful for hydrograph separation analysis and determination of region-groundwater/catchment-groundwater mixing.

8.4.3 New directions in catchment hydrology for cosmogenic nuclides

For catchment hydrologic applications, the use of all cosmogenic nuclides except ^3H and ^{14}C can be considered "new directions". The uses of ^{36}Cl and ^{129}I discussed above are all today less than 10 years old, and many of the potential applications have not yet been attempted. Several cosmogenic nuclides, including ^7Be , ^{10}Be , ^{22}Na , ^{24}Na , and ^{41}Ca (Table 8.1) have had little or no attention in hydrology and may have significant value to catchment studies.

Beryllium is a strongly lithophilic element, tending at pH levels greater than about 5.5 to sorb onto mineral surfaces rather than to exist in solution in surface and ground waters. However, since most rainwater in North America has a pH less than 5, cosmogenic Be produced in the atmosphere will enter into solution and be readily transported to the Earth's surface. As the precipitation quickly becomes more alkaline, Be drops out of solution. Cosmogenic ^{10}Be that is produced in the atmosphere thereby accumulates in the uppermost soil layer, where its long half-life (1.6 Ma) permits a long residence time. The presence of ^{10}Be , and its radioactive decay, have been used to examine soil erosion (Pavich et al., 1985; Brown et al., 1995), regolith soil formation (Barg et al., 1992), and the development of lateritic soils (Bernat et al., 1990). The use of ^{10}Be present in authigenic material in weathering soils appears to be a valuable tool for dating the soil minerals and thereby determining soil formation rates (Barg et al., 1992). Concentrations of ^7Be and ^{10}Be have been measured in precipitation samples from several locations (Dominik et al., 1987; Brown et al., 1989; Brown et al., 1992; Knies et al., 1994), and in atmospheric aerosols (Dibb et al., 1994). The ratio of ^{10}Be to the stable beryllium isotope, ^9Be , has been measured in filter retentates from river waters and associated sediments (Brown et al., 1992, 1995). The atmospheric flux of cosmogenic ^7Be (half-life ≈ 53 days) has been measured, and the input-output budget within an alpine watershed used to determine erosion rates and fluvial transport mechanisms (Dominik et al., 1987).

No studies have as yet been published reporting beryllium nuclide contents in groundwater samples. Beryllium isotopes would seem to have *potential* utility in catchment hydrology because of the different Be nuclide contents and ratios that must exist in different compartments within a catchment system. For example, precipitation will have high ^7Be contents and a fairly uniform $^7\text{Be}/^{10}\text{Be}$ ratio (measured at ~ 0.67 ; Brown et al., 1989), soil pore water will contain significantly more ^{10}Be relative to ^7Be due to accumulation of ^{10}Be and the short half-life of ^7Be , groundwater older than several months will contain very little or no ^7Be , and very old groundwater will contain no ^{10}Be . The stable Be isotope, ^9Be , would permit some constraint on observed variations in radioactive nuclide content that would be due to sorption. Thus while Be may prove analytically difficult because of its low concentrations in catchment waters, and because interpretations would require close consideration of sorption versus solution behavior, the substantial differences in nuclide contents between important catchment compartments may make Be isotopes worth examining.

Elemental *sodium* is often used as a tracer in hydrologic studies. It is a mobile element that participates in some well documented precipitation and dissolution reactions in groundwaters

(clay formation, albitization of plagioclase), and has therefore received considerable attention in hydrologic research. Substantial concentrations of two cosmogenic Na isotopes (^{22}Na , half-life = 2.605 years; ^{24}Na , half-life = ~ 15 hours) have been measured in precipitation (Roedel, 1970; Perkins et al., 1970). However, no studies have as yet been published documenting the cosmogenic sodium systematics in ground or surface waters. The short duration of their half-lives (i.e. high decay rate) makes their measurement relatively easy by common radioanalytical techniques. The high degree of mobility combined with the short half-lives suggests that cosmogenic Na may be useful in characterizing catchment processes thought to occur on short time scales. Examples of such processes would include soil water movement (macropore flow versus intergranular flow), storm hydrograph separation (overland flow versus long-duration throughflow), fracture-facilitated fast path infiltration, and chemical mixing in lakes and rivers.

Calcium is one of the most useful elements to hydrologic studies, participating in a wide variety of hydrochemical processes. For this reason, ^{41}Ca may have utility in hydrologic studies. Unlike the Be and Na nuclides discussed above, ^{41}Ca is not primarily produced in the atmosphere, but rather is produced by neutron activation of ^{40}Ca . Most of its production is in the upper meter or so of the soil column where the cosmogenic neutron flux is still sufficiently strong. Because the half-life of ^{41}Ca is about 100,000 years, the hydrochemical cycling of ^{41}Ca atoms could be substantial. The geochemical behavior of Ca is closely related to calcite formation and dissolution. This would suggest that ^{41}Ca may be useful in studies that are focused on the carbon cycle. Natural levels of $^{41}\text{Ca}/\text{Ca}$ are on the order of 10^{-16} to 10^{-13} , within the analytical abilities of modern accelerator mass spectrometry (Kutschera, 1990). No published studies have as yet applied ^{41}Ca to hydrology.

8.5 Lithogenic and Cosmogenic Tracers in Catchment Hydrology: Concluding Remarks

This chapter provided a broad overview of the applications of lithogenic and cosmogenic nuclides to hydrology in general, and to catchment hydrology in particular. In spite of the fact that reference is made to many tens of studies in isotope hydrology, the ability of lithogenic and cosmogenic nuclides to provide valuable information to hydrologists has been investigated only rather recently. In many cases, the systematics of behavior of the nuclides within natural waters is still largely undocumented. This means, unfortunately, that the time has not yet come when lithogenic and cosmogenic nuclides can be used on a routine basis wherein interpretations become standard and easily referenced to other similar studies. This does mean, fortunately, that the study of lithogenic and cosmogenic nuclides in catchment systems is still exciting and new, with important observations and discoveries still lying ahead.

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Chapter 9

Dissolved Gases in Subsurface Hydrology

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9.1 Introduction

Dissolved gases have been used as tracers of water residence times, recharge temperatures and elevations, ground-water/surface-water interactions, and injected directly to evaluate mass transport processes. Many dissolved gases are essentially geochemically conservative making them ideal tracers of physical transport in the subsurface. Furthermore, modern analytical methods are capable of detecting extremely small quantities of dissolved gases (e.g. ca. 1000 atoms of ^3He) and as a result, the introduction (either naturally or via intentional injection) into watersheds seldom results in significant changes in fluid properties (e.g. density and viscosity).

Several books have discussions on the use of dissolved gases as environmental tracers: *Noble Gas Geochemistry* (Ozima and Podosek, 1983), *Applied Isotope Hydrogeology, A Case Study in Northern Switzerland* (Pearson et al., 1991), *Chemical and Isotopic Groundwater Hydrology: The Applied Approach* (Mazor, 1997), *Isotopes of Noble Gases as Tracers in Environmental Studies* (IAEA, 1992), and *Regional Ground-Water Quality* (Alley, 1993). Nearly all studies of dissolved gases in the subsurface have examined water under fully saturated conditions. Undoubtedly, there are potential applications of dissolved gases in partially saturated porous media, but the focus of this chapter will be fully saturated conditions in shallow groundwater.

9.2 Occurrence and Transport of Dissolved Gases

Dissolved gases in groundwater can be either of atmospheric or subsurface origin. Recharging water will tend to equilibrate with a gas phase in the unsaturated zone. In general, gas composition in the unsaturated zone will be similar to the atmosphere (with the exception of oxygen and carbon dioxide that are consumed (O_2) and produced (CO_2) in the soil zone) and thus recharging groundwater will have dissolved gas concentrations that are close to air saturation.

The solubility of gases in water varies considerably with the molecular weight of the gas and the temperature of the water. Figure 9.1 shows the Bunsen coefficient of several gases as a function of temperature. A strong positive correlation between molecular weight and solubility is apparent in Figure 9.1. Therefore, the Bunsen Coefficient at 0°C for He (MW = 4) and Xe (MW = 131.3) is 9.5 and 226, respectively. The solubility of gases shown in Figure 9.1 can be computed using empirical data from Benson and Krause (1976), as reported by Andrews (1992).

$$S = \frac{1.244 \times 10^6 \cdot \rho \cdot p \cdot \exp(-M K_s)}{1000 \cdot K}$$

$$\frac{1}{K} = \exp \left[A \left(\frac{T_1}{T} - 1 \right) + 36.855 \left(\frac{T_1}{T} - 1 \right)^2 \right] \quad (9.1)$$

$$K_s = a \left(\frac{T}{100} \right)^3 + b \left(\frac{T}{100} \right)^2 + c \left(\frac{T}{100} \right) + d$$

where S = the amount of gas dissolved in cm^3 (STP) per cm^3 of water; ρ = the solution density in g/cm^3 ; p = the partial pressure of gas in the atmosphere in atm; K = the Henry coefficient; T = absolute temperature ($^\circ\text{K}$); K_s = the salting coefficient; M = Cl^- molarity of the solution; A , T_1 , a , b , c and d are empirical constants shown in Table 9.1. For salinities less than 1 g/L the term $\exp(-M K_s)$ is near unity and is often neglected.

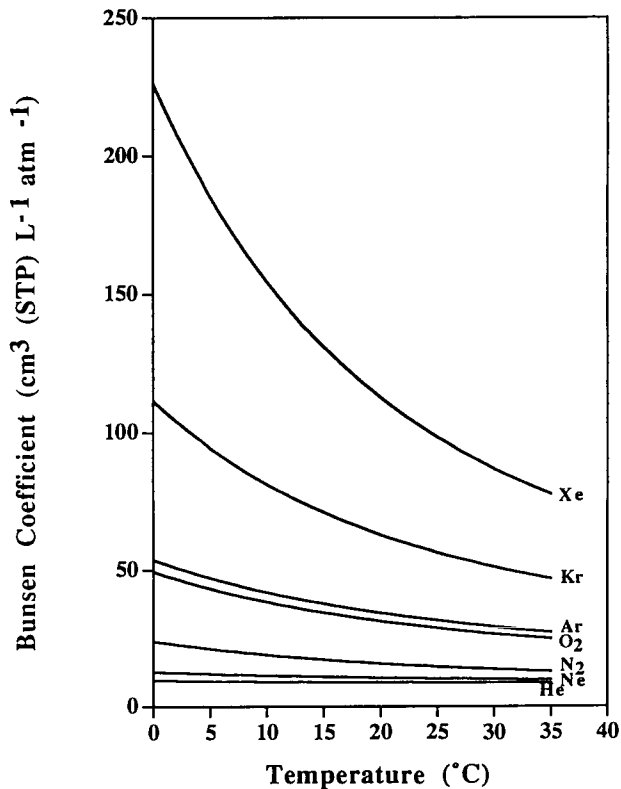


Figure 9.1. Variations of the solubility of atmospheric gases as a function of temperature. The Bunsen Coefficient is the volume (ml) of gas (measured at STP) dissolved per volume (L) of solution when the partial pressure of the gas is 1 atm.

Determination of recharge temperatures

Because the solubility of dissolved gases depends on temperature, it is possible to estimate recharge temperatures of groundwater based on measurements of the dissolved concentration of atmospheric gases (Sugisaki, 1961; Mazor, 1972; Stute et al., 1992a). The recharge temperature is the temperature at which groundwater equilibrates with a gas phase. Final gas equilibration occurs theoretically at the top of the capillary fringe (as defined in Chapter 1) which is generally near (10 to 50 cm) the water table. Although fluctuations in temperature at land surface propagate downward, high frequency fluctuations (annual and greater) are virtually attenuated at depths greater than 10 m (Hillel, 1980). Thus, the temperature at the top of the capillary fringe (i.e. recharge temperature) is generally near the mean annual surface temperature.

Table 9.1. Empirical constants and atmospheric partial pressure for computing dissolved concentrations of various gases using Equation 9.1.

	He	Ne	N ₂	O ₂	Ar	Kr	Xe
A	41.824	41.667	41.712	40.622	40.404	39.781	39.273
T _i	131.42	142.5	162.02	168.85	168.87	179.21	188.78
Partial Pressure	5.24E-06	1.82E-05	0.781	0.209	9.34E-03	1.14E-06	8.60E-08
a	-0.2304	-0.3022	-0.2427	-0.3616	-0.4050	-0.1124	-0.1611
b	2.2951	3.6278	2.1504	3.3454	3.8471	1.3282	1.9007
c	-7.7154	-13.6641	-6.6100	-10.5501	-12.3389	-5.1432	-7.3019
d	9.0060	16.8309	7.4294	11.6687	13.6921	6.8403	9.5072

The precision of calculated recharge temperatures depends on the precision and accuracy of dissolved gas measurements along with the validity of the gas-water equilibrium assumption described above. Modern analytical measurements can provide dissolved gas data with an uncertainty of less than 1% which corresponds to a temperature uncertainty of less than 1 °C under conditions of thermodynamic equilibrium.

While gas-water equilibrium can occur, measured dissolved gas concentrations are often greater than expected for equilibrium conditions. In a study of 81 groundwater samples from South Africa, Heaton and Vogel (1981) show that concentrations above equilibrium can be explained by the occurrence of small air bubbles trapped by infiltrating water in the unsaturated zone. These bubbles are thought to dissolve as they are transported below the water table due to an increase in total fluid pressure. The amount of dissolved gas above the equilibrium solubility value is referred to as “excess air.”

Typical amounts of excess air observed in groundwater range from zero to about 30 cc (STP)-air/kg-water. The influence of a fixed amount of excess air on dissolved gas concentrations is

greatest for gases having low solubilities. For example, the addition of 10 cc (STP)-air/kg-water will cause the dissolved concentration of Ne to differ from equilibrium solubility (at 0°C) by about 85%, but the dissolved Xe concentration will differ by only 4%. If air bubbles dissolve completely and no fractionation occurs, it is possible to estimate the amount of excess air using dissolved Ne data. This is possible because the temperature dependence of Ne solubility is minor compared to that of heavier gases and thus equilibrium solubility for Ne can be estimated without an a priori estimate of recharge temperature. If fractionation occurs during bubble dissolution, it is not possible to estimate the amount of excess air and hence the recharge temperature estimate may be erroneous. Stute and Sonntag (1992) compared noble gas recharge temperatures to actual soil temperature measurements and for most samples found agreement to within 1°C indicating that fractionation is minor.

Dissolved gas transport through fully saturated porous media is similar to ionic species as far as advection, dispersion, and diffusion are concerned. However, when both liquid and gas phases exist, dissolved gases having low solubilities will tend to partition into the gas phase which will strongly influence dissolved gas transport (Fry et al., 1995). Water that is at saturation with a gas at the water table becomes undersaturated below the water table as a result of rising fluid pressure. As a result, gases that are of atmospheric origin are typically undersaturated in shallow groundwater systems below the annual low water table. In laboratory columns however, the existence of both liquid and gas phases is common as it is extremely difficult to avoid trapping air upon saturation of the column. Trapped gas may also be prevalent near the water table in aquifers that experience significant water table fluctuations. When a trapped gas phase does exist, Fry et al. (1995) have shown that dissolved gases are retarded relative to bulk fluid movement. Assuming a linear equilibrium mass transfer, Fry et al. (1995) show that the retardation factor for dissolved gases is given by:

$$R = 1 + H' (V_g / V_w) \quad (9.2)$$

where H' is the dimensionless Henry's coefficient, and V_g and V_w are the volumes of trapped gas and water phases, respectively. Fry et al. (1995) determined retardation factors for dissolved oxygen ranging from 1 to 6.6 as V_g/V_w increases from 0 to 0.1.

9.3 Shallow Groundwater Dating

A direct measure of the travel time of groundwater from recharge to discharge points is of considerable use for evaluating fluid flow, mass transport, and water quality in watersheds. Plummer et al. (1993) summarized ground water dating methods (see Figure 9.2) and recognized two classes of chronologic tracers: (1) those that mark the occurrence of a particular event, such as fallout from nuclear activities, and (2) those that are present worldwide as a result of continuous inputs from the atmosphere and allow a continuum of age determinations. Event markers can provide an unambiguous measure of groundwater age, but generally suffer from the limitation that very detailed profiles of samples are required to locate these events. In this section we treat only the methods that allow a continuous measure of age such that measurements from even a single sample can be useful. Of the continuous age tracers shown in Figure 9.2, those that range from 0 to about 50 years are likely to be the most useful for watershed studies, and all of these employ dissolved gases.

Water molecules are continually associating and disassociating and thus the term “groundwater age” has little meaning in the usual sense as the elapsed time since formation. We use the term groundwater age to imply the mean travel time of water from the point of recharge to the point of collection. The dating methods described in this chapter use dissolved gases and thus zero age is generally taken to be the water table (or top of the capillary fringe) where water becomes isolated from a gas phase. Because of hydrodynamic dispersion, individual water molecules in a given sample will experience different travel times. In cases where dispersion is a strong process (i.e. when the range of travel times in a sample is large), a mean travel time may be of limited value. Furthermore, the results of hydrodynamic dispersion are tracer specific, and thus the apparent age determined by a particular tracer may not coincide with the mean travel time in the above definition of groundwater age (although as discussed below, this difference is thought to be small for many hydrogeologic situations).

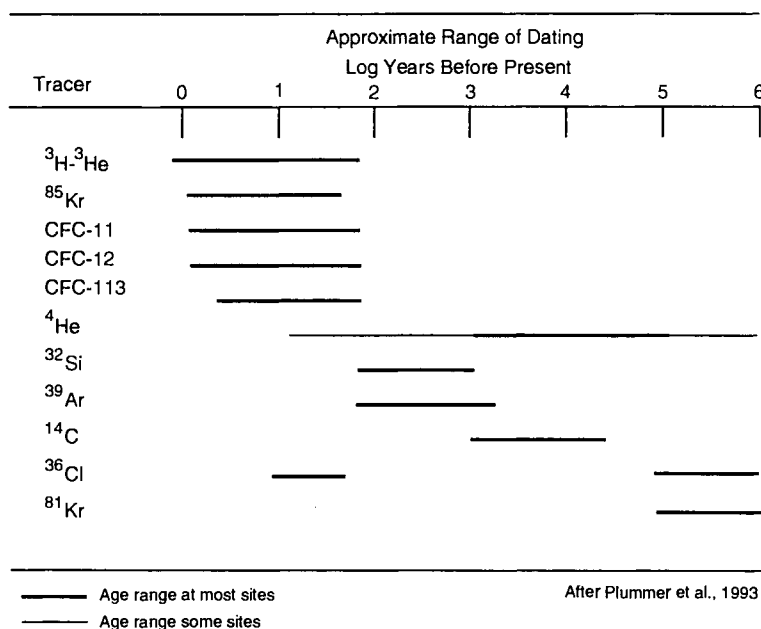


Figure 9.2. Approximate range (in years) of dating applications of dissolved-gas age tracers; modified from Plummer et al. (1993).

The distribution of groundwater age in different types of aquifers is depicted in Figure 9.3. If recharge is constant across the aquifer, then the age profile will be also be constant, and contours of groundwater age will be horizontal (Figure 9.3a). The groundwater age profile will be concave upwards. If recharge decreases downgradient, then groundwater age contours will rise towards the surface (Figure 9.3b). Where a unit of low conductivity overlies one of high conductivity, the groundwater age profile may display an apparent age inversion (Figure 9.3c). The distribution of groundwater age within an aquifer system allows estimation of many groundwater parameters, including recharge rates and flow velocities.

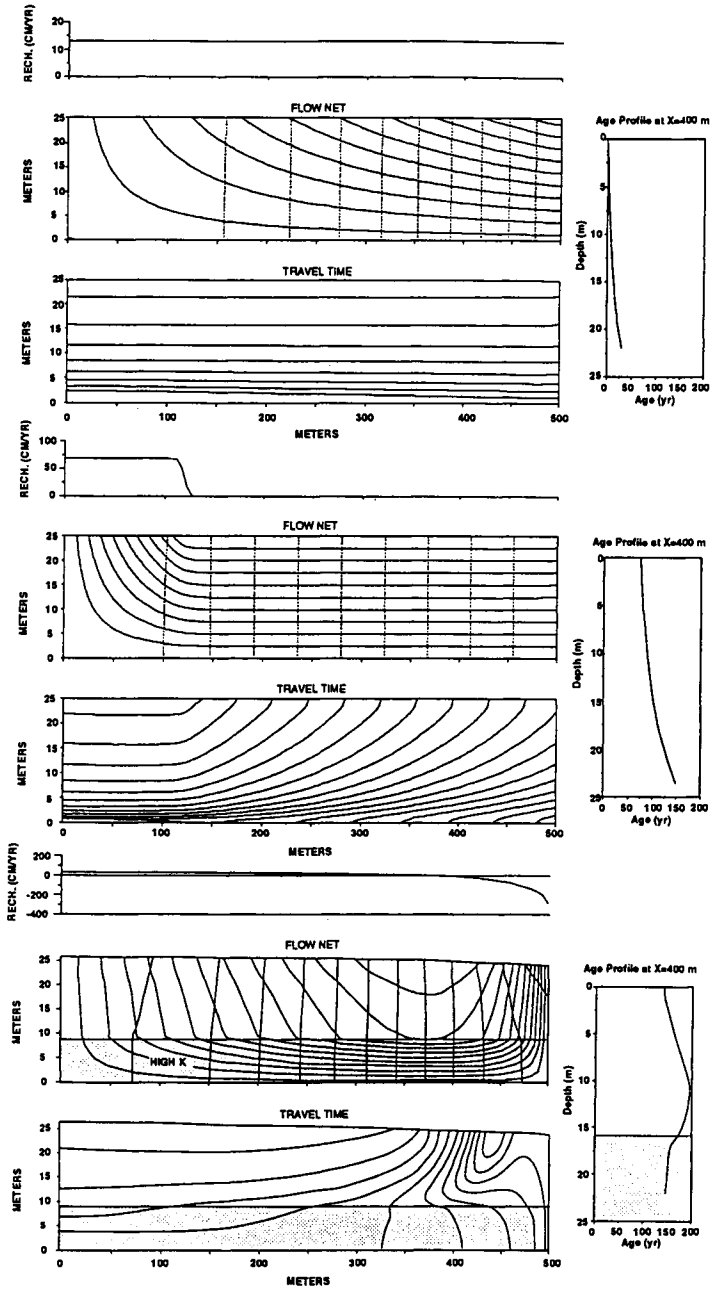


Figure 9.3. Groundwater age (travel time) distributions in generic aquifers for purely advective transport: (a) constant recharge, (b) recharge decreasing downgradient, (c) recharge decreasing downgradient (discharge downgradient of 400 m), low conductivity over high conductivity layering. (The left hand and lower boundaries for all simulations are no flow. For (a) and (b) the right hand boundary is constant head, and for (c) it is no flow.) Figure 9.3c is similar to a simulation presented by Goode et al. (1996).

Reilly et al. (1994) demonstrate the use of age data to calibrate a groundwater flow model, which was then used to provide estimates of flow rates, flow paths and dispersive properties of the groundwater system. Similarly, Robertson and Cherry (1989) and Solomon et al. (1993) used age data to calibrate a groundwater flow and transport model of the Sturgeon Falls aquifer, and hence estimate spatial variations in recharge, dispersivity and tortuosity values. Cook et al. (1995) used the same model to simulate chlorofluorocarbon profiles, and hence estimate groundwater recharge rates, with an estimated accuracy of 20%.

In order to use dissolved-gas tracers to determine recharge rates, however, advective transport must dominate over diffusive transport. Solomon and Cook (1994) calculated that when fluid velocities are less than about 100 mm/yr diffusive transport becomes significant for many tracers, and at fluid velocities of 10 mm/yr, diffusion dominates the transport. Thus, recharge rates > 30 mm/yr (assuming a porosity of 0.3) can be determined after correcting for diffusion, but lower recharge rates cannot be reliably determined using dating methods.

In some cases, groundwater dating using dissolved gas tracers can also provide estimates of horizontal flow velocities. Solomon et al. (1995) used age dating of a groundwater contaminant plume at Cape Cod, MA to estimate the horizontal groundwater velocity, as well as the recharge rate. Because recharge estimates were made from a flow divide to a point of interest (and local recharge is the only source of water to this unconfined aquifer) it was possible to estimate horizontal groundwater velocities by integrating the spatial recharge patterns and then invoking conservation of mass. A direct determination of horizontal velocity from age data may not be possible at locations far from a flow divide, or where sources of water from other than local recharge exist (e.g. upward leakage through an aquitard).

Groundwater dating has also been used to reconstruct past releases of contaminants to aquifers. Bohlke and Denver (1995) and Johnston (1994) used age dating methods to reconstruct past nitrate loads to unconfined aquifers beneath agricultural land. Solomon et al. (1995) used age dating to estimate the year in which a solvent spill to groundwater occurred. Measurement and interpretation of chlorofluorocarbons (CFCs), ^{85}Kr and ^4He concentrations and the $^3\text{H}/^3\text{He}$ ratio in groundwater are techniques which have become available within recent years that allow direct dating of single groundwater samples. These tracers are often able to estimate groundwater ages with an uncertainty of only a few years for groundwaters recharged since the 1950s (except for ^4He which is applicable to older waters). Both the CFC and $^3\text{H}/^3\text{He}$ methods are now widely used in oceanography (Wallace et al., 1992) and limnology (Torgersen et al., 1977; Kipfer et al., 1994) to study the circulation of water masses. The discussion that follows on $^3\text{H}/^3\text{He}$, CFC, and ^{85}Kr dating follows closely the review by Cook and Solomon (1996).

9.3.1 $^3\text{H}/^3\text{He}$

The large increase in atmospheric ^3H (12.4 y half-life) that resulted from above-ground testing of thermo-nuclear weapons in the 1960s has been used in a variety of groundwater studies (see Chapter 7). Chemically bound to water molecules, ^3H has generally been considered to be relatively conservative geochemically. Unfortunately, the historic concentration of ^3H is not accurately known globally as atmospheric measurements were only made in a few locations. Furthermore, local sources of ^3H , such as nuclear fuel research and reprocessing facilities, can be significant and are generally not well quantified. The absolute concentration of ^3H in

groundwater is very sensitive to the historic atmospheric concentration and the magnitude of recharge. Because ^3H decays to ^3He it is possible to use ^3H as a quantitative tracer even if the source function is not accurately known, by measuring both ^3H and ^3He . In the unsaturated zone, dissolved ^3He generated from ^3H decay can be lost to the atmosphere. (The atmosphere is a sufficiently large reservoir that its ^3He content is not measurably altered by ^3H decay.) Once isolated from the atmosphere below the water table, dissolved ^3He concentrations will rise as groundwater becomes older. Although groundwaters contain ^3He from several sources other than ^3H decay (see below), determination of both ^3H and tritiogenic ^3He ($^3\text{He}^*$) can be used as a dating tool (Tolstikhin and Kamensky, 1969; Torgersen et al., 1977; Takaoka and Mizutani 1987; Poreda et al., 1988; Schlosser et al., 1988). The $^3\text{H}/^3\text{He}$ age is defined as:

$$t = \lambda^{-1} \ln \left(\frac{^3\text{He}^*}{^3\text{H}} + 1 \right) \quad (9.3)$$

where t is the estimated groundwater age, λ is the ^3H decay constant, and ^3H and $^3\text{He}^*$ are measured in tritium units. For ^3H , one tritium unit (TU) represents one atom of tritium in 10^{18} atoms of hydrogen. For ^3He , one TU is approximately equal to $0.402 \text{ pcm}^3 \text{ kg}^{-1}$, i.e. one TU of ^3H will decay to $0.402 \text{ pcm}^3 \text{ kg}^{-1}$ of ^3He . The method is independent of the ^3H input function when only advective transport is considered, and requires only that measurable concentrations of ^3H and ^3He exist in the groundwater.

The tritiogenic ^3He component is calculated by subtracting from the measured value that due to atmospheric solubility (a function of recharge temperature), excess air and radiogenic production (by decay of U/Th-series elements). These different sources of ^3He are identified by measuring concentrations of ^4He and other noble gases (Torgersen et al., 1977, 1979; Weise and Moser, 1987; Schlosser et al., 1989). Analytical uncertainties usually result in errors in age estimates of less than 10% (Solomon et al., 1993). Sensitivity of $^3\text{H}/^3\text{He}$ age to recharge temperature is less than 0.5 years per $^{\circ}\text{C}$. Sensitivity to excess air is approximately -5.0 years per $\text{cm}^3 \text{ kg}^{-1}$ of excess air for very young water, decreasing to -0.25 years per $\text{cm}^3 \text{ kg}^{-1}$ for water approximately 25 years old. While in theory, excess air and radiogenic ^3He can be estimated and corrected for, in practice this is not always so straightforward. Air entrapment or gas stripping during sampling is also a possible source of error (Solomon et al., 1992b, 1993; Ekwrzel et al., 1994).

Effects of physical transport

In a groundwater system with piston flow and negligible mixing, $^3\text{H}/^3\text{He}$ ages will accurately reflect hydraulic ages (subject to the uncertainties discussed above). However, because ^3H and ^3He concentration gradients will usually be different, and because the diffusion coefficient for helium in water ($5.74 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 10°C ; Jahne et al., 1987) is much higher than that of tritium ($1.57 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 10°C ; Wang et al., 1952), the concentration ratio of these isotopes at any discrete point will not always accurately reflect the groundwater age. Diffusive loss of ^3He to the atmosphere has been shown to lead to underestimates of ages of surface water bodies (Wuest et al., 1992), and will similarly lead to underestimates of groundwater ages (Schlosser et al., 1989).

Diffusive loss of ^3He to the atmosphere is greatest when helium concentrations near the water table are largest, such as when a large ^3H spike is injected in the aquifer and begins to decay.

Consequently, $^3\text{H}/^3\text{He}$ ages near the tritium bomb peak are most seriously affected. Measured vertical profiles of $^3\text{H}/^3\text{He}$ often show much younger ages below the ^3H bomb peak (e.g. Schlosser et al., 1988, 1989), suggesting that this technique should not be used to date water older than the mid 1960s. The effects of dispersion on the $^3\text{H}/^3\text{He}$ age reduces as the ^3H input becomes nearly constant in time, such as during the past 15 years. Thus Solomon et al. (1993) used the vertical $^3\text{H}/^3\text{He}$ age gradient immediately below the water table as an indicator of the vertical water flux.

Long well screens will have a similar effect on $^3\text{H}/^3\text{He}$ dating as high values of the dispersion coefficient. If large screens sample a mixture of water from different depths, then $^3\text{H}/^3\text{He}$ ratios may not reflect the mean age of the groundwater. Ideally, the ratio of the screen length to the vertical water velocity should be not greater than 2 to 3 years. Since vertical velocities generally decrease with depth, the importance of small well screens increases, especially near impermeable boundaries.

Although decay of bomb tritium commences in the unsaturated zone, it is not until it enters the groundwater that ^3He is preserved. This is because gas transport in the unsaturated zone is rapid relative to transport in groundwater. For this reason, a zero $^3\text{H}/^3\text{He}$ age should occur at the water table, and ages should increase with depth below that. In the case of a fluctuating water table, it appears that the $^3\text{H}/^3\text{He}$ clock is set at the seasonal low water table position (Solomon et al., 1993).

9.3.2 Chlorofluorocarbons

Chlorofluorocarbons (CFCs) are man-made organic compounds which are produced for a range of industrial and domestic purposes (Rowland, 1990). Chlorofluorocarbons CFC-11 (CFCl_3), CFC-12 (CF_2Cl_2) and CFC-113 ($\text{C}_2\text{F}_3\text{Cl}_3$) have relatively long residence times in the atmosphere (44, 180 and 85 years, respectively; Cunnold et al., 1994; Ko and Jackman, 1994), and so their atmospheric concentrations are uniform over large areas, and are steadily increasing. Concentrations of these CFCs in ocean basins have been used to study mixing processes, and the movement of deep ocean currents (Trumbore et al., 1991; Wallace et al., 1992). CFC concentrations in groundwater have been used to estimate groundwater age (Thompson and Hayes, 1979; Busenberg and Plummer, 1992; Dunkle et al., 1993).

As shown in Figure 9.4, concentrations of CFC-11, CFC-12 and CFC-113 in the atmosphere have been increasing steadily over the past 50 years (Prinn et al., 1983; Cunnold et al., 1994; Rasmussen and Khalil, 1986.) Atmospheric concentrations show little spatial variation, with only 10% variation observed between average concentrations in Ireland, Oregon, Barbados, Samoa and Tasmania (Cunnold et al., 1994). As a result the atmospheric input of CFCs to the groundwater can be known with a high degree of precision, even at remote sites which is in strong contrast to the spatially variable nature of ^3H concentrations in rainfall. Atmospheric concentrations for the period before their regular measurement have been reconstructed from estimates of worldwide production of chlorofluorocarbons and their rate of release to the atmosphere (McCarthy et al., 1977; AFEAS, 1993).

As a result of various regulations regarding the use of CFCs, production of CFC-11, CFC-12 and CFC-113 is declining. Production estimates for 1992 are approximately half of late 1980s

peak values (AFEAS, 1993). Modeling suggests that atmospheric concentrations of CFC-11 and CFC-12 will reach a maximum before the turn of the century, after which they will slowly decline (Elkins et al., 1993; Khalil and Rasmussen, 1993). The sensitivity of the CFC dating method depends on the rate of change of the atmospheric CFC concentration with time, and thus the ability to date very young water will diminish with time. However, the ability to date groundwater that entered the saturated zone prior to the Year 2000 will not change for several decades.

Apparent CFC ages are obtained by converting measured CFC concentrations in groundwater to equivalent air concentrations using known solubility relationships (Warner and Weiss, 1985; Bu and Warner, 1995) and the recharge temperature. Corrections for excess air are made if appropriate (Busenberg and Plummer, 1992). These concentrations are compared with the atmospheric concentration curve (Figure 9.4) to obtain an apparent CFC age.

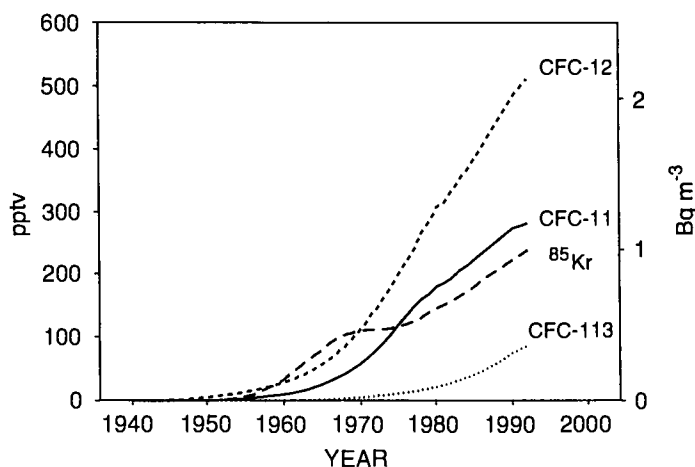


Figure 9.4. Atmospheric concentrations for CFC-11, CFC-12 and CFC-113 (pptv), and specific activity of ^{85}Kr (Bq m^{-3}) from 1940 through to the present. Data for CFC-11 and CFC-12 between 1975 and 1985 is from measurements at the Pacific North West station (USA). Between 1985 and 1990, a linear rate of increase of 10 and 20 pptv yr^{-1} has been assumed for CFC-11 and CFC-12, respectively (Rasmussen and Khalil, 1986). After 1990, a linear increase of 4 and 14 pptv yr^{-1} respectively has been assumed. Concentrations before 1975 are derived from the release data of McCarthy et al. (1977), normalized to concentrations measured in 1975. Atmospheric concentrations of CFC-113 are from Smethie (pers. comm. to pge). The specific activity of ^{85}Kr is modified from Rath's (1988) two-dimensional model simulation, which is fitted to atmospheric observations (Smethie et al., 1992; from Cook and Solomon, 1996).

Concentrations of chlorofluorocarbons in groundwater samples are measured by gas chromatography (Bullister and Weiss, 1988) with an analytical precision that is approximately $\pm 3\%$ for concentrations above 50 pg kg^{-1} . This corresponds to an error in apparent CFC ages of less than 1 year for groundwaters recharged since the mid 1960s (Dunkle et al., 1993). The sensitivity of apparent CFC age to excess air is less than 0.1 year per $\text{cm}^3\text{-air kg}^{-1}\text{-water}$ at 0°C and less than 1 year per $\text{cm}^3 \text{ kg}^{-1}$ at 20°C for CFC-12 and CFC-113. Sensitivity of apparent CFC age to recharge temperature is less than 2 years per $^\circ\text{C}$ for CFC-12 and CFC-113 (for

recharge temperatures below 20°C) and less than 1 year per °C for CFC-11 (Cook and Solomon, 1996). Hence, allowing for analytical precision and uncertainty in atmospheric concentrations, the accuracy of apparent CFC ages in a purely advective flow system is better than ± 4 years, provided that excess air can be estimated to within $1 \text{ cm}^3 \text{ kg}^{-1}$, and recharge temperature to within 1°C.

Effects of physical transport and biochemical processes

The effect of dispersion on apparent CFC concentrations and ages has been discussed by Busenberg and Plummer (1992), Plummer et al. (1993), Ekwurzel et al. (1994) and Reilly et al. (1994). Because the atmospheric concentration curve is approximately linear with time, dispersion has a minimal effect on concentration profiles. Modeling results show that only waters older than 20 years are significantly affected. For dispersivities of less than 0.5 m, the age error will be less than 3 years for groundwaters recharged since 1955 (Plummer et al., 1993; Ekwurzel et al., 1994).

Sorption of CFCs to aquifer materials may cause CFC velocities to be lower than water velocities in some aquifers. This will result in apparent CFC ages which are older than groundwater ages. In particular, Cook et al. (1995) observed significant retardation of CFC-113 in a shallow, silty sand aquifer, resulting in apparent CFC-113 ages being greater than CFC-12 ages by between 30 and 50%. Sorption of CFC-12 appeared minimal in this system. In contrast, Busenberg and Plummer (1993) found good agreement between CFC-12 and CFC-113 ages in a shallow, coarse sand aquifer on the Delmarva Peninsula. In both cases, the organic carbon content of the aquifer (which often controls the amount of sorption) was very low and thus CFC sorption mechanisms are unclear. Significant sorption of CFC-113, and to a lesser extent CFC-11, to aquifer materials has also been reported in column studies by Ciccioli et al. (1980), Brown (1980) and Jackson et al. (1992). Although further work is still needed, sorption of CFC-11 and CFC-12 do not appear to be important processes in low organic carbon aquifers.

Degradation of chlorofluorocarbons under anaerobic conditions has been widely reported in landfills and laboratory studies (e.g. Khalil and Rasmussen, 1989; Semprini et al., 1992; Lovley and Woodward, 1992). Cook et al. (1995) reported degradation of CFC-11 under natural conditions, where dissolved oxygen concentrations were below approximately 0.5 mg/l. CFC-12 and CFC-113 were not significantly degraded at this site. Similarly, Dunkle et al. (1993) and Katz et al. (1995) observed apparent CFC-11 ages which were considerably older than CFC-12 ages from wells with dissolved oxygen below 0.5 mg/l.

One of the assumptions of groundwater dating with CFCs is that concentrations in the soil gas immediately above the water table are in equilibrium with the atmosphere. However, this is not necessarily the case, particularly if the unsaturated zone is thick (Weeks et al., 1982; Severinghaus et al., 1994). Cook and Solomon (1995) showed that there is a time lag associated with diffusion of these gases through the unsaturated zone. The magnitude of the time lag is strongly dependent on the soil water content and CFC solubility, and to a lesser extent on the recharge rate. The time lag is negligible if the unsaturated zone thickness is less than 5 m, and varies between 0.5 and 3 years for a unsaturated zone thickness of 10 m. For a 30 m thick unsaturated zone, the time lag ranges between 5 and 20 years. Johnston (1994) found groundwater ages beneath a 25 m thick unsaturated zone in southern Ontario determined using CFC-11 to be consistently greater than $^3\text{H}/^3\text{He}$ ages by approximately 8 years, which he attributed to this effect.

Contamination of groundwater with chlorofluorocarbons appears to be the greatest limitation to CFC dating. Other organic contaminants may contain small quantities of CFCs, sufficient to cause serious contamination at the parts per trillion level. If not already present in the contaminants, large quantities of CFCs may partition from the atmosphere into other organic liquids, possibly resulting in high measured concentrations in the groundwater. Groundwater samples from residential and industrial sites often contain concentrations of CFCs above modern atmospheric levels, in some instances by several orders of magnitude (Thompson and Hayes, 1979; Jackson et al., 1992; Busenberg and Plummer, 1992). Concentrations of CFCs in excess of those in water at equilibrium with the atmosphere were observed by Russell and Thompson (1983) and attributed to sorption onto aquifer solids. However, the occurrence of excess CFCs and the mechanisms leading to this condition have not been well studied. Elevated atmospheric concentrations may occur close to industrial centers (Lovelock, 1972; Cook et al., 1996; Johnston, 1994). It is possible that some well construction materials and sampling methods may also contaminate samples (Thompson and Hayes, 1979; Reynolds et al., 1990; Dunkle et al., 1993).

9.3.3 ^{85}Kr

^{85}Kr is a radioactive noble gas, with a half-life of 10.76 years. It is produced by fission reactions, mostly in nuclear reactors. Worldwide emission of ^{85}Kr increased from less than 5 PBq/yr (peta-becquerels per year) before 1950 to approximately 350 PBq/yr in 1986 (Weiss et al., 1992). ^{85}Kr releases are concentrated over North America, Western Europe and the former Soviet Union, with no significant releases in the Southern Hemisphere (Jacob et al., 1987). Atmospheric concentrations of ^{85}Kr have increased from less than 10^{-2} Bq/m³ before 1950 to approximately 0.8 Bq/m³ in 1986 (Figure 9.4). Concentrations in groundwater have been used as a dating tool over this time scale (e.g. Rozanski and Florkowski, 1979; Smethie et al., 1992; Ekwurzel et al., 1994). There are no significant sources or sinks (besides radioactive decay) for ^{85}Kr in the subsurface and thus the decay-corrected concentration in groundwater is directly related to the atmospheric concentration at the time of recharge.

The specific activity of ^{85}Kr in the atmosphere over the Northern Hemisphere is shown in Figure 9.4. Regular measurements have been made since 1973 in Freiburg, Germany, and more recently at stations in Poland, USA, Spain, South Africa, Austria, Australia and Antarctica (Weiss et al., 1992). Latitudinal variations have been successfully predicted by global atmospheric transport models (Jacob et al., 1987; Zimmerman et al., 1989). Concentrations of ^{85}Kr in the lower atmosphere show considerable spatial variability, primarily reflecting the locations of the major sources. A strong concentration gradient also exists between the northern and southern hemispheres. Concentrations at the North Pole are approximately 30% higher than the South Pole in January, when convective mixing is least important (Jacob et al., 1987; Zimmerman et al., 1989).

Groundwater ages are obtained by correcting the measured ^{85}Kr activity in groundwater for radioactive decay, until a point on the atmospheric curve is obtained. A nomograph is often used for this purpose (Smethie et al., 1992). Because it is the ratio of ^{85}Kr to stable krypton which is measured, the method is independent of both the recharge temperature and excess air trapped during recharge. Similarly, the method will not be sensitive to partial sample loss either in sampling or analysis, provided that contamination with modern atmospheric air does not

occur. Detection limit is 0.05 Bq/m^3 , which is about the ^{85}Kr activity groundwater recharged in 1963 (Smethie et al., 1992).

The primary difficulty with using ^{85}Kr , is that because of its low solubility and low atmospheric concentration, very large volumes of water are required for analysis. At least 100 liters of water are usually required, and contact with the atmosphere must be avoided (Rozanski and Florkowski, 1979). Dissolved gases are extracted from the water samples in the field by vacuum extraction. Sampling and analytical methods are discussed by Smethie and Mathieu (1986). Analytical precision is approximately $\pm 4\%$. Recent technical developments suggest the possibility of accurate ^{85}Kr measurements on water samples of 10 - 20 liters by laser-based resonance ionization spectroscopy (Thonnard et al., 1992). However, the cost of such a method is currently prohibitive for most hydrogeological investigations. Uncertainty in the atmospheric concentration curve at remote sites may result in an uncertainty in age of up to 5 years.

Effects of physical transport processes

As with chlorofluorocarbons (see above), dispersion within the aquifer will tend to cause elevated concentrations in older waters and hence result in underestimation of groundwater ages. However, for dispersivities less than 0.5 m, the error will be less than 1 year for groundwaters recharged after 1970 (Ekwurzel et al., 1994).

The use of ^{85}Kr dating assumes that soil gas immediately above the water table is in equilibrium with the atmosphere. If this is not the case, then groundwater ages may be overestimated. The error is likely to be negligible if the unsaturated zone thickness is less than 5 m, but increases from approximately 1.5 years to over 20 years as the unsaturated zone thickness increases from 10 to 40 m (Cook and Solomon, 1995).

9.3.4 Radiogenic ^4He

Observed concentrations of ^4He in deep groundwater often exceed the concentration in equilibrium with the atmosphere by many orders of magnitude due to subsurface production (Davis and De Wiest, 1966; Marine, 1979; Andrews and Lee, 1979; Torgersen, 1980; Stute et al., 1992b). This production results mostly from the α -decay of natural U- and Th-series elements in rocks and sediments. Mass transfer between aquifer solids and groundwater occurs resulting in a relationship between groundwater travel time (or contact time) and the ^4He concentration in groundwater. If the ^4He solid to liquid mass transfer rate is known, it is possible to use ^4He as a quantitative tracer of groundwater travel times (e.g. Marine, 1979; Andrews and Lee, 1979; Torgersen, 1980; Andrews et al., 1982; Andrews et al., 1985; Torgersen and Ivey, 1985; Balderer and Lehmann, 1989; Mazor and Bosch, 1990, 1992; Fu et al., 1990; Bottomley et al., 1990; Ballentine et al., 1991; Stute et al., 1992b; Marty et al., 1993). If the solid to liquid mass transfer rate is governed by the radioactive decay of U and Th, significant (i.e. measurable) amounts of radiogenic ^4He will exist in groundwater after a contact time on the order of 1000 years, and ^4He can theoretically continue to accumulate for millions of years. Thus, ^4He has generally been considered to be a hydrologic tracer over time scales of 10^3 to 10^6 years (e.g. Mazor and Bosch, 1992); however, a recent study by Solomon et al. (1996) has shown that the ^4He solid to liquid mass transfer rate is more than 100 times greater than can be supported by U- and Th-series decay in numerous shallow aquifers. Solomon et al. (1996) show that some aquifer solids are currently losing ancient ^4He (that was previously

trapped within crystal lattices) at rates that are controlled by solid state diffusion. If quantified, such high solid to liquid mass transfer rates allow groundwater dating with ^4He for water as young as 10^1 years and possibly as old as 10^3 years.

Groundwater ages using ^4He are computed by determining the solid to liquid mass transfer rate, and then measuring the ^4He content of groundwater samples. The solid to liquid mass transfer rate can be determined directly in the laboratory or by calibration using groundwater age data obtained using a different (i.e. CFCs or $^3\text{H}/^3\text{He}$) dating method. The laboratory procedure used by Solomon et al. (1996) involves the placement of aquifer solids into an “on-line” stainless steel tube furnace that was then put under high vacuum to remove air (including He) from the pore space. The sample is then sequentially heated with an external resistive heater while measuring both the isotopic composition and total amount of He released using a noble gas mass spectrometer (see Poreda and Farley (1992) for more complete details of the analytical procedure). The He solid state diffusion coefficient increases dramatically with increasing temperature and thus heating allows measurements to be made in a relatively short amount of time. The results are plotted as the He release rate versus temperature and extrapolated to the in-situ temperature to obtain an estimate of the solid to liquid mass transfer rate in the aquifer.

The calibration procedure involves the collection of groundwater samples of various ages (as determined using CFCs, $^3\text{He}/^3\text{H}$, or ^{85}Kr) along with measurements of the radiogenic component of ^4He (see below). The mean solid to liquid mass transfer rate can then be computed for young waters, and this value can be extrapolated to older waters (assuming the mass transfer rate is spatially uniform).

Once the solid to liquid mass transfer rate has been estimated, groundwater ages are determined by measuring total He and Ne in groundwater samples, and computing the component of radiogenic ^4He . Because groundwater contains ^4He from the atmosphere as well as that released from solid phases, it is necessary to separate radiogenic from atmospheric ^4He . The component of ^4He that results from in situ production can be determined as (e.g. Schlosser et al., 1989):

$$^4\text{He}_{\text{rad}} = ^4\text{He}_m - ^4\text{He}_{\text{sol}} - [N_{\text{e}_m} - N_{\text{e}_{\text{sol}}}] \cdot R_{\text{He-Ne}} \quad (9.4)$$

where $^4\text{He}_{\text{rad}}$ = radiogenic component of ^4He ; $^4\text{He}_m$ = measured ^4He concentration; $^4\text{He}_{\text{sol}}$ = solubility ^4He concentration; N_{e_m} = measured Ne concentration; $N_{\text{e}_{\text{sol}}}$ = solubility Ne concentration; $R_{\text{He-Ne}}$ = He/Ne ratio in the atmosphere. Groundwater age is then estimated as simply $t = ^4\text{He}_{\text{rad}}/G$, where G is the solid to liquid mass transfer rate.

The uncertainty in groundwater ages determined using radiogenic ^4He results mostly from uncertainty in the solid to liquid mass transfer rate. Solomon et al. (1996) suggested that with carefully conducted laboratory tests it may be possible to determine the ^4He mass transfer rate to within about a factor of 2. Determining the in situ release rate using age vs $^4\text{He}_{\text{rad}}$ data can likely be accomplished with an uncertainty of 10 or 20 %; however, such results by themselves have to be extrapolated to older parts of the flow system for dating beyond about 40 years. By combining in situ release data with laboratory measurements Solomon et al. (1996) speculate that the uncertainty in the ^4He age may be less than 50%; however, this has not yet been evaluated directly. While the age uncertainty using ^4He is much greater than with CFCs, $^3\text{He}/^3\text{H}$, or ^{85}Kr , the potential for dating waters in the range of 50 to 1000 (where no other dating methods are practical) makes the use radiogenic ^4He attractive.

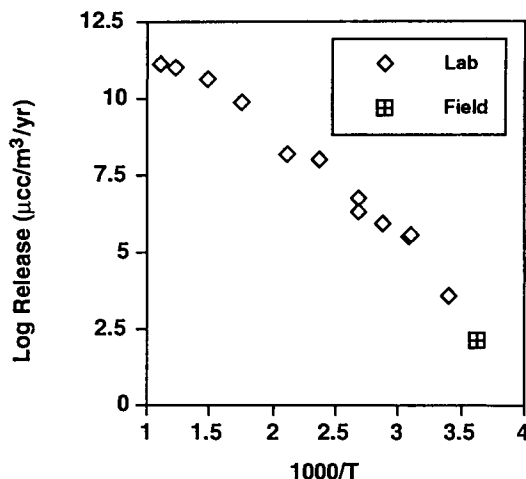


Figure 9.5. Radiogenic ^4He release from during laboratory heating experiments. Also shown is the release derived from in situ ^4He concentrations and groundwater ages. (After Solomon et al., 1996).

9.3.5 Field examples of groundwater dating

Solomon et al. (1993) measured ^3H and ^3He profiles in a shallow, silty sand aquifer near Sturgeon Falls, Ontario. The water table depth varies seasonally, between approximately 0.2 m in spring, and 2 m depth in late summer. The aquifer thickness is approximately 35 m. Groundwater at this site was sampled at 11 discrete depths, using multi-level piezometers with 15 cm long screens. In 1991, ^3H and ^3He peaks both occur at approximately 11 m depth, and indicate the position of 1963 rainfall (Figure 9.6). The location of the ^3H peak was combined with two-dimensional flow modeling to yield a recharge estimate of 0.15 m/yr. The $^3\text{H}/^3\text{He}$ age gradient suggests a vertical velocity of approximately 0.45 m/yr near the water table, and decreases slightly with depth. Assuming a porosity of 0.35, the recharge rate is estimated to be about 0.16 m/yr. This is in good agreement with that estimated from ^3H alone. However, detailed vertical profiling was required to accurately locate the position of the 1963 ^3H bomb peak. With $^3\text{H}/^3\text{He}$ dating, a few samples obtained close to the water table were sufficient to estimate the recharge flux.

The CFC-12 profile measured at the Sturgeon Falls site is depicted in Figure 9.7 (Cook et al., 1995). Concentrations decrease almost linearly with depth, from 510 pg kg^{-1} at 0.6 m to less than 50 pg kg^{-1} below 10 m. The concentration measured in the uppermost sample is not significantly different from that which would be expected for water in equilibrium with the atmosphere (in 1993) at a recharge temperature of 3°C . The apparent CFC-12 age increases with depth, from zero at 0.6 m, to 34 years at 11.9 m. The apparent age of 36 years for the sample from 19.1 m appears too young, which is attributed to low levels of contamination, probably introduced during sampling. Apparent CFC-12 ages of 27 and 33 years at 9.8 and 11.9 m depth are in good agreement with ^3H data obtained at the site (Figure 9.6).

Figure 9.8 depicts ^{85}Kr profiles obtained at Borden, Ontario (Smethie et al., 1992). The specific activity was measured to be $0.87 \pm 0.03 \text{ Bq/m}^3$ in the air, and $0.89 \pm 0.03 \text{ Bq/m}^3$ in soil gas. The

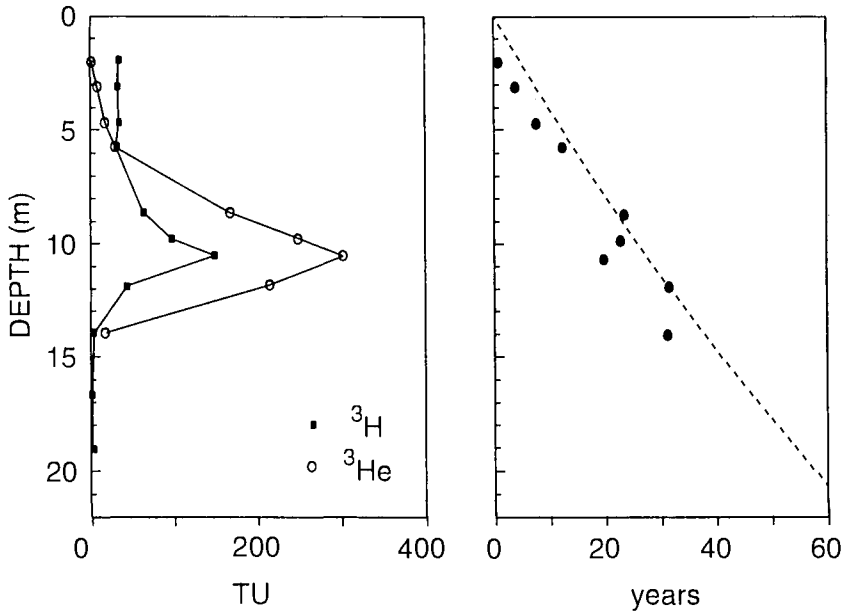


Figure 9.6. Groundwater ^3H and ^3He concentrations and $^3\text{H}/^3\text{He}$ age profiles at Sturgeon Falls, Ontario. The broken line represents results of a two dimensional flow model calibrated using tritium data. (Modified from Solomon et al., 1993).

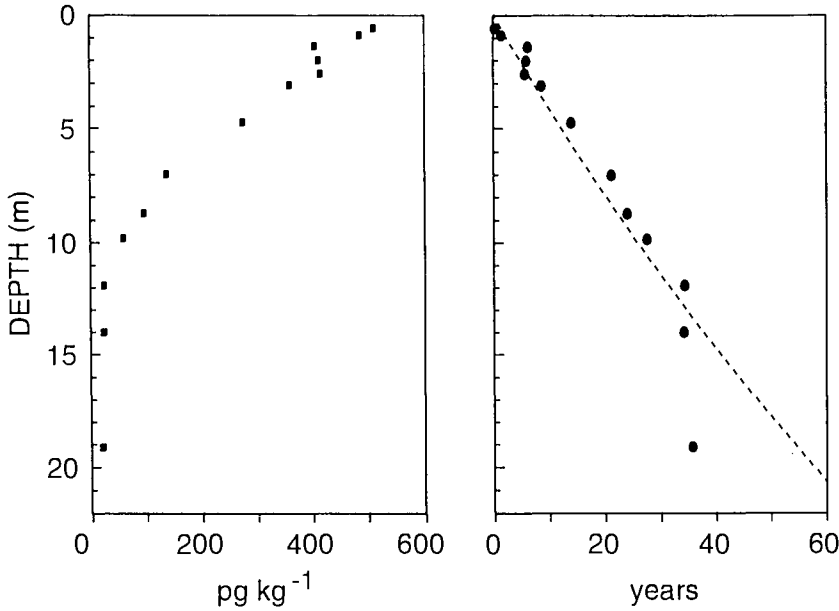


Figure 9.7. Profiles of CFC-12 concentration and apparent CFC-12 age in the Sturgeon Falls aquifer. The broken line represents results of a two dimensional flow model calibrated using tritium data. (From Cook and Solomon, 1996).

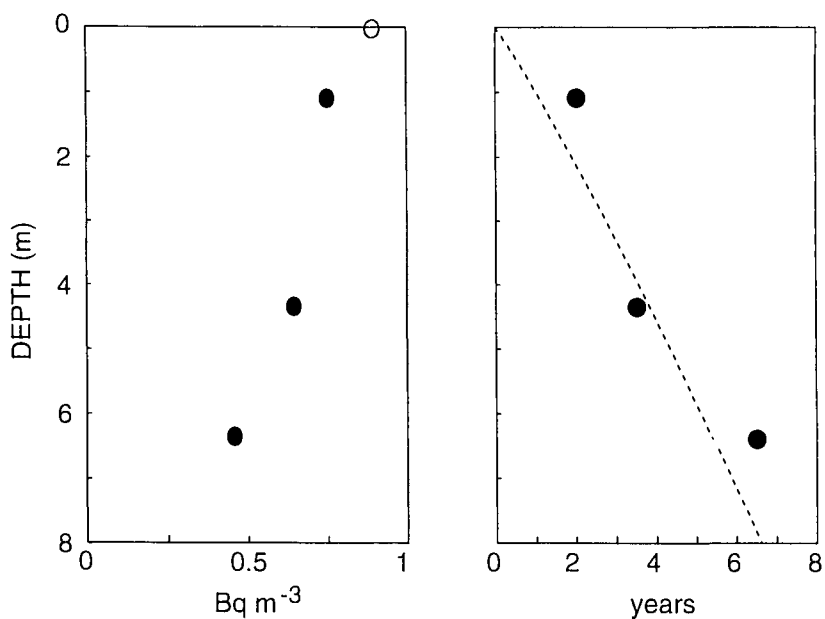


Figure 9.8. Specific activity of ^{85}Kr , and apparent ^{85}Kr age in a vertical profile in the Borden aquifer. The open circle depicts the measured concentration in the soil gas and in the atmosphere. The broken line depicts the groundwater age profile determined using a two-dimensional flow model. (Modified from Smethie et al., 1992).

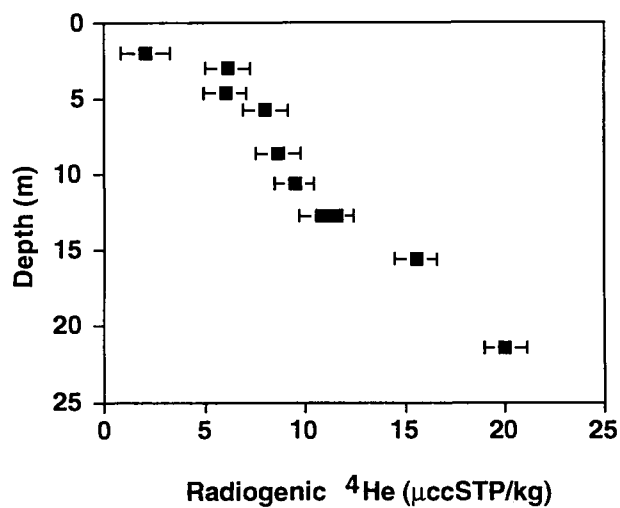


Figure 9.9. Profile of radiogenic ^4He at the Sturgeon Falls site, Ontario. (Modified from Solomon et al., 1996).

specific activity in the groundwater decreased from $0.75 \pm 0.06 \text{ Bq/m}^3$ at 1.1 m depth, to $0.45 \pm 0.04 \text{ Bq/m}^3$ at 6.4 m. Apparent ages increase from 2.0 ± 1 years at 1.1 m to 6.5 ± 1 years at 6.4 m. Apparent ^{85}Kr ages are equal to hydraulic ages determined using a numerical flow model within experimental error (Smethie et al., 1992). These ages are also in good agreement with $^3\text{H}/^3\text{He}$ ages reported by Solomon et al. (1992b).

Figure 9.9 shows a vertical profile of radiogenic ^4He concentrations at the Sturgeon Falls site in Ontario (Solomon et al., 1996). Groundwater dating (using CFCs and $^3\text{H}/^3\text{He}$) at this site has shown that flow is nearly vertical with an average downward velocity of 37 cm/yr. The underlying bedrock at this site is rich in radiogenic ^4He ; however, the downward fluid velocity is too great to allow upward transport (via diffusion) of ^4He and thus Solomon et al. (1996) argued that the increase in ^4He with depth is a result of mass transport out of the solid phases within the aquifer. Using the age versus depth data the ^4He solid to liquid mass transfer rate was computed to be $130 \text{ } \mu\text{ccSTP m}^{-3}$ (of aquifer) yr^{-1} which is close to the value obtained by conducting laboratory release experiments on the aquifer solids (see Figure 9.5).

9.4 Groundwater Surface-Water Interactions

Dissolved gases have been used to evaluate interactions between groundwater and surface water systems. High concentrations of ^4He and ^{222}Rn are common in deep (old) groundwaters as a result of the decay of U- and Th-series nuclides. The dissolved concentration of these gases in surface water bodies can be elevated due to groundwater discharge. Mass balance permits quantitative evaluations of ground water discharge provided that dissolved gas concentrations are sufficiently elevated above equilibrium solubility with the atmosphere.

9.4.1 ^4He

Helium-4 in both the soil atmosphere and dissolved in pore fluids has been used to locate areas of deep groundwater discharge into watersheds. A study by Gascoyne and Sheppard (1993) of the Whiteshell Laboratories in Manitoba was conducted in the context of evaluating a potential high-level nuclear waste disposal site in the Canadian Shield. Samples were collected by placing ping-pong balls inside a sampling probe that was driven 0.5 m into the overburden. The ping-pong balls act as a semi-permeable membrane and thus air within the balls equilibrates with He in the surrounding soil solution. After a seven-day equilibration period, the balls were removed, placed in a water-filled container, and later pierced with a syringe and then analyzed using a modified He leak detector.

The maximum anomaly along the transect observed by Gascoyne and Sheppard (1993) is approximately 8 times greater than equivalent atmospheric levels. Vertical profiles collected within 1 m of maximum surface ^4He anomaly showed that the concentration of ^4He at a depth of 2 m is nearly 1500 times greater than atmospheric values. Using the vertical profiles to estimate the ^4He flux density, and assuming a ^4He concentration in deep groundwater of 10 ml/L (Gascoyne et al., 1992), Gascoyne and Sheppard calculated an approximate groundwater discharge of 26,000 L/yr.

At the Experimental Lakes Area (ELA) in northwestern Ontario, profiles of ^4He concentrations in lake sediments have been used by Stephenson et al. (1994) to calculate groundwater velocities and discharge. The ELA is located on Archean age rocks of granitic composition. More than 1000 lakes ranging in depth from < 2 m to 175 m exist over jointed and faulted bedrock. ^4He is generated from U- and Th-series decay and is released into groundwater via fractures in the rock matrix. Stephenson et al. (1994) measured bottom-water He concentrations of 45 lake basins during summer stratification. Most contained little excess He (He concentrations greater than equilibrium solubility with the atmosphere) indicating little groundwater discharge. However, 3 lakes had He-rich bottom waters and were selected for subsequent investigations by installing sampling probes to a depth of 2 m in the lake sediments. The probes consisted of series of He-permeable ping-pong balls placed inside PVC casing.

Helium profiles from one site (Lake 239) show concentrations are near atmospheric solubility at the sediment-water interface, then increase with depth up to 1000 times solubility in one profile. The rate of increase as well as the shape of the ^4He concentration profile depends on the magnitude of groundwater discharge into the lake or groundwater recharge from the lake. Stephenson et al. (1994) evaluated groundwater discharge/recharge by solving a one-dimensional form of the advection dispersion equation. By fitting the model to the observed data, Stephenson et al. (1994) calculated groundwater discharge rates ranging from near zero to about 22 cm/yr. Integrated ^4He fluxes into the lake using the calculated discharge rates were in reasonable agreement with ^4He accumulation in lake bottom waters during summer stratification.

9.4.2 ^{222}Rn

The use of ^{222}Rn to evaluate groundwater discharge into streams is discussed in Chapter 20; examples include the use of injected gases such as sulfur hexafluoride and propane to correct for ^{222}Rn exchange with the atmosphere prior to sampling.

9.5 Injected Dissolved Gas Tracers

The use of applied tracers has been a common method of tracing groundwater flow paths and investigating transport processes for many years. Ideal tracers are ones that are nonreactive, have little or no effect on the physical or chemical properties of the aquifer or groundwater, can be detected at concentrations that range over several orders of magnitude, are readily soluble in water, and lend themselves to easy sample collection and analysis. The most common nonreactive tracers are the anions chloride and bromide. Salts of these anions are readily soluble in water and simple methods exist for analyses; however, in order to obtain a range of detection limits greater than 2 - 3 orders of magnitude, the source concentrations must be high causing the density and ionic strength to often exceed that of natural groundwater.

An alternative to anionic tracers is dissolved nonreactive gases. Inherent advantages of dissolved gases are numerous and include: 1) the source solution can typically be saturated many orders of magnitude above background concentrations without significant changes in the physical and chemical properties of the injection water; 2) many gases (e.g. noble gases) are inert and nontoxic in hydrologic systems; 3) a relatively constant source concentration can be

maintained for extended periods of time with very little maintenance; 4) multiple tracers can be injected and analyzed with the same equipment; and 5) both natural and forced gradient field experiments can be performed. The most commonly used inert gases include helium, neon, krypton, sulfur hexafluoride (SF_6), chlorofluorocarbons (CFCs), and perfluorocarbons (PFCs).

Carter et al. (1959) documented the use of dissolved helium as an injected tracer. In their study, helium was detected at a distance of 188 feet from the injection point in a confined aquifer and they concluded that helium was a feasible groundwater tracer. However, they had reservations about the methodologies of injection and sampling and were concerned about large errors associated with their analytical measurements (made with a mass spectrometer). Many of these problems have been overcome and the use of dissolved gases as groundwater tracers has increased steadily over the past few years (e.g. Upstill-Goddard et al., 1991; Eikenberg et al., 1992; Sugisaki and Aoki, 1993; Wilson and Mackay, 1993, 1995; Sanford and Solomon, 1995; Sanford et al., 1996).

Noble gases

Noble gases are the most appropriate of the naturally occurring gases to use as groundwater tracers. He, Ne and Kr are the most commonly used because of their relatively low background concentrations. Ar is not generally used because of the high background concentration. Xe is a potentially powerful tracer having the advantage that 9 isotopes exist in natural waters and it may be possible to have multiple injections of Xe each having a unique isotopic composition. However, Xe gas and especially isotopically-enriched gas, is rather expensive limiting the use of this tracer. Very precise measurements of dissolved gas ($\pm 0.5\%$) are possible using mass spectrometric methods, and at higher concentrations gas chromatography can be very precise and inexpensive.

Gupta et al. (1994) tested the applicability of helium as a tracer in a basaltic aquifer in Hawaii and found it to behave similarly to bromide. They also reported on the use of a specialized portable helium analyzer which allowed for field measurements. Sanford et al (1996) describe simplified techniques for injection, sampling and analysis of dissolved gases in groundwater (see discussion of field experiment below) which has allowed extensive use of He and Ne to investigate groundwater flow and transport processes within shallow aquifers that are contaminated with radioactive wastes (Sanford et al., 1994; Jardine et al., 1995; Sanford and Solomon, 1995). Advantages of these methods are that they use equipment that is readily available and relative inexpensive. Kr is perhaps the best of the noble gases to use because it has a much greater solubility in water than either He or Ne; however, it is much more expensive. Kr was used by Jones et al (1995) as a tracer to determine groundwater velocities during pumping in fractured crystalline bedrock in north Georgia. Analysis of dissolved Kr was performed in the laboratory using a GC-MS.

Fluorinated compounds

The man-made fluorinated compounds (SF_6 , CFCs, PFCs) are quite ideal for dissolved gas tracer studies. They are relatively inert in groundwater, nontoxic, and can be detected down to extremely low levels using a gas chromatograph equipped with an electron-capture detector. A suite of three CFC-compounds (CFC-114, CFC-113, and CFC-112) were tested as groundwater tracers in the highly weathered shale saprolite in Tennessee (Cooper, 1981). Sulfur hexafluoride has recently been used as a tracer in both karstic and clastic aquifers. Hirth (1995)

reported on the successful application of SF₆ as a tracer to indicate distinct recharge zones in a karst terrain in Florida. During this study, SF₆ was detected in springs at distances of 11 km. SF₆ has been used in fractured shale aquifers in Tennessee to aid in investigating the migration of transuranics (Knowles et al., 1995) and to study fracture flow dynamics and interconnectivity (Moline et al., 1995). Currently there is interest in using SF₆ in studies designed to detect and locate DNAPLs in the subsurface (Nelson and Brusseau, 1995). Sulfur hexafluoride has been shown to partition into immiscible-liquid phases of DNAPLs (Wilson and Mackay, 1995) and is being studied as a possible partitioning tracer to indicate the presence and location of residual phase liquids in the aquifer.

9.5.1 Field example: noble gas tracer experiment

The burial of wastes on the U.S. Department of Energy's Oak Ridge Reservation (ORR) generally has been in shales of the Conasauga Group, which is one of the units comprising the ORR aquitards (Solomon et al., 1992a). It is believed that shallow subsurface groundwater flow and transport of contaminants occur in discrete, fractured zones of relatively high permeability within the water table interval. The saprolite in the upper portion of the water table interval can be described in broad terms as having a low permeability yet a relatively large porosity.

The West Bear Creek Valley noble gas tracer test was designed to study the effects of matrix diffusion on transport in the groundwater using dissolved He and Ne. The two noble gases have different molecular diffusivities so diffusion into and out of the matrix porosity will cause a separation of the gases. He has a molecular diffusion coefficient 1.5 times larger than Ne, indicating that for any given time period, He will diffuse farther than Ne. Modeling of the breakthrough and elution of the gases will provide valuable information on fracture spacing and aperture and matrix porosity for groundwater models developed for the optimization of remediation. In addition, the test was used to develop the technique of using dissolved gases as groundwater tracers in the shallow subsurface.

Materials and methods

Sanford et al. (1996) developed and tested a passive in situ headspace sampler for use in field-scale dissolved gas tracer tests. This device is similar in concept to the ping-pong ball samplers used by Gascoyne and Sheppard (1993). The sampler is simple and easy to use and does not require the collection of water samples, which is especially advantageous for use in contaminated areas. The passive diffusive gas samplers can be used to collect any gas which can diffuse through the silicone tubing, including He, Ne, H₂, Ar, O₂, N₂, CH₄, Kr, and SF₆. The equilibration time for these samplers can be controlled by varying the membrane thickness and/or the surface area to volume ratio. Equilibration times ranging from several hours to several weeks are possible. Gases were analyzed using gas chromatography with a thermal conductivity detector (Sugisaki et al., 1982).

The gas injection system was constructed of 100 m of Teflon tubing coiled around a 3-m length of slotted 1.3-cm diameter PVC pipe. The Teflon tubing was connected to a gas cylinder at the surface with copper tubing. The tracer gas was a mixture of 60% Ne and 40% He which flowed continuously through the tubing at a rate of 30 - 40 cc/min, and then diffused through the Teflon tubing resulting in a bubble-free injection system.

Multilevel groundwater sampling wells were installed at depths determined from the subsurface distribution of a fluorescent dye Rhodamine-WT that was injected as part of an earlier study at the same site (Lee et al., 1992) and from the results of a series point dilution tests used to identify zones of higher groundwater flux (Sanford and Moore, 1994).

Tracer experiment

The natural gradient tracer test started on March 11, 1994. Breakthrough of the gases was first seen in Well 487 (14 m from the source) in 4 days (Figure 9.10), yielding a minimum velocity of greater than 3 m/d. This time includes the time it takes to saturate the source well and to have the sampler come to equilibrium.

The breakthrough curve for Well 487 in Figure 9.10 is for the first 83 days after injection started and shows a separation of He and Ne, as expected. The enrichment in Ne relative to He is interpreted to be a result of the larger diffusivity of He causing it to be lost to the matrix faster than Ne. Also plotted on Figure 9.10 is the daily rainfall amount for the same period of time. Around Day 15 there was a storm in which nearly 150 mm of rain fell over a weekend. The sample collected from Well 487 was below detection; however the next sample, collected 2 days later, had concentrations nearly as high as before the rain. This behavior suggests a flushing of water at a fast rate through the permeable interval, causing a decline in concentration. As the flushing slows, the concentrations rise rapidly because the matrix between the source and Well 487 already contains He and Ne, thereby slowing the rate of diffusion from the permeable interval into the matrix. Sharp decreases and increases in concentrations just after heavy rains are also seen around Days 30 and 35.

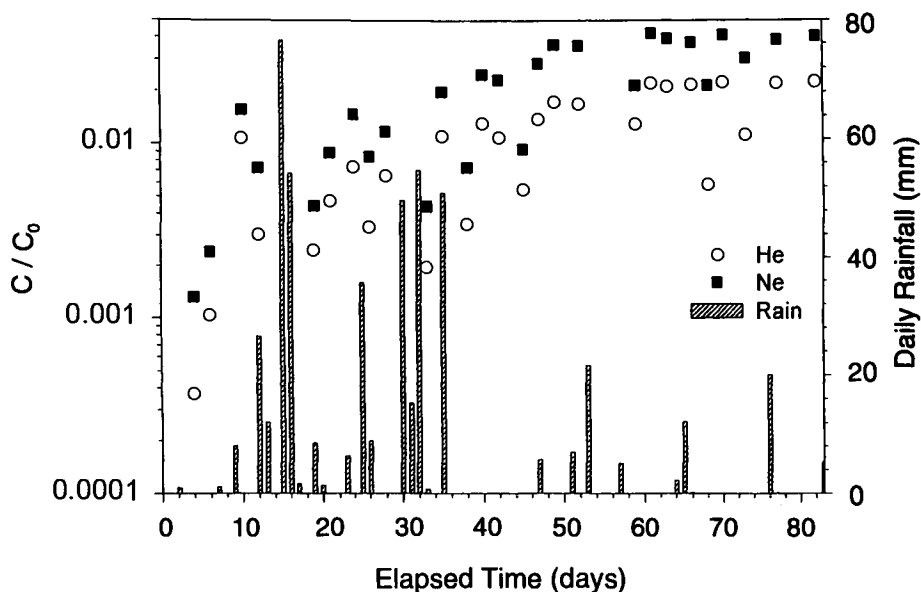


Figure 9.10. Breakthrough curves for He and Ne that were injected into the West Bear Creek Valley watershed. (Modified from Sanford and Solomon, 1995).

This example of a dissolved gas tracer experiment illustrates how important long-term continuous injection tracer experiments can be in investigating flow and transport processes in heterogeneous shallow aquifers. The simplified methods of dissolved gas injection, sampling and analysis have allowed for the implementation of similar experiments in contaminated sites (Jardine et al., 1995). These methods will make it much easier to perform dissolved gas tracer tests during hydrological investigations in practically any hydrogeologic setting, especially in pristine settings where the use of other types of dissolved tracers may be harmful to the environment.

9.6 Future Directions

Concepts of using dissolved gases as tracers in subsurface hydrology are not new; however, these techniques remain underutilized. Consequently, the prospect for new discoveries and enhanced hydrologic understanding resulting from the use of dissolved gases is high. In particular, advances in sample collection and analysis methods are overcoming most of the practical problems associated with using dissolved gases. We expect the use of dissolved gases to increase significantly in the coming decade.

The greatest increase in the use of dissolved gases is for dating shallow groundwater. Significant progress has been made in developing dating methods and in understanding their limitations. While it is likely that further progress will be made in methodologies, the most significant advances will probably result from combining dissolved gas chronologies with other measurements. For example, it may be possible to determine effective field-scale rate constants for water-rock reactions, spatial variations in recharge rates and the controls on preferential flow may be mapped, and the calibration of flow and transport models improved by obtaining a groundwater chronology.

Currently, most dissolved gases used as tracers are applied when the gases are geochemically conservative. Thus, most tracers yield information regarding the physical hydrology of the system. In the future, it is likely that geochemically conservative gases will be combined with reactive gases in order to understand various geochemical processes. For example, the degradation of CFC-11 under anaerobic conditions when combined with a conservative age tracer such as tritium/helium-3 may help characterize the subsurface microbiology.

Finally, little use of dissolved gases in the unsaturated zone has occurred to date. Because the partitioning between water and gas is highly variable among the common gas tracers (due to differences in solubility), differential transport of dissolved gas will occur in the unsaturated zone with the differentiation being a strong function of water content.

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Oxygen and Hydrogen Isotopes in Rainfall-Runoff Studies

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10.1 Introduction

Knowledge of the hydrologic pathways by which water moves over and through the ground to streams represents an important component of our hydrological, geochemical, and ecological understanding of the Earth's surface. Streamflow generation (the drainage of water to streams and rivers) is a key component of the hydrologic cycle, and as such it is of fundamental scientific interest in itself. In addition, as in most areas of hydrology, there are areas in which fundamental scientific knowledge can be applied for the benefit of society and the environment. For example, a thorough understanding of streamflow generation can clearly be useful in designing computer models for streamflow prediction, and predicting streamflow is of importance in land use planning, flood contingency planning, and dam construction and operation. Also, the nature of water storage and drainage on hillslopes has important implications for slope stability, erosion, and related aspects of geomorphology. Finally, prediction of the chemical impacts of non-point source pollutants also requires an understanding of the pathways through which water moves on its way to the stream, because different pathways provide different opportunities for contact with organic detritus, soil, and rock. For example, the chemistry of water in an organic surface soil may be very different from that of water in the underlying mineral soil (e.g., Hooper et al., 1988), and both may be very different still from water in the local bedrock (e.g., Mulholland, 1993; Genereux et al., 1993). For these and other reasons, the field study of streamflow generation remains a significant topic in hydrology.

Naturally-occurring stable isotopes of oxygen and hydrogen are among the most effective tools available for delineating and constraining hydrologic flowpaths on watersheds. The basis for this application of $\delta^{18}\text{O}$ and δD is the temporal variation in the isotopic composition of precipitation. It is well known that the isotopic composition of rainfall varies from storm to storm at a given site (e.g., Pionke and DeWalle, 1992; Chapter 3); thus, the rainfall in any one storm may differ isotopically from the water stored in the subsurface at the start of the storm. This contrast in isotopic composition has proved useful in analysis of streamflow generation on storm event time-scales. The isotopic composition of precipitation also varies with season, leading to a variation of the isotopic composition of streamwater on this longer time-scale as well. This chapter seeks to provide an overview of traditional hydrograph separation applications on storm event time-scales. Beginning with an introduction to terminology and assumptions inherent to hydrograph separation, we will address the requirements for successful separation and discuss the results of several isotopic hydrograph separation studies. We

conclude by considering other frameworks for application of isotope data, on storm-event and longer time-scales.

10.2 Hydrograph Separation

10.2.1 Terminology

Two-component hydrograph separation provides the simplest means (conceptually and computationally) for use of oxygen and hydrogen isotopes in analysis of streamflow generation. Sklash et al. (1976) and Sklash and Farvolden (1979) provide a simple, logical, and widely-used framework for the relationship between isotopic and other types of hydrograph separations. As Sklash et al. (1976) wrote: "Storm runoff in a stream consists of a number of component parts, which may be categorized in three ways: *time source* components, *runoff mechanism* components, and *geographic source* components". Event and pre-event water are the time source components of isotopic hydrograph separation. Event water refers to rain falling and/or snow melting during a storm and/or melt event of interest, whereas pre-event water refers to liquid water present on the watershed before the start of the event of interest. More recently the terms "new water" and "old water" have come into use as synonyms for event and pre-event water, respectively (Obradovic and Sklash, 1986; Pearce et al., 1986; Sklash et al., 1986; Hooper and Shoemaker, 1986). However, the terms "event" and "pre-event" are somewhat preferable in that they are more explicit and they serve as a reminder that the time source separation may be applied only to rain and/or snowmelt events, and not to baseflow between events.

Returning to the framework of Sklash et al. (1976), and modifications in Sklash and Farvolden (1979), each "runoff mechanism" component represents water arriving at a stream through operation of one of the physical mechanisms described in the streamflow generation literature (see Chapter 1), such as Hortonian overland flow, variable source area overland flow (or saturation overland flow), groundwater flow, or perched saturated flow. "Geographic" (or what was renamed "historical" in the 1979 paper) source components are somewhat less well-defined, but generally distinguish among different possibilities for where the water was located before arriving at the stream (e.g., in the saturated zone or in the vadose zone).

This general framework is a useful starting point for investigation of streamflow generation with isotopic data. Strictly speaking, a two-component isotopic hydrograph separation yields the proportions of event and pre-event water in a stream, nothing more. Because it is runoff mechanisms (or in some cases, geographic sources) which are of more fundamental significance in watershed hydrology, finding meaningful relationships between these components and time source components (event and pre-event water) has been and remains one of the fundamental priorities in extracting as much hydrologic information as possible from isotopic data. As is discussed in Section 10.2.3, relationships between time source and other components have often been built around quasi-quantitative observations or arguments concerning physical characteristics of a particular study site. In any case, it is important to bear in mind that isotopic data do not necessarily distinguish, for example, groundwater (a geographic source component) and new water (a time source component); as Genereux and Hemond (1990) point out, "not all old water is groundwater and, during and after storms, not all groundwater is old water."

10.2.2 Requirements and assumptions in hydrograph separation

Oxygen or hydrogen isotopes may be used to separate a hydrograph if the difference in the isotopic compositions of event and pre-event waters is "large" relative to the isotopic variability within each component and the analytical uncertainty associated with the isotopic analyses (the same general condition could be stated for any mixing problem involving use of a tracer). The requirement for a "large" difference in isotopic composition between event and pre-event waters is not specified in quantitative fashion here, because it depends on the amount of uncertainty one is willing to incur in the final hydrograph separation results (see Section 10.2.5). Most authors that have addressed the requirements for successful hydrograph separation have listed specific criteria rather than the general condition given above. For example, according to Sklash and Farvolden (1979), successful isotopic hydrograph separation requires that:

1. The isotopic content (^{18}O , D, T) of the event component is significantly different from that of the pre-event component.
2. The event component maintains a constant isotopic content.
3. The groundwater and vadose water are isotopically equivalent or vadose water contributions to runoff are negligible due to hydrogeologic constraints.
4. Surface storage contributes minimally to the runoff event.

(D and T in item 1 refer to ^2H and ^3H , respectively.) Item 1 in this list obviously states the requirement for an isotopic difference between event and pre-event waters. The other items refer to intra-component isotopic variability, specifically the requirements that the isotopic composition of event water not vary with time and that the composition of pre-event water not vary in space or, if it does, that only one pool of pre-event water (e.g., groundwater and not vadose zone water or surface storage) contribute significantly to storm runoff.

Failure to meet all of the requirements for successful separation is one of the main drawbacks of isotopic hydrograph separation. Event and pre-event waters are often too similar in composition, and one or the other may exhibit significant internal variability (see Section 10.2.4). Another limitation of the technique is that it may be applied only to stormflow. The major strength of the technique is that stream isotope data offer a watershed-scale signal that is linked to hydrologic pathways. Like the rate of streamflow itself, the isotopic composition of streamwater is an integrated signal responsive to streamflow generation processes in the watershed upgradient of the stream measurement point.

10.2.3 Findings

General Result

Table 10.1 summarizes the findings from a number of studies in which oxygen and/or hydrogen isotopes were used to separate storm streamflow into pre-event and event water. Table 10.1 includes only studies which focused on analysis of precipitation events; studies aimed at snowmelt and combined snowmelt-plus-precipitation events are considered in Chapter 11. Also excluded from Table 10.1 are studies in which hydrograph separations were not computed though isotopes were applied in a descriptive fashion (e.g., Kennedy et al., 1986) or in some other quantitative framework (e.g., Turner and Macpherson, 1990). Many studies in Table 10.1 present graphical examples of hydrograph separation results, as in Figures 10.1 and 10.2.

Table 10.1. Each value in the column labeled "volume" is a volume-weighted average percentage of pre-event water over the hydrograph; values in the column labeled "peak" refer to peak flow, except for two studies (Bottomley et al. (1984) and Mook et al. (1974)) which reported the minimum percentage of pre-event water for the hydrograph (i.e., 100 minus the peak in event water percentage). * indicates summary data were taken from Table 1 of Jordan (1994), not from the original paper. Some of these studies could have involved snowmelt, though this is not specifically indicated in any of the titles. For studies reporting more than two values for a given watershed, the table contains the lowest and highest values separated by a hyphen. Watershed areas shown as approximate for Sklash et al. (1976) were estimated by the present authors using a map in the original paper. For Bonell et al. (1990), values were calculated from Q_{10} and Q_{20} data in their Table IV and taken from p. 31 of the text.

Study	Location	Catchment area (ha)	Tracer	Percentage pre-event water	
				peak	volume
Jordan (1994)	Switzerland	3.6	^{18}O		45, 75
Waddington et al. (1993)	Ontario	160	^{18}O	87, 93	
McDonnell et al. (1991)	New Zealand	3.8	D	92-100	
O'Gunkoya & Jenkins (1991)*	United Kingdom	1000	D		54-90
McDonnell et al. (1990)	New Zealand	310	D		21-33
Nolan and Hill (1990)	California	1060	D		57
Bonell et al. (1990)	New Zealand	218	D		59
		310	D	38	38 to >97
Blowes and Gillham (1988)	Ontario	0.75	^{18}O	9, 45	22, 50
Turner et al. (1987)	W. Australia	82	^{18}O , D		69-95
Herrman et al. (1987)*	Germany	76	^{18}O		84
Rodhe (1987)	Sweden	3	^{18}O		81, 87
		4	^{18}O		81, 96
		17	^{18}O	87	
		50	^{18}O		85-99
		400	^{18}O		68-86
		660	^{18}O		75-95
Pearce et al. (1986)	New Zealand	3.8	^{18}O		≥97
Sklash et al. (1986)	New Zealand	3.8	D		73-79
		1.6	D		74, 86
Bottomley et al. (1984)	Ontario	41.8	^{18}O	85-90	
		124	^{18}O , D		~40
		176	^{18}O	70-88	
Merot et al. (1981)*	France	10	^{18}O		88
Sklash & Farvolden (1979)	Quebec	120	^{18}O	>65, >80	

Table 10.1. Continued.

Study	Location	Catchment area (ha)	Tracer	Percentage pre-event water	
				peak	volume
		390	^{18}O	>80	
	Ontario	100	^{18}O	>80 (two)	
Sklash et al. (1976)	Ontario	~70,000	^{18}O	70	
		~40,000	^{18}O	71	
		~10,000	^{18}O	55	
		~35,000	^{18}O	69	
		~17,000	^{18}O	52	
		10,800	^{18}O	70	
		7300	^{18}O	75	
Fritz et al. (1976)*	Canada	180	^{18}O		45
		2200	^{18}O		60
		13,500	^{18}O		>50
Mook et al. (1974)	Netherlands	650	^{18}O	~70	
Crouzet et al. (1970)*	France	570	T		97
		1500	T		99
		9100	T		46

In almost all cases pre-event water accounts for over half (and usually about three-quarters) of the runoff and/or peakflow associated with rainstorms. Except for the Glendhu 2 catchment in New Zealand (McDonnell et al., 1990) and two small catchments near Babinda, Queensland, Australia (see Chapter 11) the similarity of the fraction of pre-event water (f_{pe}) holds true for watersheds of different area, vegetation, and geology. The basins in Table 10.1, located in Europe, North America, Australia, and New Zealand, range over five orders of magnitude in area (0.75 to 7×10^4 ha). Most of the watersheds studied were predominantly forested, though at least one was mixed forest and grassland/pasture (Nolan and Hill, 1990) and one all grassland (Bonell et al., 1990). The 3.8 ha M8 catchment in New Zealand was clear-cut, leaving only a 3–10 m wide strip of riparian vegetation, before the studies conducted there (Pearce et al., 1986; Sklash et al., 1986). Most of the sites in Table 10.1 receive annual precipitation of 1000–1300 mm. Permanente Creek (Nolan and Hill, 1990) is the driest, with 400–800 mm/yr (depending on elevation within the watershed), while the wettest sites are Hafron Forest (Neal and Rosier, 1990) and the M8 catchment referred to above, receiving 2400 and 2600 mm/yr, respectively. Sites in Table 10.1 span a wide variety of bedrock types (metamorphics of various grades, intrusive and extrusive igneous rocks, limestone, and clastic sedimentary rocks).

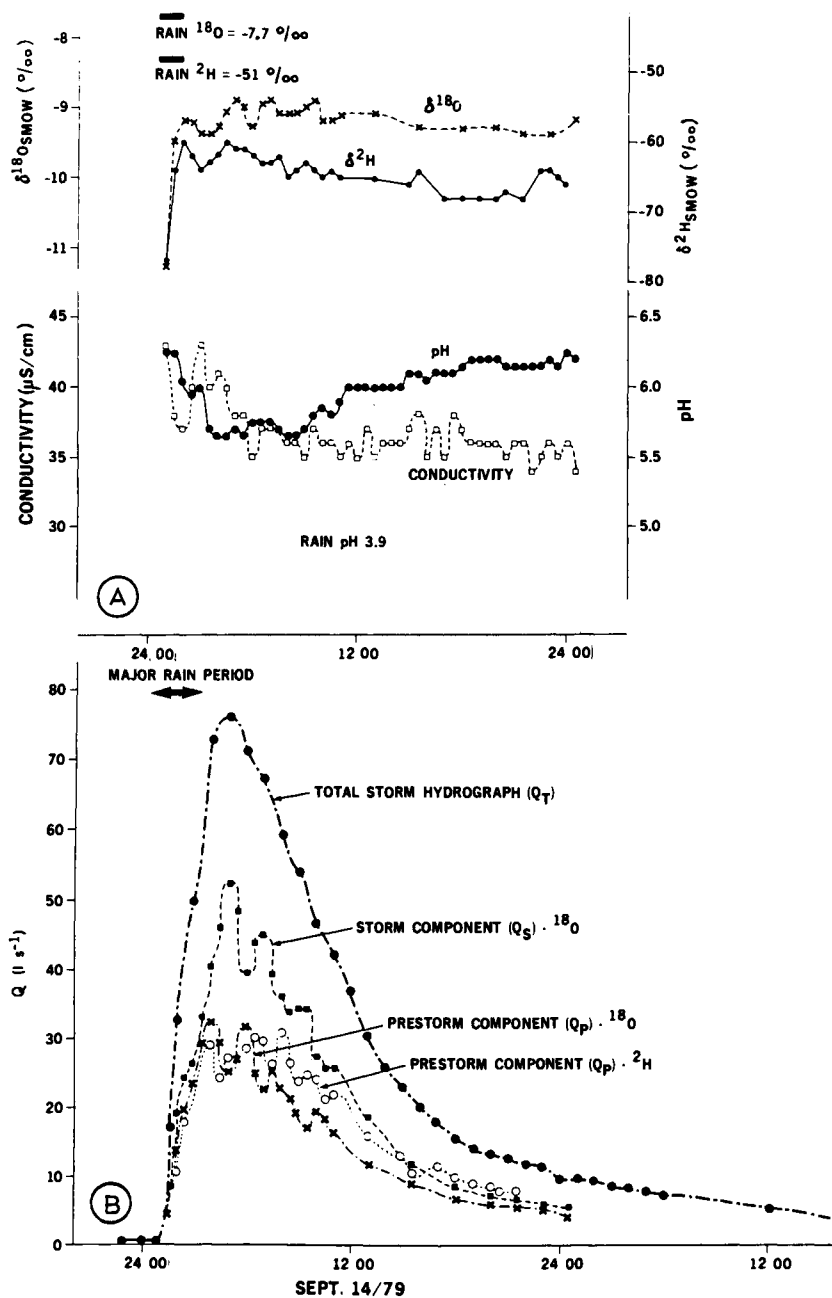


Figure 10.1. Electrical conductivity, pH, δD , and $\delta^{18}\text{O}$ data for storm runoff from Harp Lake sub-basin number 4 in Ontario, Canada, and separation of the resultant stream hydrograph into "storm" (event) and "pre-storm" (pre-event) components, for the rainfall event of 14 September 1979 (from Bottomley et al., 1984). The volume-weighted proportion of pre-event water for the hydrograph was about 40%.

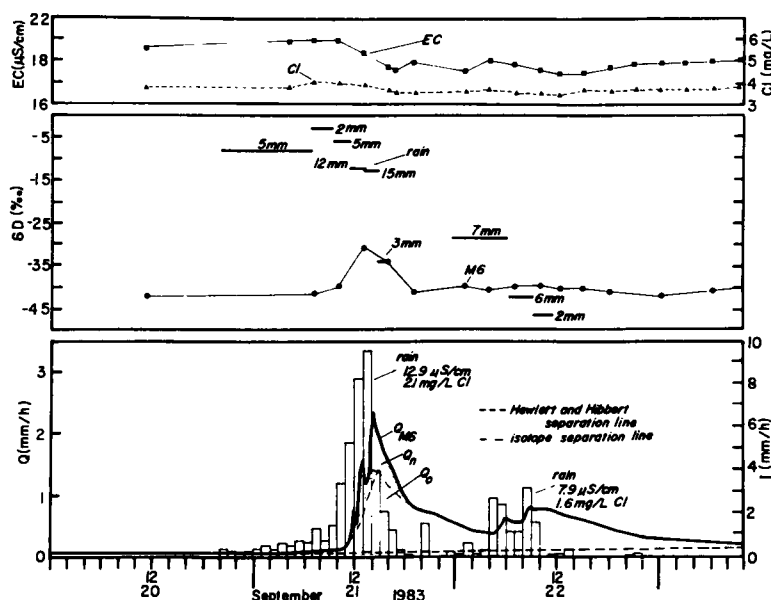


Figure 10.2. Electrical conductivity, chloride, δD , and discharge data for the stream, and δD and rainfall rate data for precipitation, for the M6 catchment at Tawhai State Forest, New Zealand during the rainfall event of 21-22 September 1983 (from Sklash et al., 1986).

The most significant finding of the studies in Table 10.1 is the consistently large fraction of pre-event water in storm streamflow. The discharge of significant amounts of pre-event water to streams during storms is unequivocal proof of the importance of subsurface stormflow in generating stream hydrographs. In this respect, the isotopic studies are in accord with the substantial body of hydrometric studies indicating the importance of subsurface stormflow (e.g., Hursh, 1936; Hursh and Brater, 1941; Hoover and Hursh, 1943; Roessel, 1950; van't Woudt, 1954; Whipkey, 1965, 1969; Weyman, 1970; Troendle and Homeyer, 1971; Harr, 1977; Anderson and Burt, 1978). Nevertheless, many of the subsurface flow studies highlight the importance of rapid throughflow of rain water through soil macropores: the body of isotopic evidence suggests that this is not possible mechanically (see Section 10.2.3). Because Hortonian overland flow would necessarily be composed of new or event water, the isotopic data preclude the dominance of (but not the contribution to) storm runoff by this mechanism at the sites investigated. This is in accordance with other work that has relied on the large difference between rainfall and potential infiltration rates to argue against the widespread occurrence of Hortonian overland flow (e.g., Hewlett and Hibbert, 1967; Freeze, 1972b).

While oxygen and hydrogen isotopic data indicate that subsurface stormflow is important and Hortonian overland flow does not dominate runoff on humid forest and grassland watersheds, one could argue that hydrometric studies had already provided solid support for both of these conclusions by the time the isotopic approach and results started to become widely known (see reference list in previous paragraph). Of course, confidence in the conclusions regarding subsurface stormflow and Hortonian overland flow is enhanced by reaching them independently with both hydrometric and isotopic data, but it is fair to ask whether the isotopic data can offer something more than confirmation of conclusions already well-established

through hydrometric investigations. Hydrometric data alone could never reveal the proportions of event and pre-event water in streamflow, but most hydrologists would probably agree that quantitative knowledge of physical runoff mechanisms is the primary goal and isotopes are only useful insofar as they contribute toward this goal. We believe that isotopic data do have something unique and significant to offer beyond the capabilities of hydrometric data: the potential to constrain the hydraulics (mixing and flow) of the subsurface storm response to improve understanding of how infiltration mixes and moves down gradient with pre-event water. We return to this theme later in the chapter.

While the isotopic composition of storm streamflow is sensitive to the type of runoff mechanisms feeding the stream, it is also true that the relative volumes of event and pre-event water influence stream isotopic response. As Pearce et al. (1986) stated, "even a shallow soil profile 1 meter thick will commonly contain 300-500 mm of water at field capacity. It is a reasonable assumption that in any catchment there is some magnitude of runoff event which exceeds the maximum possible storage capacity of the catchment. If events of this size or larger occur, rainfall from the current storm must appear substantially in and eventually dominate the hydrograph." Thus, part of the reason for the large f_{pe} values in Table 10.1 seems to be the small amount of precipitation, relative to the storage of pre-event water, in the events studied.

Examples

One of the best examples of the investigation of stormflow using isotopic and hydrometric methods at a single site is the work done at the M8 catchment in New Zealand. Mosely's (1979) hydrometric work involved monitoring storm response in 8 soil trenches, 1 seep, and two stream channel sites. Dyed water was also injected under wet conditions, and the response monitored at several of the trenches. Rapid subsurface flow in amounts capable of accounting for stream hydrographs was observed at the seep and soil pits. Downslope seepage was observed at the base of the organic soil, above the mineral soil. Also, "where roots, decayed root channels, and other macropores...provide pathways across the interface between the organic and mineral horizons, water moves rapidly into the mineral soil..." (Mosely, 1979). From there it eventually reaches the interface between the mineral soil and the relatively impermeable underlying sediments (compacted Old Man Gravel). This water was found to then move downslope above the Old Man Gravel both as rapid macropore or "pipe" flow and slower seepage through the soil matrix (the latter continuing between storm events).

Sklash et al. (1986) reported on the isotopic and streamflow response of M8 to 3 storms in September 1983. As indicated in Table 10.1, pre-event water accounted for 73-79% of the runoff associated with these events. Sklash et al. (1986) also collected water samples at 6 of Mosely's hillslope sites (5 trenches and the seep). Pre-event water was found to dominate stormflow at all of the sites, accounting for about 60-70% of subsurface stormflow at site A and pits 1, 2, and 3, and > 90% at pit 5 and the seep. The storms studied were of moderate size and duration, having return periods of about 4 to 13 weeks, and occurred over wet, dry, and intermediate conditions. Clearly, the macropore flow observed by Mosely (1979) (and seen "infrequently" by Sklash et al., 1986) was not new (event) water, in contrast to Mosely's assertion in his conclusions. Pearce et al. (1986) and Sklash et al. (1986) discounted Mosely's observations as unimportant to storm runoff and proposed a hypothesis of pre-event storm runoff that relied on the concept of "groundwater ridging", a rapid rise in the water table associated with infiltration in the riparian zone. However, while the isotopic data showed that

Mosely's use of the phrase "new water" had been an inappropriate description of the macropore flow on M8, it did not otherwise discredit Mosely's observations of macropore flow. Clearly the stage was set for development of a theory of pre-event water flow in macropores.

McDonnell (1990) built on the work of Mosely (1979), Pearce et al. (1986), Sklash et al. (1986) and others to provide a plausible explanation for the contribution of pre-event water to stormflow via macropore flow. McDonnell used nests of continuously recording tensiometers to observe the response of soil moisture during storms. Data indicated that water perched above the interface between organic soil and mineral soil (as reported previously by Mosely) and moved quickly as "bypass flow" (bypassing the soil matrix) to the base of the mineral soil along preferential flowpaths (vertical cracks). There, above the top of the Old Man Gravel, the infiltrated water filled the small amount of available air-filled pores (usually less than 10% of the total porosity, as reported previously by Mosely), creating a saturated zone at the base of the mineral soil. This saturated zone was then drained by rapid macropore or pipe flow in the lower mineral soil. Because the saturated zones thus created would consist of 90% or more pre-event water (the percentage of total porosity occupied by water at the start of the storm), the downslope macropore flow would be mostly pre-event water, in accordance with isotope data from Pearce et al. (1986) and Sklash et al. (1986). In the case of the M8 catchment, McDonnell's synthesis of the hydrometric and isotopic data reveals how event and pre-event waters may mix in the subsurface and how the latter may be displaced from the soil matrix into macropores where it may move rapidly through the subsurface to contribute to stream hydrographs. Taken alone, neither type of data (hydrometric or isotopic) could have advanced the understanding of storm runoff on M8 as much as the combination of the two together.

In addition to the analysis of pre-event water flow in macropores, McDonnell (1990) also documented the response of the near-stream zone during storms, in particular the rapid increase of pressure heads at the beginning of storms and the much slower decrease following cessation of rainfall. The quick response of the water table was attributed to the high soil moisture (i.e., low available storage) of riparian soils on the M8 catchment. While the near-stream response was rapid, order-of-magnitude calculations with Darcy's equation showed that this response was not sufficient to explain the peak discharge of pre-event water to the stream during many storms (including those studied by Sklash et al. (1986)). Storm runoff of pre-event water was dominated by seepage and macropore discharge from small hollows adjacent to deeply-incised, ephemeral first-order streams feeding the main perennial channel, rather than by displacement of riparian groundwater.

Rapid increases in riparian groundwater levels (so-called groundwater "mounding" or "ridging") have often been invoked to explain the increased fluxes of pre-event water that are observed during storms (Sklash and Farvolden, 1979; Sklash et al., 1986; Blowes and Gillham, 1988). The assumption is that the combination of increased hydraulic gradient and larger saturated cross-sectional area adjacent to the stream channel is adequate to account for increased discharge of pre-event water to the stream. The focus on the near-stream area may seem reasonable, given the fact that pre-event water flow has in some cases been observed to peak before event water or total stream flow (e.g., Bonell et al., 1990; Waddington et al., 1993). Most authors invoking the rapid groundwater mounding mechanism explain its occurrence by reference to the conversion of a capillary fringe to positive (greater than atmospheric) pressure upon infiltration of event water. While laboratory studies (e.g., Abdul and Gillham, 1984) show this phenomenon to be possible in principle, we know of no evidence that it has or does

actually occur in any field setting. McDonnell (1990) notes that:

In the soil physics literature...the notion of a soil having a tension-saturated zone, or capillary fringe, has been questioned. Field retention data have failed to observe significant zones of tension saturation in clays and loams (Perroux et al., 1982), and Clothier and Wooding (1983) even question the presence of such zones in laboratory media.

However, the groundwater ridging mechanism need not rely on the existence of a capillary fringe. It requires only that available storage (air-filled porosity) in the vadose zone be low, through some combination of proximity of the top of the saturated zone to the ground surface (which may be affected by a capillary fringe) and/or high soil moisture.

Even when there is a significant response of the near-stream water table to infiltration, that response may still be insufficient to explain storm discharge of pre-event water to the stream (e.g., McDonnell, 1990). In at least one case, increases in groundwater head were contemporaneous with decreases in head gradient toward the stream. While Sklash and Farvolden (1979) found that "very large and rapid increases in the hydraulic head in the near-stream groundwater occur soon after the onset of rain", they also noted "that the near-stream hydraulic gradient may decrease slightly from its pre-storm value." From the standpoint of water fluxes to the stream, the observation concerning gradient is clearly the more salient one.

In a manner similar to McDonnell (1990), Waddington et al. (1993) argued that the near-stream water table response at their site in Ontario was too small to account for storm fluxes of pre-event water to the study stream. Based on observations at one soil pipe, Waddington et al. (1993) concluded that discharge from soil pipes at the bases of hillslopes was a significant source of pre-event water to the study stream during storms, but that this flow responds too slowly to account for the large f_{pe} at peak flow. Their explanation for the large fraction of pre-event water in storm streamflow (87% and 93% at peak flow for the two streamflow hydrograph separations reported) was based on their "rapid surface water mixing" hypothesis. Evidence for the hypothesis comes largely from work on a 190 m² wetland plot about 40 m from the stream channel. About one-third of the plot (60 m²) was a groundwater discharge area covered with an average depth of 13 mm of water. It was found that "piezometric heads (on the wetland plot) remained virtually unchanged during and after storm events of varying intensity and duration" (Waddington et al., 1993). Storm runoff from the plot seemed to be dominated by saturation overland flow consisting of a mixture of event and pre-event water, with the mixing proportions determined by the rate of throughfall on the saturated ground surface (4.5 to 11.3 mm/hr) and the (nearly steady) rate of groundwater discharge to the ground surface (6 to 18 mm/hr at baseflow).

Waddington et al. (1993) also write that:

...peak (overland) flow from the saturated area was dominated by pre-event water (more than 77%). Hydrograph separation of the basin outlet storm discharge showed peak flow pre-event water fractions of over 87-93%, which is consistent with the saturated area response *and indicates that the same process is operating at the basin scale.* (Italics are ours.)

While the conclusions regarding runoff processes on the saturated wetland plot are probably correct, one must be skeptical of the extrapolation of these processes to the entire 160 ha watershed based solely on the similarity of f_{pe} values at the plot and watershed scales. For example, we have already discussed how Sklash et al. (1986) and Pearce et al. (1986) found f_{pe} values of 73-97% at a site in New Zealand dominated by subsurface runoff, as more recently described by McDonnell (1990). Waddington et al. (1993) found values within this range (77-93%) for saturation overland flow on their wetland plot, illustrating a critical point mentioned earlier: there is not a unique relationship between runoff mechanisms and the fraction of pre-event water in runoff. Furthermore, Buttle (1994) discussed in detail how different mechanisms may lead to similar f_{pe} values. Saturation overland flow may be an important runoff mechanism basin-wide at the study site of Waddington et al. (1993), but this is not necessarily indicated (and is not proved) by the similarity of f_{pe} values at plot and basin scales.

The results of Blowes and Gillham (1988) provide an interesting contrast to those of Waddington et al. (1993), in the sense that near-stream water table response was much larger yet the fraction of pre-event water in the stream hydrograph was much smaller for the former study. For example, for one May storm involving 8.8 mm of precipitation over a 12 hour period, Blowes and Gillham (1988) used ^{18}O data to show that 50% of the hydrograph volume was due to pre-event water (called "groundwater" by the authors). Water table elevation rose 19 cm during this storm. Waddington et al. (1993) found negligible water table response for storms resulting in hydrographs with 87% and 93% pre-event water. The contrast underscores the point that there is not a unique relationship across study sites between the magnitude of water table response and the fraction of pre-event water in the associated hydrograph. Relationships between f_{pe} values and flowpaths will generally vary from site to site, and should in general be worked out in the field with the combined use of hydrometric and isotopic measurements.

A particularly vivid example of the lack of correspondence between f_{pe} and run-off mechanism is provided by Kendall (1993) reporting on a storm event at the artificially constructed Hydrohill catchment at the Chuzhou Hydrology Laboratory located in northeastern China near Nanjing. After a hillslope was excavated to bedrock, a concrete aquiclude consisting of two intersecting slopes dipping towards each other at a 10-degree angle was constructed with an overall downslope gradient of 14 degrees. Sidewalls were constructed of concrete to prevent any lateral infiltration from the surrounding bare rock areas to define a 490 m² catchment. The area was filled with a silty loam to a depth of approximately 1 m. During infilling the bulk density of the soil was maintained to approximate the natural soil profile; grass was planted over the entire basin. The soil was allowed to settle for 3 years. After this time, a drainage trough was dug at the intersection of the two slopes. Five fiberglass troughs, each 40 cm wide and 40 m long, were installed longitudinally in the trench, staked on top of one another to create a set of long zero-tension lysimeters that isolated five different flowpaths: rain, surface run-off, the 0 to 30 cm soil layer, the 30 to 60 cm soil layer and the 60-100 cm soil layer. This facility presents a unique opportunity to directly observe separate flowpaths.

During the rainstorm reported by Kendall (1993), the groundwater levels never reached above the soil surface, so two physically distinct flowpaths can be unambiguously defined: surface runoff and subsurface runoff. Table 10.2 contains the proportion of new water contained in these two physically defined flowpaths as calculated by isotopic and two commonly used chemical tracers, Cl and SiO₂. The surface runoff was entirely event water, consistent with

physical observations. However the overall proportion of event water (88%) did not correspond with the physical flowpath proportions (62% subsurface runoff, 38% surface runoff). Kendall (1993) was able to close a mass balance for ^{18}O in this storm using well and soil moisture data. From these calculations, she found that subsurface runoff contained more event water than expected. She suggested that rain followed preferential flowpaths to the troughs during the event and that the entire catchment did not respond uniformly to the input.

Table 10.2. Comparison of Chemical and Isotopic Hydrograph Separations at Hydrohill (modified from Kendall, 1993).

Physically Measured Flow	Percent of Total Flow	Percent Event Water Calculated With:		
		SiO_2	Cl	^{18}O
Surface	38	65	80	100
Subsurface	62	32	39	84
Total	100	36	45	88

If one had sampled only the outlet of the catchment, it would appear that the chemical tracers did capture the physical flowpaths: the proportions of new water calculated from these tracers (36 and 45%) tightly bracket the observed proportion from the surface trough. The values from the individual troughs, however, indicate that this is a fortuitous occurrence: the tracers are highly non-conservative, with both silica and chloride being rapidly dissolved in the event water, as indicated by fact that the surface-runoff component did not contain 100% new water. Even in this highly controlled artificial catchment, there is a high degree of heterogeneity in water movement through the porous medium. Determining the proportion of event water alone does not constrain the possible hydrologic mechanisms sufficiently to uniquely distinguish subsurface and surface flowpaths through the catchment.

10.2.4 Scale dependence of f_{pe} values

While spatial scale is widely recognized as one of the most important parameters in hydrologic studies, there are at present very few data on the variability of f_{pe} within a single watershed over the range of scales most relevant to watershed modeling. The data of one of the earliest studies (Sklash et al., 1976) come closest to fitting this description. Measurements were made at seven different points in two adjacent watersheds; the largest number of points on any individual branch of a drainage system was three. Watershed areas upstream of these three points were roughly 100, 400, and 700 km^2 (see Table 10.1), and f_{pe} values were 55, 71, and 70 percent, respectively (at the Otterville, Tillsonburg, and Vienna sites, respectively, in Figure 10.3), for the one storm reported. Mook et al. (1974) measured ^{18}O concentrations at three points in the stream draining their study site; the three points defined watersheds of roughly 0.25, 1.5, and 6.5 km^2 (estimated from their map). Data were reported only for the site farthest downstream, though it was stated that data from the other two sites were similar. Pearce (1990) found similar

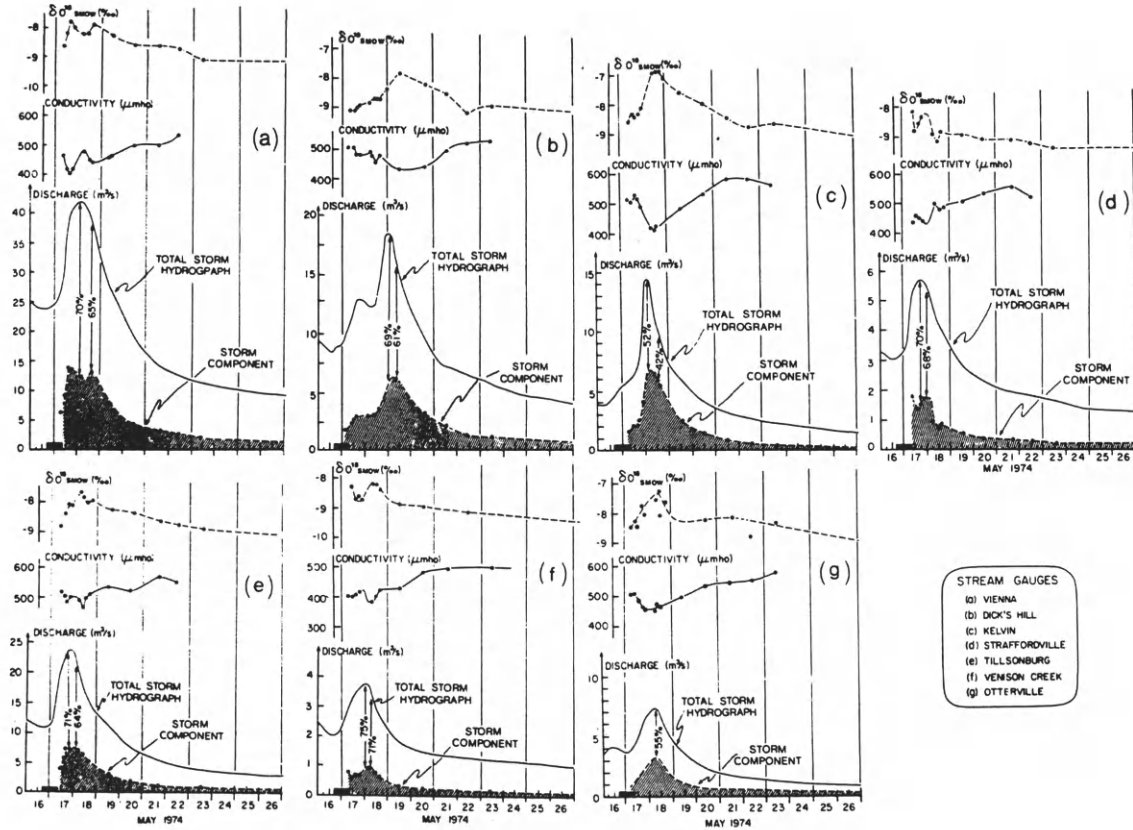


Figure 10.3. Electrical conductivity and $\delta^{18}\text{O}$ data, and event/pre-event hydrograph separations, from seven different sites in the Big Creek and Big Otter Creek watersheds in Ontario, Canada, for the rainfall event of 16 May 1974 (from Sklash et al., 1976).

f_{pe} values decreased with catchment size for the 0.038 km² M8 catchment (discussed earlier) and a 0.003 km² subcatchment within it, though the larger 2.8 km² catchment containing M8 showed smaller f_{pe} values at peak flow. This behavior is opposite to that shown by Sklash et al. (1976), where the smallest watershed had the smallest f_{pe} . Two studies (Sklash et al., 1986; Waddington et al., 1993) report measurements at plots or soil pits within a watershed, in addition to measurements made at the watershed outlet. The few available data do not provide a clear picture of the dependence of f_{pe} values on spatial scale, making this an issue to be resolved by ongoing and future work. New work suggests that results continue to be equivocal. Brown et al. (1998) reports that for 7 nested catchments (5 - 200 ha) in the Catskill Mountains of New York, that new water decreases with catchment size. McDonnell et al. (1998) report for 4 nested catchments in New Zealand (ranging in size from 0.05 - 1000 ha) that new water *increases* with catchment size.

10.2.5 Intra-component variability in tracer concentrations

Implications for uncertainty in calculated pre-event water fractions

As stated in Section 10.2.2, ¹⁸O, D, and T may be used in a two-component mixing model if the isotopic difference between event and pre-event water is large relative to the intra-component variability of each and the measurement uncertainty associated with the isotopic analyses. The mixing equation used to determine f_{pe} for a stream or other water sample is:

$$f_{pe} = \frac{C_s - C_e}{C_{pe} - C_e} \quad (10.1)$$

where C_{pe} , C_e , and C_s are the concentrations of the isotopic tracer in pre-event, event, and sample water, respectively. Either δ values in parts per thousand (‰, per mil) or isotope ratios such as ¹⁸O/¹⁶O can be used as "concentrations" in Equation 10.1. The uncertainty in f_{pe} (W_{fpe}) can be expressed in terms of the uncertainties in the tracer concentrations (Genereux, 1998):

$$W_{fpe} = \sqrt{\left[\frac{C_e - C_s}{(C_{pe} - C_e)^2} W_{cpe} \right]^2 + \left[\frac{C_s - C_{pe}}{(C_{pe} - C_e)^2} W_{ce} \right]^2 + \left[\frac{1}{(C_{pe} - C_e)} W_{cs} \right]^2} \quad (10.2)$$

where W_x corresponds to the uncertainty in x . From inspection of Equation 10.2 it is apparent why a large difference between the isotopic composition of event and pre-event waters is beneficial; the larger $C_{pe} - C_e$, the smaller W_{fpe} . Also, it can be seen that the uncertainty in f_{pe} is most sensitive to uncertainty in C_s , since the multipliers on W_{cpe} and W_{ce} differ from the multiplier on W_{cs} by factors of $(C_e - C_s)/(C_{pe} - C_e)$ and $(C_s - C_{pe})/(C_{pe} - C_e)$, respectively, ratios whose absolute magnitudes are always less than one for mixtures of event and pre-event water. This is fortunate because C_s is generally the tracer concentration with the smallest uncertainty (typically just the analytical uncertainty of the isotope measurement). Inspection of the error terms for C_{pe} and C_e shows that W_{fpe} is more sensitive to error in the component (event or pre-event water) accounting for more than half of the mixture (pre-event water in most cases).

Table 10.3 shows the results of some example calculations with Equation 10.2 for a hypothetical case in which precipitation of $\delta^{18}\text{O} = -6\text{‰}$ falls on a watershed where pre-event water has $\delta^{18}\text{O} = -12\text{‰}$, and a stream sample with $\delta^{18}\text{O} = -10\text{‰}$ is collected. The stream sample would of course have $f_{pe} = 0.67$; the last column in Table 10.3 gives the uncertainty in this f_{pe} value, given different values for the uncertainty in C_{pe} (-12‰) and C_e (-6‰). The uncertainty in C_s is taken to be ± 0.1 , the approximate value of the analytical uncertainty in $\delta^{18}\text{O}$ measurements. Results show that f_{pe} is more sensitive to error in C_{pe} than error in C_e (because pre-event water accounts for more of the stream sample than event water), but significant amounts of uncertainty in either C_{pe} or C_e (around $\pm 1\text{‰}$ or more) introduce sizable error in calculated f_{pe} values. Thus natural intra-component variability of this magnitude is of concern for isotopic hydrograph separations and resultant conclusions regarding runoff mechanisms. Genereux (1998) presents a detailed analysis of tracer-based uncertainty for those readers seeking additional detail on the topic.

Table 10.3. Uncertainty in f_{pe} calculated using selected values of W_{cpe} and W_{ce} in Equation 10.2. The value of W_{cs} is taken to be ± 0.1 . See text for discussion.

W_{cpe} (error in C_{pe})	W_{ce} (error in C_e)	W_{fpe} (error in f_{pe})
0.1	0.1	0.021
0.2	0.1	0.028
0.3	0.1	0.038
0.5	0.1	0.058
1.0	0.1	0.112
2.0	0.1	0.223
0.1	0.2	0.023
0.1	0.3	0.026
0.1	0.5	0.034
0.1	1.0	0.059
0.1	2.0	0.113
0.2	0.2	0.030
0.3	0.3	0.041
0.5	0.5	0.064
1.0	1.0	0.125
2.0	2.0	0.249

Variability in pre-event water

Several examples from the literature document spatial variability in the isotopic composition of pre-event water (while the isotopic composition of pre-event water may vary in time from

season to season, only spatial variability at a given time is relevant to isotopic hydrograph separation during and following a particular storm). Blowes and Gillham (1988) found that the $\delta^{18}\text{O}$ of pre-event water varied between -5.3‰ at about 10 cm below ground surface to -9.5‰ at 3 m below ground surface in May, 1982. Blowes and Gillham (1988), like other authors, chose the $\delta^{18}\text{O}$ of pre-storm streamflow (-7.9‰ for May 1982 storms) as the best $\delta^{18}\text{O}$ value to use for pre-event water in hydrograph separations. The $\delta^{18}\text{O}$ of baseflow represents an integrated average $\delta^{18}\text{O}$ for the pre-event water actually arriving at the stream, and as such may represent the best practical choice for isotopically defining pre-event water. However, if flowpaths change during a storm, the flow-weighted average $\delta^{18}\text{O}$ of pre-event water discharging to the stream may also change, introducing error into hydrograph separations which assume the isotopic signature of pre-event water reaching the stream during the storm is unchanged from that of baseflow.

Sklash and Farvolden (1979) found $\delta^{18}\text{O}$ values of about -11.9‰ in jointed gneiss bedrock at their study site in Quebec (Ruisseau des Eaux Volées), while groundwater in the overlying glacial deposits had $\delta^{18}\text{O}$ values around -12.8‰ . Probably even more significant with respect to hydrograph analysis was the fact that " ^{18}O analyses of the vadose water indicate ... values are consistently heavier than the groundwater by as much as 6 ppt" (Sklash and Farvolden, 1979). Because this large isotopic variability in pre-event water could lead to a substantial uncertainty in hydrograph separation, Sklash and Farvolden (1979) sought to undertake separations only for those hydrographs without a significant contribution from vadose zone water. However, the graphical procedure applied to detect such hydrographs was faulty in that it could lead to both "false positives" (incorrectly identifying a hydrograph as having a significant contribution from vadose zone water) and "false negatives" (failing to identify hydrographs with a significant contribution from vadose zone water). The procedure (Sklash and Farvolden, 1979) relied on plots of $\delta^{18}\text{O}$ vs. streamflow rate (Q). It was assumed that mixtures of groundwater and precipitation would fall along a straight line connecting baseflow and peakflow on such a plot; further, it was assumed that contributions from isotopically-heavy vadose zone water would cause data to plot above this straight line. However, both of these assumptions may be violated. Stream samples composed of water from three distinct components (groundwater, vadose zone water, and precipitation) could potentially fall along a straight line on a plot of $\delta^{18}\text{O}$ vs. Q . In addition, time-varying samples of a two-component mixture (groundwater and precipitation) will not necessarily fall along a straight line on the $\delta^{18}\text{O}$ vs. Q plot. Hysteresis in flowpaths between the rising and falling limbs of a hydrograph could produce different isotopic signatures for the mixture (streamwater) at the same Q . This phenomenon is well known for the storm response of chemical solutes; in addition, it is apparent in more recent isotope data (published after Sklash and Farvolden's paper) showing that the peak in event water discharge sometimes follows the peak in total hydrograph discharge (Bonell et al., 1990; Waddington et al., 1993). This phenomenon could also explain some of the results of Sklash and Farvolden (1979).

Turner et al. (1987) found smaller differences between vadose zone water and groundwater. The ^{18}O content of "deep" groundwater was found to be highly uniform and equal to 5.0‰ ("deep" was not defined, but appears from the text and Figure 2 of the paper to be greater than several and less than about 25 meters below ground surface), while "shallow" groundwater was slightly more variable and heavier on average (-4.1‰). Vadose zone water was said to have been highly uniform and "depleted by about 0.4 ppt in $\delta^{18}\text{O}$... relative to the deep groundwater samples" (Turner et al., 1987). Neal et al. (1992) used isotopic data for rainfall and streamflow to indirectly demonstrate variability in the isotopic composition of pre-event water at their site. During two of three storms studied, the isotopic composition of streamwater shifted away from

that of precipitation, indicating there were contributions to storm streamflow from pre-event water with an isotopic composition distinct from that of pre-event baseflow. Any simple mixing model for storm runoff would require at least three components on such a basin.

DeWalle et al. (1988) used a three-component model to account for variability in pre-event water on the Fish Run catchment in Pennsylvania. Soil moisture in the vadose zone was found to be 2-3‰ heavier than stream baseflow prior to two events in November 1986. Precipitation associated with these storms resulted in the isotopic composition of streamwater shifting away from that of throughfall and toward that of soil water at some sampling times. As the authors noted, the standard two-component mixing model can not be applied to such situations. The three-component model separated storm streamflow into groundwater, soil water, and channel precipitation (a "geographic source" separation, in the terminology of Sklash et al. (1979)). A three-component model requires one additional constraint (a second tracer or a physical measurement of the flow from one component) beyond what is needed for a two-component model. DeWalle et al. (1988) supplied this extra constraint by calculating the rate of channel precipitation as the product of the throughfall rate and the surface area of the stream. The surface area of the stream was based on a regression equation of stream surface area versus streamflow rate, determined by surveying the stream surface area at four different streamflow rates and fitting a curve to the four points. Results from six storms showed that channel throughfall accounted for 0-14% of storm streamwater, groundwater was 69-100%, and soil water accounted for 0-40%. This work documents the significance of shallow soil water stormflow during precipitation events. In fact, the soil water fluxes are probably underestimated because of the way in which the groundwater component was defined. As pointed out by Genereux and Hemond (1990b):

In their analysis of storm runoff, DeWalle et al. ... defined the groundwater component to be isotopically equivalent to the pre-storm streamwater... Using this definition with the 3C (three-component) model of DeWalle et al. requires the assumption that soil water does not contribute to baseflow. Results from several hydrometric studies have concluded that unsaturated lateral flow is important in baseflow maintenance (e.g., Hewlett and Hibbert, 1963; Weyman, 1970, 1973; Mosely, 1979)... Unless there are valid reasons to exclude the soil water contribution to baseflow on Fish Run, the ground water $\delta^{18}\text{O}$ used by DeWalle et al. will be biased toward that of soil water, and the net effect on stormflow analysis will be to underestimate the true soil water contribution.

Variability in event water

In principle either spatial or temporal variability in the isotopic composition of event water could pose a problem for isotopic hydrograph separation. There are well-known large-scale variations of the isotopic composition of precipitation with latitude and elevation (see Chapter 3 of this volume). These spatial trends could be significant in isotopic analysis of runoff in large basins, though intra-storm temporal variability is probably more troublesome to traditional hydrograph separation studies on small watersheds. Pionke and DeWalle (1992) documented intra-storm variability in the ^{18}O content of precipitation during ten storms at a site in Pennsylvania. Summary data (Table 10.4) show very large ranges in $\delta^{18}\text{O}$ for some storms, particularly the larger, longer storms. As shown earlier, variability of this magnitude can have a significant effect on the uncertainty in a calculated f_{pe} value. Pionke and DeWalle (1992) found that the ^{18}O content of precipitation changed most rapidly during periods of high rainfall rate, the same effect observed by Matsuo and Friedman (1967) for at least some of their monitored storms (their storm 3, in their Figure 1a).

Table 10.4. Total rainfall depth, duration, and range and mean of $\delta^{18}\text{O}$ for ten storms, from Table 1 of Pionke and DeWalle (1992).

Depth (mm)	Duration (hr)	$\delta^{18}\text{O}$ (‰)		
		mean	maximum	minimum
3.8	0.7	-10.00	-9.94	-10.43
9.9	0.5	-9.91	-9.60	-10.90
10.2	0.7	-4.04	-3.71	-4.60
10.6	1.1	-3.51	-3.48	-3.57
17.5	9.0	-3.97	-2.34	-5.78
18.5	4.8	-7.40	-3.86	-9.63
31.0	11.0	-15.41	-4.00	-19.97
31.7	3.0	-8.48	-7.21	-12.42
48.2	9.7	-9.33	-2.53	-12.11
58.2	1.8	-4.89	-2.70	-5.91

McDonnell et al. (1990) studied the effect of intra-storm isotopic variability in precipitation on separation of a hydrograph from the Glendhu 2 catchment in New Zealand. δD of the precipitation became heavier during the storm, from -94.8‰ at the start to -61.9‰ at the end about ten hours later. Three different hydrograph separations were performed (Figure 10.4), each using a different method to determine the δD value of event water (i.e., C_e) for use in Equation 10.1:

1. *Standard weighting*: the depth-weighted average δD of the precipitation was calculated and used as C_e at every time during the storm (this is the approach traditionally used).
2. *Incremental mean*: C_e at a particular time was determined as depth-weighted mean δD up to that time. In this way precipitation not yet fallen does not affect the hydrograph separation.
3. *Incremental intensity*: similar to incremental mean, except that δD values were weighted by average rainfall rate over an interval rather than total rainfall amount over the interval.

Results showed that the standard weighting procedure significantly underestimated the contribution of pre-event water, relative to the other two techniques, during the rising limb of the hydrograph. The f_{pe} determined by standard weighting started off about 30% lower than the values derived from the two incremental methods (which gave very similar results throughout), and eventually merged with the results from the incremental methods around or shortly after peak flow. In the absence of detailed information on the travel time of new water through a catchment, the two incremental approaches are presently the best approach to handling the temporal variability in the isotopic composition of precipitation (at least they improve on the simple standard weighting approach by not allowing C_e at a given time to be affected by precipitation falling after that time).

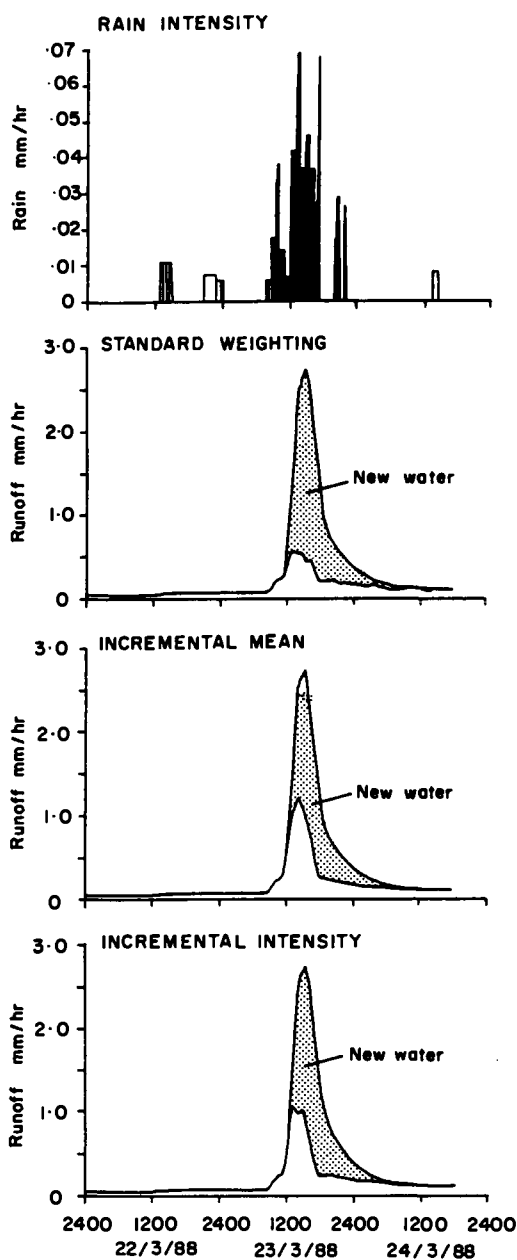


Figure 10.4. Rainfall rate and three different hydrograph separations (based on the same δD data) for the 23 February 1988 storm at the Glendhu 2 watershed in New Zealand (from McDonnell et al., 1990). The three separations are based on different methods for handling the temporal variability in the δD of rainfall (see text for discussion).

10.2.6 Recommendations for field studies

Perhaps the most important and general recommendation that can be made regarding hydrograph separation studies with oxygen and hydrogen isotopes is to respect the limitations of the approach. This begins with an appreciation for the basic logic of the separation (that one is distinguishing water falling as precipitation during a particular storm from water stored on the watershed before the start of the storm), and is reinforced through use of language that is strictly consistent with this logic (e.g., "old" vs. "new" water, or "pre-event" vs. "event" water, as distinguished from other hydrologic terms such as groundwater and overland flow (Sklash et al., 1976)). While it is true, as argued earlier, that much of the impetus for "time source" separation of event and pre-event water is to constrain other separations of more fundamental hydrologic significance ("geographic source" and/or "runoff mechanism" separations), realization of that goal will, in practice, usually require additional measurements beyond oxygen and hydrogen isotopes. Thus, combination of hydrometric measurements (of water flow, head, or storage) with isotopic measurements is strongly recommended. The work done in New Zealand and summarized earlier demonstrates the value of this approach; the work of Waddington et al. (1993) provides another good recent example.

Recent studies demonstrate the significant isotopic variability within both event and pre-event water. Because this variability may control the uncertainty in the hydrograph separation, it is of prime importance to have some data with which to evaluate it. In general this calls for sequential sampling of rainfall (or more specifically, throughfall; see below) to evaluate the temporal variability of event water composition, and spatially distributed sampling of pre-event water in the subsurface. As Pearce et al. (1986) point out, evaporation from intercepted water on a forest canopy could result in throughfall being enriched in the heavier isotopes of oxygen and hydrogen relative to precipitation. Spatial variability in the isotopic composition of pre-event water has been evaluated in several studies, and found to be significant. Some authors have taken the isotopic composition of pre-event streamflow as representative of pre-event water, on the supposition that even if there is a heterogeneous distribution of pre-event isotopic composition in the subsurface, streamflow generation processes operate to provide the true flow-weighted average composition of water reaching the stream, the composition that is of interest from the standpoint of the hydrograph separation. The major concern with this approach is that subsurface flowpaths likely change during the storm, and if these changes affect the flow-weighted average isotopic composition of pre-event water reaching the stream (e.g., isotopically heavier water from higher in the soil profile becomes relatively more important) they will introduce error into the hydrograph separation. Efforts should be made to minimize (by working under conditions when pre-event water is relatively homogeneous, and there is a large difference in event and pre-event composition) and quantify (through spatial sampling of pre-event water to determine its variability, and quantitative propagation of this variability to estimate uncertainty in f_{pe}) this error in hydrograph separation. Ideally, at least several subsurface sampling sites would be used, with a greater site density toward the lower slopes and riparian areas which water must traverse *en route* to the stream. A formal geostatistical approach to quantification and modeling of pre-event water variability has not been attempted, but it would be a useful addition to understanding the structure of this variability.

10.3 New Directions

10.3.1 Subsurface mixing and residence time

Some authors have sought out frameworks other than separation of event and pre-event water for use of oxygen and hydrogen isotope data in streamflow generation studies. Several studies have applied stable isotope data to the determination of water residence times or apparent streamflow "ages" on catchments. Most of the work on water residence times involves deconvoluting the time course of isotope input (i.e., the isotopic composition of precipitation or throughfall) with a system response function (also called weighting function) to calculate the time course of isotope output (i.e., the isotopic composition of streamwater) from the catchment. Adjusting the response function to optimize the fit between measured and computed streamwater isotope content gives a mean residence time for water (τ) and possibly, depending on the form of the response function used, an additional "dispersion" parameter (see below). τ and, if applicable, the dispersion parameter, can be used in the response function to calculate the distribution of water residence times. Chapter 21 reviews these techniques in some detail.

Rose (1993, 1996) adopted a somewhat different approach in his use of tritium to constrain water residence times on four catchments in Georgia. Rose (1993) found the mean T content of baseflow to be about 20-30 tritium units (TU) on three catchments of the Upper Ocmulgee basin. This information was used to constrain the mean residence time of water providing baseflow as follows:

- It was assumed that water discharged as baseflow had a normal distribution of residence times.
- A mean τ and standard deviation S_τ were chosen for this normal distribution (τ values chosen ranged between 10 and 45 years, S_τ values ranged from 1 to 15 years).
- The area under the normal distribution with the chosen τ and S_τ values was taken to be 1, and was divided up into time intervals to give weighting fractions for the contribution of water from each time interval (since 1953) to the baseflow in 1991 (the year of data collection). (It was somewhat unclear from the original paper whether the time intervals were 1 or 2 years).
- The weighting fraction for each time interval was multiplied by the decay-corrected T content of rainfall during that interval (i.e., the T content water from that rainfall would have had in 1991) to give the fractional contribution of T from that time interval to the 1991 baseflow.
- The fractional contributions were added to give the model-computed T content of 1991 baseflow, which was then compared to the true T content of 1991 baseflow to evaluate how realistic the chosen τ and S_τ values were.

This procedure was applied to combinations of τ values between 10 and 45 years and S_τ values between 1 and 15 years, yielding agreement between true and model-computed T values in baseflow for τ values between 15 and 30 years. Rose (1993) suggested that these residence times are consistent with expected rates of vertical downward flow through saturated regolith, though a specific argument was not offered for why τ would be controlled by rates of vertical rather than horizontal flow. Rose (1996) carried out a similar procedure to constrain the range of possible residence time values for groundwater sampled near a ridge on Falling Creek basin (187 km²) in Georgia. Residence times from 5 to 100 years were investigated using the computational procedure outlined above, and those in the range 20 - 40 years gave good agreement between measured and model-computed T content.

Harris et al. (1995) proposed a new hydrograph method for source area modeling based on continuous open system isotopic mixing using a variable source area and three isotopic reservoirs. These three reservoirs were 1) direct precipitation onto saturated areas, 2) a near-stream saturated zone, and 3) subsurface water in upslope areas (Figure 10.5). They allowed the reservoir sizes and isotopic compositions to evolve due to continuous, open system mixing. They found that streamflow was composed of rainfall on saturated areas and water exfiltrated in the near-stream zone. The contributing source fractions were determined using the observed isotopic compositions of the stream and the modeled isotopic compositions of the contributing reservoirs, which were functions of time. The near-stream saturated zone received inflow from the upslope areas which were not surface saturated (Figure 10.5). The surface saturated area was allowed to change dynamically based on the difference between lateral inflow and contributions to streamflow from the near-stream saturated zone. The upslope zone (reservoir 3) evolved by mixing with rainfall. The Harris et al. (1995) hydrograph separation model required 1) a function which relates the amount of water stored in the near-stream saturated zone to saturated area, 2) a function which relates saturated area fraction to total streamflow (similar to that used by DeWalle et al. (1988) as discussed in Section 10.2.5), and 3) knowledge of the water storage capacity in reservoirs 2 and 3.

The hydrograph separation method was applied by Harris et al. (1995) to oxygen isotope data for rainfall and runoff during a 36-hour storm at the Gårdsjön F1 catchment in southwestern Sweden (described in Chapter 12). This method was used to estimate parameters for relations between saturated area fraction and streamflow, and saturated area and subsurface water storage. Harris et al. (1995) showed that streamflow contributions from overland flow could be described by a simple analytic function of antecedent conditions and catchment processes. This approach is of interest as many new studies highlight the importance of the riparian zone on imparting the chemical signal of streamwater (Hooper et al., 1998). The mixing of distinct reservoirs is now being attempted in several current projects.

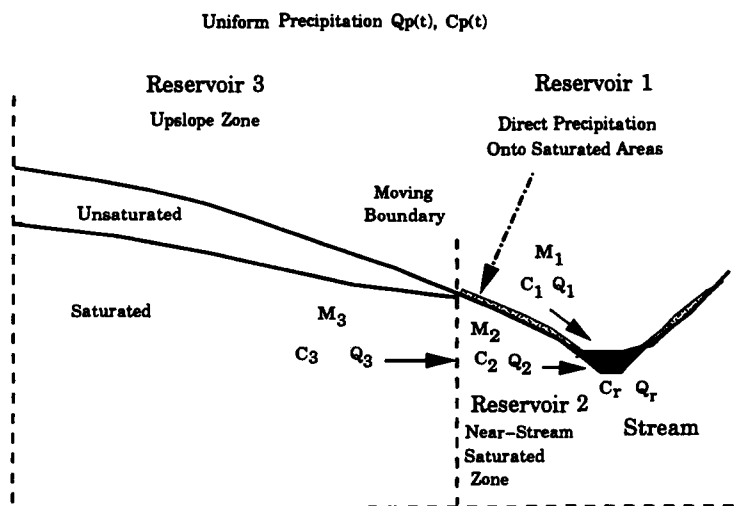


Figure 10.5. Schematic diagram of continuous open system isotope mixing model (From Harris et al., 1995). Arrows indicate model flux directions; dashed line indicates boundary limiting surface-saturated areas of catchment; hachured area is surface saturated; and solid area represents the stream.

10.3.2 Use of isotopes in model calibration

In addition to their application in hydrograph separation and residence time studies, oxygen and hydrogen isotopes have been used in the calibration of catchment rainfall/runoff models, particularly "conceptual" hydrochemical models. These are lumped-parameter models where the catchment is divided into compartments that represent different conceptual units, such as soil horizons, which are thought to influence streamwater chemistry. Predictions of streamwater chemistry are more sensitive to the routing of water through these internal compartments than are predictions of the quantity and timing of streamflow. The main impetus for this research was the prediction of the effects of acid deposition on streamwater chemistry, but the problem is generic to determining the effects of any non-point source pollutant on surface waters.

In this application, only the conservative behavior of the isotopes is assumed; that is, the isotopes move as the water moves and do not fractionate between the time the water reaches the ground and the time the water exits the catchment as streamflow. This assumption is generally supported for catchments with little surface water (Dinçer and Davis, 1984; Sklash and Farvolden, 1979). None of the other assumptions for hydrograph separation, as outlined above, are needed. The isotopic tracer is being used to provide more insight into the movement of water through the catchment, and to provide additional information for model calibration. The central issue is "parameter identifiability"; that is, do the data that are available define a unique parameter set for the model or are multiple parameter combinations able to reproduce the data equally well? Model predictions become increasingly uncertain as the range of acceptable parameter values widens.

The Birkenes model (Christophersen and Wright, 1981; Christophersen et al., 1982) has been most extensively evaluated using isotopic tracers. It represents the catchment as two linear reservoirs. For the snow-free periods of the year, the hydrologic model contains essentially six adjustable parameters: three dimensional parameters describing the threshold and size of the reservoirs, two rate parameters relating hydrologic flux to the head in the linear reservoirs, and a routing parameter to determine the proportion of the flow from the upper reservoir that goes directly to the stream (Figure 10.6). In the initial application of the model to the Birkenes catchment (located in southern Norway), where only reactive solutes were included, parameter sets were identified that made physical sense and adequately reproduced the catchment hydrograph and chemographs. A strong correlation existed between discharge and solute concentration, with high flow being more acidic and aluminum rich. The model reproduced this pattern by routing acidic rainfall through the more acidic upper soil horizon. However, conservative tracers exhibited a much more dampened response, reflecting the predominance of pre-event water in runoff at Birkenes, as has widely been observed. Christophersen et al. (1985) found it difficult to reproduce both the dampened response of the conservative tracers and the rapid variations in the concentration of reactive solutes using manual model calibration.

To explore the model behavior more systematically, de Grosbois et al. (1988) developed a multi-signal automatic calibration methodology that used a weighted least squares objective function to determine the optimal parameter values for reproducing both the observed streamflow and oxygen-18 signal. For error-free artificial data, de Grosbois et al. (1988) found that the parameters could be determined uniformly better when both oxygen-18 and streamflow were used for calibration than when streamflow alone was used. At the best weighting for the tracer and streamflow signals, all six parameters could be determined to within 10% of their true value in 80% of the trials where the starting parameter values ranged from one-tenth to ten times the true parameter value.

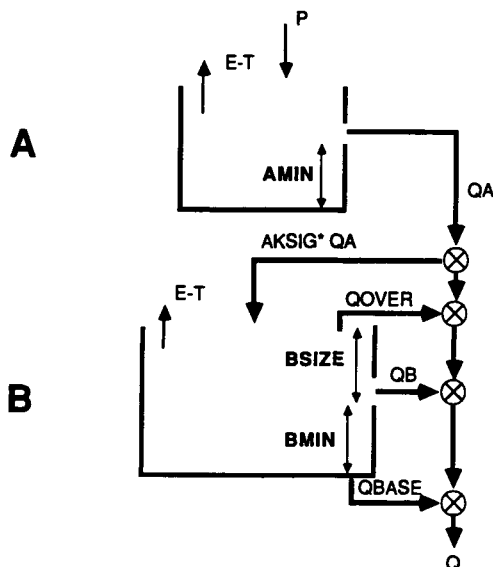


Figure 10.6. Schematic diagram of the hydrologic module of the Birkenes model (from Hooper et al., 1988). Outflow is generated from each of the two linear reservoirs (A and B) when a storage threshold (AMIN or BMIN, respectively) is exceeded. In addition, the B reservoir may generate overland flow (QOVER) if net inflow occurs when the maximum storage (BMIN + BSIZE) has been reached; it may also generate outseepage to baseflow (QBASE). The proportion of flow from the A reservoir (QA) that is routed to the B reservoir (instead of directly into the stream) is equal to AKSIG times QA, where AKSIG varies linearly from 1 (when the water level in B is less than BMIN) to a minimum of AKSMX (when the water level in B is at its maximum).

Hooper et al. (1988) applied this multi-signal calibration technique to real data from the Birkenes catchment. Inclusion of the conservative tracer improved the observability of the threshold parameters, a logical result because the tracer dynamics indicate the effective mixing volume in the catchment. Only the sum of the parameters, not two separate values as the model was originally posed, could be uniquely identified. Additional tracers would be required to identify more than one passive store. However, the tracer did not help to identify the routing parameter, which remained poorly constrained. Hooper et al. (1988) concluded that hydrologic and isotopic data could identify only a four-parameter model, which included only a single passive store and eliminated the routing parameter.

Kleissen et al. (1990) provided a more systematic examination of parameter identifiability in hydrologic models similar to the Birkenes model using both deterministic (Pohjanpalo's method) and stochastic (extended Kalman filter) approaches. This study attempted to understand what aspects of the data signal determined the parameter values, and therefore the most important field observations. This is termed an "a priori" model structural analysis that is not dependent upon the specific choice of parameter values as is an "a posteriori" analysis such as that performed by Hooper et al. (1988). Kleissen et al. (1990) demonstrate that if thresholds are included in the model, a tracer must be used to identify the model parameters. In general, they conclude that threshold and routing parameters are the most difficult to determine from the data, consistent with the results of Hooper et al. (1988). The deterministic

method becomes algebraically intractable as the model becomes more non-linear. The extended Kalman filter can be applied to more complex models, but parameter values must be specified. Using this approach, Kleissen et al. (1990) found that inclusion of a tracer uniformly decreased the standard deviation of the parameter estimates.

Another hydrochemical model, the PULSE-model (Bergstrom et al., 1985) was modified to better simulate oxygen-18 concentration by Lindstrom and Rodhe (1986). The additional damping required to explain the oxygen-18 concentration was obtained by adding mixing in the unsaturated zone and storage volumes that do not affect runoff calculations. The storm response was modeled using a bypass mechanism that represents saturation overland flow.

10.4 Conclusions

Stable isotopes of oxygen and hydrogen have proven to be useful tools in determining the contribution of rainfall to stormflow, the residence time of water on catchments, and other aspects of watershed hydrology. The separation of contributions from event and pre-event (or "new" and "old") waters to stormflow adds a constraint on streamflow generation that physical (hydrometric) measurements never could. The large contribution of pre-event water to storm streamflow (usually 70-80% of hydrograph volume and peak flow rate) is entirely consistent with the importance of subsurface stormflow as documented by hydrometric studies on forested catchments before isotopes became widely used. In addition, isotopic studies clearly show that, through some combination of mixing and displacement, pre-event water usually makes up the bulk of stormflow, even discharging to streams through macropores and soil pipes. While stream pH and alkalinity are generally depressed during stormflows, the stable isotope data point out that this depression could be much more severe if subsurface mixing and flowpaths were different, and high-pH, high-alkalinity pre-event water made up less of storm streamflow.

Recent studies suggest that application of oxygen and hydrogen isotopes to hydrograph separation may be limited in many places and times by the significant temporal (intra-storm) variability in the isotopic composition of rainfall, and the spatial variability in the isotopic composition of subsurface (pre-event) water. This variability may impose severe constraints on the accuracy of hydrograph separations. One of the original attractions of two-component hydrograph separations was that they were based on spatially-integrated signals measured in the stream, potentially avoiding the logistical pitfalls (familiar from hydrometric studies) of point measurements on hillslopes. However, it now seems that subsurface sampling is necessary to evaluate the isotopic homogeneity of pre-event water. Fractional sampling of precipitation to gauge intra-storm isotopic variability is also beneficial, and is much simpler than spatially distributed sampling of pre-event water.

In development of lumped-parameter hydrologic models, stable isotopes have provided information that influenced the conceptualization of streamflow generation mechanisms and improved model calibration. Parameter identifiability was improved with tracers, but the model structures that could be supported by hydrologic and isotopic data remain quite simple. Other tracers, such as reactive solutes, could provide additional information for model calibration; however, inclusion of these solutes requires the introduction of additional model parameters. The salient question is whether the information provided by the additional data series is greater than the information required by the additional parameters. This question is an area of active

research that requires advances in both numerical and analytical approaches to the problem of parameter identifiability.

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Chapter 11

High Rainfall, Response-Dominated Catchments: A Comparative Study of Experiments in Tropical Northeast Queensland with Temperate New Zealand

Michael Bonell, Christopher J. Barnes, Clive R. Grant, Andrew Howard and John Burns

11.1 Introduction

Isotopic studies in catchments are most useful when used in combination with multiple techniques that assess structure of the catchment and its hydrological processes. In this chapter we present results of a hydrological investigation involving two paired catchments in a high rainfall area of the humid tropics of north-east Queensland (near Babinda). The isotopic techniques were fully integrated with other hydrometric techniques, playing mutually supportive roles. We saw the need for detailed understanding of the underlying geology, lithology, soil structure and process information (e.g. hydraulic conductivity), as well as climate and topography to appreciate the spatial and temporal heterogeneity in hydrological response to monsoon rainfall. The latter required measurements of the hydraulic response of the stream to storm events (hydrographs), groundwater (well hydrographs), soils (soil moisture contents, tensiometer and piezometer data), and rainfall intensities, as well as measurements of isotopic concentration. All measurements were taken at what we considered to be appropriate spatial and temporal scales and then compared to data from other catchments in high rainfall areas.

We begin the chapter with a brief overview of earlier isotopic studies in other catchments, with specific reference to the Maimai catchments (New Zealand), and the pertinent questions raised by these studies. This is followed by a detailed description of the geology, soils and hydraulic properties that were previously undescribed and supported by summaries of the rainfall and hydrological characteristics. An important message of the foregoing review is the need to undertake *a priori* hydrometric studies for setting up the appropriate hypotheses for the described environmental tracer study. Subsequently, a brief section on experimental and analytical methods follows, before attention then focuses on the contrasting responses of the paired, tropical rainforest catchments (disturbed, undisturbed) to a monsoon storm which occurred on February 16, 1991. This storm is typical of those events which exceed 250 mm in total over a 24 hour period and which coincide with very wet antecedent conditions (Gilmour, 1975; Bonell et al., 1991). During the interpretation of such responses reference will also be made to data collected during the 1990-91 wet season including hydrometric and isotopic information from the hillslope monitoring plots. An appropriate modeling strategy for analyzing the observed responses will also be discussed and some early results presented. Our principal conclusion is that the observed major differences in hydrology between these and other well-studied catchments are due to very high rainfall intensities, interacting with a complex, heterogeneous soil matrix. This results in contrasting spatial and temporal responses

in slope sections in terms of runoff generation coupled with the corresponding domination of the storm hydrograph by event (or 'new') water. To achieve these objectives, and because it is a case study, it will be necessary to provide a detailed description of the studies aforementioned.

11.2 Previous Studies in High Rainfall, Response - Dominated Catchments

11.2.1 The Maimai Catchments

Two benchmark studies discuss the use of environmental isotopes in runoff generation studies and hydrograph separation (Bonell, 1993). First, Sklash and Farvolden (1979) used the groundwater ridging mechanism hypothesis (Ragan, 1968) to explain the temporal variability of isotopic concentrations in the storm hydrograph, and to explain the large contributions from pre-event (Rodhe, 1987) or 'old' (Obradovic and Sklash, 1986) water stored in temperate drainage basins. Second, Pearce and co-workers (Pearce et al., 1986; Sklash et al., 1986; Pearce, 1990) presented isotopic evidence of predominance of 'old' water in the storm hydrographs even in the very wet, highly responsive Maimai catchments of New Zealand where quickflow/precipitation (QF/P) ratios (expressed as a percentage) could exceed 70% in individual storms. As noted by Pearce (1990), previous environmental tracer studies had concentrated on temperate environments where equivalent QF/P ratios are 20% or less. Moreover, there are very few *comprehensive* studies which attempt to reconcile the traditional input-output hydrogeochemistry data with hydrometric information and the water chemistry on the hillslopes. McDonnell's (1989) work in the Maimai catchment is one of the few exceptions. Based on detailed monitoring of various hillslope features, McDonnell (1990) built a conceptual model to explain the rapid mixing of 'new' (Obradovic and Sklash, 1986) or 'event' (Rodhe, 1987) water in macropores with pre-event matrix water, and then subsequently the displacement of 'old' water by both pipeflow and a groundwater ridging mechanism (which did not exhibit the capillary-fringe characteristics put forward by Sklash and Farvolden, 1979).

McDonnell (1989) evaluated the conflicting arguments of Mosley (1979, 1982) who favored a rapid delivery mechanism of event water by macropore flow in contrast to a displacement mechanism of pre-event water put forward by Pearce et al. (1986) and Sklash et al. (1986). Such opposite views were both considered to be technically correct by McDonnell (1989), but *the frequency of occurrence of each type of delivery mechanism was strongly dependent on the frequency of specific ranges of hourly rainfall intensities*. Mosley's (1979, 1982) rapid delivery occurs during infrequent high intensity storms where hourly rainfall intensities exceeded 15 mm/h, as described for a 90 mm event. (Mosley, 1979). McDonnell (1989) observed that hourly intensities greater than 15 mm were only recorded for 29 clock hours over a 13 year period. In contrast, the maximum hourly rainfall intensities reported by Pearce et al. (1986) and Sklash et al. (1986) were less than 3.2 mm/h. Thus the divergent interpretations of flow pathways may partly be due to the rainfall characteristics. Significantly, 99.9% of the cumulative frequency for Maimai storm rainfall hourly intensities were < 9 mm/h while 90.1% of the cumulative frequency was, < 3 mm/h. Thus the short-circuiting (Bouma and Dekker, 1978) or bypass flow (Smettem and Trudgill, 1983) mechanism, noted mostly from artificial tracer experiments (Mosley, 1979, 1982; McDonnell, 1989), and the 90 mm event (Mosley, 1979), maybe much less important for the majority of rainfalls in that particular environment.

11.2.2 Linkages between the Maimai and Babinda studies

Despite escalating interest in the application of hydrogeochemistry in runoff generation studies, the tropical moist forests have largely been neglected in the literature (Bonell, 1993; Bonell with Balek, 1993). The Babinda catchments are similar to Maimai (Pearce, 1990) in that the former are also characterized by high QF/P ratios which commonly exceed 45% for individual storms (Bonell et al., 1991). Prevailing short-term rainfall intensities during the summer wet season (Bonell, 1991) however, are at least an order magnitude higher than those of Maimai. Such characteristics, in combination with the persistently high antecedent volumes of soil moisture and groundwater storage associated with the wet season, provide the basis for an interesting comparison with the previous Maimai study. More importantly, the north-east Queensland study extends our knowledge of stream hydrogeochemistry to both undisturbed and disturbed tropical rainforest environments.

11.3 Physical Background

The paired catchments of this study are located at 17°20'S, 145°58'E, about six km east of Babinda (Figure 11.1a,b). The physical characteristics of the disturbed (North Creek) and undisturbed (South Creek) catchments are summarized in Table 11.1. The vegetation is tropical rainforest -- Mesophyll vine forest according to the classifications of both Webb (1959) and Tracey (1982). The canopy is uneven due to frequent damage by tropical cyclones. Over the period 1971-1973, 12.8 ha of North Creek was logged and cleared. Natural forest regeneration followed until the same area was cleared again by the landowner in 1987, only to be abandoned a second time, thus allowing a second regeneration of the forest to resume.

The underlying geology of the catchments consists of basic metamorphic rocks which belong to the Babalanghee Amphibolite of de Keyser (1964). This geological unit exhibits a strong and complete schistosity with a coarse grained texture (Richards, 1977; Arnold and Fawckner, 1980). Further it is conceivable that differences in the kind and degree of deformation, and therefore the schistosity (Hammond, 1986; Yardley, 1989), may affect the spatial pattern of resulting weathering, and by implication the preferred hydrologic pathways in the catchment (Riesen, 1993, pers. comm.).

The soils of both North and South Creek are dominated by kaolin-dominated silty clay loam to clay soils which may continue to 6 m in depth depending on the geomorphology. South Creek would seem to be actively downcutting the principal channels resulting in more shallow soils on the lower slopes and considerable exposure of ortho-amphibolites outcrops (Riesen, 1993, pers. comm.). The depth to the weathered bedrock increases with distance upslope from the principal stream channel. North Creek has not been surveyed in the same detail. Nevertheless, the steeper upper slopes, which still retain undisturbed forest, include some exposures of weathered bedrock, although not on the same scale as in South Creek. The complex origins of the geology are also reflected in the soil descriptions. Murtha (1986) provided a more comprehensive soils description of the wet tropical coast. A total of 98 soil series (as defined by the Soil Survey Staff, 1975) were established into seven broad units. Based on the classification of Murtha (1986) and the report for the Babinda region (Murtha et al., 1996), the field descriptions indicate completely different soils for each of these two catchments. North Creek has been studied in less detail, but from field descriptions (Murtha,

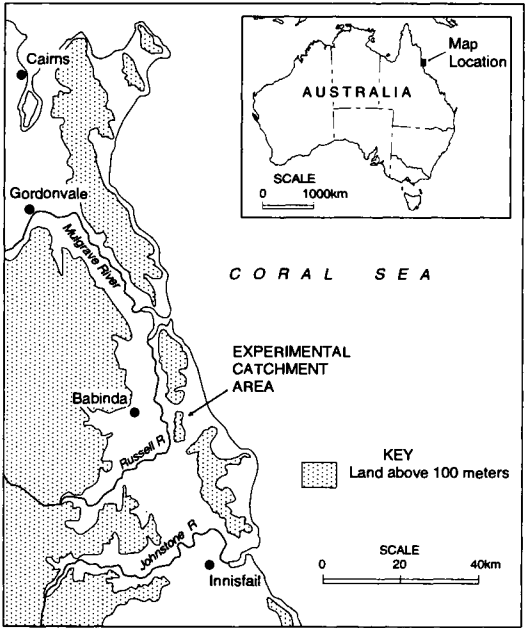


Figure 11.1a. The physical setting and location of the paired catchment study near Babinda.

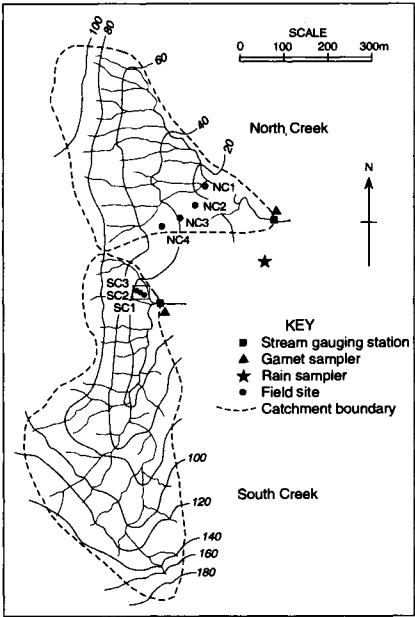


Figure 11.1b. The experimental plan in both North Creek and South Creek.

Table 11.1. Geomorphological characteristics of the experimental catchments.

Item	North Ck.	South Ck.
Area (hectares)	18.3	25.7
Minimum elevation (m)	9.2	21.4
Maximum elevation (m)	118.3	198.7
Median elevation (m)	62	87.5
Dominant-trend direction of principal stream channel	South-east	North
Maximum valley side slope (m/m)	1.27	1.63
Minimum valley side slope (m/m)	0.03	0.03
Mean catchment slope (m/m)	0.26	0.4
Mean hillslope length (m)	159.8	157.8
Mean specific catchment area (m ²)	235.1	217.6
Maximum stream order	4	4
Proportion of catchment area drained by first order streams	71.5	71.5
Bifurcation ratio	3.37	5.25
Drainage density (m/m ²)	.22	.23
Length of principal stream channel (m)	845	976

Source: Modified from Gilmour (1975) using additional information from TOPOG (O'Loughlin, 1986).

1991, pers. comm.) the soil has been mapped as part of the Bingil series of Murtha (1986) (Krasnozern of Stace et al., 1968; Haplorthox of Soil Survey Staff, 1975). South Creek is more complex. On a broader scale, Murtha (1993, pers. comm.) considers the soils to be part of the Galmara series (Red Podzolic of Stace et al., 1968; Tropeptic Haplorthox of Soil Survey Staff, 1975) with additional small areas of the Bicton series (Xanthozem of Stace et al., 1968; Tropeptic Haplorthox of Soil Survey Staff, 1975) which have yellow B horizons. More detailed profile descriptions (Riesen, 1993, pers. comm.; Elsenbeer et al., 1994) tentatively classify the more prevalent, steep sideslopes as Inceptisols, but this depends on subtle differences in criteria adopted (see Murtha, 1986). There is soil mineralogical evidence for surficial processes controlling pedogenesis (Elsenbeer et al., 1994) following Murtha's (1981, pers. comm. reported in Bonell et al., 1982) earlier observations that only remnants of the A2 and A3 horizons survive on the steeper slopes.

Detailed reports of the soil hydraulic properties have been presented elsewhere (Bonell et al., 1982, 1983a, 1987) for South Creek. The field saturated hydraulic conductivity, K^* characteristics for North Creek have also been summarized (Bonell, 1991; Bonell with Balek, 1993). Despite differences in the soil series, there is a consistent order of magnitude change of K^* down the profile when considering the 0-0.1 m, 0.1-0.2 m and 0.2-0.5 m depth layers. For South Creek the logarithmic means are respectively 843 mm/h ($n = 65$), 60 mm/h ($n = 60$) and

3.5 mm/h ($n = 219$). For the disturbed area of North Creek the 0-0.1 m depth, K^* had been reduced to 184 mm/h ($n = 34$) (measurements taken 10 years after logging and clearing), whilst the smaller sample from the undisturbed forest had a mean K^* of 1145 mm/h ($n = 10$). The logarithmic means of K^* for the 0.1-0.2 m depth (57 mm/h, $n = 28$) and 0.2-0.5 m depth (3.3 mm/h, $n = 155$) are almost the same as for the respective depths in South Creek.

The rainfall climatology has an important bearing on the runoff generation process. Mean annual rainfall for the period 1970-83 inclusive was 4009 mm (median 3630 mm, range 2654 mm (1980) to 5496 mm (1973)), and 63.5% occurred between December to March. The latter is commonly associated with tropical cyclonic perturbations triggered by the proximity of the monsoon trough (Bonell et al., 1991). When considering the rainfall frequency, intensity, and duration for the Babinda catchments over the period 1971 to 1983, the 0.1 h equivalent hourly intensities range from 95 to 247 mm/h and absolute hourly intensities (rain amount falling over one hour) lie between 46 and 104 mm/h for return periods one to 14 years (Bonell, 1988).

The high rainfall intensities and relatively low subsurface hydraulic conductivities suggest that saturation overland flow and subsurface stormflow (Chorley in Kirkby, 1978) will occur over large areas of the catchments. High values of surface K^* suggests that infiltration-excess (Hortonian) overland flow (Chorley in Kirkby, 1978) is unlikely to be significant in these catchments, except in the disturbed areas of North Creek during storms of high short-term intensity. Figure 11.2 shows the simulated percentage area of each of the catchments which are saturated using a steady-state version of TOPOG (O'Loughlin, 1986) for specific delayed flow discharges. Accepting that the delayed flow estimates are based on the arbitrary hydrograph separation procedure of Lyne and Hollick (1979) (using a filter factor of 0.899), it is evident that for discharges of 20 mm/day (typical of long duration monsoon storms) there are extensive areas of both catchments which are capable of generating saturation overland flow.

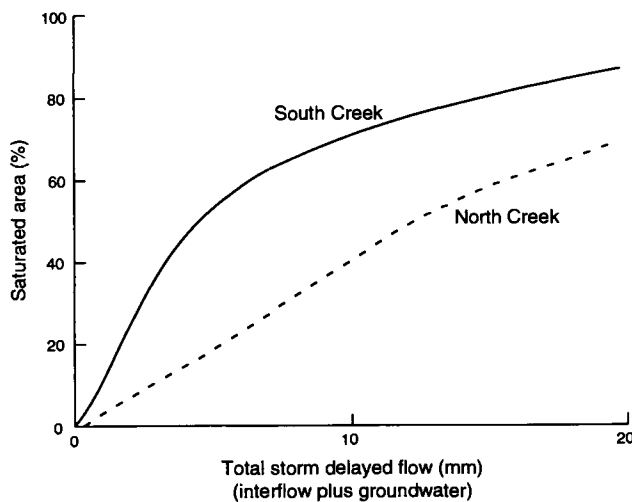


Figure 11.2. Saturated area vs total delayed flow (interflow plus groundwater), calculated using TOPOG (O'Loughlin, 1986), illustrating the effect of different topographies for North and South Creek.

However, the assumption of uniform transmissivities over the respective disturbed and undisturbed areas of North Creek, and also for South Creek, probably results in an overestimation of the extent of these areas. Furthermore the steeper South Creek catchment produces a non-linear, convex increase in saturated area compared with the more linear trace shown for North Creek. In common with the Maimai catchments, low matric potentials persist in the soils of the Babinda catchments during the wet season. Furthermore these soils are capable of storing between 1.2 to 1.5 m equivalent depth of rain as a typical upper limit in the top 3 meters (Gilmour, 1975). More comprehensive details of experimental methods and scientific results from previous hydrometric studies investigating the runoff generation process have been presented elsewhere (Gilmour et al., 1980, 1982; Bonell and Gilmour, 1978; Bonell et al., 1981, 1982, 1983a,b, 1984, 1991; Bonell, 1988). Particular emphasis was made in the previous literature on the subsoil K^* acting as an 'impeding' layer to the prevailing rain intensities, and in turn, initiating saturation overland flow as a dominant flow pathway. Previous results using injected tritiated water, however, indicated the existence of short-circuiting (Bouma and Dekker, 1978) or 'by-pass' flow (Smettem and Trudgill, 1983) at least down to 1.2 m depth (Bonell et al., 1982, 1983a, 1984) associated with the moderate to fine blocky structure of the subsoil (Murtha, 1981, pers. comm.) in experiments undertaken in South Creek. *This aspect will be an important consideration in the current work using new data.*

11.4 Experimental Methods

11.4.1 Precipitation

Precipitation was recorded automatically by a Rimco tipping-bucket raingauge (0.25 mm capacity) linked to a Wesdata single-channel data logger, centrally located between the two Creeks (see Figure 11.1b). Rainwater was sampled for isotopic analysis using two parallel methods. First, a design attributed to Kennedy et al. (1979) was used whereby successive increments of 15 mm are collected using an 84 mm funnel in a setup outlined by Bonell et al. (1990). Second, a modified Manning streamwater sampler was used with a 24 sample capacity and adjustable sampling frequency. For rainfall samples, recorded times are indicated as lines joining the start and end of the sampling period. A more appropriate procedure may have been to assign the time of the "center of mass" of the associated rainfall, but this has not been attempted here.

11.4.2 Streamflow

Stream discharge was measured at North and South Creeks by V-notch weirs described by Gilmour (1975). Stage height was recorded by capacitance water level probes connected to Wesdata single-channel loggers. A Stevens chart recorder was used as a backup measure for water level recording. Gammet water level samplers (24 bottle capacity) were time-programmed in linkage with float mechanisms for unattended streamwater sampling of both creeks. Sampling was generally set at 30 min intervals after the float reached a set level, while background sampling was set at either 12 or 24 hr intervals. During the latter period of the study, three Gammets were 'daisy-chained' at each Creek, allowing for the unattended collection of seventy-two samples. Time of sampling of automatically collected samples was

estimated from the sampling protocol, and the time at which the event hydrograph reached the pre-assigned level.

11.4.3 Hillslope instrumentation

The locations of sampling points (rain gauges, wells, suction lysimeters, weirs etc.) and monitoring points (piezometers, tensiometers etc.) are shown in Figure 11.1b with a more detailed plan for the South Creek transect included in Figure 11.3.

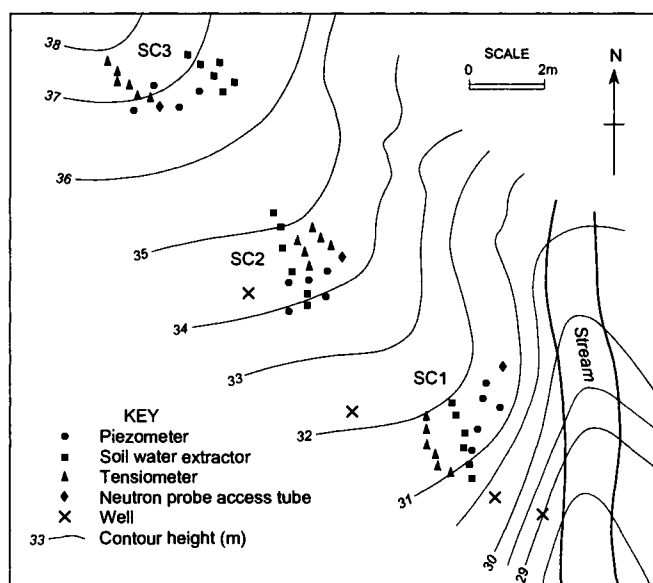


Figure 11.3. The detailed plan of the hillslope monitoring system in South Creek.

Wells

Wesdata capacitance water level probes were used in conjunction with Wesdata single channel loggers to record water table elevations at 10 min intervals during periods of groundwater level fluctuation. Plastic tubing extended to the base of each well facilitated the extraction of groundwater samples for isotopic analysis. The depths of the wells ranged between 1.90 - 4.86 m below the surface along the South Creek hillslope transect and 6.93 - 7.56 m in the corresponding North Creek monitoring plots. The shallower depths in South Creek reflected the difficulties in auguring within the underlying weathered rock.

Pressure transducers and piezometers

Honeywell 130 pressure transducers were installed at 15 cm, 30 cm, 45 cm, 60 cm, 90 cm and 120 cm depths at each site on both Creeks for monitoring the tensiometers. In the case of the piezometers, Wesdata capacitance water level probes were installed at each site at depths of 30 cm, 60 cm, 100 cm, 200 cm and 300 cm, except at South Creek site 3, where auguring to 3 m

was not possible (as with the wells) because of rock, preventing installation of a probe at this depth. Sets of both pressure transducers and piezometers were linked to multi-channel data loggers at each site (designed by I. Durham of CSIRO Division of Water Resources).

Soil moisture suction lysimeters were installed at each site to the same depths as the pressure transducers to provide for the collection of soil water samples for isotopic analysis. Sample timing represents the actual time of sampling; for suction lysimeters this represents the prior time period, in contrast to the procedure for rainfall. During relatively dry weather, it was often not possible to obtain samples (especially near the surface); and missing samples also often resulted from failure of the samplers to maintain a vacuum.

Samples were analyzed for D/H ratios on a VG Micromass 602E mass spectrometer by on-line reduction of 10 μg aliquots of water over a uranium furnace. External precisions of about 1‰ on repeated samples were typical.

11.5 Results: Event of February 16, 1991

11.5.1 Antecedent catchment storage and rainfall-runoff of sample storm

It is common practice to use different versions of an Antecedent Precipitation Index (API) to indicate the moisture status of a catchment (e.g. Mosley, 1979; Taylor and Pearce, 1982). Because of the huge range in time constants discernible from the hydrograph (discussed in Section 11.6.1), ranging from minutes to months, representing rates at which different parts (stores) of the catchment are drying out, defining the moisture status of the catchment as a whole is not practical. In this study, we consider several measures of catchment wetness, appropriate to different time scales. None of which are universally adequate, due to the complex nature of the catchment, but each can be used in a limited context. One measure of the catchment moisture status is simply the background streamflow, which varies over a period of several days, and probably represents the status of the upper soil stores and perched water table. Another measure, appropriate to the seasonal time-scale, is the estimated change in catchment storage, using a simple rainfall-runoff water balance model starting from a date just prior to the onset of the wet season (December 1, 1990). Figure 11.4 shows the cumulative rainfall-runoff for the 1990-91 wet season. Initially, runoff is only a small proportion of rainfall, but as the wet season progresses, there is a tendency for closer convergence to a line given by assuming a constant runoff coefficient of 0.88. There is significant replenishment of the permanent groundwater during the initial part of the season (approximately 1000 mm rainfall), and a gradual discharge of this water body as the dry season is approached (which presumably continues until the start of the next wet season, but was not observed during this study). The corresponding changes in catchment storage are shown in Figure 11.5 (calculated by assuming a constant rate of water loss due to evapotranspiration). This seasonal increase and decrease in catchment storage provides the background on which individual event hydrographs are superimposed. Such considerations must be taken into account if catchment responses (particularly to isotopic tracers) at various times during the season are to be understood.

Attention will now focus on the various hydrological responses which took place during the February 16, 1991 event (or Julian Day (JD) 47, 1991), under very wet antecedent conditions. Such conditions are typical of the summer wet season during a period of persistent storms.

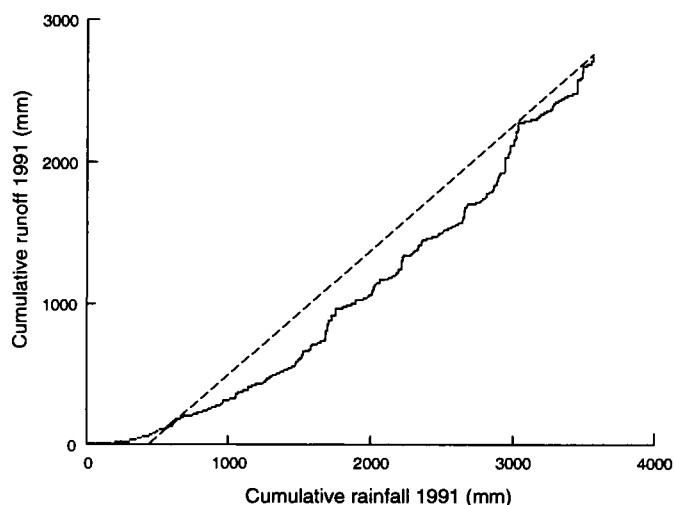


Figure 11.4. Cumulative rainfall - runoff for South Creek for the period December 1, 1990 to April 30, 1991.

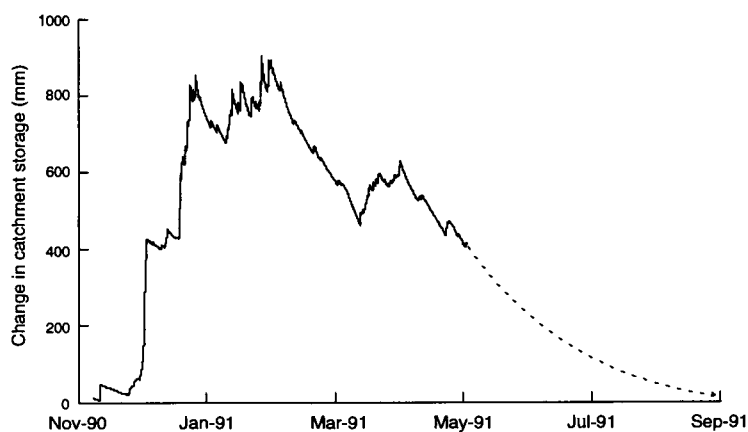


Figure 11.5. Changes in catchment storage in South Creek for the period December 1, 1990 to April 30, 1991.

Later when consideration is given to the well responses, it will be necessary to extend the period of consideration to include several days prior to and following the storm.

The sudden onset of the Australian wet season often coincides with the southward movement of a tropical cyclone permitting the intrusion of monsoon air into the continent, and the formation of the monsoon trough (Davidson et al., 1983). The ensuing heavy rainfalls also commonly ensure only a short period of catchment recharge in an average wet season before soil matric potentials ψ are close to 0, and water levels in wells tapping the deeper permanent water tables are at maximum elevations (Bonell and Gilmour, 1978; Bonell et al., 1981; Gilmour et al., 1980). Figure 11.5 similarly indicates a dramatic increase in catchment storage

following the occurrence of tropical cyclone Joy in late December 1990. By late January 1991 over 800 mm had been added to catchment storage, and from then onwards very wet antecedent catchment conditions exist until the beginning of March 1991, coinciding with the abrupt northwards retreat of the monsoon trough. The February 16 event described here is *representative of monsoon storms under maximal wet season conditions*. In conformity with the emphasis on the close linkage between synoptic climatology-rainfall intensity-hillslope hydrology to differentiate contrasting responses across the humid tropics (Bonell, 1993), brief reference is made to the synoptic situation of the event under consideration. The distribution of rain cells are well organized (Figure 11.6), as recorded by the Australian Bureau of Meteorology radar at Cairns at 11.19 h (Australian Eastern Standard Time) during the storm. At that time, a significant convective cell was over the catchments. This cell was part of the southward movement of the monsoon trough (otherwise known as the southern monsoon shearline, McAlpine et al., 1983) over the area, activated and connected to a tropical depression (Figure 11.7).

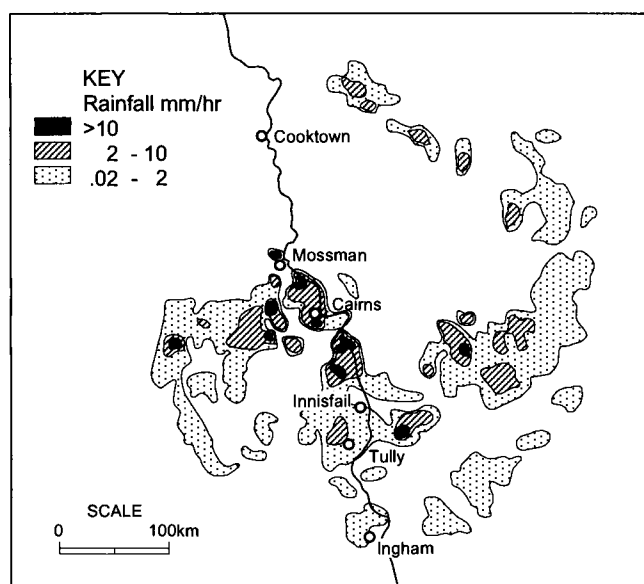


Figure 11.6. The distribution of rain cells at 11.19 hr Australian Eastern Standard Time, February 16, 1991 recorded by Cairns radar.

The hydrometric characteristics of the precipitation are summarized in Table 11.2. Short term rain intensities (minimum 6 min to maximum 60 min) approximate to the 1 year return period based on rainfall intensity-frequency-duration analysis (1971-83) presented by Bonell (1988). It is also necessary for later discussion to draw attention to the structure of the hyetograph (see, for example, Figure 11.8) for the February 16 storm). The storm consists of initially two smaller peak pulses which precede a third more intense pulse towards the end of the event. Particular emphasis will be placed on the impacts of these succession of pulses on changes in soil matric potential and stream isotopic response.

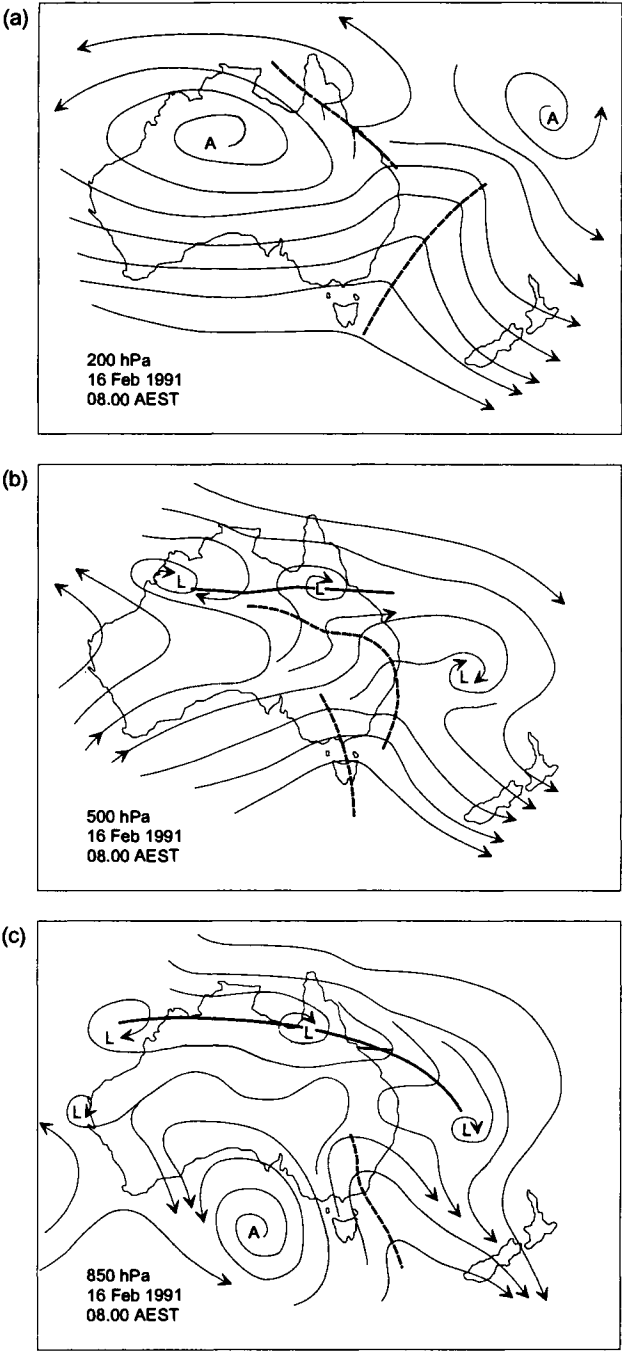


Figure 11.7. Meteorological streamline charts for the 850 hPa, 500 hPa and 250 hPa levels at 04.00 GMT (14.00 hr Australian Eastern Standard Time), February 16, 1991. The tropical depression embedded on the monsoon trough is shown extending up to the 500 hPa level.

Table 11.2. Rainfall characteristics of the February 16, 1991 storm.

Total (mm)	Maximum depths for specific durations (mm/h equivalent)					Duration (hrs)
	6 mins	10 mins	20 mins	30 mins	60 mins	
259.8	90	78	67.5	57	52.8	21.09

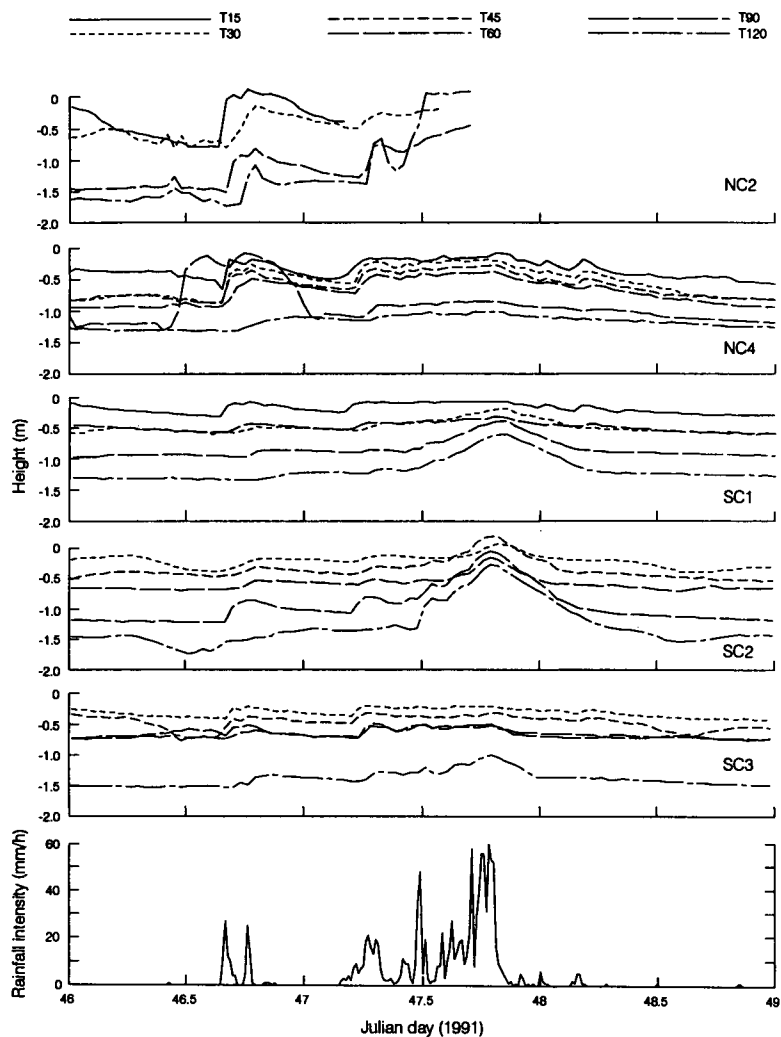


Figure 11.8. The temporal variability of rain and hydraulic potential (Φ) in tensiometers for (a) NC2, (b) NC4, (c) SC1, (d) SC2, and (e) SC3 on February 16-17, 1991. Hydraulic potential, $\Phi = \psi - z$ where ψ is the matric potential and z is the distance from the soil surface. Times at which the hydraulic potential trace is less than the depth of the respective tensiometer indicates when Φ has moved into the saturated phase.

11.5.2 *Matric and hydraulic potential changes on sample slope transects*

The persistence of near-saturated conditions in the period of high catchment storage is demonstrated in Figures 11.8 and 11.9 which includes changes in hydraulic potential (Φ) in tensiometers and piezometers for sites NC2, NC4, SC1, SC2 and SC3 during the February 16 storm. Unfortunately equipment failure caused selective gaps in record for various tensiometer depths and excludes consideration of all tensiometers and piezometers at sites NC1 and NC3. There are also gaps in record at NC2, but the broad pattern of Φ over time remains discernible. The above Figures also allow direct comparisons between the tensiometers and piezometers for corresponding depths.

For slopes exceeding about 4° , hydraulic potential (Φ , units of length) is conventionally expressed as $\Phi = \psi + z$, where ψ is the matric potential (units of length), and z is the elevation from a datum such as mean sea level or the lowest elevation in the drainage basin (Chapter 2; Bonell with Balek, 1993, p. 194). In this presentation however, interest is directed more towards identifying within-site zones of downward or upward fluxes to compare with isotopic changes in soil water. Consequently, the soil surface (which varies slightly between individual piezometers or tensiometers at the same site, due to the slope) was used as the reference level (leading to $\Phi = \psi - z$ where z is the depth from the surface to the mid-point of the tensiometer cup or base of piezometer). This is equivalent to the assumption that the local water table gradient is approximated by that of the soil surface, and is more meaningful for assessing when exfiltration might be occurring during the storm.

Several aspects related to the tensiometer and piezometer responses need to be considered. Movement from the negative to positive matric potential in the tensiometer records identifies the temporal development of saturation within the top 1.2 m of soil. Such changes can be detected when the magnitude of Φ is less than the depth, z , (with z taken as negative downwards from the surface) of each tensiometer. Where temporary water levels are established in piezometers, obviously a regime of positive matrix potentials has taken over at the base of the cavity. In common with the tensiometers, the corresponding Φ are always less than z (obeying $\Phi = \psi - z$) in these circumstances. More pertinent, the preferred direction (upward or downward) of soil water fluxes in the vertical plane can be determined from the hydraulic potential gradients. In addition, Hvorslev (1951) established that a time lag in the responsiveness of water levels in piezometers and wells occurs. This lag increases when water progresses from coarser- to finer-textured soils. In contrast, tensiometers do not experience this problem and are therefore expected to be more responsive.

We will present only a summary of the more pertinent characteristics observed within Figures 11.8 and 11.9. A persistent theme will be the impact of the aforementioned complex geology and pedogenesis on the temporal and spatial variability on ψ and Φ ; thus highlighting the need for such information and at the same time challenging the simplistic assumptions embodied in topographically-based, runoff generation models such as TOPOG (O'Loughlin, 1986) and TOPMODEL (Beven et al., 1995).

North Creek

Despite previously measured low K^* connected with the subsoil, a common feature is the rapid response and large increases in ψ and Φ throughout the profile. Saturation is quickly attained soon after the commencement of the storm, and some of the largest increases in Φ occur for

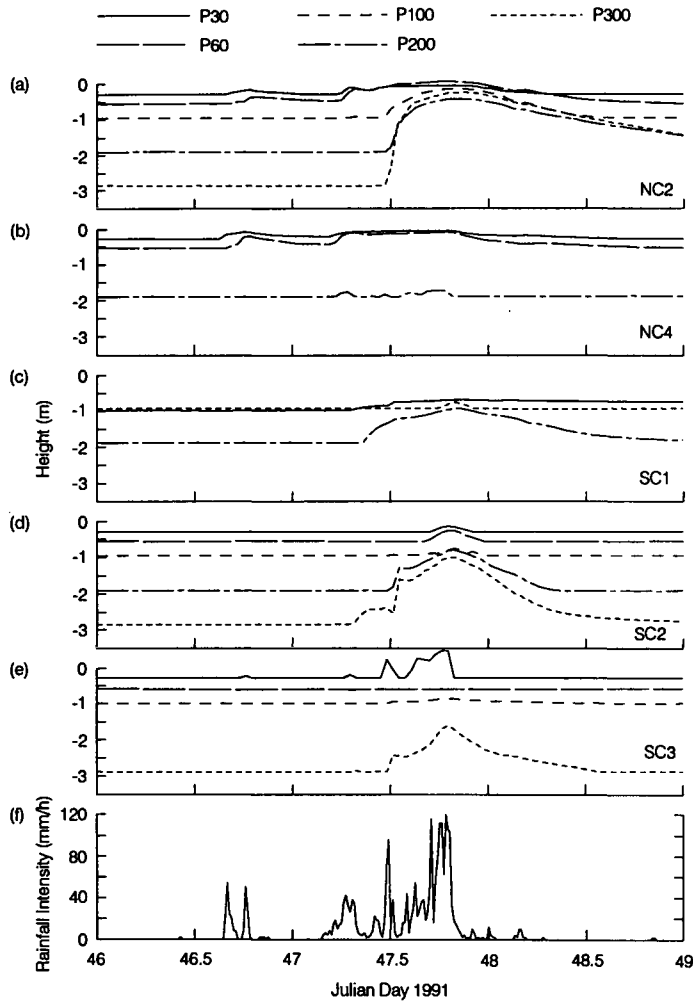


Figure 11.9. The temporal variability of rain and hydraulic potential in piezometers for (a) NC2, (b) NC4, (c) SC1, (d) SC2, and (e) SC3 on February 16-17, 1991.

example in the deeper piezometers such as P200 and P300 at NC2. In addition, there is also an interesting time lag with depth in the initial response of the respective tensiometers down the profile at NC4.

The piezometer and tensiometer Φ records also provide examples of downward and upward fluxes converging at different depths. For example, at NC2, there is convergence of downward flow from P100 with upward flux from P300 towards P200. Actual movement of water has to be lateral into, or out of, the cross-section at this point. Similarly, adjoining tensiometers also show upward flow between T120 and T60 during the second rain pulse. Even more pertinent, the Φ values of P30 and P60 show a reversal in gradient which exceeds that of the soil surface showing the occurrence of exfiltration, especially during the main pulse of the event.

In contrast, the records for NC4 in both the tensiometers and piezometers indicate prevailing downward fluxes. Nevertheless despite the more elevated position of this site, saturation exists throughout the profile down to 2.0 m depth during the most intense pulse of the storm. Such evidence provides an indication of extensive saturation over the catchment, and challenges the notion of a slow progression upslope of a saturated wedge commonly associated with humid temperate environments (Dunne, 1978; O'Loughlin, 1986). In addition, the tensiometer trace indicates the presence of a semi-confining layer between T60 and T90 at this site. This is supported by the piezometric data where P60 has almost the same hydraulic head as P30 in contrast to the weaker responses at greater depths.

When comparing the tensiometer and piezometer records for similar depths, there is not universal consistency in hydraulic gradient down the profile. At NC2 for example, downward flow between P60 and P100 contrasts with the upward flow suggested between T90 and T60 during the early part of the storm. On the other hand, there is more consistency in record between the respective Φ responses in T30/P30 and T60/P60.

The overall picture from the North Creek piezometers and tensiometers is of a highly heterogeneous system, with local confining layers (lenses) of less permeable soil interspersed with regions of high vertical conductivity. These physical characteristics lead on the one hand to regions of exfiltration (or '*return flow*', Kirkby, 1978) and lateral interflow, and on the other to rapid recharge of the groundwater body during prolonged and intense rainfall. *In the former case, there will inevitably be mixing of pre-event ("old") and event ("new") water within the saturation overland flow and thus, in turn, modifying the isotopic composition of this flow. We will need to consider this factor during the analysis of storm hydrographs.*

South Creek

The above tentative conclusions about the local behavior of the North Creek catchment are also corroborated by corresponding South Creek observations. The tensiometer record at SC1 and SC3 shows a progressively delayed response to the commencement of the storm with depth, on similar lines to that noted at NC4. With the exception of T30, all tensiometers at SC1 show transient saturation during the storm. Movement into the saturation phase is complete (except for T30) by the second intense pulse of rain, and peaks in ψ and Φ occur towards, or shortly after, the end of the final rain pulse. The contrast in responses between T30 and T60 is evidence for some hydraulic discontinuity between these two layers at SC1. Similarly, all tensiometers have $\psi > 0$ m by the third intense pulse at SC3. However, the shape of the Φ peaks are flat in contrast to SC1, suggesting a relatively high porosity and/or rapid lateral movement of water. The delayed response in the deepest tensiometer, T120, evident at SC3 and particularly SC2 when $\psi < 0$ m during the early part of the storm, is particularly interesting. Subsequently, both tensiometers show the greatest increase in Φ to the most intense pulse of rain, suggesting a direct hydraulic connection to the surface through macropores which operate only under saturated conditions.

These temporal changes in T120 at SC2 and SC3 are also reflected in the records from the deeper piezometers. For example, the trend of some of the deeper piezometers being the most responsive (as noted earlier for NC2) is continued in SC2 (P300, P200) and SC3 (P300). Consistent with this pattern are the weaker responses in the shallower cavities. For example, P30, P60 and P100 at SC2 do not respond until the third, more intense rain pulse. At SC3, P30 is much more responsive than in SC2, and in fact shows evidence of exfiltration (return flow,

c.f. NC2) following the second intense pulse of rain. On the other hand the weak response of P100 follows the description for SC2. These observations suggest the progressive filling up (from below) of a relatively well defined store, connected hydraulically to the surface by a network of macropores.

As with the North Creek sites, the prevailing downward flow is disrupted by various sections of the soil profile indicating upward flow at SC1 and SC2 (the lower sites). Apart from substantial differences in hydraulic potential between P300 and P200 at SC1, upward movement is also indicated at this site by the substantial Φ difference between T60 and T30 following the second intense rain pulse of the storm. The tensiometer records at SC2 also indicate hydraulic gradients favoring upward flow occurring between T90 and T60, and between T45 and T30 at the final peak of the storm, where the substantial hydraulic potentials indicate the occurrence again of return flow or exfiltration. On the other hand, a confining stratum is considered to exist between P300 and P200 at SC1 with P300 being connected directly to the water table. Consequently, the suggested upward flux may not be as significant to the runoff generation process as might appear. At higher levels in SC1, the weak response in P100 suggests that this piezometer is located in a more permeable layer, and is directly connected to the layer represented by P200 where a more significant response is evident.

For the most part, comparisons between tensiometers and piezometers are consistent in terms of prevailing hydraulic gradients and peak responses. Any differences in detail are probably due to local heterogeneity combined with small differences in position on the steeply sloping sites.

The well records

Only records for wells NCC, NCD, SCA and SCB were available for the February 16 storm. To gain better understanding of the characteristics of the saturated zone, Figure 11.10 shows the situation over the period February 14-24 (JD 45-55). The location of NCC and NCD on the more elevated parts of the North Creek transect meant that the pipe depths, although substantial, were insufficient to connect with the permanent water table for long periods. Both NCC and NCD were effectively dry before the February 16 storm. In contrast SCA and SCB were continuously connected with a permanent water table.

During the February 16 storm, NCC shows a sharp response of 1 meter head and an equally sharp recession when the cavity once again becomes dry. In contrast only a weak response occurs in NCD at the time of the storm, but subsequently there is a progressive increase in head until it peaks on February 22 (JD 53) following additional rainfall. Over the latter period there is negligible response in NCC. These records suggest very different flow pathways responsible for the responses of these two wells: the response of NCC is consistent with an area with highly conductive macropores which fill rapidly only under saturated conditions in response to the most intense rainfall, and also drain rapidly as soon as rainfall intensity decreases; while NCD, with an attenuated and delayed response, is indicative of a much less conductive region and a more indirect connection to the surface.

SCA and SCB are both responsive, but because of the location of the former (hydraulically well connected to the stream) it shows only a narrow range in water level fluctuation in the well hydrograph. In contrast, SCB responds rapidly to rainfall inputs and shows a much larger range in water level change (exceeding 0.5 m) which peaks towards the end of the February 16 storm (high frequency "noise" sometimes evident on the SCB trace appears to be an artifact of the

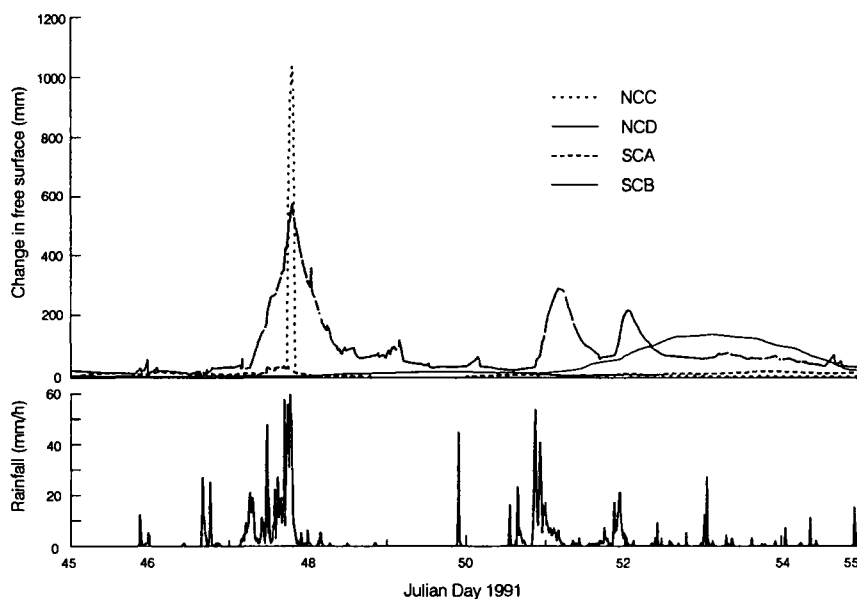


Figure 11.10. The change in depth to the water table with rain between February 14–25, 1991 for wells NCC, NCD, SCA and SCB.

electronic data recording system, but does not seem to have significantly affected the trace). The well hydrograph peaks also occur at the end of events on February 21 and 23 (JD 52 and 54). It is also significant that well hydrograph peak times of SCB and NCC are almost coincident during the February 16 event, suggesting that both are responding to macropore flow due to saturated surface conditions, but that drainage is somewhat slower in the case of SCB.

Some clues concerning the roles of possible groundwater contributions to the storm hydrograph are provided by crude water table profiles (Figure 11.11) for selected events from the South Creek wells. Two contrasting periods, a comparatively dry period from 17/1/90 to 17/3/90, and a relatively wet period from 8/11/89 to 8/12/89, were chosen, and the range of water table elevations in the wells were compared, although data logger problems preclude complete reconstruction of the profiles for the "wet" period. Nevertheless, there is the suggestion that the water table 'pivots' in the neighborhood of SCA in response to rapid and direct infiltration, and shows a progressive increase in the hydraulic gradient with increasing storm size and antecedent streamflow (another indicator of antecedent catchment wetness). Furthermore, the maximum hydraulic gradient occurs near or soon after the stream hydrograph peak. These observations, including the rapid relaxation of the water table profile, imply substantial contributions of groundwater into the adjacent tributary, although it is not clear from this reasoning whether such contributions are largely event water, or displaced pre-event water.

Despite the lack of direct comparability between K^* and K_{sat} , there is some support for the above reasoning by the higher saturated hydraulic conductivities, K_{sat} determined for wells SCB (K_{sat} logarithmic mean 14.2 mm/h, $n = 2$, depth range below the surface 2.7–3.1 m) and SCA1 (subsequently located post-1991 between SCA and SCB) which has a K_{sat} logarithmic mean

22.1 mm/h, ($n = 2$, depth range below the surface 1.97-2.19 m) using the auger hole pump test method (Ernst, 1950; described in detail by Maasland and Haskew, 1957; and van Beers, 1958). Groundwater inflow into SCA exceeded the pump capacity during testing, indicating an even higher K_{sat} , which provides a good connection between the well and the tributary creek. Further upslope the K_{sat} of SCC is an order of magnitude lower (K_{sat} logarithmic mean 4.4 mm/h, $n = 2$, depth range below the surface, 3.35-3.60 m) which may contribute to the greater water table recoveries during storms. These K_{sat} values are in the same range as those previously measured on an upper slope site (4.4-18.1 mm/h range for site 2 in Bonell and Gilmour, 1978; Bonell et al., 1981) despite the diverse geology and pedogenesis which exists in these catchments.

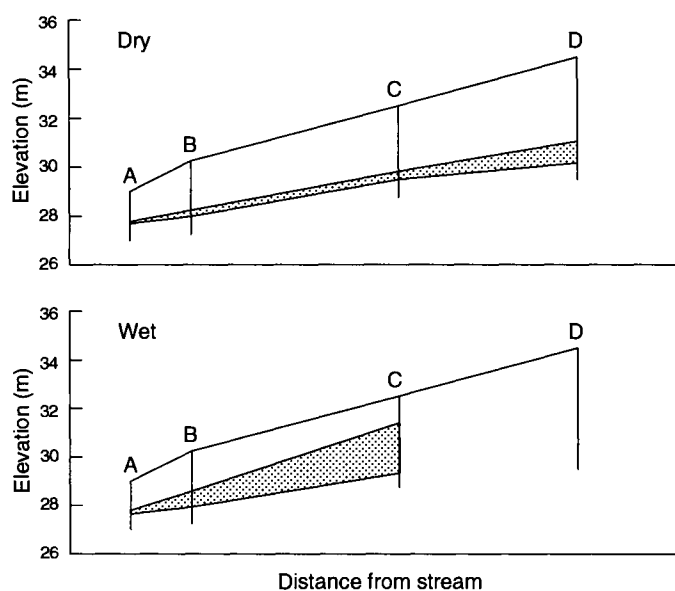


Figure 11.11. Changes in the position of the water table along the cross-section of the South Creek hillslope monitoring system during the periods 1/17/90-3/17/90 (a "dry" period) and 11/8/89-12/8/89 (a "wet" period). The upper line shows the soil surface, while the vertical lines indicate the depth of penetration of the wells. The shaded area indicates the range of water table movement in the respective period. Note that in the "wet" period, hydraulic gradients are more than doubled.

It is significant that the water table profiles (Figure 11.11), do not show evidence of groundwater ridging (Abdul and Gillham, 1989). There is, however, evidence of considerable and rapid influx of groundwater into the stream network. However, because there are gaps in the record due to well logger failure, this evidence cannot be regarded as conclusive. On the basis of previous studies (Perroux et al., 1982; Clothier and Wooding, 1983) and moisture release characteristics (volumetric moisture content, matric potential, $\theta(\psi)$) determined in the laboratory on soil cores collected from the Maimai catchments, McDonnell (1989) argued against the notion of a tension-saturated capillary fringe inducing the observed groundwater ridging close to the main stream. Similar moisture release characteristics were presented earlier for selected sites in South Creek (Bonell et al., 1982; 1983a) and the $\theta(\psi)$ changes support McDonnell's (1989) observations down to 0.75 m depth.

Summary

The hydrometric information presented in this section provides evidence of heterogeneous catchments with a very complex response to precipitation. Information derived from piezometer and tensiometer data suggest that during periods of intense rainfall, exfiltration and saturation overland flow occur from parts of the catchment due to low conductivity layers in the soil. Additionally, there is evidence of lateral interflow in the soil profile. Thus there is considerable potential for the transfer of rainwater over the surface towards organized drainage, via saturation overland flow, *dominated by contributions of event water mixed with some pre-event water discharged from return flow*. The implications of this conclusion in terms of the appropriate modeling strategy will be considered briefly here. In other parts of the catchment, rapid percolation to the water table occurs, causing marked variations in the permanent water table. Even at these locations, saturation overland flow continues to occur. Relaxation times in well hydrographs of a few minutes (NCC) to attenuated responses with delay times of several days (NCD) attest to the complex effects of the heterogeneity induced by the weathered, metamorphic geology. The higher hydraulic conductivities and rapid changes in groundwater gradients in the vicinity of the stream network during major events suggest significant groundwater contributions to event hydrographs.

11.5.3 Hydrograph analysis

It is pertinent to place the preceding observations within the framework of hydrograph response to events preceding and immediately following the sample storm of February 16 (Figure 11.12). Although event hydrographs will be discussed in detail as a necessary aid to interpreting the stable isotopic data below, some observations from the event hydrographs are appropriate at this point. As suggested previously, South Creek appears more responsive to smaller storms whereas North Creek releases greater volumes of delayed flows between events. As the magnitude and *duration* of storm increases, however, there is a tendency for the storm hydrograph characteristics to converge. The short time lags between rain and streamflow previously discussed (see also Bonell et al., 1979; 1981) are also evident in the data of Figure 11.12. A detailed comparison of the North and South Creek hydrographs over this period with the rainfall input indicates a number of features.

It is apparent that small rainfall inputs usually result in negligible streamflow response, even during very wet conditions a few hours after a major event. For example, following the large event of February 3 (JD 34), 7 mm of rain fell over 3 hours, commencing only 3 hours after the previous event, when stream flows were still 1-2 mm/h. However, there is no discernible response from South Creek, and only a barely discernible one from North Creek. Similarly, for a small event eleven days later on February 14 (JD 45) (with antecedent stream flows around 1 mm/h and two days after another major event), 18 mm of rain falling over 1 hour (with a peak 15 min intensity of nearly 40 mm/h) produced negligible responses in both streams. This tendency is continued for larger events with higher rainfall intensities, which lead to disproportionately higher peak streamflows. For example, 140 mm falling on the first three days of February (JD 32-34; peak 15 minute intensity 10 mm/h) succeeded in raising background flow levels substantially (from 0.3 mm/h to 1 mm/h), but peak flows did not exceed 3.2 mm/h and 2.2 mm/h for South Creek and North Creek, respectively. A further 79 mm falling over the first four hours of February 4 (JD 35; peak intensity 20 mm/h) generated peak flows an order of magnitude higher (33.1 mm/h and 22.6 mm/h for South Creek and North Creek, respectively).

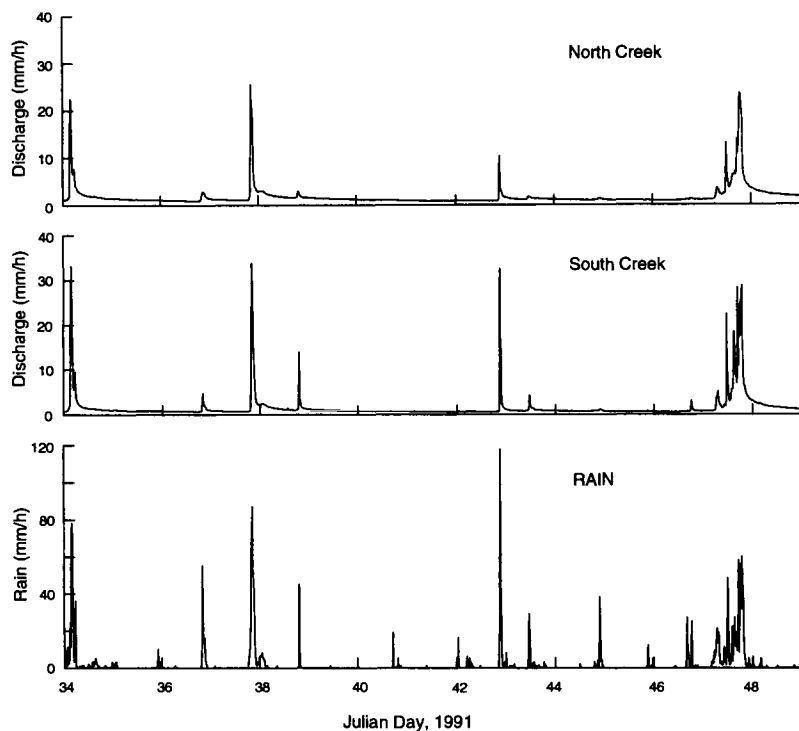


Figure 11.12. Rainfall and streamflow for North and South Creek for the period January 30-February 19, 1991 (Julian Day 30-50).

Catchment responses are not simply related to rainfall intensities per se. There are three separate events on February 6, 7 and 8 (JD 37, 38, 39, respectively), each event separated by almost exactly 24 hours, following a period of more than a week without substantial rainfall. Rainfall amounts (peak 15 min intensities) for each event are 35 mm (55 mm/h), 131 mm (87 mm/h) and 24 mm (45 mm/h) respectively, whereas peak streamflows for South Creek (North Creek) are 4.8 mm/h (2.8 mm/h), 33.7 mm/h (25.6 mm/h) and 13.9 mm/h (2.9 mm/h), respectively. For South Creek, the ratio of the peak flow rate to peak rainfall intensity for the third event (0.31) is slightly lower than for the second (0.39), as expected from the lower rainfall intensity. This is more than three times higher than for the first event (0.09). For the less responsive North Creek, however, the ratio for the third event (0.05) is less than that for either the second (0.29) or the first event (0.06).

These non-linearities in the rainfall-runoff relationships of the catchments indicate that the catchment response is not stationary, but depends on both the distribution and intensity of the rainfall. The analysis of this subsection is consistent with the previous ones, implying the existence of a surficial store which overflows into the stream network during prolonged periods of intense rainfall. With reduced rainfall intensity this store rapidly drains: either through lateral subsurface flow towards the drainage network, or vertically to the permanent water table through areas of high vertical conductivity.

The above data presents a consistent picture of South Creek as a very responsive catchment which responds rapidly to precipitation, and also recedes rapidly; North Creek responds somewhat more slowly, has lower peak flows, but releases greater volumes of delayed flows between events.

11.6 Stream Hydrograph Analysis and Isotopic Response

Of necessity, the isotopic data is of lower temporal resolution than much of the hydrometric data, and hence is more suitable for confirming or refuting conclusions from the latter on the relative role of various catchment processes on catchment behavior. In particular, whereas hydrometric data is well suited to defining the natural time constants of the system, analysis using isotopic and tracer data is much more suited for determining the relative contributions and proportions of different storages contributing to overall catchment response. The isotopic analysis is mainly restricted to the event of February 16 but some reference to the wet season of 1990-91 will be made to support conclusions from the soil water extractors and wells, and the hydrometric data which has been discussed in detail above.

11.6.1 Event analysis - general considerations

One of the suggestions of the previous section was that the rapid responses noted in the hillslope hydrometric system and the previously noted highly responsive storm hydrographs (Bonell et al., 1979, 1981) are due to saturation overland flow - the preferred pathway during monsoon storms. If one can assume for the moment that the volumes connected with return flow are minor compared with the direct contributions from precipitation over saturated surfaces, then saturation overland flow should be characterized almost exclusively by event or "new" water (due to the high rain intensities), as most precipitation runs directly off the saturated areas, bypassing pre-event water stored beneath the surface. It can be shown (see Chapter 2) that the fraction of event water in the hydrograph can be rigorously defined:

$$q_N(t)/q(t) = \frac{\delta(t) - \delta_o(t)}{\delta_N(t) - \delta_o(t)} \quad (11.1)$$

where q_N and q are the flux of event ("new") water and total streamflow, and δ , δ_N , and δ_o are the D/H delta-values in streamflow, event ("new") water and pre-event ("old") water, respectively. If the overland flow hypothesis for this catchment is correct, the rapid response part of the hydrograph obtained using classical hydrograph separation should be slightly less than the quantity of event water obtained using this equation, allowing for some contribution of event water arriving in the stream by slower pathways. All quantities in Equation 11.1 are implicitly functions of time, but usually hydrograph separation using isotopes is obtained by assuming a two point mixing model, where both the pre-event and event water (originating in pre-event precipitation and precipitation from the current event, respectively) have constant compositions. In the current circumstance, although it does appear reasonable to assume a constant pre-event water isotopic composition (background streamflow isotopic concentrations show almost no change over the whole season), it is clear that the assumption that event water has constant isotopic composition is violated, with the range of isotopic composition of rainfall

exceeding that of the streamflow. In fact, because rainfall deuterium concentrations were almost always significantly lower than stream concentrations (except towards the end of the event at about JD 47.8 where rainfall concentrations 'cross-over' the stream isotopic trace and become heavier), the error in using the amount-weighted mean rainfall D concentration for event water of -96‰ (cf. McDonnell et al., 1990) would be only moderate, although this procedure will overestimate the event water proportion when rainfall D concentrations are low (i.e. in the hydrograph peaks) and underestimate it otherwise. Use of a moving average of rainfall composition, calculated from the beginning of the storm (c.f. McDonnell et al., 1990) is inappropriate, given the *exceptionally rapid response times* evident here (unlike in the Glendhu catchments of New Zealand (Bonell et al., 1990)), and will give far too much weight to the early rainfall concentrations. Such a moving average is equivalent to assuming a well mixed store for event rainfall, with a size that is large compared to runoff, and hence mean residence times that are large compared to the length of the event. The latter approach is little more appropriate for this catchment than the assumption of a constant isotopic composition for event water (with similar implications for residence times), although the moving average does at least preserve causality!

A possibly more appropriate assumption for the current data is to assume that the event water isotopic composition corresponds to the composition of current rainfall, lagged by a constant amount. This is equivalent to replacing the actual distribution of residence times with a (constant) mean residence time for the event water component of the hydrograph, which is equal to the lag time. The latter would represent the observed lags between rainfall and the hydrograph peaks, and between the hydrograph peaks and the isotope extreme. Alternative models which allow a spread in residence times (e.g. using a Poisson or Gaussian distribution) require the determination of at least one further parameter, which is difficult to justify given the time resolution of this data. The assumption of a relatively short and constant residence time is supported by the observations of the small lags between peak intensities of rainfall and hydrograph peaks, ranging from 15 to 30 min for minor peaks in South Creek and North Creek hydrographs respectively, to only a few minutes for major peaks (Bonell, unpublished data); and from the evident effect of current rainfall on the streamflow isotopic signature. Further support can be obtained from an analysis of the rapid recession rates of the hydrographs, obtained by fitting an exponential to the peak, and calculating the time taken for the peak to decay to certain fraction of its maximum; for simplicity, the fraction chosen was $1/e$ (where $e = 2.71828\dots$), appropriate to an exponential decay (Note: $1/e$ is chosen because recessions of hydrographs are often observed to decay approximately exponentially). Thus the recession takes the form:

$$q = q_0 e^{-\alpha t} \quad (11.2)$$

where q_0 is the discharge at the beginning of the recession (at time zero), q is the discharge at time t and α^{-1} is the time constant (units of time). Time constants so obtained ranged from approximately 2 min for recession from a peak flow rate of 55 mm/h, to 12 min for a peak flow rate of 15 mm/h for South Creek. Corresponding time constants for North Creek ranged from 15 min (30 mm/h) to 40 min (8 mm/h).

Some difficulties still remain, because it is not clear what value to use for event water during hydrograph recession, when there is no rain, but stream isotopic concentrations still have not

returned to pre-event levels. The somewhat arbitrary choice of the amount-weighted mean rainfall concentration for the event was used, because previous calculations on other storms suggest that by the end of events, only 20-30% of the current rainfall has left the catchment. We argue that new water arrives at the stream network in this latter period via the shallow subsurface groundwater, where it is increasingly well mixed - the majority of the event water becomes mixed with the large groundwater store, whose isotopic concentration is barely altered by a single event, and therefore has a very long residence time. The proportion of event water in the hydrographs at any time, calculated according to Equation 11.1, will be shown, with corresponding hydrograph separations. Not surprisingly, it will be established that event water proportions closely follow the shape of the hydrograph, with proportions in South Creek somewhat higher than in North Creek during the storm, but converging during the recession. An interesting characteristic that will be demonstrated from the hydrograph separation is that the flux of pre-event water in the hydrograph rises at the beginning of each major hydrograph peak, before falling abruptly back to initial levels while the total hydrograph continues to rise. This will be shown to be consistent with the lags between isotopic response and hydrograph peaks already discussed, and with observations previously made in other geographical/climatic settings (e.g. New Zealand, Bonell et al., 1990; USA, Nolan and Hill, 1990). The difference between these results and those observed earlier is the much higher proportion of event water in the total hydrograph observed here.

The dependence of lag-times and recession time-constants on peak height, and the non-proportional response of both the hydrograph and the isotopic response to rainfall intensity rule out a simple interpretation of precipitation routing through the catchment, where the response time distribution is independent of catchment wetness and precipitation intensity, such as is assumed in applications of the unit hydrograph technique. For both catchments, the data suggest that the rapid response component of the hydrograph (typically characterized by time constants and lags of less than one hour) largely corresponds to the direct input of event water into the streamflow, rather than the displacement of pre-event water; but the time lag between peak flows and maximum isotopic response implies that this explanation alone is not completely adequate. *The above analysis suggests that pathways and residence times depend critically on rainfall intensity, with a "first-in-first-out" routing protocol being progressively replaced by a "last-in-first-out" protocol (Gamble et al., 1990a,b) as the intensity increases, and the slower low-intensity pathways are short-circuited.* The precise mechanisms and flow pathways by which this is achieved requires a more detailed and thorough examination of the catchment response through the linkage of the hillslope hydrometric information with the isotopic concentrations of the soil and groundwater, together with hydrograph analysis. This is demonstrated below for the event of February 16, 1991.

11.6.2 Soil and groundwater isotopic changes

Soil water

Examination of changes in the soil water and groundwater isotopic concentrations provide some clues to explain the subsequently described rainfall-runoff responses. Figure 11.13 shows the isotopic variations for the soil water lysimeters for selected dates in the 1991 study period. These include samples taken on February 6 and 13, 1991 reflecting antecedent conditions. Field logistical problems delayed sampling until March 5 following the storm of interest, but yet the

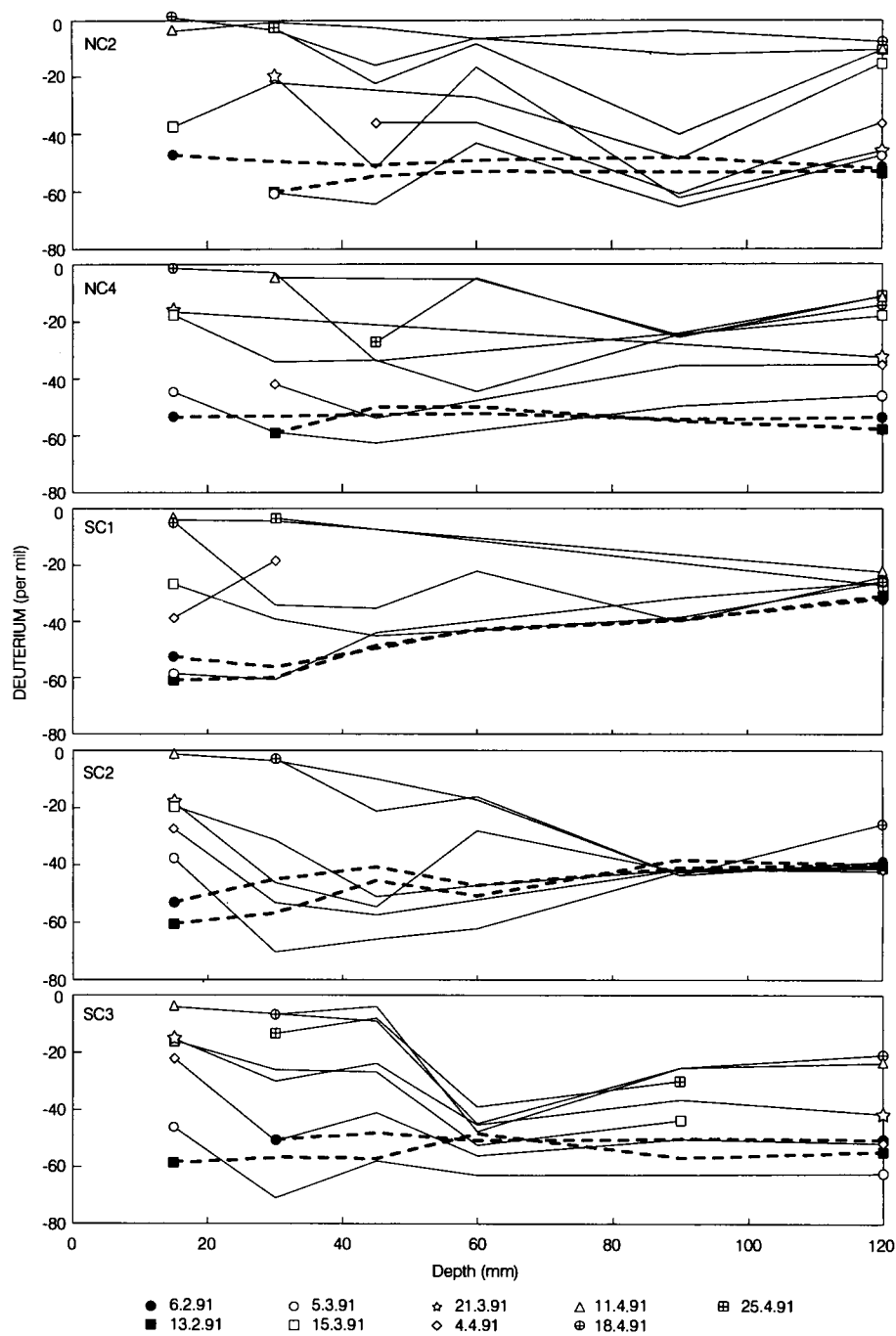


Figure 11.13. Isotopic data from soil lysimeters from North and South Creek catchments (see Figure 11.1b for lysimeter locations).

temporal variations in deuterium concentrations still provide indications of the ability of rain inputs to pass through the soil profile.

The relative lack of variation with depth of isotopic concentrations for a particular time at NC2, coupled with the marked variations between different times is fully consistent with the reported piezometer (and tensiometer) traces. Collectively, this indicates that the soil profile readily saturates during intense rainfall, and drains slowly. During saturation, existing water at all levels will be equilibrated with virtually the same body of water, and then subject to very similar concentrations of rainfall and residual water during the recession phase.

There is considerable temporal variability for the whole period at all depths at NC4. Changes between February 6 and 13 and March 5 between 0.30 to 0.60 m depth are erratic. The first period shows little change, the second shows considerable differences in isotopic signature. There is only the suggestion of an impeding layer at 0.9 m affecting the concentrations, and relatively uniform isotopic depth profiles are supportive of the free draining profile inferred from the hydrometric information. The isotope profiles could be produced either as a result of a receding water table, or (for the more variable ones) of the percolation from less intense rainfall.

Despite the 270 mm of rain input between February 6 and February 13, and an additional 635 mm between February 13 and March 5, 1991, SC1 shows virtually unchanged isotopic concentrations at 0.45 m depth and below. Apart from the one result from March 5 (possibly due to analytical or transcription error), results from the 0.6 m and 0.9 m depths show no significant variation throughout the relevant period, although some variation in isotopic concentration is evident at 1.2 m. These results are taken as strong evidence for a layer that impedes percolation at these depths; whereas hydraulic potentials from the tensiometer record seemed to indicate a prevailing downward flux at SC1, with an impeding layer between 0.30 m and 0.60 m depth. The lack of isotopic evidence in Figure 11.13 for the inferred upwards flux (between T30 and T60, and between P200 and P300 (Figures 11.8 and 11.9)) at SC1 is probably due to the long sampling period of the suction lysimeter, when the hydraulic gradient is mostly downward. Taken together, and bearing in mind variations in position of only a few meters between nests of piezometers and tensiometers, these results show the strong influence of local heterogeneity in this hydraulically active part of the catchment.

SC2 shows virtually unchanged isotopic concentrations at 0.90 m depth and below for the entire season, which also indicates an impeding layer at this site. In contrast, there is marked temporal variability observed in the isotopic concentrations within the surface soil, down to a depth of 0.60 m. Once again, the lack of evidence for exfiltration (which should result in isotope profiles with relatively small variation with increasing depth) at this site is probably due to the highly transient nature of this process. Nevertheless, significant lateral flow is strongly suggested.

At SC3 soil water isotopic concentrations show temporal variability throughout the record at all soil depths (indicating deeper percolation), and which also includes the period prior to and following the February 16 storm. There is a slight restriction in isotopic variation at 0.6 m corresponding to the minor irregularity of tensiometer T60. Downward percolation is thus favored at least to 1.20 m, which conforms with the preceding observations from the tensiometers and piezometers.

Well Data

It is usually assumed that the isotopic signature of streamflow during periods of low flows corresponds to that of the groundwater in the catchment. It is therefore of interest to investigate the range and variability of isotope concentrations in groundwater from various parts of the catchment, and the relationship to streamflow at the time. The isotopic response of the groundwater in the four South Creek wells SCA, SCB, SCC and SCD, and the North Creek well NCB during the period of interest is shown in Figure 11.14, with samples taken at approximately weekly intervals; some duplicate analyses are shown. Also shown for comparison in Figure 11.14 are the stream background concentrations for the same dates, with sampling intervals of 12 or 24 hours.

As may be expected from this sampling strategy, the range of deuterium concentrations in individual well samples is much less than either in the rainfall or the stream samples, but is still appreciable (up to about 10‰). Variations within particular wells are also less than in the group as a whole, with individual wells appearing to have distinctly different mean D concentrations and ranges. SCA shows a somewhat smaller range than NCB, but a similar mean (c. -25‰), about 5‰ higher than the means of either SCB or SCD, and 10‰ higher than SCC. SCC and NCB exhibit the greatest range (10-15‰), and hence the greatest influence of recent rainfall, with the other wells having similar ranges of about 5‰.

Well deuterium concentrations broadly follow low-flow background sample concentrations over this period. Comparison of NCB with North Creek background samples (NBG) indicates a consistently higher value for NCB, with an offset of approximately 5‰. Similarly, comparisons of SCA, SCB, SCC and SCD with the South Creek background samples (SBG) indicate average offsets of approximately 8‰, 2.5‰, -2‰ and 1‰, respectively. In addition, background samples over this period show a consistently higher concentration in NC, with an average difference of approximately 4‰ over the period.

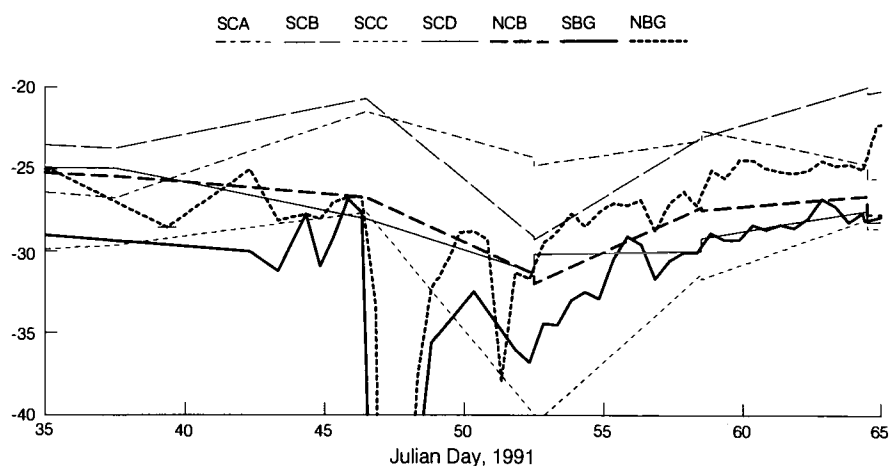


Figure 11.14. Isotopic data for well samples taken during the period February 4-March 6 (JD 35-65), 1991 for South Creek (SCA, SCB, SCC and SCD) and North Creek (NCB) (see Figure 11.3 for well locations). Also shown are background stream samples for North Creek (NBG) and South Creek (SBG) for the same period.

The consistent differences between isotope concentrations in different wells, and the differences between the wells and the associated stream (particularly for SCA, adjacent to the main channel of South Creek) *indicates a complex groundwater body, with different areas of the catchment contributing groundwater of significantly different concentrations to streamflow.* The origin of these distinct isotopic signatures for different wells and streams could be due to local variations in precipitation amounts and/or concentrations. More likely it is due to *different residence times of the groundwater in different parts of the catchment arising from the aforementioned complex geology of these catchments.* The resulting spatial heterogeneity of recharge via preferential flow, previously noted in the piezometer and tensiometer results, will cause the indicated variable residence times. The reduced variation of concentrations in the wells when compared to rainfall variations, coupled with the recovery of wells and streams to almost exactly their prior values (even after more than 950 mm of rain) both argue for a very large groundwater store with a long turnover time. The significant responses of NCB and SCB after rain, and subsequent slow recovery paralleling the streamflow indicates a gradual mixing of the newer water with the old water within the groundwater bodies.

Rainfall and streamflow

Figure 11.15 shows rainfall and streamflow, and the isotopic concentrations for North and South Creek for February 16, 1991 (JD 47). Marked differences between background isotopic concentrations in the antecedent streamflow and the subsequent rain increments persisted throughout the storm, making it a good example to assess runoff sources. Antecedent flow concentrations were similar in both streams (i.e., close to -30‰), and rain concentrations ranged from -78‰ down to -133 ‰ at the peak of the storm. The stream isotopic signatures also show considerable temporal variability, with a range of about -28‰ down to a low of -105‰ (NC) and -109‰ (SC). Allowing for the somewhat lower temporal resolution of the rainfall concentration series, *it is evident that the stream signatures are highly correlated with that for rainfall.* In a subsequent study, based on non-isotopic environmental tracers, Elsenbeer et al. (1994) demonstrated the same high association between rain and the stream signature for South Creek. In addition, all three deuterium time series are closely correlated with the rainfall intensity or stream discharge (as appropriate). For example, at about 1500 hr (during the first rain pulse) South Creek shows a small response in the hydrograph which is absent in the North Creek trace; the isotopic record for South Creek shows a similar response to the hydrograph, but no response is evident in the North Creek data. In contrast, North Creek shows a more responsive hydrograph in the second rain pulse, but South Creek continues to show higher discharges. There is also an isotopic response in North Creek, showing an initial lag in relation to the South Creek trace. Additionally, the higher peak flow and more rapid recession of South Creek compared to North Creek is reflected in the isotopic data, with timings of crossovers of the traces of the two catchments consistent in both sets of data. The preceding observations continue to be appropriate for both hydrograph and isotopic responses during the third, most intense, rain pulse.

The close correspondence between streamflow and deuterium concentration is made even more clear in Figure 11.16 by scaling the negative of the isotopic concentration onto the North Creek hydrographs. Within the limits of the somewhat lower resolution of the concentration data, the two sets of data give a mutually excellent fit! Rainfall concentration data plotted in the same way (Figure 11.16b) also appears to mimic the intensity data, though the low temporal resolution of the concentration data and the high variability of rainfall intensity result in a much less impressive fit. As rainfall sampling was effectively intensity based, higher resolution is

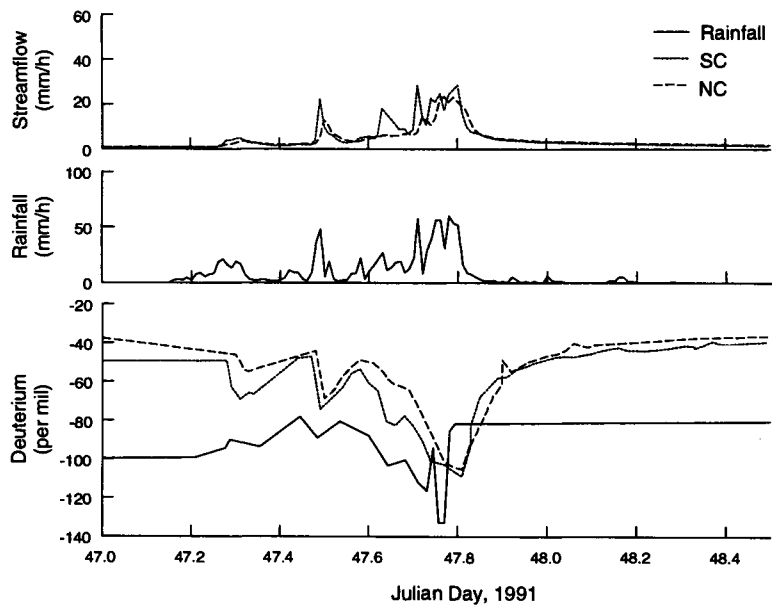


Figure 11.15. Data from the event of February 16, 1991, showing details of (a) rainfall intensity and stream discharge, and (b) deuterium concentrations in rainfall and stream flow, as a function of time.

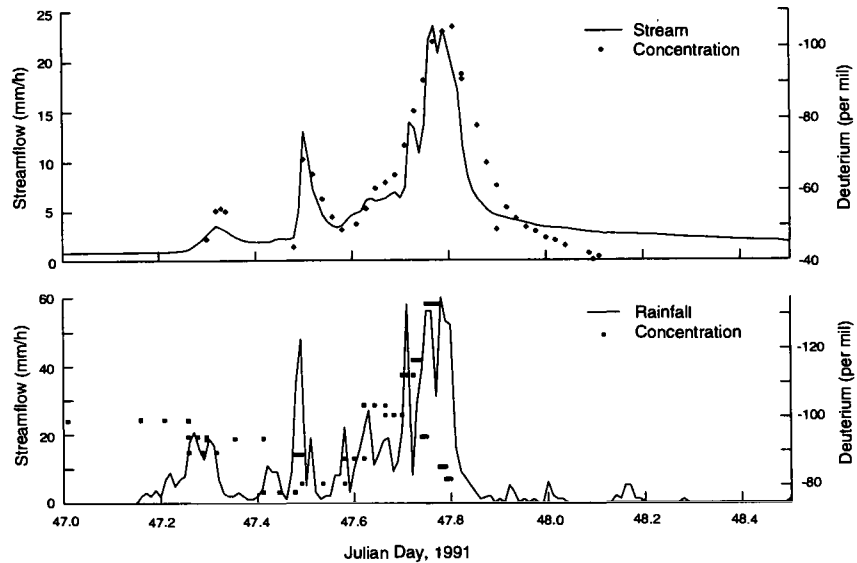


Figure 11.16. Data from the event of February 16, 1991. (a) North Creek streamflow and deuterium concentration, and (b) rainfall intensity and deuterium concentration, as a function of time. Note the reversal of the concentration axes.

obtained during the more intense rainfall. Even where the deuterium concentration is not simply related to intensity during the most intense rainfall (i.e. the third pulse near the end of the event); contrary to the suggestion at the beginning of this section, the concentrations coincidentally appear to anticipate the imminent drop in rainfall intensity, and so preserve the general shape of the intensity record.

Observations on lag times between rainfall peaks (roughly corresponding to isotopic lows in rainfall) and isotopic response indicated for other large storms earlier also apply here. Unfortunately, the temporal resolution for the two events are similar, so although isotopic extremes occur consistently later than their discharge counterparts, it is not possible to improve on the 10-30 min average lag time already reported. The time lag between the rain and stream isotopic signatures at the lowest (most negative) concentrations is about 75 min in both streams.

Coincident with a quite abrupt change in the rate of recession for South Creek, beginning about 2.5 hours after the end of the intense rain, South Creek isotopic concentrations also show an abrupt change in their rate of recovery, and tend almost linearly (with time) towards pre-storm values of about -30‰. It can however take several days (sometimes weeks) for the pre-storm values to be recovered, depending on the temporal occurrence and magnitude of rain events. The time-scale in this slower phase of recovery is similar to that of the deeper piezometers, such as SC1 and NC2, and appears to be due to lateral flow of event water through the upper parts of the groundwater system.

Hydrograph separation

The proportion of the total hydrograph which contains event water from current rainfall is of interest as an indicator of the relative importance of the contribution of overland flow to the total streamflow. Following the analysis of Section 11.6.1, and given the close correspondence between deuterium concentration and rainfall intensity and streamflow, the previously described procedure involving a constant residence time was used. Taking into account the lags between rainfall and streamflow discussed earlier, event water isotopic composition was chosen as that of the rainfall, but a lag of 75 minutes for both catchments was introduced for the purposes of hydrograph separation, in order to best match the rainfall and streamflow signals. For calculating the proportion of event water during the hydrograph recession after the cessation of rain, the amount-weighted mean concentration in rainfall was again used. The proportion of event water in the hydrograph at any time, calculated according to Equation 11.1 is shown in Figure 11.17, together with the hydrograph separation. Background concentrations for the deuterium concentration of old water were chosen according to the data of Figure 11.15.

Initial stream concentrations in South Creek appear to be still affected by a small event occurring late in the previous day (JD 46), by which North Creek was unaffected. New water proportions calculated in this way are clearly very sensitive to changes in streamflow, and exceed 50% in South Creek following the initial pulse of rain to the end of the event, except for a brief period where some low intensity rainfall just prior to the second major rainfall peak appears to have allowed some pre-event water to be displaced, temporarily reducing the event water contribution to less than 30%. This feature does not seem to have occurred in North Creek. The major rainfall and streamflow peaks are associated with very high event water contributions, especially for South Creek, where event water proportions appear to exceed 90% for short periods. Significantly, in a subsequent study which applied EMMA to South Creek

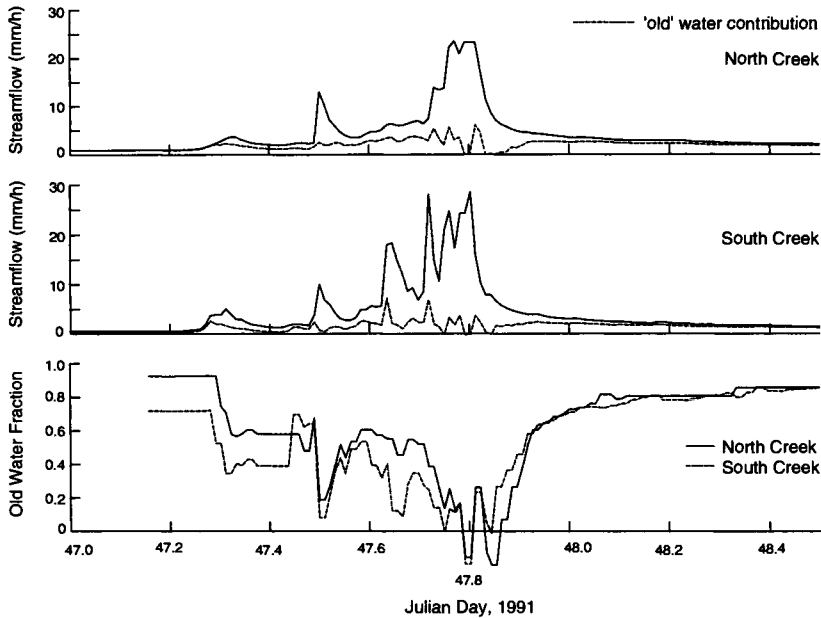


Figure 11.17. (a) Hydrograph separations (North and South Creek); also showing (b) the variation with time of the proportion of pre-event water for the event of February 16. Background (or pre-event) water deuterium concentrations were -28‰ , and -30‰ (NC and SC, respectively), and event water composition was taken as that of rainfall 75 min earlier. Also shown for comparison are the streamflow hydrographs.

data (based on non-isotopes), Elsenbeer et al. (1995) remarked for one event that "... the contribution of saturation overland flow reaches almost 80% near peak flow at which time the groundwater contribution nearly vanishes."

Examination of the event water proportion associated with the major streamflow peak reveals a major problem with this analysis. The calculated proportion of event water for both North and South Creek exceeds 100%, a physically meaningless result. It is natural to ask whether this is an artifact of the particular assumptions made in the analysis; in particular, with the identification of the event water isotopic composition with the lagged rainfall composition. A detailed analysis shows that the difficulty appears because of the high resolution, and hence variability, in rainfall isotopic composition during this period of intense rainfall. Isotopic composition of both streams approaches that of the rainfall, but in reality is somewhat smoothed by the distribution of travel times within the catchment (particularly in North Creek). As a result, when the rainfall concentration briefly rises from -117‰ to -94‰ (above that of the stream minimum), and then falls abruptly to -133‰ over a period of 15 minutes, the effect of this on the streamflow is attenuated, and the simple application of Equation 11.1 leads to the physically impossible result reported. The problem is repeated shortly afterwards near the end of the storm as rainfall concentrations rise rapidly, and stream concentrations briefly fail to keep pace. These difficulties result in some confusion for hydrograph separation in the major peak, at about JD 47.8 (Figure 11.17), resulting in zero or near-zero pre-event water contributions on three occasions.

Use of existing alternative ways of calculating event water concentrations would not improve matters, however. For instance, the amount-weighted mean isotopic concentration of rainfall for the event is -96‰, a value which is significantly heavier (less negative) than the minimum isotopic concentrations in both streams. Use of this value in Equation 11.1 would not only also lead to the same unphysical results (but over a much more protracted period), but would also seriously underestimate the proportion of event water in the hydrograph during the early part of the event. The use of a cumulative amount-weighted average is not much better, and does not take account of the rapid response of the streamflow to recent rainfall. *Our assumption of a simple delta-function distribution with constant lag over corrects for the sins of the alternative techniques.* What is actually required is a more realistic residence time distribution with a finite "width" as was discussed at the end of Section 11.6.1. The use of the delta-function distribution is reasonable here because of the short residence times; in other catchments with a wider spread of residence times in the rapid response component (and hence a more attenuated isotopic response to rainfall) a more sophisticated distribution would be imperative (but requires higher quality data or further information than is available here). Other writers have observed similar problems with the 2-component mass balance equation and have put forward the need for a third component to take into account soil water contributions (e.g. DeWalle et al., 1988; Ogunkoya and Jenkins, 1993). In fact, it was Turner and Macpherson (1990) who particularly emphasized the 'collapse' in the use of the 2-component model when the temporal deuterium concentration of rain 'crossed over' the stream signature and became heavier (less negative). Not surprisingly, they found that the use of the traditional amount-weighted average estimate for rain (which mathematically avoids the aforementioned difficulties but is less physically realistic) was more 'reliable' and showed the closest agreement with an alternative model (Kalman filter method). It is important to recognize however that consideration of any of the preceding measures need to be supported by *independent observations of the hillslope processes* to justify the inclusion of additional components, *via* soil water. Otherwise they prove to be only mathematical corrections and lead to misleading conclusions during hydrochemical hydrograph separation.

Of interest also is the previously mentioned characteristic of an initial rise in pre-event water at the start of each hydrograph pulse: at JD 47.3, 47.45, 47.5, 47.63 (SC) and 47.72. These peaks, though clearly related to the same phenomenon observed in other storms (Bonell, unpublished data), are significantly less pronounced in this event, and peak pre-event water contributions are lower despite the significantly greater overall fluxes for the February 16 event, while mean pre-event water fluxes are almost identical in the two events for the respective catchments. After previously assessing the water table profiles, any notion of 'groundwater-ridging' or of the occurrence of the maximal increase in the water table gradient early into the event would seem to be unlikely explanations for the 'displacement' of this old water. The alternative mechanism put forward by Nolan and Hill (1990), whereby sudden inputs of new water upstream sets up a flood wave composed of old channel water which reaches locations downstream ahead of the translation of the subsequent event water, might be at least a credible part-explanation. Such a mechanism where wave celerity is larger than the water velocity is well known in channel hydraulics.

Figure 11.18 shows cumulative rainfall and streamflows for both catchments against time from the beginning of the event. Also shown are the calculated contributions to total streamflow from the current rainfall. It is clear that South Creek, with the higher peak flows, discharges significantly greater quantities of event water during the storm, and that the greater quantities

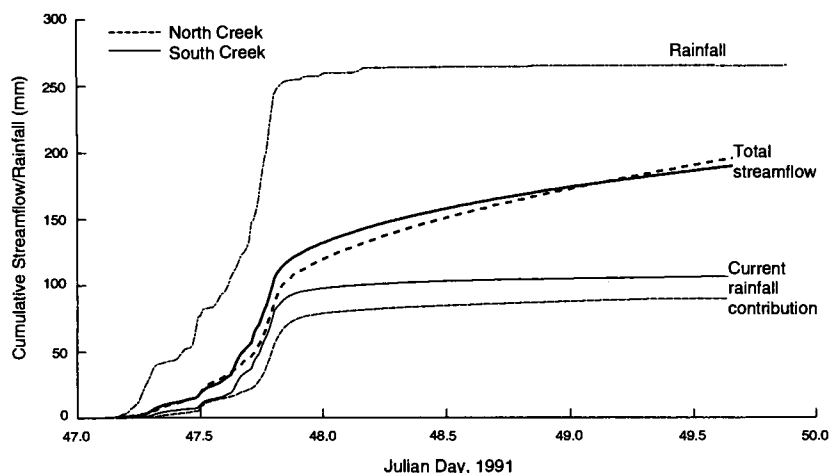


Figure 11.18. Cumulative rainfall and streamflow for North Creek and South Creek from the beginning of the February 16 event. The lower curves show the rainfall contributions to the total flows.

of delayed flow in North Creek are largely made up of older water. Maximum cumulative proportions of event water in both hydrographs occur shortly after the cessation of rain, and amount to nearly 70% in North Creek, and 80% in South Creek. Total discharge of event water up to two days after the event is 34% and 40% for North Creek and South Creek, respectively.

11.7 How High Rainfall Catchments Work

11.7.1 The Babinda model

The sensitivity of the temporal variations in the isotopic concentrations of both streams to rainfall intensity show that above a critical application rate, saturation overland flow is likely to prevail from wet areas over large parts of each catchment. The close correlation between rain and stream signatures at the peak of this storm is particularly impressive, and to our knowledge has not been reported before from either a forested or recently converted forested environment. At such times, the hydrographs must be dominated by 'new' water and isotopically confirm earlier reports of the ability of this environment to generate saturation overland flow (Bonell and Gilmour, 1978; Bonell et al., 1981).

The observation of slower recovery to pre-background isotopic concentrations in comparison to the steeper hydrograph recession at the termination of the storm is highly significant. There seems to be mixing of 'new' water draining off the catchment with other sources to cause the protracted isotopic recession in both streams. Possible clues to explain this pattern emerge from consideration of both isotopic and hydrometric evidence from the South Creek transect. *It is clear that vertical percolation to the permanent water table is much more significant during storms than previously credited* (because of the lack of continuous data, Bonell and Gilmour, 1978; Bonell et al., 1981). The basis for previously discounting the possibilities of such recharge were the measured (Talsma and Hallam, 1980) low subsoil K^* across both catchments

(Bonell et al., 1987; Bonell, 1991) and some comparability with the limited K_{sat} values then available from previous pumping tests (Bonell et al., 1981). Consequently, there would seem to be credibility in the earlier suggestion of Topalidis (1983) that measurements made using the Constant Head Well Permeameter (CHWP) of Talsma and Hallam (1980) were providing estimates principally of the matrix K^* , especially taking into account the effects of smearing within the auger holes (Talsma, 1987).

During the February 16 storm, the sensitivity of temporal changes in hydraulic potential, as recorded by the tensiometer and piezometers, provide clear evidence that preferential flow paths are propagating water quickly through the soil profiles. These observations reinforce the currently expressed notion that the surface hydrology is very much more connected to the permanent water table than was previously recognized (Bonell and Gilmour, 1978). Such characteristics could only be detected with the use of the improved technology available for the present study. In addition, previous evidence showed negligible piezometer response below 1 m depth (see Gilmour et al., 1980; former upper slope site 2) which *further demonstrates the heterogeneity in soil hydraulic properties arising from the complex geology of these catchments*. It is also clear that such preferential flow occurs both in the unsaturated phase (by-pass flow of Smettem and Trudgill, 1983; short-circuiting of Bouma and Dekker, 1978) and especially the saturated phase. Such mechanisms cause the deeper piezometers to be as responsive as those in the more shallow layers at most sites. Furthermore whilst the tensiometers at NC4 and SC3 indicate a progressive time lag in response to rain with depth, such lags are still very short. McDonnell (1989) also noted the significance of preferential flow in the Maimai catchments of New Zealand in producing larger changes in the matric potential with depth. McDonnell (1989) attributed such trends due to the build-up of preferential flow water at the base of the soil profile overlying the more permeable Old Man Gravels. Thus the temporal occurrence of positive matric potentials generally only occurred in his deeper tensiometers *and then only in circumstances of higher rain intensities which were mostly simulated using artificial sprinklers* (McDonnell, 1989). The infrequent occurrence of such rainfalls was one of the reasons attributed by McDonnell (1989) to the domination of the storm hydrographs in his study by old water. By contrast, in the Babinda environment positive matric potentials are more universal throughout the top 1.20 m depth of soil (tensiometers) and also at 2 and 3 m based on the piezometers. There is, however, evidence for higher hydraulic potentials in the deeper piezometers possibly caused by the accumulation of preferential flow. Spatial as well as temporal heterogeneity in soil hydraulic properties also causes reversals in hydraulic potential gradients, thus encouraging upward fluxes of soil water in some of the profiles. *Exfiltration was also noted at NC2, and possibly SC2, indicating the potential for subsoil contributions to saturation overland flow, which thus could modify the isotopic signature of this flow vector*. In addition, records presented for smaller events at NC2 showed only saturation at 0.15 m depth (as shown by Figure 11.8 preceding the February 16 storm) so that saturation overland flow and subsurface stormflow can occur independent of the hydraulic status of the deeper subsoil. Such observations are in agreement with preceding work (Bonell and Gilmour, 1978; Gilmour et al., 1980). Similar flow characteristics were reported from earlier experiments undertaken elsewhere in South Creek using water artificially tagged with tritium (Bonell et al., 1983a, 1984).

Reconciling the changes in hydraulic potential through time with the more limited isotopic information is less clear. It has to be recognized that the hydrometric data base is much more sophisticated in describing temporal variability of soil water movement than the corresponding

isotope data. Furthermore one cannot assume that the collected soil water samples are more representative of matrix rather than preferential flow. DeWalle et al. (1988) presented evidence that there was no statistical significant difference in isotopic concentrations collected from soil water lysimeters (assumed to favor matrix water) and pan lysimeters (assume to favor macropore water). Leaney et al. (1993) noted that suction lysimetry preferentially removes soil water from the larger capillaries.

Isotopic information from the suction lysimeters can generally be taken as confirming the more detailed information available from the tensiometer and piezometer network, and appears to have particular sensitivity to variations in conductivity, etc. Despite the lack of temporal resolution, the isotope data also suggest the existence of lateral flow in some locations, in contrast to evidence of vertical flow at other locations. *On the other hand, providing acceptable interpretations of this data would have been very difficult without the supporting hydrometric information.*

The soil water lysimeters nevertheless further reinforce evidence for the local heterogeneity in recharge, especially along the South Creek transect. SC1 shows isotopic concentration profiles which change little over time at 0.45 m depth and below. In these circumstances, shallow subsurface flow and saturation overland flow can quickly develop in storms. At SC2 isotopic concentrations change between events down to 0.60 m depth, but are invariant below that. Subsurface stormflow is more favored above 0.60 m, with the possibility of saturation overland flow during the most intense part of storms. In contrast, SC3 shows isotopic concentrations changing down to 1.20 m depth after events indicating a recharge area to the deeper permanent water table.

The preceding observations of spatial variability in recharge of the permanent saturated zone and the ability of preferential flow paths to connect this zone with the surface hydrology is supported by Figures 11.10, 11.11 and 11.13. The well hydrographs and corresponding isotopic concentration changes were more responsive than expected. Previous studies (Bonell and Gilmour, 1978; Gilmour et al., 1980) only presented weekly observations. The fact that the permanent water table was located at considerable depth below the surface previously led to the reasoning that it had no immediate role in the runoff generation process in hillslopes (Bonell et al., 1981). Whilst the latter may still be correct for the bulk of the hillslopes, the continuous records not previously available now provide contrary evidence at least when considering the point of hydraulic connection between groundwater and stream hydrograph. The wells are highly responsive, and plots of changes in the water table profile with time through several other storms indicate a progressive steepening of the water table gradient, until about the time of the stream hydrograph peak or soon afterwards. Consequently, contributions to the stream network from the adjoining permanent water table should progressively increase towards the end of the storm. However, the hydrograph separation analysis indicates that, although pre-event water fluxes do rise during a storm, almost all the rapid flow component of the hydrograph is due to event water.

The exception noted at the beginning of each pulse of streamflow cannot be due to the above mechanism of steepening hydraulic gradients either, because of the observed short duration of the pre-event water contribution, and lack of correlation with the decay of the hydraulic gradient. As an explanation for these pre-event water peaks (which are relatively much more significant in the early part of the storm) we hypothesize the mechanism of displacement of

pre-event water already existing within the main stream channel early on in the storm (as a flood wave, Nolan and Hill, 1990) supplemented by the entrainment of pre-existing water displaced from the surficial soil layers by the beginning of the overland flow component. During periods of less intense rainfall when overland flow ceases, the relatively slow exfiltration of subsurface water results in fresh quantities of pre-event water which are subsequently flushed out at the front of the next pulse of overland flow.

Anderson and Burt (1982) have described a conceptual model of an upper layer of the saturated zone mixing with preferential inputs through the unsaturated zone. We envisage a similar mechanism in these catchments with the mixing layer linked hydraulically to the stream network. This mechanism is responsible for the significant but diminishing component of event water in the recession phase of the hydrograph, and is also seen in the isotopic response of the wells (Figure 11.14). The absence of significant quantities of pre-event water in the early stages of the recession, but after overland flow is assumed to have ceased (cf. Figures 11.8, 11.15 and 11.17), suggests that much of the water with a subsurface flow pathway which must now dominate the hydrograph is also event water; presumably water which is held in the highly transmissive upper regions of the soil store, adjacent to the stream network. The implication is that both the primary and secondary stores (storage due to overland flow and the upper, normally unsaturated soil store, respectively) responsible for the stream response largely consist of event water, and that the tertiary, deep groundwater, store responds only slowly because of a relatively low transmissivity. Where the secondary and tertiary stores interact directly, at the interface with the stream network, the greater conductivity of the upper layers, filled mainly with event water, in combination with the intensity of the rainfall, overwhelm the tendency to hydraulic displacement of pre-event water seen elsewhere.

11.7.2 The secondary store issue

The role of the unsaturated zone (the "secondary store" above) is not altogether clear in terms of being capable of supplying significant quantities of lateral flow to the storm hydrograph. Tensiometers show that positive matric potentials quickly develop in the shallow soil layers following a storm onset. In contrast to McDonnell (1989) some of the deeper tensiometers are the slowest to move into the positive matric potential phase. Thus there is need at these locations for time for preferential flow to pass through the subsoil to build up pressure at depth, in contrast to the much shallower Maimai soils. The subsequent convergence of flow, indicated from the equipotentials, favors lateral flow. Previous runoff trough evidence (Bonell and Gilmour, 1978; Bonell et al., 1981; Gilmour et al., 1980) however showed only negligible contributions from the 0.25 m-0.50 m, and 0.50 m-1.00 m depths, respectively. Therefore the volumes of fluxes involved maybe quite small. The low field saturated hydraulic conductivities determined using the CHWP (Bonell et al., 1987) supported these previous findings. Such notions however, conflict with the present evidence for preferential flow (certainly in the vertical component) being more significant in these horizons than previously credited, and attest to the complex heterogeneity present in these catchments.

The fact that both streams (and the wells) do eventually return almost to pre-storm background isotopic concentrations confirms the suggestion of a large, deeper groundwater body which sustains the dry weather flow, and which is itself sustained by the residual event water from individual events: 60-70% for South Creek, and 70-80% for North Creek, for the event reported

here and others analyzed (Bonell and Barnes, unpublished data). (Incidentally, this difference in retention rates, and hence residence times, for the deep groundwater stores is the most likely cause of the consistently higher background isotope concentrations in North Creek during 1991, see Figure 11.15). Previous water balance work taken over a four-year period (mean annual rainfall 3900 mm) by Gilmour (1975) indicated an annual average of 1275 mm of delayed flow out of a total of 2375 mm streamflow in South Creek. Such large volumes substantiate the argument for a large aquifer within the catchments. At the end of the 1991 wet season, background streamflow samples are within 5‰ of their initial values, even after more than 3000 mm precipitation; *and show no significant change at all as a result of the February 16 event of 260 mm. These observations suggest residual active storages of at least several meters depth of water.*

11.7.3 New water dominance at Babinda vs old water dominance at Maimai

The conclusions of the Babinda study are in stark contrast to the Maimai study and other humid temperate environments (Section 11.2). Previously, hydrograph separations based on isotopes and other tracers have tended to conflict with those based on the more traditional (if somewhat arbitrary) hydrometric techniques, indicating considerably greater proportions of pre-event water in the hydrograph. Our conclusions, indicating very high proportions of event water, are much more in line with traditional expectations. The principal reason for this is the domination of the hydrographs of major events by the saturation overland flow mechanism, resulting in almost complete bypassing of existing catchment storage during intense rain. Additional hydrometric evidence from the hillslopes also supports this hypothesis that saturation overland flow emanating from 'wet' areas of the catchments is the principal contributor to the stream hydrograph at times of high rainfall intensities. Such wet areas are considered to incorporate a large proportion of each catchment on the basis of TOPOG simulations (O'Loughlin, 1986) and hydrometric evidence presented here. Even NC4, located in a 'drier' part of North Creek, showed positive matric potentials throughout the upper soil profile at the peak of the storm. Ultimately, **the chief factor which causes the behavior of these catchments to differ from that of previously studied catchments is the high rainfall intensities associated with monsoon trough disturbances**, a point previously emphasized from earlier hydrometric work (Bonell and Gilmour, 1978; Bonell et al., 1981; Howard, 1993). *Such conclusions also reinforce earlier arguments for greater attention being given to the linkages between synoptic climatology-rainfall intensity-hillslope hydrology to differentiate varying runoff responses across the humid tropics* (Bonell et al., 1991; Bonell, 1993). In contrast the weak rain intensities coupled with the large antecedent soil moisture and dominant subsurface pathways, such as pipe flow, encourage hydrographs mostly dominated by old water in the Maimai catchments, as outlined in the conceptual model of McDonnell (1990). It is poignant however that despite the strong criticism of the previous arguments of Mosley's (1979, 1982) earlier conclusions by Pearce et al. (1986) and Sklash et al. (1986), the Babinda study lends strong support to the former writers interpretations. The principal difference being that Mosley centered his arguments on a rare, extreme event (in terms of rain intensity) coupled with unrepresentative application rates (for the Maimai environment) using artificial rain simulators more suited to the humid tropics of north-east Queensland. The lesson is to analyze a comprehensive range of storm types before being certain of drawing together comprehensive conclusions.

Displacement flow, due to enhanced hydraulic gradients caused by rapid infiltration to groundwater, was also observed; but the combination of soil heterogeneity, and declining hydraulic conductivities with depth, results in only small proportions of pre-event water being displaced. The results do not support the groundwater ridging process as a mechanism for inducing rapid influxes of groundwater into the stream network; unlike in the Maimai catchments (McDonnell, 1989, 1990) - though the latter writer argued against the capillary-fringe mechanism of Sklash and Farvolden (1979).

For the Babinda catchments, paradoxically, the groundwater storage plays as much a part during the relatively dry "shoulder" period of the annual cycle, as in the intense monsoonal events when catchment storage is far higher. One explanation may be that, when overland flow occurs over large parts of the catchment, shallow water tables adjacent to the stream network will be virtually identical in terms of their mechanisms of development (and possibly isotopic signature), irrespective of the overall status of the deep groundwater system. Hence similar perched water table behavior may be expected at any time of the year, provided rainfall intensities and durations exceed a certain threshold.

Despite the preceding uncertainties, it is clear that the simplistic assumption of two separate well-mixed reservoirs supplying contributions to the storm hydrograph, as assumed in the traditional two-component mass balance model, are not met in this example. There is considerable temporal variability in the rain isotopic concentration, although McDonnell et al. (1990) did discuss a simple model to attempt to address this problem. This approach, however, does not solve the problem encountered near the peak of the February 16 event. The assumption of a constant isotopic signature within the deeper groundwater body is more nearly met due to the very large apparent size of the active residual groundwater store in this catchment.

The above discussion is probably best understood in terms of the idealized non-linear conceptual model of the upper and lower soil stores, shown in Figure 11.19, which is similar to storage elements introduced by Boughton (1984) to represent the behavior of the groundwater store. At low rainfall intensities, precipitation is routed to streamflow via the groundwater/soil water system, which can be characterized as a predominantly "first-in-first-out" system. However, at high precipitation rates, the flow capacity of these pathways is exceeded, and alternative pathways involving rapid flow are invoked which effectively short-circuit the former pathways, provided that the threshold storage represented by H_1 is also full, resulting in a "last-in-first-out" type of behavior. The invocation of these rapid flow pathways therefore depends on both the rainfall intensity and the amount of rainfall, and explains the very rapid transition between the two types of behavior evident from the isotope data.

Simulation of the data using the above conceptual model requires a value for the threshold H_1 of approximately 12 mm for both catchments. Allowing for the differences of scale in measurement, this is of the same order of magnitude as, and compatible with, measured values of the available water storage capacity (AWSC) from soil cores for South Creek (AWSC for the top 0.2 m ranged from 19-52 mm) (Bonell et al., 1982, 1983a). Further, Bonell et al. (1981) using a lag regression model, had earlier inferred the existence of a limited, upper water storage capacity in order to explain their data.

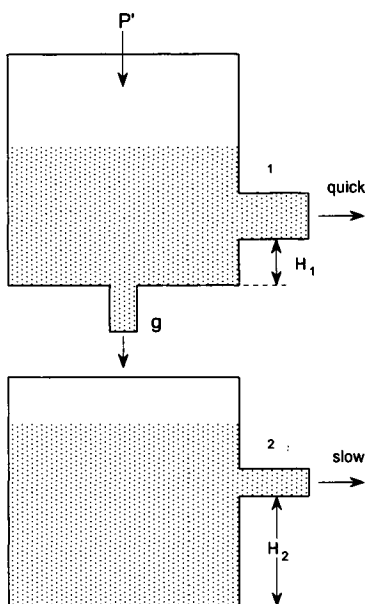


Figure 11.19. Conceptual model of catchment behavior using non-linear storage elements. The parameters α_1^{-1} and α_2^{-1} represent the quick and slow flow recession time constants, while the time constant g^{-1} determines the partitioning between the two reservoirs. The non-linearity of the system is represented by the two threshold storage depths H_1 and H_2 . For South Creek, approximate values of these parameters are: $\alpha_1^{-1} = 1$ d; $\alpha_2^{-1} = 50$ d; $g^{-1} = 0.5$ d; $H_1 = 0.12$ m; $H_2 > 3$ m.

11.8 Future Research Directions

Although it is possible to infer the qualitative result that substantial volumes of 'new' water are released from the catchments under conditions of high antecedent moisture and high rainfall intensities, it is difficult to quantify this result. This is because of two confounding effects: under prolonged, intense rainfall, saturation overland flow results in substantial variations in stream isotopic concentrations due to the addition of event water. On the other hand, the fact that the concentration of the event water more or less mimics the intensity of the rainfall results in similar variations, even if the proportion of event water were to remain constant. In general, variations in rainfall concentrations, even if uncorrelated with intensity, will confound attempts at hydrograph separation. In order to separate unambiguously these two effects, *what we require is an estimate of the time (or distribution of times) which rainfall of a particular isotopic composition takes to travel through the catchment.* For instance, if recession time constants are sufficiently large, event water can be characterized by the isotopic signature of current rainfall. This is appropriate if the temporal rate of change of the rainfall isotopic signature relative to that of the stream is small compared to the rate of change in stream discharge, but this is by no means always the case, as evidenced by the above difficulties during the peak of the February 16 storm, and is a severe restriction on the accuracy of an analysis using this assumption.

As suggested above, what is required for successful hydrograph separation is the residence time distribution of rainwater within the catchment. The Unit Hydrograph technique, in use by hydrologists for more than half a century, is a suitable tool, because the Instantaneous Unit Hydrograph (IUH) gives the response time distribution for rainfall input to catchment runoff. Simple techniques for obtaining an IUH now exist (cf. Jakeman et al., 1990). Assumptions inherent in the IUH approach include linearity and stationarity; i.e. twice as much rainfall results in twice as much runoff etc., and the distribution does not change with catchment wetness. Although neither of these assumptions generally hold (see analysis of Figure 11.12 above), the predictive power of an empirically determined IUH is often significantly better than that of "physically-based" models of rainfall-runoff. A more significant criticism of this approach is the lack of identity between the response time distribution (measuring the hydraulic response) and the residence time distribution required. For instance, an empirically determined IUH based on the events considered here fails to recognize the magnitude of the deep groundwater store, and predicts residence times which are far too short. However, using non-linear conceptual storage elements similar to those portrayed in Figure 11.19 it is possible to devise simple modifications to the IUH theory which largely overcomes this complication. Such modifications are described in detail elsewhere (Barnes and Bonell, 1996; Barnes et al., 1997). Alternatively, most physically based models of catchment behavior implicitly model water movement rather than hydraulics, and so are capable of yielding a prediction of residence times.

The most effective use of isotopic information is in conjunction, not only with other hydrometric data both demonstrated here and elsewhere (Bonell and Fritsch, 1997), but also in conjunction with sophisticated (not necessarily complicated) models which reflect the deepest understanding of catchment behavior and data limitations. An example of the difficulties of using such models is that, whereas when predicting water yield from catchments, it is possible to group losses in one lumped parameter, to predict isotope concentrations it matters where (vertically, horizontally) such losses occur, so that further assumptions have to be made. Unless careful attention is paid to the formulation of such models, it is possible to introduce more unknown parameters than can be evaluated using the extra information from the measurements! Applying the best of these models to predicting isotopic responses as well as the usual hydrological ones, ensures the fullest use of information represented by the data, and the most stringent test of our current understanding of catchment behavior.

Finally, the question of the transferability of the results and conclusions of this study needs to be addressed. Whereas many previous studies in other climatic and geographic regions have concluded that much of the event hydrograph consists of pre-event (or "old") water (including studies in highly responsive catchments such as Maimai), this study has shown that in these catchments the rapid response part of the hydrograph is closely associated with event water from the current precipitation. Moreover, the observed transition from "first-in-first-out" to "last-in-first-out" routing protocols with increasing rainfall intensities needs to be addressed. We have suggested that a particular mechanism (overland flow) is dominant in major events in this catchment; and that catchment behavior is largely determined by the duration and intensity of rainfall events, as well as hydraulic conductivity and slope angle. Are the observed differences and range of catchment behaviors primarily due to the climatic differences (precipitation), complexities of catchment morphologies, or an interaction between the two; and is it possible to predict *a priori* whether a catchment response is likely to be event- or pre-event- water dominated? More experience with catchments with responses intermediate

between the ones reported here and the New Zealand Maimai catchments (for instance) is required, with careful attention to actual flow pathways.

The challenge then is to develop models of catchment behavior which adequately represent our understanding of whole catchment behavior, as obtained from detailed studies such as reported here, without necessitating huge amounts of data on catchment heterogeneity, etc. Such models will depend on catchment scale parameters (for example, the time constants of the hydrograph recession, and the threshold storages H_1 and H_2 of Figure 11.19) rather than parameters derived from point scale conceptual models (such as water contents and potentials, and hydraulic conductivities). On the other hand, a complete understanding requires that these catchment scale parameters can in principle be related to point scale parameters, at least for idealized hillslopes etc., even if in practice they are "measured" directly using catchment scale data, rather than calculated as some sort of average of point scale. The approach based on the distribution of residence times alluded to throughout this chapter represents a possible first step in this direction.

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Snowmelt-Dominated Systems

Allan Rodhe

12.1 Introduction

Seasonal snowcovers occur over about one fourth of the Earth's land surface, at high latitudes and at high altitudes. The temporary storage of precipitation in snowpack, and the subsequent melting, greatly influences the hydrologic regime (see Chapter 1). Precipitation falling over several months may be stored on the ground in the catchment and released during a few weeks of intense spring snowmelt. During the period of snow storage there will be little or no water input to the ground. The groundwater reservoir will gradually decline by draining to the stream, whose discharge recedes in proportion to the falling groundwater level and flow. During snowmelt the groundwater reservoir recovers and stream discharge may reach its annual peak by contributions from groundwater as well as overland flow. In arctic and high altitude areas, practically all stream runoff may be generated by snowmelt, with some addition of rainfall during the melting period. In many temperate humid catchments with seasonal snowpacks, the main part of the yearly runoff takes place in connection with the spring snowmelt.

The winter storage and spring release of precipitated water, and the hydrological regime that follows, also have important consequences for the water chemistry in the catchment. Wet- and dry-deposited salts and acids will be stored in the snowpack and, partly due to redistributions within the snow crystals, they tend to leave the snowpack with the first meltwater which may be much higher in solutes than the original snowfall (see Chapter 4). The high groundwater level, caused by the large and prolonged water input during melting, may result in very shallow flowpaths for the majority of the water and few possibilities for chemical reactions between the discharging water and the mineral soil. Acid meltwater may remain acid, causing low pH-values in the stream with health hazards for the biota, the so-called acid surge.

Isotope studies have made important contributions to our understanding of catchment flow processes during snowmelt. One paradoxical finding is that the spring flood, so clearly connected with the melting of the snow cover, may well be dominated by old water, i.e., liquid water that existed in the catchment prior to the melting. Other results concern mixing processes in the unsaturated zone, rate of groundwater recharge, flow paths, and particle velocities and transit times along various parts of the water flow through a catchment. The effects of those processes on the isotopic composition of runoff are discussed in Chapter 4. The intention of this chapter is to present and discuss findings of isotope studies in catchments where snowmelt accounts for an important part of the total water input, with the focus on isotopic and hydrologic conditions related to meltwater input.

The chapter is based on the author's experience of seasonal snowpacks in Scandinavian catchments. Some general comments may therefore refer to Scandinavian conditions rather than global conditions.

12.1.1 Basic hydrological processes

Characteristics of snowmelt as compared to rainfall

The water input from snowmelt differs from that from rainfall in several aspects. The snowmelt intensity is comparatively low, seldom more than a few mm/h and the melting takes place over many hours during the day and commonly over many consecutive days. The rate of melting is determined by the energy flux to the snowpack. (Physical snowmelt processes are discussed in detail in Chapter 1.) The main components of this energy flux are net radiation and sensible and latent heat fluxes from the air and its water vapor. Favorable conditions for melting are thus sunny days and cloudy nights giving large net radiation, and warm and moist air with strong winds, generating large turbulent fluxes of sensible and latent heat. Other, less important, energy fluxes are heat conduction from the ground and advective heat flux by rainfall. The former can be important in the autumn when the ground is comparatively warm, but it decreases during the winter as the soil temperature gradient close to ground surface decreases. The advective heat flux from rain is small even for large rainfalls. The energy from a rainfall of 20 mm, having a temperature of + 4 °C (= assumed air temperature), generates only 1 mm of meltwater. [This is contrary to the common opinion that the snow is "raining away" during rainy days in spring. The underlying conclusion is understandable, however, since the air is warm, moist and often windy when it rains, giving large melting by sensible and latent heat fluxes.]

The water input to the ground is not directly given by the rate of melting, since the snowpack is a porous medium with an ability to store liquid water by capillary forces. This capacity, which is equivalent to the field capacity of a soil, is about 4% of the water equivalent of the snowpack (Snow Hydrology, 1956). There will thus be no meltwater drainage from the snowpack until the accumulated melt exceeds about 4% of the snowpack water equivalent. Before this meltwater amount has accumulated in the snowpack, the air temperature might, however, have dropped so that the liquid water has frozen and more melting is needed to give drainage. Thus, the liquid water storage and the amount of refreezing have to be taken into account when the meltwater production of a snowpack is to be calculated.

The regular variation of energy flux to the snowpack during the day gives a characteristic variation in the meltwater production (i.e., in the water input to the ground) with the maximum in the afternoon and minimum at night. This variation is, to a greater or lesser degree, preserved in the stream discharge (Figure 12.1), with a damping and delay increasing with the catchment area. An example of the time delay is given in Figure 12.2, showing the hour of daily streamflow maximum in several adjacent catchments and subcatchments.

Characteristic hydrologic conditions in the catchment during snowmelt

In addition to the different characteristics of the water input during snowmelt and rainfall, snowmelt takes place when the conditions in the catchment normally are different from those during rainfall events, producing a different response to a given water input. The main difference is that evapotranspiration normally is very small and that the soil might be frozen.

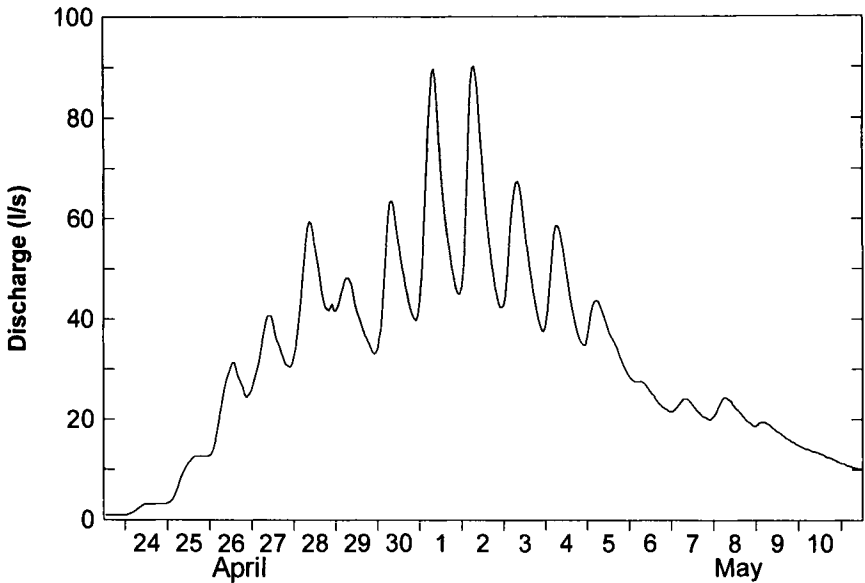


Figure 12.1. Stream hydrograph during spring flood 1993 based on hourly mean values. Svartberget Nedre, Sweden. Catchment area: 0.50 km². Very little precipitation fell during the period shown (< 1 mm/day during three of the days). After Bishop et al. (1995).

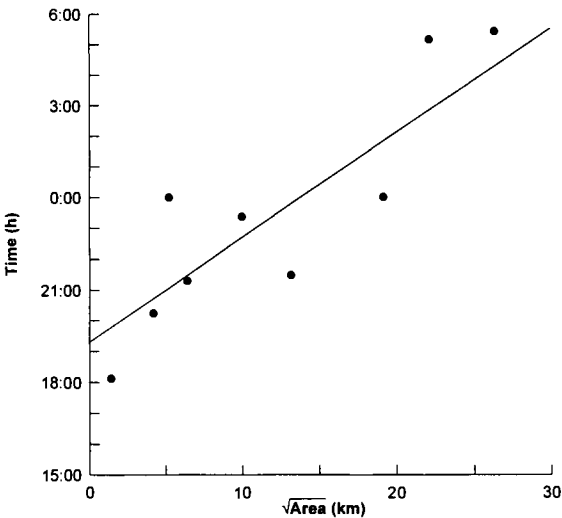


Figure 12.2. The hour of daily stream discharge maximum during spring snowmelt plotted against the square root of the catchment area, representing characteristic lengths of the catchments. Subcatchments within Lappräsket catchment, Sweden 1969-1974. From Persson (1976).

The transpiration is small since the seasonal canopies have not yet developed, and the perennial conifers have low activities owing to low soil temperature. The snow temperature can not exceed 0 °C even if the atmosphere may be warm (and moist). Warm air will therefore give a small or negative vapor pressure difference between the snow and the atmosphere, and thus a small or negative evaporation (i.e., condensation). Evaporation from open surface water reservoirs, if such exist, is also small due to the low water temperature, and evaporation from water under the snowpack is negligible due to low temperature and lack of turbulent exchange with the atmosphere (Chapter 1). The minor loss of water to the atmosphere makes the meltwater input very efficient for soil water and groundwater recharge and for streamflow generation.

In many places, snowmelt occurs on a soil in which the upper layers are temporally frozen. In a frozen soil the water is partly frozen, reducing the pore volume available for liquid water flow. The infiltration capacity of a frozen soil is therefore smaller than if it were unfrozen, but the infiltration capacity may still be large enough to allow all meltwater to infiltrate. Some characteristics of soil frost and water movement in frozen soils are discussed below.

The occurrence of seasonal soil frost at a particular site may vary largely from year to year and there may be large spatial variations within a catchment. The growth of the frost is driven by the heat loss from the ground surface, which in turn is large when the air temperature is low and the net radiation negative. Both of these factors may vary considerably at the micrometeorological scale. The forest canopy, for instance, reduces the radiation heat loss from the ground surface, so that there may be little or no soil frost in the forest, but a considerable frozen layer in a nearby open field or clearing. Snow is a poor heat conductor and effectively reduces the heat loss from the ground surface and thus frost growth. A snowfall giving a few tens of cm of snow on a bare soil may stop the frost growth or, in some cases, even cause the frost to start melting by the heat flow from the ground below. Apart from the meteorological conditions, the frost depth depends on the water content of the soil. The more water in the soil, the more heat has to be conducted away to freeze a certain layer and the slower will be the deepening of the frost. This relationship is reflected by differences in frost depth in various soil textures. The largest frost depths are thus found in coarse soils, which, due to their restricted water holding capacity, normally have the lowest water content at freezing.

The process of freezing is in some ways equivalent to the drying of a soil. The water in the largest pores freezes first, decreasing the pressure of the remaining water and thereby lowering its freezing point (Miller, 1980). In a soil that is saturated at the time of freezing, the hydraulic conductivity falls drastically after freezing. Although there remains some liquid water which can conduct water, it is the large pores, which gave the largest contribution to the conductivity, that are frozen. Snowmelt infiltration, on the other hand, normally takes place in soils that were unsaturated at freezing. Depending on the water content at freezing there may or may not be a sufficiently large open pore space to allow the meltwater to infiltrate. If freezing in the autumn starts directly after a heavy rainfall, the infiltration capacity of the frozen soil may be small and Hortonian overland flow will occur next spring. But if the same soil freezes at a lower water content, all meltwater may infiltrate (Kane and Stein, 1983a, b).

It is thus not the frost depth, but the water content of the upper soil layers at the time of freezing, that determines the infiltration capacity. Since the water content of the upper soil layers to a large degree is governed by the topography, we can expect the most permeable

frozen soil on ridges and in the upper parts of the hillslopes. All meltwater may infiltrate in such areas, whereas Hortonian overland flow may be generated on frozen areas in the lower parts of the hillslopes, where the water content at freezing was high due to very shallow groundwater table. During snowmelt periods with repeated melting and freezing, particularly in connection with large rainfalls on the melting snow, concrete ice can form on the ground surface. Such ice, often occurring in agricultural land, is impermeable and generates overland flow.

Current understanding of streamflow generation

Various theories on streamflow generation, i.e., the process by which rainfall or snowmelt in a catchment is transformed into streamflow, are discussed in Chapter 1. Most isotope studies on snowmelt runoff in Scandinavia were performed in the most common soil type of the region, comparatively coarse textured till soils on fractured gneiss or granite. As a background to the interpretation of these isotope studies, a hypothesis for streamflow generation in such till soils is presented (Rodhe, 1987).

The infiltration capacity of the till soil is usually larger than the intensity of rainfall or snowmelt. Thus all water on unsaturated areas infiltrates. The water table largely follows the topography, with a depth below ground surface of a few meters in elevated areas. In the lower parts of certain hillslopes and in some low-lying areas, the water table is at or above the ground surface. These saturated areas generally, but not always, occur in connection with the streams. Depending on whether the water flows into or out from the groundwater zone, the area of a catchment can be divided into recharge and discharge areas for groundwater, with the discharge areas normally constituting a minor part of the catchment. The areal extent of discharge areas is highly variable, expanding with rising groundwater level. During dry periods the discharge area may constitute only the stream itself and some permanently wet areas.

The outflow of groundwater in discharge areas may respond rapidly to rainfall or snowmelt on recharge areas, causing a substantial groundwater component in stream stormflow. This groundwater reaches the stream either as overland flow on saturated areas or directly through the stream bottom and sides. All rainfall on discharge areas (except water lost by evapotranspiration, particularly during interception, and precipitation which falls directly into the stream channel) reaches the stream as overland flow. Together with the groundwater discharged outside the stream, it forms saturation overland flow.

When the water table in a hillslope rises as a result of water input, the groundwater flow increases for two reasons: increased total head gradient due to increased slope of the water table and increased transmissivity due to contribution by additional soil horizons. Since the water table largely follows the topography, the relative increase in the slope of the water table is normally small. But the hydraulic conductivity often increases drastically towards the ground surface, giving a dramatic increase in the transmissivity as the water table approaches the ground surface. With the hydraulic conductivity profile reported for a till soil by Lundin (1982), the groundwater flow increases manifold by a small rise of a shallow water table, even if the slope of the water table remains essentially the same (Figure 12.3). The mechanism has been termed transmissivity feedback by Bishop (1991), who tested the mechanism for consistency between the isotopic, chemical and hydraulic potential signals in a hillslope and the runoff from that hillslope.

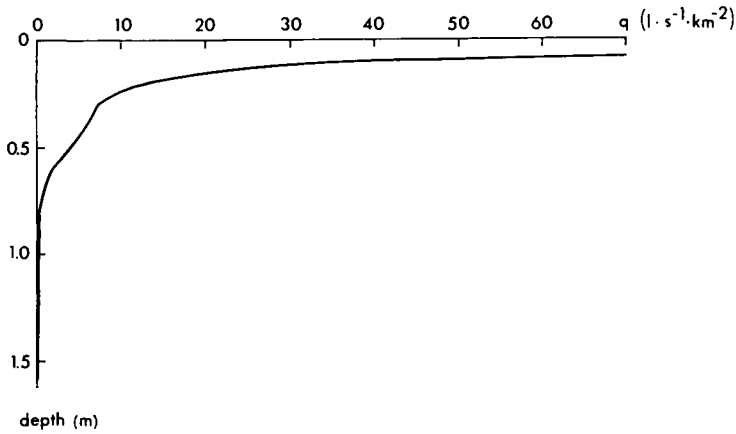


Figure 12.3. Total lateral groundwater flow as a function of the depth to the water table calculated from a hydraulic conductivity profile in till soil (data from Lundin, 1982). The hillslope is assumed to be 50 m long and the slope of the water table 0.1 m/m at the base. From Rodhe (1987).

The increase in hydraulic conductivity towards the ground surface has a profound impact on the flowpaths of the water. Even if the near surface high conductivity layers are unsaturated for most of the time, with little or no lateral flow, the majority of the annual groundwater flow in the profile may take place in these layers during short periods with high groundwater tables (Figure 12.4). These superficial “spate-specific flowpaths” (Bishop et al., 1990) are of great importance for the hydrochemical processes in the soil.

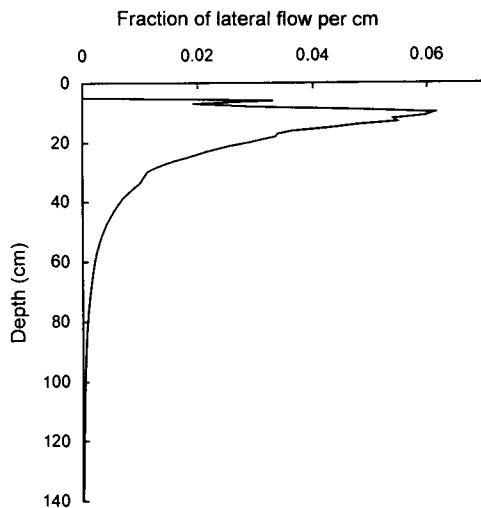


Figure 12.4. Vertical distribution of the annual lateral groundwater flow calculated from an observed hydraulic conductivity profile and the frequency distribution of groundwater levels. Catchment G1 at Lake Gårdsjön, Sweden, April 1991 to May 1992. From Seibert (1993).

Discharge areas can be defined as areas in which the groundwater has a flow component directed away from the groundwater zone, which normally is equivalent with an upward flow component. In the corresponding way, recharge areas have a downward groundwater flow component. With this definition, a discharge area may be saturated or unsaturated, depending on whether or not the groundwater table reaches the ground surface (Grip and Rodhe, 1994). In a saturated discharge area, no infiltration can take place and all rainfall or snowmelt generates saturation overland flow together with the outflowing groundwater. In an unsaturated discharge area, the upflowing groundwater is either lost by evapotranspiration from the unsaturated zone or diverted laterally through layers of high hydraulic conductivity. During wet periods there may be a downward flow in the unsaturated zone and at the same time an upward flow in the saturated zone. A prerequisite for this lateral diversion of the upflowing groundwater is that the saturated hydraulic conductivity increases towards the ground surface. The ground surface may therefore remain unsaturated also during wet periods at locations where one, from a topographic point of view, would expect groundwater discharge.

12.1.2 Global geographical distribution

Areas in which seasonal snowpacks have an important influence on the hydrological regime are situated mainly in the northern hemisphere. High latitude results in snowpacks in Canada and Northern United States, Scandinavia, Finland, many Eastern European countries, Russia and Japan, whereas high altitude gives snowpacks in many other areas, notably the Himalaya and its surroundings in Central Asia, the Alps in Central Europe, and the Andes in South America.

The isotope studies of snowmelt referred to in this chapter have been carried out exclusively in Europe (the Alps and Scandinavia with Finland) and in North America (Canada and United States). As noted above, glacial till soils with shallow groundwater on gneiss or granite dominate in the Scandinavian and Finnish catchments. This geology is similar to some of the Canadian study catchments, but other studies have been performed in geological surroundings with quite different groundwater conditions.

12.1.3 Isotopic characteristics of snowmelt

Stable isotope catchment hydrology is based on the transformation of the input isotope signal during the various stages of water flow through a catchment. The input signal is the temporal variation in the ^{18}O and D concentration of precipitation, which can be seen at different time scales: a slight variability between years around a climatically determined mean value, a seasonal variation, a variability between precipitation events, and a variability within rainstorms or in the course of snowmelt. The seasonal variation of the stable isotope content of precipitation (discussed in detail in Chapter 3), with comparatively low δ -values in the snowfall, is largely reflected in the ^{18}O and D contents of meltwater. Although isotope changes take place in the precipitated water during both snowpack storage and melting (see Chapter 4), meltwater is normally considerably depleted in stable isotopes as compared to the annual mean of precipitation or groundwater. This deviation provides a useful tracer signal for hydrological studies. During snowmelt, the catchment gets a large input of isotopically depleted water, which can either be traced directly in the soil water and groundwater or be used in

mixing calculations. In comparison with rainwater, snowmelt is favorable for isotope hydrograph separation, because its ^{18}O and D contents normally are consistently lower than those of the groundwater or pre-event water. The isotope content of rainfall, on the other hand, may or may not deviate from that of the groundwater, and may be either higher or lower in its isotope content.

As pointed out in Chapter 4, liquid water in isotopic equilibrium with ice is depleted in heavy isotopes as compared to the ice, by about 3‰ in $\delta^{18}\text{O}$ and by about 16‰ in δD (from fractionation factors given by O'Neil (1968)). Fractionation during melting is, however, normally restricted by incomplete mixing. During melting of a snowpack, the original melting of the topmost layer may be non-fractionating, but as the meltwater percolates through the snowpack, melting-freezing will tend to establish isotopic equilibrium between water and ice. The effect depends on the time of contact between snow and water, and also on the isotopic layering of the snowpack. For this reason, the fractionation processes do not give a unique relationship between the δ -value of a snowpack and the δ -value of the meltwater generated at the same moment. Several investigations have shown depleted meltwater (Arnason et al., 1973; Stichler and Herrman, 1977) in accordance with the expected direction of fractionation, but also enriched meltwater has been reported (Martinec et al., 1977; Hooper and Shoemaker, 1986). Since the time of contact between the percolating meltwater and the snow decreases as the melting intensity increases, the difference between the δ -values of the snowpack and meltwater decreases as the melting intensity increases (Herrmann and Stichler, 1978). These phenomena may give a considerable short term variation in the isotope content of the meltwater from a certain snowpack. Rain-on-snow is also an important component of the melting period in many areas. Such a rainfall, which often is enriched as compared to the snowpack, may greatly influence the isotope content of the water draining from the snowpack.

Regarding the above isotopic changes during meltwater production and the changes of the isotope content of the snowpack due to molecular exchange with the atmosphere, both during the accumulation period and during the melting periods, estimates of the δ -value of meltwater from the δ -values of the winter precipitation or from the δ -value of the snowpack are very uncertain. If it were only for the fractionation during melting, the total isotope input to the soil would be given from the isotope content of the snowpack at the onset of melting, although the time variation would be different from that of the isotope content of the melting snowpack. But due to enrichment of the snowpack by evaporation and molecular exchange between the snow and the atmosphere, the mean isotope content of the meltwater is normally higher than that of the original snowpack.

In order to obtain useful δ -values of the water input to the ground, it is thus necessary to collect meltwater for isotope analysis. Snow lysimeters, consisting of impermeable sheets or plates on the ground draining to a sampling device, may also give the volume and intensity of the water input. A detailed description of a 25 m² snow lysimeter is given by Herrmann (1978) and a 5.2 m² lysimeter is described by Arnason et al. (1973). One or more snow lysimeters, with areas ranging from 1 to 6 m² have been used in catchment studies (e.g., Hooper and Shoemaker, 1987; Bengtsson et al., 1989; Maulé and Stein, 1990; Wels et al., 1990; Mast et al., 1995). One important advantage of snow lysimeters is that the effect of rain on the δ -value of the snowpack drainage is included in the samples.

12.2 Hydrograph Separation Studies

12.2.1 Historical studies

In the early development of the use of environmental isotopes in hydrology in the 1950's, stable isotopes in snow were most often studied in glaciated areas, i.e., in snowpacks not melting completely during spring and summer. These glacier-related studies have played an important role in enhancing the present-day knowledge of fractionation processes and the occurrence of stable isotopes in water (Epstein and Sharp, 1959; Dansgaard, 1961). Behrens et al. (1971, 1979) investigated the runoff from three partly glaciated Austrian catchments. By using tritium and deuterium they were able to determine the contribution of fresh snowmelt water, glacier ice and subglacier groundwater.

Early isotope studies of catchment response to melting of seasonal snowpacks are those by Dinçer et al. (1970) and Martinec et al. (1974) performed in mountainous areas of Central Europe. Dinçer et al. investigated the runoff from the 2.65 km² Modry Dul catchment in the Czech Republic using tritium and ¹⁸O, and Martinec et al. made a follow-up study in the 43.3 km² Dischma catchment in Switzerland. These studies gave important contributions to the development of the modern view of streamflow generation in humid catchments in that they gave evidence to a dominance of old water in snowmelt runoff. Flow components of the runoff could be separated due to the seasonal variation of the T concentration of precipitation, reflected in a low tritium concentration in the snowpack as compared with the winter base flow, assumed to represent the subsurface flow component. According to a two-component hydrograph separation (using the tritium concentrations of the streamwater, snowpack and winter base flow), the water from the snowpacks constituted only a minor part of the spring snowmelt runoff. Dinçer et al. compared the discharged meltwater volume with the water equivalent of the snowpack and concluded that "about two-thirds of the meltwater replenishes the subsurface storage, pushing an almost equal amount of water from the storage to the drainage network of the basin."

Indications of large contributions by groundwater to stream runoff during rainfall generated events had been given also by other studies using electrical conductivity or major ions (Newbury et al., 1969; Pinder and Jones, 1969), ⁸⁹Sr/⁹⁰Sr ratios (Yamagata et al., 1963; Miyake and Tsubota, 1963) and also by tritium (Crouzet et al., 1970). But the snowmelt studies by Dinçer et al. and Martinec et al. provided the first striking evidence of the indirect mechanism of streamflow generation. The results contradicted the traditional view, based on infiltration excess (Horton, 1933), as well as the newly formulated view based on saturation overland flow (Dunne and Black, 1970), which both saw new rain or meltwater as the main contributor to stream stormflow. Since the indicated rapid response of groundwater outflow to infiltration could not be simulated by mathematical hillslope flow models (Freeze, 1972a, b), the isotope results were questioned and debated (Freeze, 1974; Martinec, 1975). The findings of Dinçer et al. and Martinec et al. have been supported by several later isotope studies, some of which will be discussed in this chapter. But even if our understanding of the subsurface response mechanism has increased substantially over the years (see Chapter 1), the statement of Martinec that "the exact nature of the propagation is not known" still holds and the debate must continue.

The tritium studies in Modry Dul and Dischma were carried out at a time when the T content of precipitation was declining after the peak concentration in 1963, generated by the hydrogen

bomb tests in the atmosphere (see Chapter 1). The decline, which was caused by precipitation and molecular exchange with the oceans (and which was much more rapid than the radioactive decay of tritium), was followed by a delayed decline in the T content of streamwater. After correction for radioactive decay, this difference could be used for estimates of the mean transit time of the groundwater and from this the volume of the groundwater reservoir. The observed T input by precipitation was transformed by means of convolution integrals (see Zuber, 1986) using various assumed transit time distribution functions, mainly based on exponential (complete mixing) and dispersive flow models. The output was compared with the observed T concentration of the base flow (see further discussion in Chapter 21). Since there is a large seasonal variation in the T concentration of precipitation, the annual T input was calculated using a weighting function for the monthly precipitation amounts, taking into account the more efficient groundwater recharge by winter precipitation than by summer precipitation. A mean transit time of 2.5 years was obtained in Modry Dul and about 4.5 years in the Dischma catchment. The corresponding subsurface reservoir volumes, given by the product of mean transit time and mean flow, were estimated to 1.0 m and 3.0 m water depth, respectively. These reservoirs, interpreted as groundwater reservoirs but which also must include the water in the unsaturated zone, are considerably larger than those obtained by recession analysis of stream hydrographs using the theory of linear reservoirs. This difference was pointed out by Martinec (1975) noting that recession analysis gives mean transit times on the order of days, in contrast to those on the order of years obtained by isotopes. The difference is quite natural, because the isotope studies give the total volume of water participating in the flow, whereas recession analysis only gives the groundwater volume above a certain threshold level and only the drainable part of this volume, i.e., the difference between porosity and field capacity. The isotopes give the mixing reservoir, influencing the chemical response of the catchment, while the volume from recession analysis determines the dynamic response.

The above tritium studies were followed by a detailed isotope study in the 18.7 km² Lainbachtal catchment in the Bavarian Alps (Herrmann and Stichler, 1978, 1980). This, and most later published isotope catchment runoff studies, used stable isotopes instead of tritium, in this case deuterium. Although isotope fractionation processes during snowmelt may cause some methodological problems in runoff studies, the stable isotopes are preferred to tritium since the analyses normally are cheaper, allowing more detailed sampling programs.

In the Lainbachtal study, two 25 m² recording snow lysimeters were used to determine the amount and deuterium content of the meltwater input. An example of a two component hydrograph separation of a snowmelt period is shown in Figure 12.5. According to the separation, the event flow component (called direct flow component) was at the most about 30% of the total flow, which occurred during the early hydrograph rise. During the main part of the event the fraction of event water was around 20%. The diurnal variations in stream discharge, caused by diurnal variation in the snowmelt, were closely related to a diurnal variation in the deuterium content of the streamwater. As one would expect, the largest fraction of event water was observed about simultaneously with the daily discharge maximum. For the whole three year period of investigation, including rainfall and snowmelt events, the direct flow component was estimated to about 1/3 of the total flow.

The sinusoidal seasonal variation of the deuterium content of precipitation input was reproduced, after damping and delay, in the seasonal variation of the deuterium content of the runoff output in Lainbachtal. From this transformation, Maloszewski et al. (1983) estimated

the mean transit time of the baseflow to be about 2 years and a groundwater reservoir corresponding to a water depth of about 2 m in the catchment. The D data were complemented with a longer, but less intense, time series of T data giving about the same mean transit time but which also allowed interpretation of the data in terms of an upper and lower subsurface reservoir with mean transit times of about 0.7 and 7.5 years, respectively.

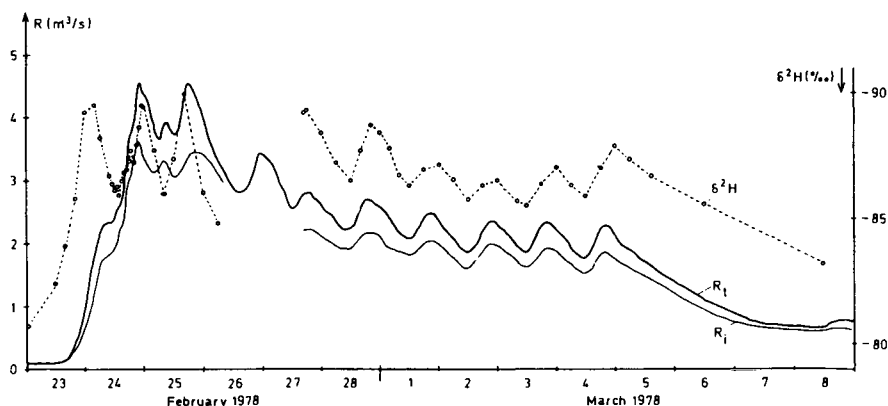


Figure 12.5. Stream hydrograph (R_t) during snowmelt, with deuterium content of streamwater ($\delta^2\text{H}$) and calculated flow of pre-event water (R_i). (Note the reversed axes for deuterium, with increasing values downwards.) Lainbachtal catchment, Bavarian Alps, Germany. Catchment area: 18.7 km², altitude 670 - 1801 m a.s.l. From Herrman and Stüchler (1980).

The Central European isotope studies of snowmelt runoff were followed by snowmelt studies based on ^{18}O or D by, among others, Rodhe (1981, 1987) in Sweden, by Bengtsson et al. (1989) and Lepistö (1995) in Finland, Hooper and Shoemaker (1986) in the United States, and Bottomley et al. (1986), Obradovic and Sklash (1986), Maulé and Stein (1990), and Wels et al. (1990, 1991) in Canada. With a few exceptions, the early findings of a dominance of old water in snowmelt runoff were confirmed, although the physiographical and hydrological conditions of the investigated catchments could differ considerably. An important extension of the method of isotopic hydrograph separation was the combined use of ^{18}O or D and Si as tracers, giving information of both the source of the water (from isotopes) and of the flowpaths (from Si) (Maulé and Stein, 1990; Wels et al., 1991). Apart from these studies on a catchment scale, the characteristic stable isotope signal of meltwater has been used to elucidate vertical flow and mixing in the unsaturated zone (Buttle and Sami, 1990; Saxena, 1987; Bengtsson et al., 1992; Lindström and Rodhe, 1992).

12.2.2 Recent studies with more complete characterization

The basic assumption for two-component isotope hydrograph separation is that the temporal variation of the input ^{18}O and D concentration is smoothed out by mixing during water flow through the ground, forming a reservoir of isotopically homogeneous water contributing to streamflow (see also discussions in Chapters 1 and 10). If the isotope concentration of this

reservoir (pre-event water) differs from that of the water input at a certain moment (event water), the fraction of event/pre-event water in streamflow can be obtained. As noted above, and exemplified in Section 12.2.1, snowmelt generated runoff events are well suited for hydrograph separation by isotopes, due to the prolonged input of water deviating isotopically from the water already existing in the catchment. The traditional formula for two-component hydrograph separation, based on mass conservation for water and tracer, reads (see Chapter 1):

$$X = \frac{(c_s - c_e)}{(c_{pe} - c_e)} \quad (12.1)$$

where X is the fraction of pre-event water in streamwater and c_s , c_e and c_{pe} are tracer concentrations in streamwater, event water (meltwater and rainwater) and pre-event water, respectively. Pre-event water (equivalently called “old water”) is liquid water existing in the catchment before a certain runoff event, and event water (“new water”) is liquid water entering the catchment during the event, i.e., new rain- or meltwater. The assumptions and limitations of this simple model are discussed in detail in Chapter 10. Often stated prerequisites for the method are areal and temporal constancy of c_e and c_{pe} . The fact that these conditions seldom, if ever, are fulfilled does not invalidate the model, since areal and temporal variability of the terms in many cases can be treated as uncertainty in the input variables to Equation 12.1. For a given uncertainty in the input variables, the relative uncertainty in X is inversely proportional to $|c_{pe} - c_e|$ (see error discussions in Rodhe (1987) and Crouzet et al. (1970)).

Rodhe (1987) performed isotopic hydrograph analysis on snowmelt and rainfall generated events in 10 small catchments and subcatchments (0.03 - 7 km²) in Sweden. All catchments were dominated by forested till soil on gneissic or granitic rock. A major shortcoming of this study was the uncertainty in the isotopic composition of meltwater. Because no direct measurements were made, the $\delta^{18}\text{O}$ of meltwater was assumed equal to the catchment mean of the $\delta^{18}\text{O}$ of snowpack at any moment, and possible deviations between these two entities were treated as errors. During snowmelt, the snowpacks were normally sampled weekly at 3-10 stations within the catchments. Daily values of the $\delta^{18}\text{O}$ of snowpack were obtained by interpolation between the days of snowpack sampling. With this procedure, the uncertainty in the $\delta^{18}\text{O}$ of meltwater was assumed to be $\pm 1.0\text{‰}$ during periods with little or no rain on snow (most of the investigated events). However, due to uncertainty in the $\delta^{18}\text{O}$ of the snowpack drainage, hydrograph separation could not be performed for snowmelt periods with considerable rain having a δ -value deviating from that of snowpack. Streamwater was normally sampled daily. In order to get conservative estimates of the pre-event fraction, streamwater was sampled in the afternoon close to the hour of daily discharge maximum, when the largest relative contribution of meltwater was expected. During a few days around the day of spring flood culmination, within-day variation of $\delta^{18}\text{O}$ was investigated by more frequent sampling. The $\delta^{18}\text{O}$ of the pre-event water was taken as that of streamwater before melting or rainfall.

Examples of hydrograph separation by ^{18}O during snowmelt are shown in Figures 12.6 and 12.7. The small runoff event in Nåsten (Figure 12.6) was caused by a short warm period, melting a few millimeters of water from a snowpack having a water equivalent of about 120 mm. The two events in Svartberget Nedre (Figure 12.7) constitute the total spring flood of the year, generated by melting of a snowpack of 200 mm water equivalent. These separations are considered accurate, due to the large difference between the $\delta^{18}\text{O}$ of the snowpack and the pre-

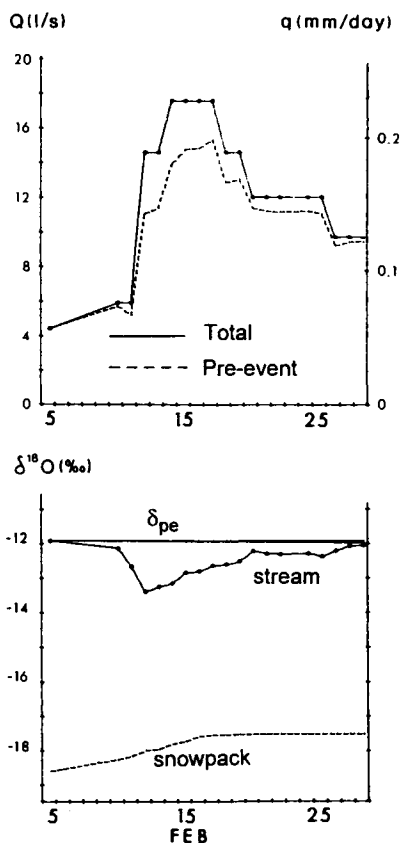


Figure 12.6. Isotopic hydrograph separation of a small winter runoff event in Nâsten, Sweden, 1982. Catchment area: 6.6 km². Stream hydrograph with calculated flow of pre-event water, and assumed $\delta^{18}\text{O}$ values for the pre-event component ($\delta^{18}\text{O}_{pe}$), streamwater and snowpack. (The hydrograph should be smooth; the step changes are an effect of the limited resolution of the water level readings.) From Rodhe (1987).

event water, particularly in the Nâsten event, and due to little or no rainfall (0 mm in Nâsten, 6 mm in total in Svartberget Nedre).

Influence of catchment physiography on the isotopic behavior of streamwater during snowmelt in two nearby catchments is exemplified in Figure 12.8, showing $\delta^{18}\text{O}$ and calculated fractions of pre-event water in two adjacent catchments (subcatchments to Svartberget Nedre, Figure 12.7). The streamwater sampling point at Svartberget Övre is located at the outlet of a bog, covering 40% of this subcatchment. Svartberget Västra, on the other hand, contains almost no bog area. The $\delta^{18}\text{O}$ of the runoff from the bog area responded rapidly to the input of meltwater with low $\delta^{18}\text{O}$, and after a few days the stream was dominated by meltwater, a condition that remained for the rest of the melting period. Svartberget Västra showed a much smaller isotopic response to the depleted meltwater input, and the $\delta^{18}\text{O}$ of streamwater almost returned to its pre-event value at the end of the first, small runoff event. The difference was certainly caused

by the presence of the bog in Svartberget Övre, but the controlling mechanisms are not known. Suggested explanations are rapid delivery of meltwater to the stream by flow in the highly conductive topmost layers of the bog, saturation overland flow or overland flow on the frozen bog. Svartberget Nedre (Figure 12.7), in which the water is a mixture between the two subcatchments with some addition from a non-bog area, shows an intermediate isotopic behavior. The same characteristic difference between the isotopic behavior of the two subcatchments was observed by Bishop et al. (1995) in a study of a later year's spring snowmelt.

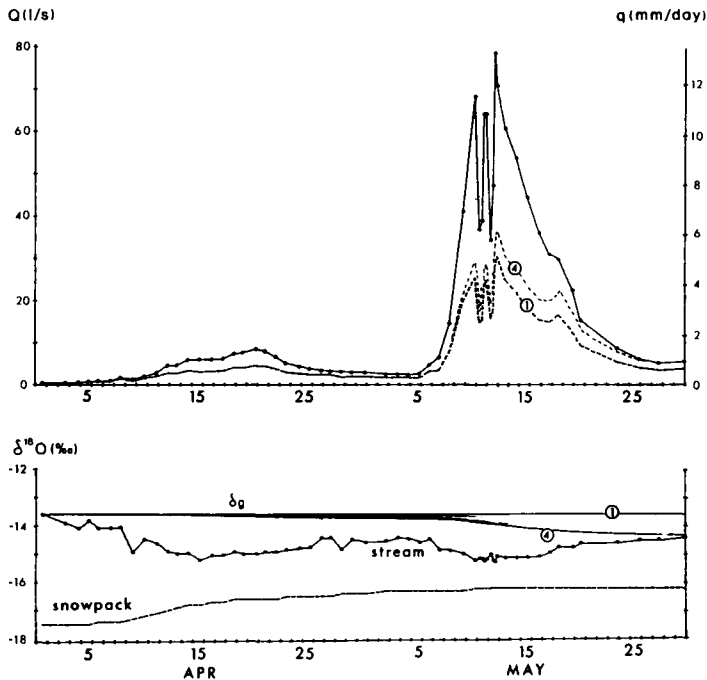


Figure 12.7. Hydrograph separation of a spring flood in Svartberget Nedre, Sweden, 1981. Stream hydrograph with calculated flow of pre-event water (dotted line 1), assumed $\delta^{18}\text{O}$ values of the pre-event component (full line 1), streamwater and snowpack (also shown in the diagram are calculated groundwater flow (dotted line 4) and a variable δ_g (full line 4) as given by Equation 12.2 using a model reservoir volume of 200 mm). The hydrograph is based on stream discharge at the hour of streamwater sampling, normally giving one value a day. For this reason diurnal fluctuations in discharge, very prominent during the main part of the snowmelt period (cf. Figure 12.1) are seen only during a few days with intense sampling, May 11 and 12. After Rodhe (1987).

Figure 12.9, presenting data from one or more events in 10 different catchments, shows that most of the snowmelt events and all rainfall events investigated by Rodhe (1987) were dominated by pre-event water, according to the estimates by ^{18}O . Although the data are scattered, there seems to be an inverse relationship between volume fraction of pre-event water and maximum specific discharge. When looking at different events in the same catchment (not seen in the figure) such a relationship could be expected for the fraction of pre-event water, but not a priori for the fraction of groundwater. This is so because a large streamflow maximum normally is associated with a large volume of infiltrated (event) water, which mixes with the

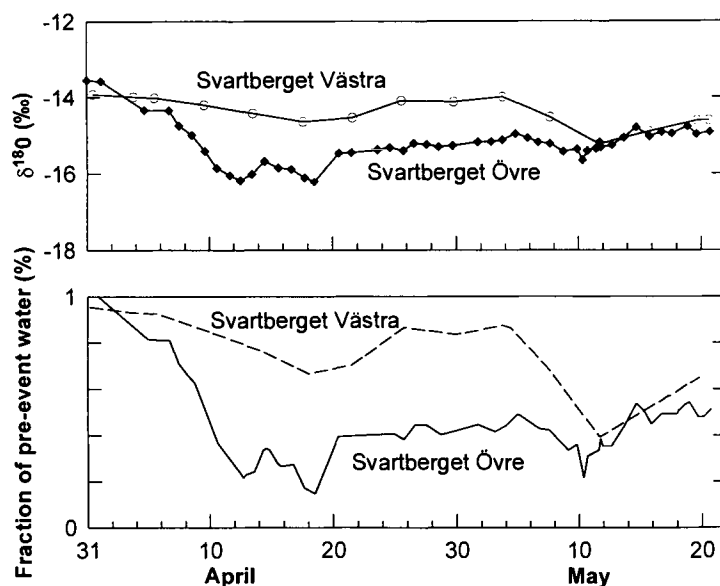


Figure 12.8. $\delta^{18}\text{O}$ of streamwater and calculated fraction of pre-event water in Svartberget Västtra (0.16 km², no bog area) and Svartberget Övre (0.20 km², 40% bog) during spring flood 1981. The two catchments are subcatchments to Svartberget Nedre (cf. Figure 12.7). Stream discharge was not measured in these streams, but the form of the hydrographs is roughly proportional to the total stream hydrograph shown for Svartberget Nedre in Figure 12.7. The $\delta^{18}\text{O}$ of snowpack, shown in Figure 12.7, was used as the isotopic composition of the event component. Daily values were obtained from interpolation between mean values of snowpack samples taken weekly at 10 locations within the main catchment (0.5 km²), with a few samples within each subcatchment. After Rodhe (1987).

soil water and groundwater and may give a large fraction of event water in the groundwater contributing to streamflow. The fraction of groundwater, on the other hand, does not necessarily decrease as the runoff increases. With the hypothesis for streamflow generation presented in Section 12.1.1, increased groundwater level gives increased saturated discharge areas and, for a given rate of meltwater production, an increased flow of meltwater to the stream as saturation overland flow. Increasing discharge areas does not, however, directly imply that the groundwater fraction of streamflow decreases; this is a consequence only if the relative increase of the groundwater discharge is less than the relative increase in meltwater flow when the discharge areas are expanding.

It is also seen in Figure 12.9 that for a certain maximum intensity of the runoff, the pre-event water fraction was larger for rainfall events than for snowmelt events. This difference was also noted by Buttle (1994) who analyzed the results of 64 isotopically separated runoff events in forest catchments reported in the literature (including those in Figure 12.9). He found that the mean value of the fraction of pre-event water at the moment of streamflow maximum was 0.77 for rainfall events and 0.58 for snowmelt events. He further observed that the fraction was independent of catchment size, but he also noted that very few studies had been undertaken in catchments larger than 100 km².

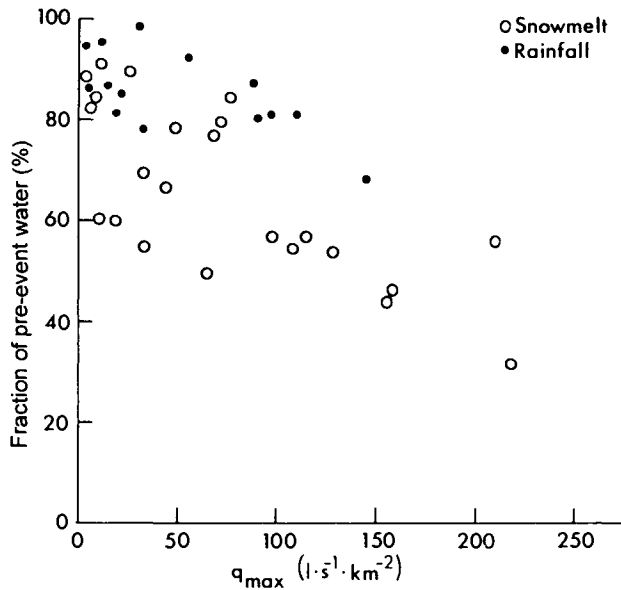


Figure 12.9. Total volume fraction of pre-event water, as estimated by ^{18}O versus maximum streamflow in 10 Swedish catchments and subcatchments. Snowmelt and rainfall events. From Rodhe (1987).

Temporal variation of c_e during the event

Temporal variations in the tracer concentration of the water input during the course of events is a problem in isotopic hydrograph separation and may prevent accurate separations (cf. discussion on the variation of the isotopic composition of the rainfall in Chapter 10). Apart from the uncertainty caused by the rough assumption of meltwater $\delta^{18}\text{O}$ being equal to that of the snowpack, Rodhe's use of daily values of c_e presumes that the flow time for meltwater to the sampling point in the stream is less than one day. Such an assumption is reasonable for overland-flowing water. But new water discharged as groundwater, as well as water flowing through temporary surface water reservoirs, may have been produced by melting several days earlier. If the δ -values of the water input approaches that of pre-event water, as is commonly the case during snowmelt, this error leads to an underestimate of the pre-event water fraction. With an assumed time lag of two days between melting and meltwater entrance to the stream, the slow rates of change of c_e in the events in Figures 12.6 and 12.7 and in other events reported by Rodhe (1987) give an underestimate of the pre-event water fraction of at most a few percentage points. Temporal variation in the tracer concentration of the water input during rainfall and snowmelt generated events has been treated in various ways in the literature. Apart from being based on momentary (daily) values of c_e , as in the snowmelt events separated by Rodhe (1987), separations of snowmelt and rainfall generated events have been based on volume weighted event mean values of the tracer input concentration, accumulated volume weighted means, and by using certain weighting factors for preceding tracer inputs in attempts to represent the temporal storage of new water (see discussion in Ogunkoya and Jenkins, (1993), McDonnell et al. (1990) and Rodhe et al. (1996)).

Pre-event fraction of the flow increase versus pre-event fraction of the total flow

When discussing the process of streamflow generation from the calculated fractions of event/pre-event water one has to distinguish between the pre-event fraction of the total flow (as given by Equation 12.1) and the pre-event fraction of the flow increase. The hydrograph from Nåsten (Figure 12.6) was strongly dominated by pre-event water, with a minimum value of 76% occurring at the early part of the discharge peak. If there had been no melting, the streamflow would have receded from slightly above to slightly below 4 l/s during this event, and the flow would have been solely pre-event water. The pre-event fraction of the flow increase is obtained by subtracting the recession flow, i.e., about 4 l/s, from the calculated flows of pre-event water and the total flow. This procedure gives a minimum pre-event fraction of the flow increase, i.e., of the runoff generated during the event, of about 65%. For most of the events investigated by Rodhe, this distinction is less important, since the relative increase in the total flow normally was large, as in the example from Svartberget Nedre (Figure 12.7). However, when analyzing the within-day variations of streamflow, often very prominent during the middle and later part of the snowmelt period, the distinction has to be made. Figure 12.10 (upper diagram) shows within-day variations of total streamflow and calculated pre-event water flow for a few days around the day of spring flood culmination in a 2 km² Swedish catchment. The pre-event fraction of total flow was about 45-50% whereas the pre-event fraction of the daily contribution was considerably smaller, about 30% (Figure 12.10, lower diagram).

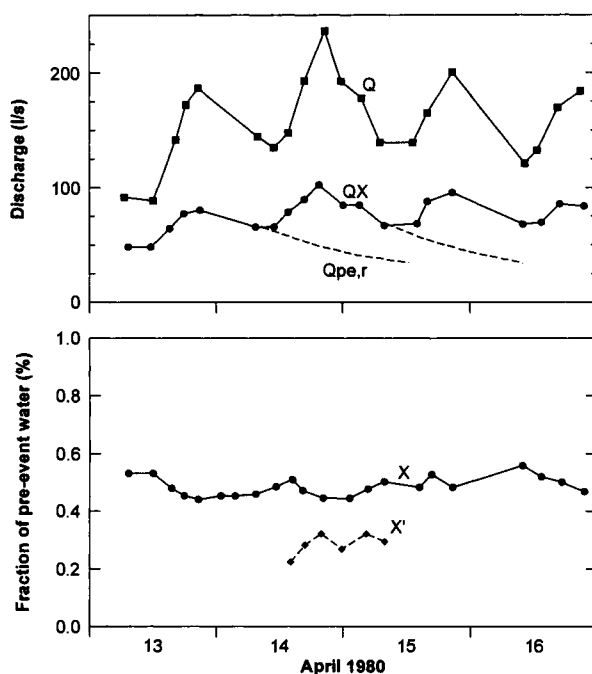


Figure 12.10. Identification of the pre-event fraction of the daily contribution to streamflow (with pre-event referring to liquid water in the catchment at the onset of snowmelt), where Q = total streamflow; QX = flow of pre-event water; $Q_{pe,r}$ = recession of pre-event water flow from the preceding day; X = pre-event fraction of total streamflow; X' = pre-event fraction of the daily contribution to streamflow. Data from Buskbäcken, Sweden. From Rodhe (1987).

Pre-event water versus groundwater

The fraction X in Equation 12.1 can be given different interpretations depending on the assessment of the term c_{pe} . In the examples above, as in many reported studies, c_{pe} is given a constant value during the event, equal to the tracer concentration of streamflow just before the event. If the tracer concentration of all pre-event water reaching the stream during the event equals the value of c_{pe} , then X really represents the pre-event fraction of streamflow. But this condition is probably seldom fulfilled for ^{18}O and D due to the occurrence of pre-event soil water of an isotopic composition different from that of the pre-event groundwater (cf. the ^{18}O layering in the unsaturated zone discussed in Section 12.3) and also due to spatial variations in the tracer concentration of groundwater. Such a variability can be treated as an uncertainty in c_{pe} , but it can also be used to get information on the contribution by pre-event soil water to streamflow (Sklash and Farvolden, 1979; DeWalle et al., 1988).

In some studies, Equation 12.1 is assumed to represent the fraction of groundwater or subsurface water. In such case c_{pe} should be replaced by c_g , the tracer concentration of groundwater or subsurface water, which is often assessed in the same way as c_{pe} . The use of a constant c_g , equal to the pre-event tracer concentration of streamwater, will tend to underestimate the groundwater fraction, since the discharging groundwater may partly be event water, having infiltrated and mixed with the groundwater during the event. Or, stated in another way, some of the new water appearing in the stream, particularly during large events, may have reached the stream as groundwater (cf. discussion on Figure 12.9). The contribution of pre-event soil water with a tracer concentration deviating from that of the pre-event streamwater may, on the other hand, influence the calculated groundwater fraction (and also the pre-event fraction) in both directions.

In Nordic till soils, with their shallow groundwater tables, the only subsurface contribution to streamflow is most probably by groundwater. In these soils, saturated zones normally build up only in connection with the groundwater. Since water can flow out of the soil only if the pressure is above that of the atmosphere, i.e., from a saturated zone, the discharging water is by definition groundwater. However, it may well partly consist of event water having infiltrated during the event or of pre-event soil water that has been transformed into groundwater during the event, by percolation or by a rising water table. If the temporal variation of the tracer concentration of the discharging groundwater within the event were known, then X in Equation 12.1 would represent the true groundwater fraction of streamflow and $1 - X$ the fraction of streamflow originating from overland-flowing rain- or meltwater.

It is regarded as impossible to calculate the temporal trend of c_g within events on the basis of groundwater and soil water sampling. This is because the relative contribution to streamflow from various reservoirs is not known. Therefore c_g can only be measured at times when the stream is fed solely by groundwater, i.e., before and after the runoff events. The temporal variation within the events has to be determined indirectly. One approach is to assume that c_g varies linearly with time between the pre-event and post-event tracer concentrations of streamwater (Hooper and Shoemaker, 1986). With this assumption the fraction X is larger than the one obtained by use of constant c_g and probably closer to the true groundwater fraction of streamwater. Rodhe (1987) attempted to calculate c_g from c_e by using a simple mixing model. Assuming a constant volume of the groundwater reservoir (here including the soil water reservoir), mass balance of water and tracer for the reservoir gives:

$$dc_g = \frac{QX(c_e - c_g)}{V_g} dt \quad (12.2)$$

where dc_g is the change of the isotope content of the groundwater, Q is total streamflow, X is the calculated fraction of groundwater, V_g is the volume of the groundwater reservoir and t is time. With this equation, a temporal variation of c_g within runoff events could be calculated. The value of V_g was chosen by trial and error so that c_g changed from the pre-event to the post-event value during the event, i.e., between the corresponding values of tracer concentration in streamwater.

In the small runoff event shown in Figure 12.6 the $\delta^{18}\text{O}$ of streamwater returned to its pre-event value after the event, indicating that the $\delta^{18}\text{O}$ of contributing groundwater did not change. This corresponds to an infinite value of V_g in Equation 12.2. In the larger events shown in Figure 12.7, the $\delta^{18}\text{O}$ of streamwater after the event deviated considerably from the pre-event value, reflecting a change in the $\delta^{18}\text{O}$ of the contributing groundwater. The figure shows the flow of groundwater in the stream estimated using variable $\delta^{18}\text{O}$ of groundwater, calculated by Equation 12.2. The inferred change of the $\delta^{18}\text{O}$ of groundwater was obtained by using various reservoir volumes, and the corresponding groundwater flow is shown in the hydrograph together with that obtained using an infinite reservoir volume (constant c_g). For the several spring floods investigated by Rodhe (1987), reservoir volumes around 100-300 mm gave the desired change in groundwater $\delta^{18}\text{O}$. The use of a constant reservoir volume, however, probably gives too slow of a change for c_g in the early part of the events. Regarding the basic relationship between groundwater level and flow, which should cause vertical as well as lateral expansion of the contributing groundwater reservoir as the flow increases, a flow-dependent reservoir volume would probably be more realistic.

Wels et al. (1990) also attempted to calculate the isotopic composition of the groundwater contributing to streamflow during spring snowmelt by Equation 12.2. Three small catchments (0.03-2 km²) on the Canadian Shield were investigated. The granitic-gneissic bedrock in the catchments was covered by sandy glacial till. The most intense study was made in Plastic 1-08, a first order catchment with thin soil cover (<1 m) and no permanent wetland. Streamwater was sampled automatically at 3 or 6 h intervals, depending on the flow intensity. At least daily or bi-daily composite samples of meltwater were collected from 1 m² lysimeters or plastic eaves troughs, installed with different degrees of exposure within the catchments. Soil water samples in Plastic 1-08 were taken bi-weekly from suction lysimeters and daily from a zero-tension lysimeter. Hydrograph separation was performed in time steps of one day, using daily values of c_e , smoothed to an input function (see Figure 12.11 showing data from Plastic 1-08). The peaks in D concentration¹ of the input on March 26 and March 31 were associated with isotopically heavy rainfalls. Figure 12.11 (upper diagram) shows the simulated D concentration of the groundwater component for various finite reservoir volumes in Equation 12.2. The best

¹Wels et al. (1990, 1991) as well as Buttle and Sami (1990), discussed below, give the D content as part per million (ppm). This unit is also used here when presenting their results. The corresponding δ -values are given by: $\delta\text{D} = [(D_{\text{ppm}}/157.6 - 1) \times 1000 (\text{‰})]$ (Buttle and Sami, 1990). A difference of 1.0 ppm thus corresponds to a difference in δD of 6.35 per mil.

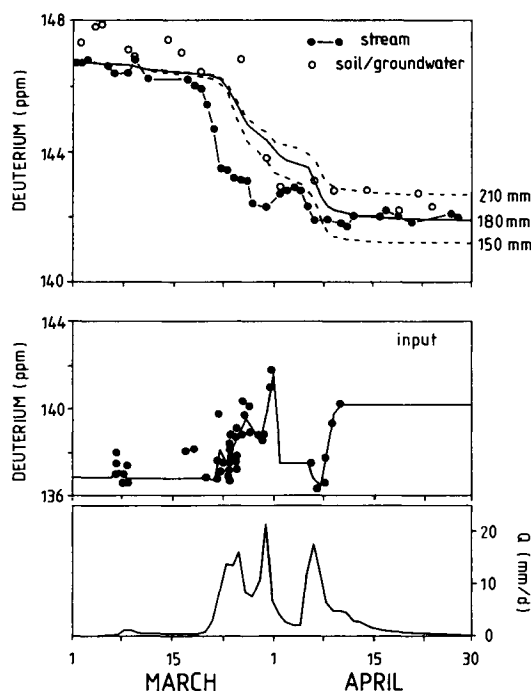


Figure 12.11. Plastic 1-08, Canada (catchment area 0.033 km^2) during spring snowmelt in 1987. Upper diagram: Temporal trends in the D concentration of soil water and groundwater samples, streamwater and of the groundwater component simulated by Equation 12.2 using a model reservoir volume of $180 \pm 30 \text{ mm}$. Middle diagram: D concentration in runoff from three melt plots in (filled circles) assumed D concentration of the new water component (full line). Lower diagram: Stream hydrograph based on daily mean values. After Wels et al. (1990).

fit to the D concentration of post-event streamwater was obtained with a reservoir volume of 180 mm, i.e., with a reservoir volume within the ranges found by Rodhe (1987). The D concentration of soil water samples from the BC horizons (3 locations) showed a temporal trend similar to the modeled values of groundwater, although the soil water was consistently enriched in comparison with the modeled groundwater, also at the onset of the simulations at the start of the event (Figure 12.11). Although the soil water samples clearly do not represent the groundwater contributing to streamflow, the agreement provides some support for the applied model. Due to the assumed gradual recharge of new water in the groundwater, the calculated groundwater fraction and flow differed progressively more from the old water fraction and flow as the events proceeded (Figure 12.12). For the total spring flood (203 mm), the fraction of old water was estimated to be 49% of the discharged volume, whereas the fraction of groundwater was estimated to be 74%.

Direct runoff from saturated areas

A simple interpretation of the isotopic hydrograph separations in terms of catchment processes is to assume that all meltwater and rainwater on recharge areas infiltrates, whereas all such water on discharge areas generates overland flow and is discharged in the stream during the

event (Rodhe, 1987) (cf. the estimates of stream width by Fritz et al., 1976). If evaporation from the surface storage during the event is disregarded, the catchment fraction of discharge area, Y , is given by:

$$Y = \frac{V_e}{V_{wi}} \quad (12.3)$$

where V_e is the discharged volume of new rain- or meltwater and V_{wi} is the volume of the water input to the catchment. The equation gives the area (expressed as fraction of the catchment area) needed for the observed amount of rainwater or snowmelt to generate the flow of rain- and meltwater in the stream as estimated by, for example, Equation 12.1.

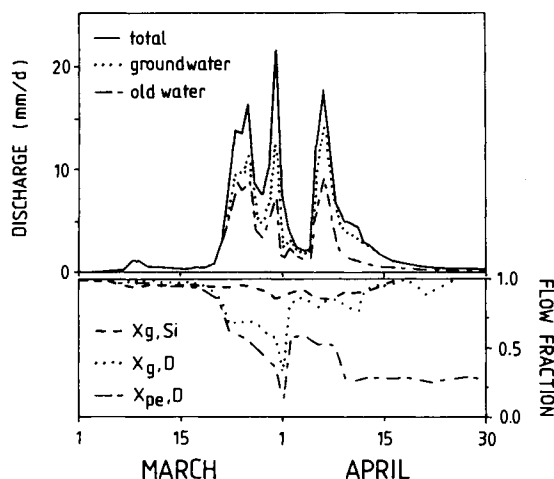


Figure 12.12. Isotopic hydrograph separation of the 1987 spring runoff for Plastic 1-08. Upper diagram: Total stream discharge with contributions of pre-event (old) water and groundwater. The fraction of pre-event (old) water was calculated using a constant D concentration of the pre-event water component. The fraction of groundwater was calculated using a variable D concentration of the groundwater component according to Equation 12.2 and Figure 12.11 (180 mm reservoir). Lower diagram: Fractions of pre-event (old) water $X_{pe,D}$, and groundwater, $X_{g,D}$, giving the flows shown in the upper diagram. Note that the fraction of groundwater is 1.0 at the end of the event by definition. Also shown in the diagram is the fraction of groundwater (subsurface water) as calculated by silica, $X_{g,Si}$, see discussion in a later section. After Wels et al. (1990) and Wels et al. (1991).

Rodhe (1987) applied Equation 12.3 for event totals of V_e and V_{wi} , to determine a quasi-event mean value of Y . Considering that some of the new water in the streamflow may have been discharged as groundwater, Y was also calculated using the volume of overland-flowing new water estimated from the variable $\delta^{18}O$ of groundwater (Equation 12.2), using the best fitting reservoir volume of 250 or 500 mm. The results for a few snowmelt periods were compared with saturated areas determined by field surveys near the dates of spring flood culmination. Saturated areas were defined as areas having water on the ground or having a water table less than about 5 cm below the ground surface. In the smallest catchments, the saturated areas were

determined by mapping. In larger catchments they were determined statistically, from observations at 200-1200 equidistant points along straight lines over the catchments. These estimates should provide upper limits of the extension of saturated areas estimated by Equation 12.3. This is because all saturated areas are not connected to the channel network. Surface stored event water in such isolated saturated areas may infiltrate as the water table falls during periods of streamflow recession. For most of the cases investigated, there was a fair agreement between fractions obtained by ^{18}O and by field surveys (Figure 12.13). The agreement was mostly better when a variable c_g was used, i.e., when attempts were made to estimate the overland flowing water rather than the event water. The values from one of the catchments differ greatly, having a five-times larger saturated area by ^{18}O than was observed in the field. This discrepancy may have been caused by an overestimation of the event fraction of streamwater by ^{18}O , or it may show that the assumed model for streamflow generation is not valid here, for instance due to the occurrence of Hortonian overland flow or rapid transmission of meltwater to the stream by macropore flow. The reasonable agreement for the other events, on the other hand, does not falsify the assumed model for streamflow generation.

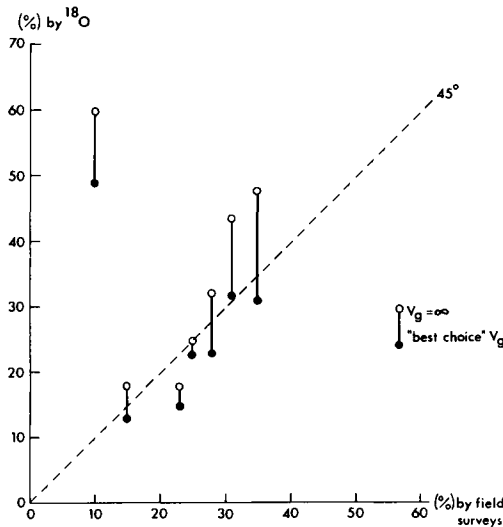


Figure 12.13. Catchment fraction of discharge area estimated by ^{18}O (Equation 12.3) and by field surveys during spring snowmelt in Swedish catchments ($0.03\text{--}7\text{ km}^2$). The “best-choice” value was calculated by using the best fitting model reservoir volume of 250 or 500 mm in Equation 12.2.

Regarding the dynamic nature of the discharge areas within events, the event mean value of Y obtained by event totals of V_e and V_{wi} is poorly defined. A better approach would be to use momentary rates of water input and new water flow in the stream, but in such case one has to take the surface water storage on saturated areas into account. This approach was used by Harris et al. (1995) in a more elaborate model for isotope hydrograph separation, based on mass and isotope balance for three dynamic reservoirs contributing to streamflow: direct precipitation on saturated areas, subsurface water in the near-stream saturated zone, and subsurface water in areas upslope of the near-stream saturated zone. With this model, temporal variations can be accounted for in the isotope content of rainfall or snowmelt within the event.

Sources versus flowpath

The isotopic response of streamwater to the input of new water (rain- or meltwater) to the catchment depends on the flowpaths and velocities of the water molecules from the water input to the ground to the sampling point in the stream. This issue is discussed in detail for rainfall events, in Chapters 10 and 11. The tracer concentration in the stream is the flow weighted mean value of the tracer concentrations of the water that has reached the stream by whatever means. When using environmental tracers in catchment runoff studies, the complex and time variable flow pattern and velocity distribution for water in the catchment has to be replaced by extremely simplified models. In most models discussed in this chapter the flowpaths are replaced by reservoirs with various degree of mixing. For conservative tracers injected uniformly over the catchment area, the input signal is transformed into an output signal only by mixing of water of different ages and thus, possibly, of different tracer concentrations. If the tracer concentrations are known only in the input (rain- or snowmelt) and in the output (streamwater), information might be obtained on transit times and reservoir volumes as discussed in earlier sections. Any conclusion on flowpaths, however, is indirect and based on the assumed model structure. Knowledge about transit times and reservoir volumes is important, for instance as a base for hydrochemical modeling, but these catchment characteristics give little information on the processes involved in streamflow generation.

Isotopic hydrograph separation is somewhat more process oriented than pure input-output considerations. The interpretation of the tracer concentration of the output is based not only on the tracer concentration of the input, but also on the observed tracer concentration of the pre-event water reservoir (from groundwater or stream baseflow). The catchment is still, however, mainly treated as a black box with an unknown interior, although the box has been opened slightly to get the tracer concentration of the pre-event water component.

The equation for two-component hydrograph separation is based on mass conservation for water and the tracer, which yields two equations and two unknowns (the flow of event and pre-event water). With more tracers it may be possible to separate the flow into more components, where the number of possible components is the number of independent tracers plus one. Since ^{18}O and D in precipitation are closely related (as expressed by the meteoric water line) and this relationship remains as long as no fractionation occurs, no extra information is normally obtained by using both instead of one of these isotopes for hydrograph separation. Environmental T may, on the other hand, be used as an independent tracer, but, except for glacier runoff studies (e.g., Behrens et al., 1971) no reports have been found on hydrograph separation based on the combined use of ^{18}O or D and T. Streamflow has been separated into more than two components by a combination of stable isotopes and dissolved chemical compounds, either conservative, such as chloride (e.g., Ogunkoya and Jenkins, 1993) or non-conservative (e.g., Wels et al., 1991, see below).

In vegetated catchments in humid areas, ^{18}O and D can normally be treated as conservative from the water input to the ground to stream runoff (although there are exceptions, cf. Rodhe (1987)). The use of ^{18}O and D in catchment runoff studies normally relies on the conservative behavior of the isotopes, whereas the use of chemical compounds as tracers may rely on their non-conservative properties. Chemical compounds may be taken up by the water through reactions with the soil and bedrock. If the reaction is sufficiently fast there will be a rapid labeling of the water in contact with the mineral soil. Dissolved silica has proved to be a useful tracer in this context for snowmelt studies in some North American catchments (Hooper and

Shoemaker, 1986; Wels et al., 1991; Maulé and Stein, 1990): its concentration in rainwater and meltwater is close to zero, but water having been in contact with mineral soil may have a considerable and fairly constant concentration. If the mineral soil is covered by an organic layer, silica can be used to separate water with subsurface pathways from water that has flown only on the ground surface or in the organic layer. Such a separation is important for the understanding of acidification processes, because the contact with mineral soil also determines the possibilities for neutralizing weathering reactions. It must be emphasized, however, as pointed out by Hooper and Shoemaker (1986), that dissolved silica is subject to biological processes and may be less suited as a tracer in other environments due to, among other things, uptake by diatoms.

Snowmelt hydrograph separations by isotopes and by suitable chemicals thus give different and complementary information. Isotopes trace the sources of water whereas chemicals trace the flowpaths of water (Wels et al., 1991). Because the use of stable isotopes is based on the temporal variation of the tracer concentration of the input, the isotopes also give a time aspect, such as event/pre-event water or information on the transit times for water and thereby on reservoir volumes (see discussion in Chapter 10). Although the isotope concentration of water is not directly related to the flowpaths, identification of various "sources" within the catchment with characteristic isotope concentrations may elucidate the flowpaths. Such sources may, for instance, be deep groundwater or soil water in the vicinity of the discharge area.

By using both isotopes and silica, three components of streamflow can be distinguished (modified from Maulé and Stein, 1990) as illustrated in Figure 12.14:

1. New surface water, having only been in contact with organic soils.
2. New subsurface water, having infiltrated during the event.
3. Old subsurface water, existing in the ground before the event.

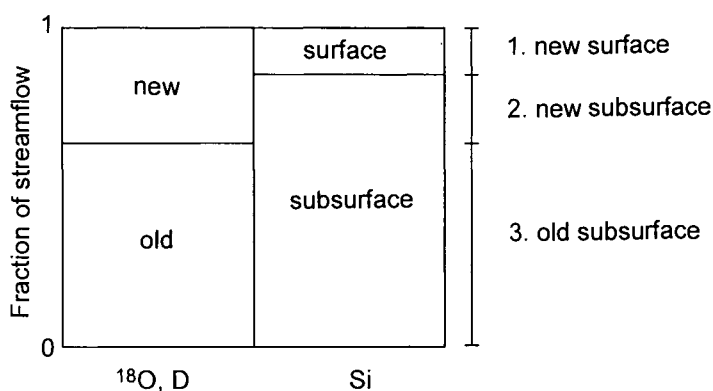


Figure 12.14. Separation of streamwater into three components by simultaneous use of ^{18}O or D and Si.

Subsurface water is here defined as water that has passed through the mineral soil. It may reach the stream directly or as overland flow and flow in the organic layer in the discharge area. There exists a fourth possibility, old surface water, i.e., old water that has never been in contact

with the mineral soil. Because wetlands normally occur in discharge areas, their water tend to be groundwater discharged from the mineral soil and thus “old subsurface water”. Water stored in or on organic soils in recharge areas, i.e., in ombrogenic bogs, would belong to the fourth category, but such water would probably have a different isotopic signature than other old water and thus prevent accurate two-component separation by isotopes.

The study by Wels et al. (1991), based on the same springmelt period as the one discussed above in connection with the variable isotope content of the groundwater component (Figure 12.12), gives instructive information on the use of silica for hydrograph separation. Plastic 1-08, which contains no permanent wetland, is a subcatchment to Plastic 1 which contains a large conifer-sphagnum swamp, to which four fifths of the catchment area is drained. The temporal trends of silica concentration of streamwater during the snowmelt period of 1987 differed largely between Plastic 1 and its subcatchment Plastic 1-08 (Figure 12.15). The fact that the silica concentration in Plastic 1-08 was about the same before and after the event indicates a constant value for the silica of groundwater, which is a prerequisite for chemical hydrograph separation. There was a gradual increase in Si at the end of the runoff event, ascribed by the authors to longer transit times for the water in the ground and/or increased weathering rates with increasing soil temperature. This increase in Si, however, had little influence on the analysis of the main runoff period. The initially high Si value from Plastic 1 and the large decrease over the snowmelt period was considered to be a result of seasonal uptake of silica by diatoms in the swamp between the two sampling points, making the swamp act as a source of silica during winter baseflow and as a sink during the later parts of the snowmelt runoff period. Similar behavior of Si was observed in the nearby Harp-5, which also contains several wetland areas. Due to the uptake and release of dissolved silica in the wetlands of Plastic 1-08 and Harp-5, silica could be used as a tracer only in Plastic 1-08, which contains no permanent wetlands. For separations in Harp-5, magnesium was used as a chemical tracer, but these separations are not discussed further here.

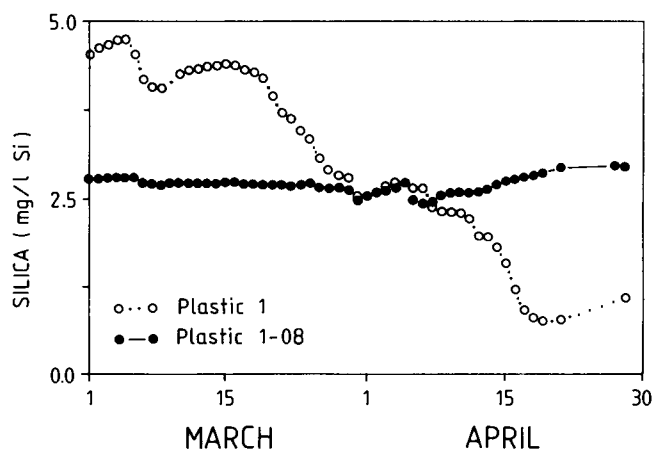


Figure 12.15. Temporal trends of silica in Plastic 1 and Plastic 1-08 during spring runoff 1987. Plastic 1-08 (0.03 km²) is a sub-catchment to Plastic 1 (0.23 km²) and the two sampling points are separated by a swamp. After Wels et al. (1991).

The silica concentration of pre-melt streamwater in Plastic 1-08 (2.6 mg/l) was lower than the observed concentration in soil water of the deeper mineral horizons in the catchment, which remained fairly constant around 3.0 mg/l during the melting period. It was, on the other hand, considerably higher than the concentration observed in the superficial organic layers during melting, being around 0.8 mg/l. For the hydrograph separations, the concentration of the groundwater component was assumed equal to that of the pre-melt streamwater. The concentration of the overland-flow component was assumed to be 0.3 mg/l, representing a value between the Si of precipitation (0.0 mg/l) reaching the stream directly and the Si of water in the top organic soil layers. The overland flow component thus included water flowing through these organic layers. Due to the large difference between the assumed Si of groundwater and overland-flowing water, the calculated groundwater fractions were not very sensitive to the uncertainties in the Si of these components.

A prerequisite for the separation by Si is that the infiltrated water rapidly obtains an equilibrium value, so that the Si of the discharging groundwater is independent of the transit time in the ground. The near constancy of the baseflow Si, shown in Figure 12.15, is one indication that this condition is fulfilled. A comparison of the temporal trends of Si and D of water in the deep mineral horizon illuminates the principal difference between these two tracers (Figure 12.16) and supports the assumption of constant Si of the groundwater component. The samples were taken from two freely draining lysimeters having a flow rate of several liters per day during the period of intense melting. Whereas the D concentration of soil water decreased as the old water was mixed with isotopically depleted meltwater, the Si concentration remained almost constant, indicating a fast equilibrium reaction. The finding that the Si concentration was independent of the flow further supports this conclusion. Rapid dissolution of silica from the soil was also shown in laboratory experiments (Wels et al., 1991).

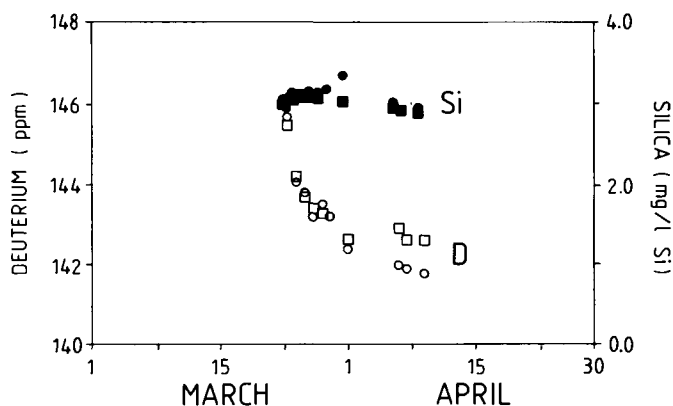


Figure 12.16. Temporal trends of Si (solid symbols) and D (open symbols) of soil water from two zero-tension lysimeter pans in the Bf₂-horizon (circles and squares refer to samples from the different lysimeter pans). Plastic 1-08, snowmelt 1987. After Wels et al. (1991).

Figure 12.12, lower diagram, compares the chemical and isotope hydrograph separations in Plastic 1-08. Both the separation by Si (marked by X_g, Si) and the one by D using a variable D concentration of the groundwater component (X_g, D) are intended to give the groundwater

fraction. In spite of this, there was a considerable difference between the two separations, particularly during the first melting period. The smaller groundwater fractions obtained by the isotopes were probably a result of a simulated change in c_g that was too slow in the early stage of the event when using Equation 12.2 with a constant reservoir volume (cf. discussion above). For the total melting period, with a total runoff of about 200 mm, the volume fraction of subsurface flow by Si and by D was 91 and 74% respectively. Almost identical results were obtained in the Harp-5 catchment, in which Mg was used as a chemical tracer instead of Si. Wels et al. (1991) discussed their findings in relation to a few other studies using both chemical and isotope tracers and concluded that there were no systematic differences between the isotopic and chemical hydrograph separations. The chemical separations could give higher groundwater fractions (Wels et al., 1991; Fritz et al., 1976), equal (Hooper and Shoemaker, 1986) or smaller groundwater fractions (Fritz et al., 1976; Kennedy et al., 1986). It has to be noted, however, that such comparisons could be misleading since the definitions of the flow components may not be identical.

Catchments with permafrost

The snowmelt runoff studies discussed so far were all performed in cold temperate climates where the soil thaws completely during the springmelt. There are a few reports of isotope studies on runoff in arctic catchments with permafrost. In such areas, the soil may thaw during summer down to a depth of several dm, below which level the ground is perennially frozen (down to a certain depth). Obradovic and Sklash (1986) used ^{18}O and major ions to investigate a springmelt period in a 60 km² catchment with permafrost on Baffin Island in Northeastern Canada and Gibson et al. (1993) made a similar study in a small catchment in Northwestern Canada, in the zone of discontinuous permafrost. Cooper et al. (1991) studied the transport of various fallout radionuclides and, by means of a limited data set on ^{18}O , the transport of water during snowmelt in the 2.2 km² Innovate Creek catchment in the tundra of Northern Alaska (discussed in Chapter 4). In a follow-up study (Cooper et al., 1993) a later year's snowmelt in the catchment was analyzed with more detailed ^{18}O observations. Unfortunately all these studies lack systematic measurements of the $\delta^{18}\text{O}$ of meltwater, which instead was assumed equal to that of the snowpack. As commented upon above, this assumption is rough and results in uncertain conclusions. Cooper et al. used the δ -value of the snowpack before melting for the event water component. The other two studies also used constant $\delta^{18}\text{O}$ of the event water, but it is not clear from which time the snow samples were taken.

Cooper et al. (1991) found that the $\delta^{18}\text{O}$ of streamwater at peakflow (-25.0‰) was very similar to that of pre-melt snowpack (-25.9‰) and concluded that the runoff was mainly meltwater. In the more detailed study (Cooper et al., 1993) it was found that the $\delta^{18}\text{O}$ of streamwater increased from -30.3‰ (which was below the pre-melt snowpack value of $-27.6 \pm 1.6\text{‰}$) to -22.5‰ at the end of the melting period. With an assumed $\delta^{18}\text{O}$ of the pre-event component of about -20‰, hydrograph separation based on the mean $\delta^{18}\text{O}$ of the snowpack would, apart from the undefined values at the early snowmelt, have given a considerable pre-event water component in streamflow. Such a contribution of pre-event water was, however, not considered possible by the authors, because the mineral soil and its organic top layer were frozen throughout the melting period. According to earlier experiences, the high ice content of the soil should exclude any meltwater infiltration and mixing with the soil water. The authors concluded that the increase of streamwater $\delta^{18}\text{O}$ throughout the event was not caused by a growing contribution of soil water, but by a gradual increase in the $\delta^{18}\text{O}$ of the meltwater due to fractionation during melting and molecular exchange with the atmosphere.

The ^{18}O data of the two other permafrost studies were, on the other hand, interpreted in terms of traditional two-component isotope hydrograph separation and the results conform with the results of most other such studies of snowmelt runoff. With a $\delta^{18}\text{O}$ of the pre-event component determined from stream baseflow samples, the isotope data gave a pre-event water contribution to streamflow of about 50% during peakflow and of 60-75% for the total volume discharged during the snowmelt periods. These sites differed from that of Cooper et al. in that the active layer thawed during snowmelt. According to Obradovic and Sklash (1986) this gradual thawing would make it possible for an increasing amount of meltwater to infiltrate and generate outflow of pre-event soil water transformed into groundwater. In the small catchment investigated by Gibson et al. (1993) permafrost was mainly restricted to northfacing slopes. The southfacing slopes were not considered to contribute to streamflow during the investigated spring melt because the snow on these slopes had melted earlier, the groundwater was deep (>3.4 m below the ground surface) and no overland flow was observed. In the permafrost slopes a shallow active layer (0.15 m) was developed in which the water table rose to the ground surface resulting in overland flow and pipe flow, i.e., flow in large frost cracks situated at or above the contact between the mineral soil and the organic layer. According to a few isotope data on overland flow and pipe flow there was a considerable mixing between meltwater and pre-event water in the active layer, with about half of both pipe flow and overland flow being old water. When these saturated superficial flows ceased, the isotopic composition of streamwater rapidly returned to the pre-event value.

12.3 Vertical Unsaturated Flow

The seasonal variation in the ^{18}O and D content of precipitation, normally very prominent in areas with seasonal snowcover, makes it possible to trace the vertical flow of water in the unsaturated zone. Spring snowmelt generates a large input of isotopically depleted water to the soil. If the unsaturated zone is sufficiently deep, meltwater can be found as a depleted layer of soil water. By following the downward movement of the depleted layer, and the seasonal variation in general, information can be obtained on the rate of groundwater recharge as well the particle velocity and the flow pattern during percolation. The isotope content of soil water is also an important factor in isotopic hydrograph separations, as it may influence the isotope content of the pre-event component of streamflow. Such an influence may introduce uncertainty into the separation, but it may also give information of soil water as a source for the flow.

One important question concerning the flow pattern in the unsaturated zone is whether the flow occurs as piston flow or along preferential flowpaths. In piston flow the water in consecutive layers is successively displaced downwards while keeping the internal order between the water layers. Due to a random variability in the mean velocities of the water molecules, as seen in a macroscale, there will be a certain degree of mixing between water in nearby layers. Together with molecular diffusion this mixing causes a dispersion of tracer signals and makes them more diffuse. Piston flow of soil water is, to a larger or lesser degree, always connected with such a dispersion. Flow along preferential flowpaths may occur in the soil under certain conditions, for instance in the presence of waterfilled macropores (Beven and Germann, 1982) or in the case of fingering due to unstable flow in profiles where a fine-textured layer overlies a coarse-textured soil layer (Hillel, 1987). In such cases, some water molecules will obtain considerably larger mean velocities than other molecules at the same level, and there will be a large, spatially discontinuous, dispersion of the tracer signal.

Another question concerns the amount of immobile water in the soil, i.e., water that is held in thin films around the soil particles or in very small pores (De Smedt and Wirenga, 1984) and which does not participate in the flow. Such water may constitute up to 50% of the total water content in very fine grained soils (Gvirtzman and Magaritz, 1986) but the fraction is considerably smaller in sandy soils. Molecular exchange between mobile and immobile water tends to increase the dispersion and retardation of hydrological tracers.

12.3.1 Estimates of groundwater recharge and particle velocity

Groundwater recharge and particle velocity for the percolating water was estimated by Saxena (1987) by tracing the vertical displacement velocity of the seasonal ^{18}O variation of precipitation in the unsaturated zone. The studies were performed at forested sites on glaciofluvial sand and glacial till in southern Sweden. Soil samples were taken at 0.1 m intervals down to 2-4 m depth by coring (in sand) or from the walls of pits (in glacial till). Water for isotope analysis was extracted by distillation. From sampling at one occasion only, rough estimates of the downward displacement velocity could be made, provided that the seasonal variation could be identified in the profile. For a more detailed analysis of the movement, profiles taken over a few month's interval were analyzed. Figure 12.17 shows two profiles in glaciofluvial sand in Uppsala. The first one was taken shortly after snowmelt, and the second one about half a year later. Monthly $\delta^{18}\text{O}$ -values of the precipitation are also shown for comparison. The seasonal variation of precipitation $\delta^{18}\text{O}$, with low values in winter and high values in summer, can be traced in the soil water, although the variation is damped. Looking at the first profile only, the snowmelt of 1981 can be found at about 2.3 m depth and that of 1982 at about 0.6 m, giving a particle velocity of the water about 1.7 m/year. Assuming that all soil water enclosed between the two depths passed through the upper level during the identified time period (in this case one year) and that no part of this water passed through the lower level, the rate of percolation, R , from the time period is given by:

$$R = \frac{\int_{z_1}^{z_2} \theta(z) dz}{t_2 - t_1} \quad (12.4)$$

where θ is the volumetric soil moisture content at a certain time and z_1 and z_2 are the depths of the water infiltrated at time t_1 and t_2 respectively. The average soil water content between the levels, determined gravimetrically from the soil water samples, was 17 percent. Equation 12.4 gives a percolation of 280 mm/year. This value falls within the range of expected annual groundwater recharge in the area. By comparing the two profiles, a similar simple analysis gives a particle velocity from May to December corresponding to about 1.6 m/year. It is to be noted that the particle velocity is the velocity of the water molecules (as seen in a macro scale), i.e., the velocity by which a perfect tracer would be transported with the water. The flow propagation velocity, i.e., the velocity determining the response of the water flow at depth and the rise of the groundwater table to the water input, is considerably larger.

Large spatial variations in the particle velocity of the percolating meltwater were found by Bengtsson et al. (1991) from the temporal trends of the $\delta^{18}\text{O}$ of soil water and groundwater during a spring snowmelt period in Teeressuonoja forested catchment in southern Finland. At the beginning of the melting period, the meltwater, collected in a 1 m² snow lysimeter, was

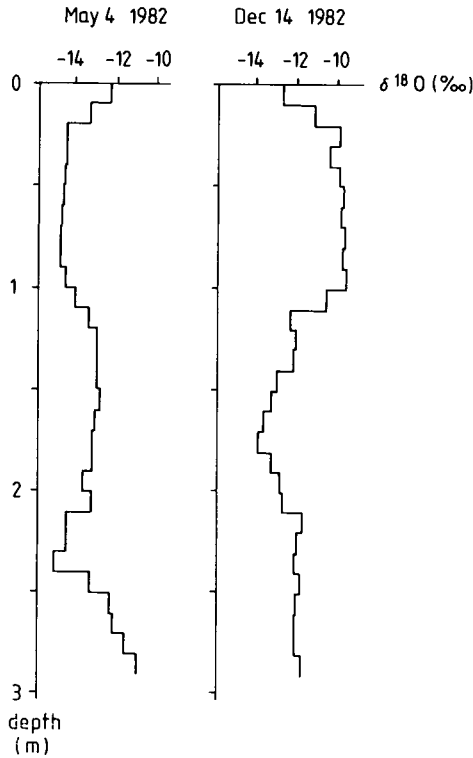


Figure 12.17. $\delta^{18}\text{O}$ of soil water in a glaciofluvial sand profile in Uppsala, Sweden, on two occasions. After Saxena (1987).

depleted in ^{18}O by about 7‰ δ -units as compared to the pre-melt soil water and groundwater, a difference that gradually disappeared as the melting proceeded. The most rapid response in the $\delta^{18}\text{O}$ of soil water was observed in a gravel formation near the water divide. In this recharge area, soil water at 1.1 m depth obtained the δ -value of meltwater in a few days, corresponding to particle velocities of a few dm per day. At a site in a sandy soil close to the stream, the arrival of the isotope signal from the meltwater to the 0.3 m sampling depth indicated particle velocities of only a few cm per day.

12.3.2 Piston flow versus macropore flow

Percolation estimates by Equation 12.4 presuppose that the vertical movement takes place by piston flow. Dispersion is not problematic as long as the tracer signal can be identified. If there is flow through preferential flowpaths, however, the equation may underestimate as well as overestimate the percolation. Some of the water molecules enclosed between the two springmelt peaks may have originated from later infiltration and have passed through the upper depleted layer by preferential flow, a condition which will tend to overestimate the percolation. In a similar way, molecules from the enclosed year that have passed the lower depleted layer

will result in underestimates. If there is immobile water in the profile, the water content in the equation should be accordingly reduced and the resulting estimated amount of percolation would be smaller.

Indications of immobile water and macropore flow in the unsaturated zone during snowmelt were found by Buttle and Sami (1990) in an isotope study on the Perch Lake watershed, Ontario, Canada. The mixing of snowpack drainage water (snowmelt and rain on snow) with soil water in the top meter of a glaciofluvial fine sand was investigated using the D content of collected drainage water, supplemented with D values of the snowpack, and the D content of soil water, sampled in 5 cm depth intervals. Profiles were taken daily during the early part of the melting period and later with intervals of 2-3 days, allowing a more detailed study of soil water recharge than the more extensive study by Saxena (1987). The gradual filling of the soil profile with newly infiltrated melt- and rainwater can be seen by comparing the rates and D content of the water input with the temporal trends of soil water content and D values shown in Figure 12.18 a and b. Due to input of isotopically depleted water, the D concentration in the top layers decreased until March 29. After this date the D concentration of the input water increased, giving an increase in the D concentration in the top layers. The D concentration of the deeper layers remained essentially unaffected by the depleted input water until March 26, although the water content increased, indicating that the increased water content was a result of the downward displacement of pre-melt soil water. The downward propagation of the tracer signal from the early drainage water (D concentration <138.0 ppm), reaching a depth of 0.85 m by April 6, gave an average water particle velocity of 5.4 cm/day. Similar considerations for the isotopically heavier water infiltrating from March 31, when the soil profile was wetter, gave an average water particle velocity of 8.6 cm/day. These particle velocities are much larger than those obtained by Saxena, corresponding to about 0.5 cm/day. Qualitatively the difference is expected, because the latter refer to percolation below the root zone and were calculated as mean values over long periods, which most probably included periods with very little percolation.

From an analysis of the vertical flow of pre-event water through various levels, based on a two-component mixing model similar to Equation 12.1, Buttle and Sami concluded that 11-19 percent of the pre-event water in the profile was immobile. This finding was used in a further analysis, in which a piston-flow model based on water and tracer budgets for 5 cm layers of the soil was used to simulate the temporal development of the D profiles from a known initial condition. Input data were the observed water and tracer input to the profile and the temporal trend of the observed water content at various levels. The general form of the simulated D profiles agreed well with observations, but during the early days of snowmelt, the simulated profile overestimated the D content in the upper 0.5 m of the profile (Figure 12.19). The isotopically depleted meltwater seemed to have progressed more effectively downwards in the real profile than was simulated by the piston-flow model. The authors ascribed this difference to the occurrence of macropore flow, by which some of the meltwater was assumed to bypass the near-surface soil matrix and diffuse into the surrounding soil further down in the profile. A similar conclusion was drawn by Bengtsson et al. (1991) in the Teeressuonoja study, which was discussed in the preceding section. At one of their sites, where the soil was mostly silt and clay, the particle velocity inferred from the ^{18}O response in the soil water to the meltwater input exceeded the one estimated from the observed hydraulic conductivity and the porosity by an order of magnitude. The difference was interpreted by the authors as an indication of macropore flow.

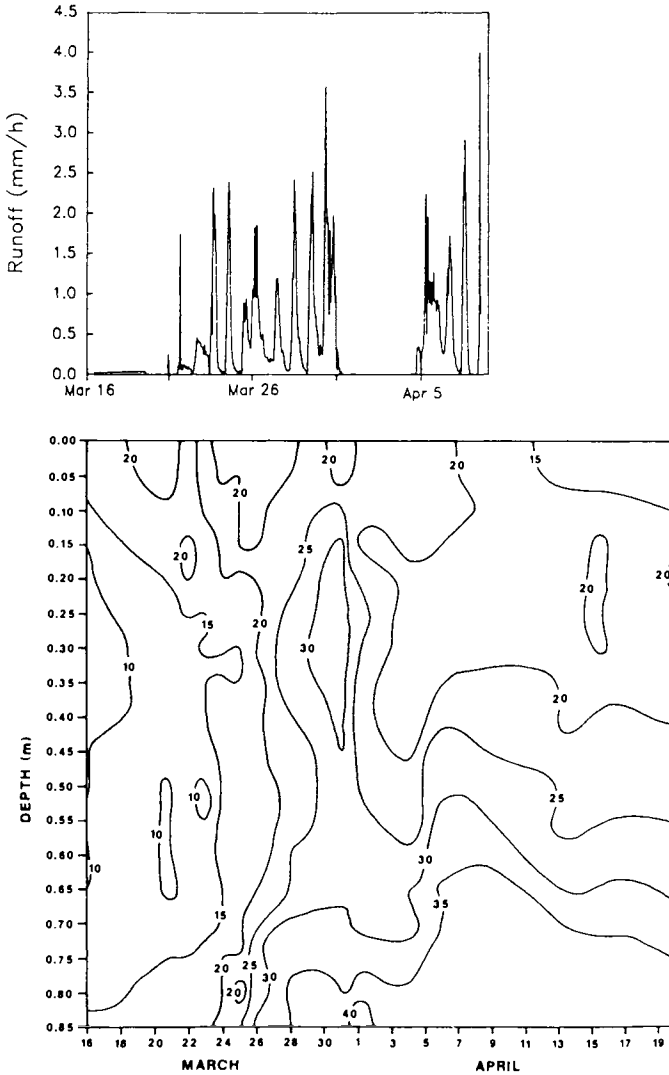


Figure 12.18a. Upper diagram: Snowpack drainage (snowmelt and rain on snow), observed as runoff from a lined plot (snow lysimeter). Lower diagram: Distribution of soil water in a glaciofluvial fine sand profile (% by volume). Perch Lake watershed, Canada, 1987. After Buttle and Sami (1990).

12.3.3 Transit times and flow pattern from lysimeter studies

In the above studies, the temporal trends in the isotope content of the water input to the soil, notably the depleted meltwater signal, were used to interpret profiles of the isotope content of soil water and their changes over time. Another approach is to analyze the temporal trend of the isotope content of the water percolating through a certain layer. A well preserved ^{18}O signal, indicating piston flow below 15 cm depth, was found in a lysimeter study in a Swedish catch-

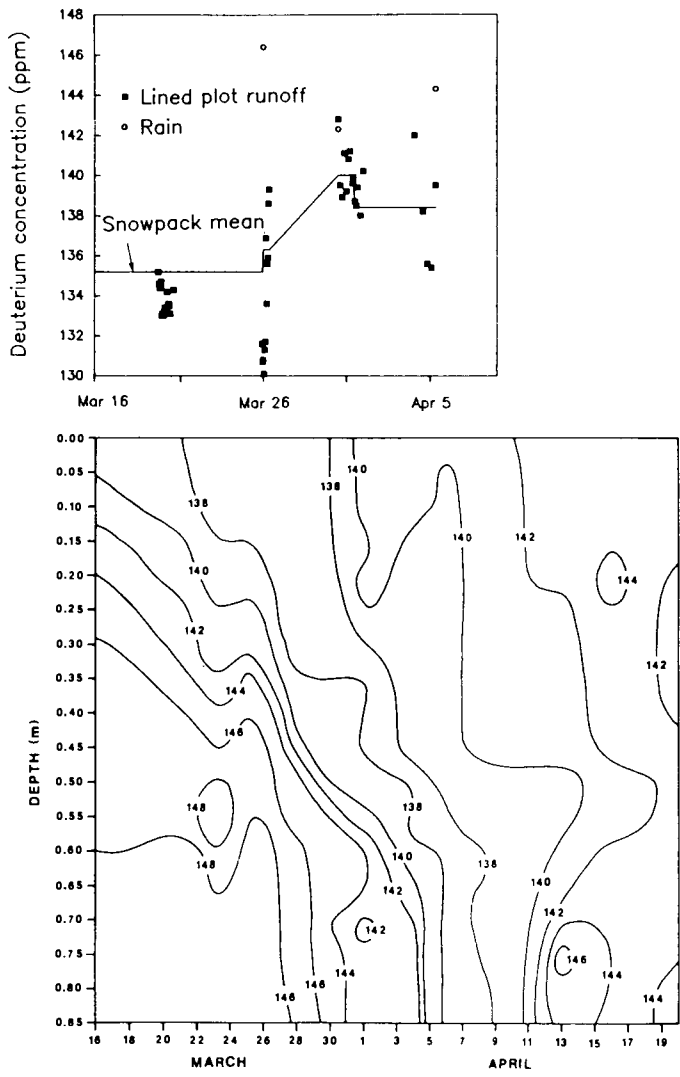


Figure 12.18b. Upper diagram: D concentration of snowpack drainage for selected periods, D concentration of rainfall, and snowpack mean D concentration throughout the melt. Lower diagram: Distribution of D concentration of soil water (ppm) in the profile. Perch Lake watershed, Canada, 1987. After Buttle and Sami (1990).

ment (Rodhe et al., 1988). Integrated drainage samples were collected from two groups of freely draining soil lysimeters of 20 cm diameter, intended to represent undisturbed columns of sandy-silty till soil, with depths 15, 40 and 85 cm. The lysimeters were installed at a forest site, with the vegetated tops at the ground level. Treating samples from the lysimeters of different depths as samples from different levels of a single lysimeter, a simple analysis of the downward tracer movement could be carried out. After a considerable damping of the scattered ^{18}O signal of the daily precipitation and snowmelt in the uppermost layer (which in part resulted

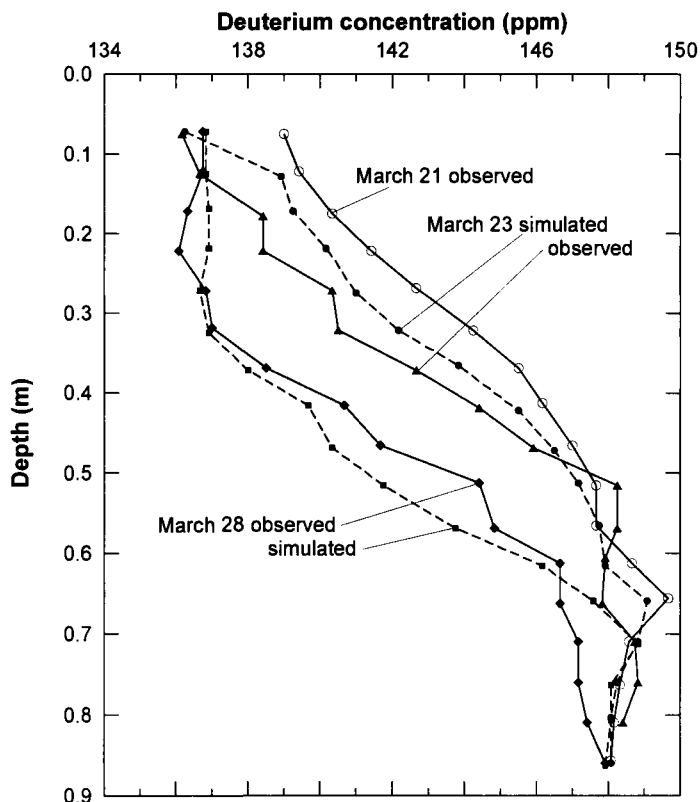


Figure 12.19. Observed and simulated D profiles during the initial phase of the snowmelt period shown in Figures 12.18a and 12.18b. The observed D and soil moisture profiles of March 21 were used as initial conditions for the simulations and 16% of the water held at a given depth at this date was assumed to be immobile and to retain its D concentration. The D concentration of the infiltrating water was 135.2–136.3 ppm. After Buttle and Sami (1990).

from the sampling, which integrated the drainage over periods from one day to about two weeks), the ^{18}O signal was displaced downwards undergoing only moderate changes (Figure 12.20). The time lag between the two curves, ranging from about 2 to 6 months, corresponds to particle velocities between 1 and 0.4 cm per day. Since the flow varied over time, in response to rainfall, snowmelt and evapotranspiration, the signal was better preserved when the $\delta^{18}\text{O}$ was plotted against the observed accumulated drainage instead of against time. In Figure 12.21 such curves have been roughly fitted by adding a start volume (150 mm) to the accumulated volume of the 15 cm lysimeter. The good fit indicates that the flow between the levels were dominated by piston flow. The volume that had to be added to the 15 cm curve can be seen as the displacement volume, i.e., the soil water volume participating in the flow between the two levels. It corresponds to a volumetric water content of 23%. The amount of immobile water in the profile would have been given by the difference between the observed water content and the volume displacement. The water content was estimated from in situ weighings of the lysimeters, but the accuracy was too low to allow safe conclusions on the occurrence and amount of immobile water.

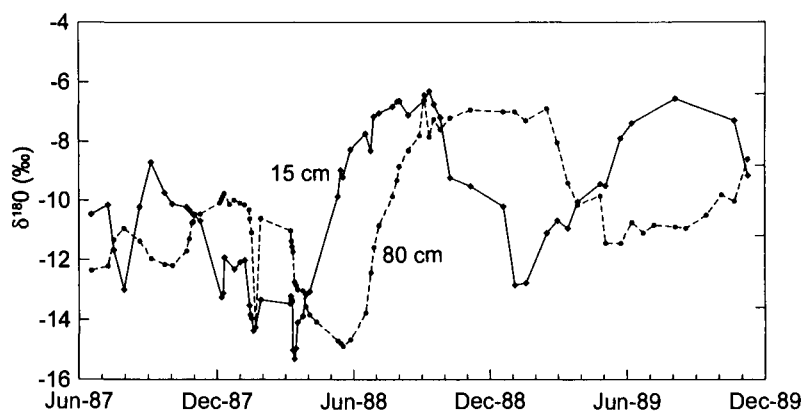


Figure 12.20. $\delta^{18}\text{O}$ of drainage from two freely draining lysimeters with sandy-silty till soil, 15 and 80 cm deep, versus time. Stubbetorp, Sweden. (Observed amount and $\delta^{18}\text{O}$ of daily precipitation and computed water equivalent of the snowpack are shown in Figure 12.22).

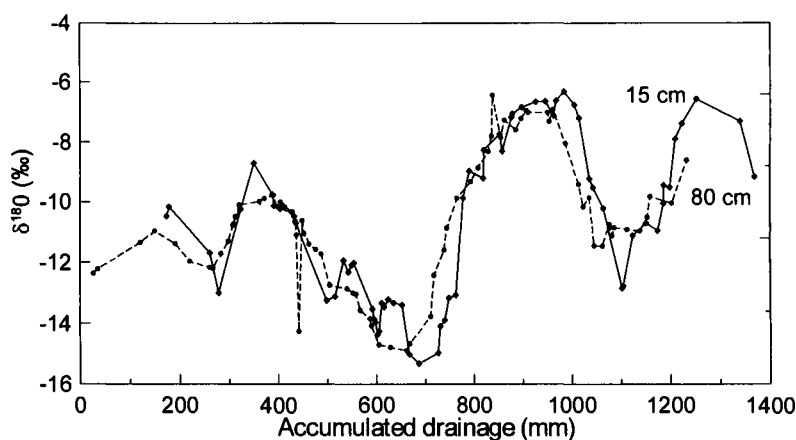


Figure 12.21. $\delta^{18}\text{O}$ of drainage from the lysimeters in Figure 12.20 versus accumulated drainage. The two curves have been fitted by the addition of a start volume of 150 mm to the drainage of the shallow lysimeter.

Flow through preferential flowpaths should have been reflected by a rapid transmission of the ^{18}O signal through the lysimeters. On a few occasions there were indications of such a rapid response, reflected in simultaneous peaks in the $\delta^{18}\text{O}$ of the lysimeters. In the example shown in Figure 12.20, negative peaks can be seen in both lysimeters in connection with snowmelt in February, 1988.

The ^{18}O flow through the Stubbetorp lysimeters was also analyzed by Lindström and Rodhe (1992) using a part of the PULSE model (Bergström, 1992), which is a rainfall runoff water balance model with simple hydrochemical subroutines. The amount and $\delta^{18}\text{O}$ of the lysimeter drainage was simulated from the daily amounts and $\delta^{18}\text{O}$ of precipitation and monthly values

of potential evapotranspiration. Air temperature was used to calculate snow accumulation and melt. The soil water routine was based on water budgets of 1-3 layers in the three lysimeters, with assumptions of either ideal mixing or piston flow within each layer. ^{18}O was assumed to be a perfectly conservative tracer, i.e., any isotope changes in the soil water and in the snowpack due to molecular exchange with the atmosphere were disregarded. The ^{18}O content of meltwater was further assumed equal to the calculated ^{18}O content of the snowpack at any moment. The best fit between observed and simulated $\delta^{18}\text{O}$ of the drainage was obtained when ideal mixing was assumed in the upper 15 cm, followed by either ideal mixing or piston flow in the 15-40 cm layer and piston flow in the 40-80 cm layer (see calculations for the 15 cm lysimeter in Figure 12.22 for an example). In order to estimate transit times of water in the lysimeters, the age of the water was set equal to zero at the moment of infiltration. In the model for ideal mixing, only the mean age in each reservoir could be calculated, but with the piston flow model it was possible to keep track of the age of each water pulse (daily input to the soil) during the flow through the profile. By treating age as a conservative property, the average age resulting from mixing of various water volumes was calculated by weighting the ages with respect to volume. The average transit time of the discharging water, which varied from day to day, was then obtained as the mean age of the discharge on that day. The simulated average transit time for the 80 cm lysimeter ranged from 2.5 to 5 months, corresponding to mean particle velocities ranging between 1.1 and 0.5 cm/day (Figure 12.23). The most important model parameter in determining the ^{18}O response was the field capacity, which to a large degree determined the water content of each layer and thus the calculated transit time. The finding that the ^{18}O flow could be simulated using complete mixing and piston flow suggests that preferential flow was not important in these lysimeters. This conclusion may be relevant for the restricted scale of the lysimeters, although preferential flow in these soil profiles may be important on a larger scale. It must also be emphasized that structures that permit macropore flow might have been destroyed in the preparation of the lysimeters. It should also be noted that although the lysimeters, as was the case here, are placed at a natural site, their hydrological conditions differ considerably from natural conditions. In this case, the water content at a certain depth was, in general, higher than in the surrounding soil. This was because a temporary saturation in the bottom of the lysimeters had to build up before water could be drained. Furthermore there were, of course, no trees but only forest ground vegetation in the lysimeters, which resulted in a comparatively small water loss by evapotranspiration.

12.3.4 Flow pattern in two and three dimensions

In the above studies the seasonal variation of the ^{18}O content of precipitation, with the depleted snowmelt water as an important component, was traced in the unsaturated zone and interpreted in terms of one dimensional vertical flow. For flow in hillslopes with shallow water tables, the interpretation of the stable isotope content of the soil water is more difficult because the flow pattern has to be treated in two dimensions. As a result of time changes of the water content and the depth to the water table, the flow at a certain point in the unsaturated zone may be either vertical or lateral (Harr, 1977; Johansson, 1985). Changes from unsaturated to saturated conditions, due to temporary water table rise may further accentuate the variations in velocity (speed and direction). The result is irregular flowpaths and a large and probably unpredictable mixing. If there are high conductive layers or large continuous pores in the saturated zone, preferential flow will occur which will further increase the dispersion of the tracer signal. As noted earlier, snowmelt events may be more suitable for isotope studies than rainfall events,

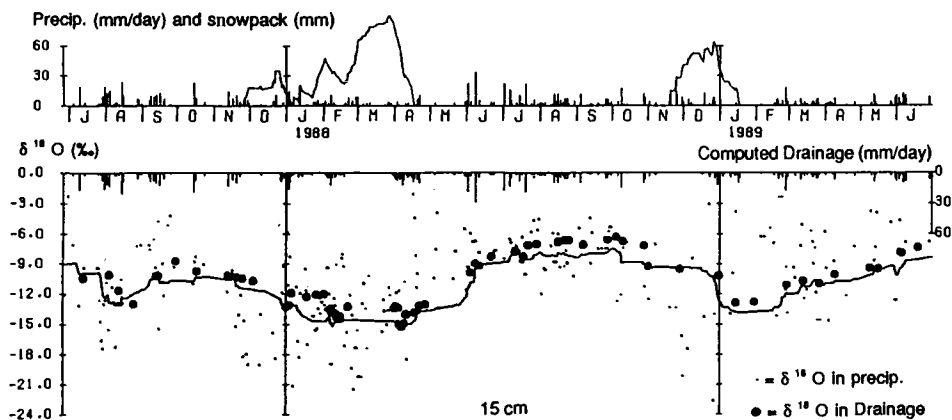


Figure 12.22. $\delta^{18}\text{O}$ simulation of the drainage from the 15 cm lysimeter in Stubbetorp, Sweden (cf. Figures 12.20 and 12.21), assuming ideal mixing in the soil layer. Upper diagram: daily precipitation and calculated water equivalent of the snowpack. Lower diagram: continuous curve = simulated $\delta^{18}\text{O}$ of the drainage, small dots = observed $\delta^{18}\text{O}$ of precipitation, and large dots = observed $\delta^{18}\text{O}$ of the drainage. After Lindström and Rodhe (1992).

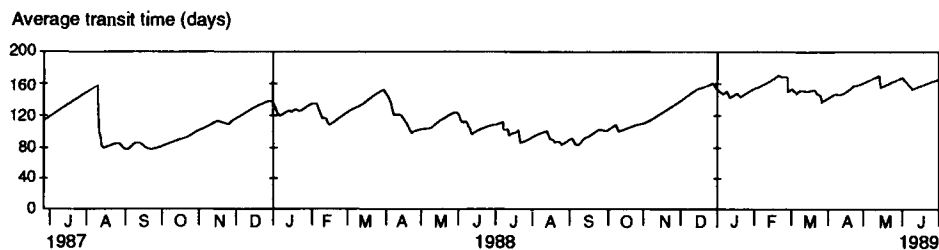


Figure 12.23. Average transit time for the drainage from the 80 cm lysimeter in Stubbetorp, Sweden, according to simulations with the PULSE-model. After Lindström and Rodhe (1992).

because the snowmelt often gives a large input of water with consistently low and comparatively constant ^{18}O and D content. Such a signal could, theoretically, be used to elucidate the two-dimensional flowpaths of the meltwater in a hillslope until enriched summer precipitation starts to complicate the signal. No such study has, however, been found in the literature. Bishop (1991) presented a cross-section of $\delta^{18}\text{O}$ in the unsaturated and saturated zones along the lower 50 m of a till hillslope in northern Sweden during a summer period. The groundwater table was 0.2–0.5 m below the ground surface during the study period and water was sampled down to about 2 m depth. The vertical stratification of $\delta^{18}\text{O}$, with depleted and comparatively homogeneous δ -values below 0.6 m and above this level increasing δ -values towards the ground surface, was similar along the hillslope. Together with data on hydraulic potentials and hydraulic conductivity, the ^{18}O profiles were used for estimates of the $\delta^{18}\text{O}$ of the groundwater contribution to streamflow from the hillslope. The absence of systematic variations in the ^{18}O profiles along the hillslope, however, prevented a two-dimensional analysis of the flowpaths.

A prolonged isotopic signal, somewhat similar to that of snowmelt but of isotopically enriched water, was obtained as a result of irrigation of a small catchment in a reversed acidification experiment (Nyberg, 1995). The 0.63 ha till catchment on the Swedish West-coast was covered by a roof and irrigated by chemically adjusted water from a nearby lake, which was enriched in $\delta^{18}\text{O}$ by about 2‰ compared to the water in the catchment at the onset of irrigation. The gradual exchange of water in the catchment was reflected by a gradual change in the isotope content of runoff towards that of the irrigation water (new water) (Figure 12.24). The soil cover in the catchment is thin (mean thickness 0.4 m), preventing a simple analysis of the vertical penetration of the enriched irrigation water into the soil profiles. The signal was, however, reflected in an areal pattern of $\delta^{18}\text{O}$ of soil water and groundwater which could be related to expected flowpaths of water. An example of two sites with different responses to the new water input is given in Figure 12.24. The most rapid isotopic adjustment to the new water was seen in the flanks and the steep sideslopes (Ly3) and the slowest in the discharge area in the valley bottom, where the $\delta^{18}\text{O}$ of soil water and groundwater consistently was close to that of catchment runoff (Ly2).

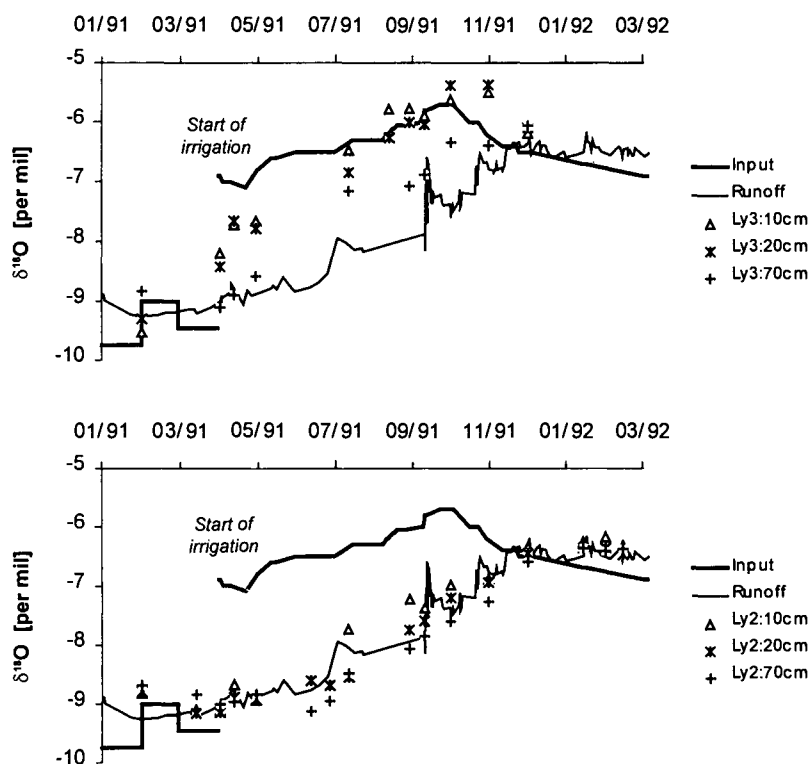


Figure 12.24. The $\delta^{18}\text{O}$ of input water (monthly mean $\delta^{18}\text{O}$ values of precipitation until April 1, 1991, thereafter $\delta^{18}\text{O}$ of irrigation), runoff, and of soil water and groundwater from two profiles (Ly3 and Ly2) in the covered catchment G1 at Lake Gårdsjön, Sweden. Ly3 is located at a sloping site on the side of the central valley and Ly2 is located in a flat area of the valley bottom. The deepest sampling points (70 cm depth) were always saturated in Ly2 and saturated for most of the time in Ly3. From Nyberg (1995).

12.3.5 Implications for catchment flow studies

The one-dimensional studies discussed above show that the isotopic variations of the infiltrated water may remain during percolation, although there seems to be a considerable damping in the near surface layers. These variations, seen as temporal as well as spatial variations in the isotope content of soil water and of groundwater recharge, might seem to violate the demand for a comparatively constant isotope content of the pre-event component in isotopic hydrograph separations. There are, however, several processes which tend to mix the water during its further flow to the discharging stream. One reason for mixing is the varying transit times in the ground for water infiltrated at different locations: Because the depth of the groundwater table, as well as the particle velocity of the percolating water, varies over the catchment, the water particles recharging the groundwater will have different age and the temporal variation in the isotopic composition of the areal mean groundwater recharge will be reduced. The isotopic variations in the groundwater contributing to streamflow are further reduced by dispersion and by the varying flowpath lengths and particle velocities for the groundwater. Even if the discharging groundwater is composed of water of different isotopic signature, the water is finally mixed in the stream itself.

12.4 Conclusions and Future Research Directions

Isotope studies have made a considerable contribution to our knowledge of catchment flow processes. The most striking result is the large and often dominating role played by groundwater in generating stream runoff in humid areas, during runoff events generated by snowmelt as well as rainfall. This finding, unequivocally shown by isotope studies since the early 1970's, has contributed to a reappraisal of the traditional view of streamflow generation, according to which runoff events in streams are generated mainly by overland-flowing rain- or meltwater on a ground surface with limiting infiltration capacity. The old view has been falsified, but several obscure points remain to be solved before we understand the response mechanism and can describe the flow-paths of water through a catchment. In Nordic till soils with their shallow water tables, the rapid response of groundwater discharge to infiltration, shown by isotope studies, seems to be explained by a rapid increase of the transmissivity as the water table rises into superficial layers of high hydraulic conductivity. In areas with other geological and climatological conditions different response mechanisms have been suggested, such as the capillary fringe model, as outlined in Chapter 1.

Many studies presented in this chapter are based on conceptually very simple models, such as the two-component model for hydrograph separation by isotopes (Equation 12.1). Simple models are attractive, since they may give a direct interpretation of the isotope data, without introduction of more or less physically based model parameters. In successful applications, such analyses give the integrated result of transport processes, which would be very difficult to describe mathematically from flow considerations. The isotopes are helpful in our attempts to describe the water flow through the particular catchments under study, and these results contribute to the development of a generalized view of the water flow through various types of catchments. In this way isotope studies have been valuable for the development of hydrological and hydrochemical models. But the isotope content is merely a result of the flow and mixing (and possibly fractionation and isotopic exchange with the surrounding medium) and has, as is well known, no influence on the water flow. They can tell us what has happened, but for any flow or transport forecast traditional hydrological methods are needed.

After more than two decades of applications in research projects, hydrograph separation by isotopes is, or at least should be, a routine method. The fact that there are several methodological problems connected with the method should not prevent it from being more widely used. In studies of snowmelt runoff, the importance of direct measurements of the isotope content of the water input to the ground, i.e., the snowpack drainage, must be emphasized. Other methodological problems concern the spatial variability of the isotope content of the pre-event water contributing to streamflow, and how to handle temporal variability of the isotope content of the water input.

In order to get a higher level of knowledge of catchment flow processes, it is necessary to combine isotope studies with detailed hydrometric observations within the catchments. From such combined studies we can begin to understand not only what has happened, but also how and why it happened. When it comes to snowmelt infiltration and runoff, it can be noted that no studies have been found where isotopes have been used in connection with measurements of soil frost and related analysis of the water flow. Such studies would fill an important gap in our knowledge. A better knowledge will also be obtained from the use of several independent tracers. Different conservative tracers, isotopes as well as chemicals, can be used to trace different sources of the water. Non-conservative chemicals, on the other hand, may tell us whether the water has passed through a certain biogeological environment or not. And, seen from the opposite side: when we have flow and transport models which can describe the output of several independent conservative and non-conservative tracers from the tracer concentration of the input, then we know how water moves through a catchment.

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Arid Catchments

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13.1 Introduction

Arid lands account for more than a third of the world's land surface and are characterized by receiving less than 200 to 250 mm/yr of precipitation, which may occur irregularly. In relative terms, Africa and Australia are the most arid continents with approximately 40% and 50% of their surfaces considered arid, respectively. At the other extreme is Europe where only 1% of the land is arid. Asia and the Americas fall somewhere in between. Characteristics of arid regions include evaporation being greatly exceeded by annual precipitation, ephemeral drainage, and the absence of regular surface runoff. Surface water, if present, is usually either transient, originating elsewhere as in large rivers, such as the Colorado River of the American Southwest and Nile River of Africa, and flows through arid regions, or collects in large quantities but usually is ephemeral as in playa lakes. Life is restricted in arid regions such that plant cover and fauna are sparse, and the vegetation is well adapted to arid conditions using water efficiently. Arid soils have low levels of biogenic processes of soil development such as observed in humid regions. Arid soils are poorly developed and dominated by upward migration of saline solutions; thus agriculture is only possible by sufficient irrigation to flush the soil of saline solutions.

Low intensity frontal type rains may occur in arid regions; in the Northern Hemisphere these usually occur only in winter. Noteworthy precipitation is produced by convective cells; it is usually of short duration, high intensity, and limited areal extent. The central core of convective cells, usually from 1 to 5 km in diameter, produces relatively uniform amounts of rain. The cell cores are surrounded by elliptical isohyets grading off to unmeasurable rain in as little as 10 km (Sharon, 1972). The total amount of rain received from the system is partially dependent on the rate at which the central core moves across the landscape.

Because of climatological relationships, arid regions worldwide have extreme ephemeral rainfall events (Jones et al., 1981), and the standard deviation of annual rainfall is much larger in arid regions than in more humid regions. In typical arid regions that receive from 200 to 300 mm/yr of rain, the range of minimum to maximum rainfall in 19 out of 20 years may be from 40 to 200% of the long-term average, whereas in more humid regions the range is closer to 75 to 125%. In drier areas where the rainfall is on the order of only 100 mm/yr, the range may be as wide as from 30 to 300% of the average annual precipitation. The correlation between mean annual rainfall and the standard deviation of annual rainfall may be modeled by a negative exponential. For example, in locations where the annual rainfall is less than 500 mm/yr in the

Near East of Asia and in North Africa, the negative correlation between the mean annual rainfall and the standard deviation of annual rainfall has been modeled by the following equation:

$$C_v = 922.3 P - 0.5992 \quad (13.1)$$

where C_v is the coefficient of variability and P is the amount of the mean annual rainfall.

The Atacama Desert in Northern Chile is an example of a site of extreme ephemeral events, where the average annual rainfall is as little as 1 mm/yr. At one time the desert received no rain for 4 years and then only 15 mm in the fifth year. However, records indicate that the region has received 64 mm in a single rain shower! Other examples of extreme rainfall variability include the Desert of Thar in northwest India, where the mean annual rainfall is only 130 mm, but the area received 860 mm of rain in only two days; in the coastal zone of the Namib desert, children can be as old as 5 years before they see rain. In central Namibia, where the mean annual rainfall is only 150 mm, a cloud burst in 1960 produced up to 489 mm in just 24 hours (Schalk, 1961).

Potential evapotranspiration, the amount of water that could be evapotranspired given a sufficient water source, far exceeds annual rainfall in arid environments. Potential evapotranspiration is usually seasonal but generally continuous throughout the year, always non-zero, and may be as high as 200 cm/yr. The Budyko ratio (Budyko, 1951), that has been developed to demonstrate the water deficit in arid regions, is the ratio of solar radiation divided by the amount of annual rainfall, both values presented in units of energy. The Budyko ratio, then, identifies the degree of surplus energy available in arid regions not used for evaporation of water. The ratio may be less than 1 in humid, cold, non-arid environments where the energy required to evaporate the amount of annual precipitation exceeds the energy received from solar radiation. In contrast, some arid environments such as the Eastern Sahara Desert have Budyko ratios as high as 200. Thus in this region, there is 200 times more energy to evaporate water than there is rain available to be evaporated.

In arid environments groundwater may represent the most important, if not the sole, source of water for sustaining life. The high evapotranspiration rate, the temporal and geographically sporadic nature of rainfall, and the possibility that several years may pass without any rain at all, render infiltration temporal and geographically sporadic. In addition, infiltration may not occur below some minimum amount of precipitation, or before some natural preconditioning. However, the timing and nature of precipitation may allow infiltration and recharge on a small scale. Groundwater tables are generally very deep in arid regions, although perched levels and shallow discharge zones may occur. Recharge has often taken place under cooler more humid conditions no longer prevalent in the area, such that withdrawal may represent depletion of the resource or groundwater mining. The balance between current recharge and withdrawal (the 'safe yield' concept) must be met in order to ensure continuous supplies. Identifying the age of the deep groundwater, timing and mode of infiltration and current recharge rates becomes important in the protection of the resource.

13.2 The Use of Isotopes in Arid Catchment Studies

Understanding the hydrology of arid catchment basins presents particular problems because of the ephemeral nature of precipitation events, high evapotranspiration, localized ephemeral or imported surface water, long infiltration path resulting in minimal recharge, and deep groundwater which may have been recharged under a more humid climate. Continued human encroachment and settlement and use of resources in arid regions requires better understanding of the impact of people on the groundwater supply and current infiltration and recharge rates.

Evaporation is probably the dominant factor in arid catchment hydrology. Isotopic methods are useful tools to understand the basic conditions of arid regions primarily because of the diagnostic stable isotopic composition imparted on water by evaporation. Rainfall, river, lake, and soil water are all affected by evaporation and the isotopic signal imparted on the water yields information concerning the degree and conditions of the evaporation. While systematics of isotopic fractionation and enrichment during evaporation have been addressed earlier in this volume (Chapters 2 and 3), this chapter explores the isotopic effect of evaporation on waters in arid catchment basins.

The hydrology of arid environments and the prevalence of evaporation requires an understanding of the arid system for proper sampling to obtain water representative of the system. The sampling of precipitation presents particular problems due to the extreme variability and sporadic nature of precipitation in arid regions, and the resultant variability in stable isotopic composition. Other waters in arid environments, such as playa lakes or rivers, albeit impressive in size, may not be hydrologically significant. They are frequently in poor hydraulic connection with the groundwater, which in turn may not be in equilibrium with local meteoric water.

13.2.1 Precipitation

While precipitation is minimal in arid regions, and may be the only supply of water to these catchments, the amount of potential evaporation will greatly exceed the average annual rainfall (high Budyko ratio). The timing and conditions of precipitation determine how much water is available for infiltration, runoff, and groundwater storage. Therefore, the origin of soil water and groundwater may be understood better by knowing the seasonality and variability of the stable isotopic composition of local precipitation in arid catchments.

The factors controlling the stable isotopic composition of precipitation are the composition of the parent condensing vapor and the temperature of condensation. The composition of the parent condensing vapor is largely controlled by the meteoric history of the condensing air mass, including factors such as the origin of the air mass, and the amount of rainout and terrestrial recycling of water along the atmospheric trajectory of the air mass (see Chapter 3 for a more complete discussion). In arid environments, an additional factor is the kinetic evaporation from raindrops before they reach the surface of the earth.

The composition of the parent condensing vapor is generally not greatly altered along the atmospheric trajectory once within the arid basin, as the lack of precipitation lessens the degree of rainout and depletion of the storm clouds. The result is little variation in the stable isotopic

composition of precipitation on a geographic basis of a single storm track. The isotopic systematics of a hydrologically-closed basin without geographic variation in the stable isotopic composition of precipitation were described for the Great Basin in Nevada, North America, by Ingraham and Taylor (1986, 1991). Similar observations have been reported for arid regions in Australia (Simpson and Herczeg, 1991).

The atmospheric trajectory of the condensing air mass prior to reaching the arid basin was found to be important in affecting the stable isotopic composition of precipitation. The isotopic composition of precipitation in the Middle East has been studied by Gat and Carmi (1970), Leguy et al. (1983), and Rindsberger et al. (1983) who demonstrated that the horizontal trajectory, whether primarily over Southern Europe, the Mediterranean Sea, or North Africa, greatly controlled the stable isotopic composition of precipitation in the region. Lawrence et al. (1982) observed variations in the isotopic compositions of precipitation along storm path trajectories and recognized the possibility of extracting a climatic signal from the isotopic compositions of precipitation.

Differences between the $\delta^{18}\text{O}$ of precipitation from different source regions and air-parcel trajectories were found to be significant for southern Nevada (Benson and Klieforth, 1989) such that Benson and Klieforth were able to assign a range of stable isotopic ratios of precipitation originating from a prescribed air mass origin and trajectory. The $\delta^{18}\text{O}$ of maritime polar, maritime polar-modified, continental polar, and arctic trajectory storms average about 2‰, 4‰, 7‰ and 10‰, respectively, lighter than maritime tropical storms. Comparison of the $\delta^{18}\text{O}$ of precipitation from these trajectories with local groundwater from the Yucca Mountain region of southern Nevada indicated that the groundwater was not derived from monsoonal air parcels as previously thought. Instead, Benson and Klieforth postulated that the oceanic source of Pacific frontal systems moved southward during the time that groundwater was recharged.

The vertical flux of meteoric water (precipitation and evapotranspiration) also plays an important role in controlling the stable isotopic composition along the atmospheric flow path. Different potential trajectories of an air mass may allow different amounts and occurrences of vertical fluxes of water. Few investigators have considered all components of the vertical flux of meteoric water when attempting to understand the evolution of the stable composition of meteoric water (see Figure 13.1). Salati et al. (1979) were some of the first researchers to recognize the importance of terrestrial recycling of meteoric water when they used the ^{18}O of precipitation to show large contributions of re-evaporated moisture to the Amazon basin's water balance. Variations in local precipitation are primarily controlled by regional-scale precipitation/evapotranspiration events upwind and that local temperature fluctuations modify the values only slightly.

Rainfall in arid environments is commonly subjected to evaporation that significantly affects the stable isotopic composition of liquid precipitation falling through dry air (the amount effect; as discussed in Chapter 3), an effect less common in more humid environments. When plotted, the isotopic composition of rainfall undergoing evaporation tends to fall on lines of lower slopes and intercepts than the slope of 8 and intercept of 10 which identifies the Global Meteoric Water Line (GMWL) of Craig (1961). Slopes from 5.5 to 6.5 for rainfall in arid regions are not uncommon (Ingraham et al., 1991; Friedman et al., 1992; IAEA, 1992). In addition, a seasonality of the slopes generated by the isotopic compositions have been observed. Summer precipitation is more susceptible to evaporation than winter precipitation;

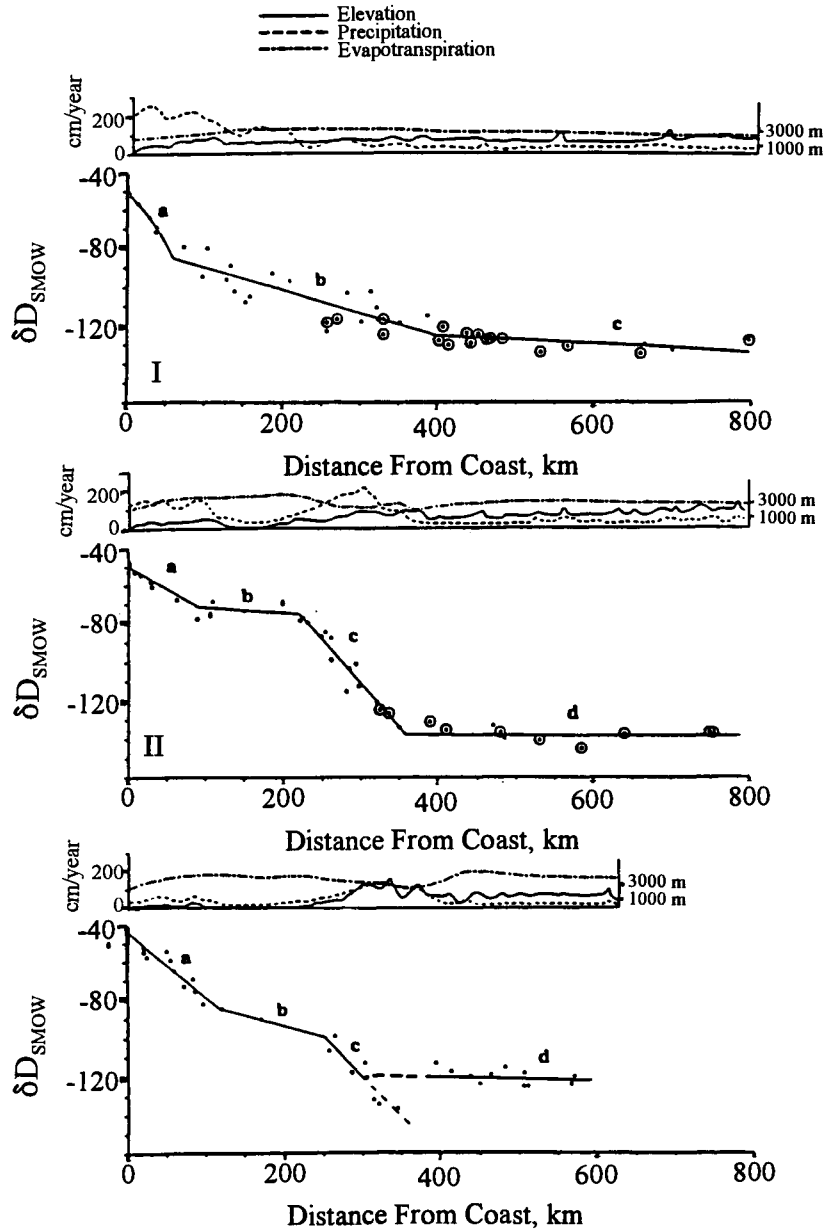


Figure 13.1. Plots of δD (SMOW) values in ground water long three W-E profiles which begin at the California (USA) coast, reflecting the history of meteoric water dominated by precipitation from the eastwards atmospheric flux. Circled data points represent samples from thermal (temperature $>40^{\circ}\text{C}$) springs. Also shown are distance profiles of topographic elevation, precipitation and evapotranspiration. Segments of low slope of δD vs. distance are interpreted as being controlled mainly by the ratio of precipitation to evapotranspiration in partially closed hydrological systems. The most pronounced is the easternmost section representing the Great Basin (Ingraham and Taylor, 1991).

whereas winter precipitation (mainly in the Northern Hemisphere) occurs under more humid conditions or may be in the solid phase which minimizes the isotopic effects of evaporation. Seasonal differences in the slopes of the meteoric water lines generated by precipitation range from 9.2 to 6.5 (Friedman et al., 1992). The average values may differ by as much as 22‰ in δD (Friedman et al., 1992) and more than 13‰ in $\delta^{18}O$ (Ingraham et al., 1991) in North America. This large seasonal nature of the stable isotopic compositions of precipitation readily enables separation of seasonal infiltration and determination of the season most conducive for infiltration and recharge.

13.2.2 Lakes

Lakes are the result of either natural or man-made impoundments, and in arid regions they may be ephemeral or perennial. In arid regions, lakes experience a large degree of evaporation due to the long residence times of water and large free-water surface in contact with the dry atmosphere. Enrichment of lake water by evaporation renders it isotopically distinctive compared to the surrounding meteoric water and allows for isotopic tracing of lake water. Lakes in arid regions are commonly terminal, having surface inflow and no surface outflow. Terminal lakes reach an equilibrium isotopic enrichment balanced by inflow, infiltration, evaporation, and isotopic exchange with the atmosphere (Ingraham and Criss, 1993). Playa lakes, which are both terminal and ephemeral, are also common in arid regions.

Ephemeral playa lakes may be either discharging or recharging. Discharging playa lakes lose most of their water to the atmosphere by evaporation and little water infiltrates lake bottoms. When evaporated to dryness, only salt flats remain. The stable isotopic values produced by this process were observed by Ingraham and Taylor (1989) for playa lakes in Surprise Valley, California, U.S.A. These playa lakes are underlain by thick (up to 1,500 m) lake deposits. The water becomes progressively enriched by continued evaporation and lake desiccation throughout the summer to a maximum of +24‰ in δD . That value is over 125‰ more enriched than the source water or groundwater in the area. The playa lake water was considerably more enriched than any other surface water or groundwater in the area, demonstrating that the lake water simply evaporated and was not in significant hydrologic connection with other waters in the basin.

Other playa lakes may be recharging the groundwater reservoir, thus they are locations of focused infiltration. As water is lost by infiltration, a non-fractionating process, the water in these ephemeral lakes does not become as enriched as the discharging playas. Nativ and Riggio (1989) studied recharging playas on the high plains of northern Texas and eastern New Mexico. The water in these playas exhibited only minor stable isotopic effects of evaporation. However, more importantly, the groundwater below the playas showed similar effects, indicating that the playas are important locations of focused recharge for the Ogallala aquifer.

Perennial lakes may also exhibit the isotopic effects of evaporation. Lake Tahoe, California/Nevada, at 1920 m above sea level, is a perennial lake that displays significant effects of evaporation. The lake receives inflow primarily from melting snow; however, the lake water is some 50‰ more enriched in δD than the source water. The isotopic enrichment due to evaporation results mainly from the long residence time of water in the lake which has been estimated to be on the order of 700 years (Goldman, 1988), rather than by a high

evaporation rate. The isotopically distinct water of Lake Tahoe is drained by the Truckee River, which flows through the arid region of the northern Great Basin. The Truckee River eventually drains into Pyramid Lake, a terminal lake that is 23‰ more enriched in δD than Lake Tahoe. In both cases, the lake waters are more enriched than the inflow water and the local groundwater.

Stable isotopes have been important in understanding the complex hydrology of regions that are transitions between rivers and lake basins such as the Okavango Delta of semi-arid northern Botswana. The Kavango River rises in humid conditions in Angola, but undergoes progressive evaporation during its passage through the delta (Mazor et al., 1977; Dinçer et al., 1979). The $\delta D - \delta^{18}O$ values lie on an evaporation trend with a slope of 5, as shown in Figure 13.2a. Although the composition of fresh groundwater in the delta reflects the evaporation of the surface water in the channels, the isotopic values of groundwater immediately outside the confines of the delta reflect local meteoric recharge. The delta therefore does not appear to have significant sub-surface outflow, or be significantly affected by the regional hydrology.

Within the Okavango Delta, small discharging playa lakes develop in the center of islands. Constant isotopic values of groundwater around the island perimeter show that the water demand of vegetation produces an inward flux of water from the surrounding channels. A strong isotopic evaporation signal is found in the small terminal hypersaline lakes in the center of the islands (Figure 13.2b; McCarthy et al., 1991). The resulting high salinity produces an increased water density, and a descending localized saline water column (recharge) into the underlying groundwater.

13.2.3 Rivers

Humid or alpine environments, where surface runoff is mostly groundwater rather than precipitation or snow melt, even during spring thaw (Dinçer et al., 1970; Sklash and Farvolden, 1979; Rhode, 1981; Bottomley et al., 1986; Ingraham and Taylor, 1989) are in contrast with arid environments where ephemeral streamflow is not composed of baseflow (groundwater). Ephemeral runoff may only have a duration of a few hours duration and is in direct response to recent large precipitation events. The stable isotopic composition of this surface water represents recent precipitation and not necessarily base flow of the arid catchment basin. Larger perennial rivers that flow through arid regions have their headwaters at significantly higher elevations or at large distances away from the arid catchment. The stable isotopic composition of the river water, then would reflect a colder and/or more humid environment with less evaporation, and is likely to be distinguishable from the local groundwaters of the arid catchment. Two large-scale examples of rivers importing water of isotopic compositions reflecting a different climate are the Colorado River of the American Southwest and the Nile River of Africa.

Large rivers in arid catchments are also susceptible to evaporation. However, because of the usual shorter residence time of water in the river as compared to lakes, and possible groundwater and tributary influx to the river, the effect of evaporation may not be as dramatic as that observed in lakes. Nevertheless, some rivers do display the isotopic effects of evaporation, in part by direct river evaporation or contributions of already evaporated water to the river by tributaries or return of irrigation waters.

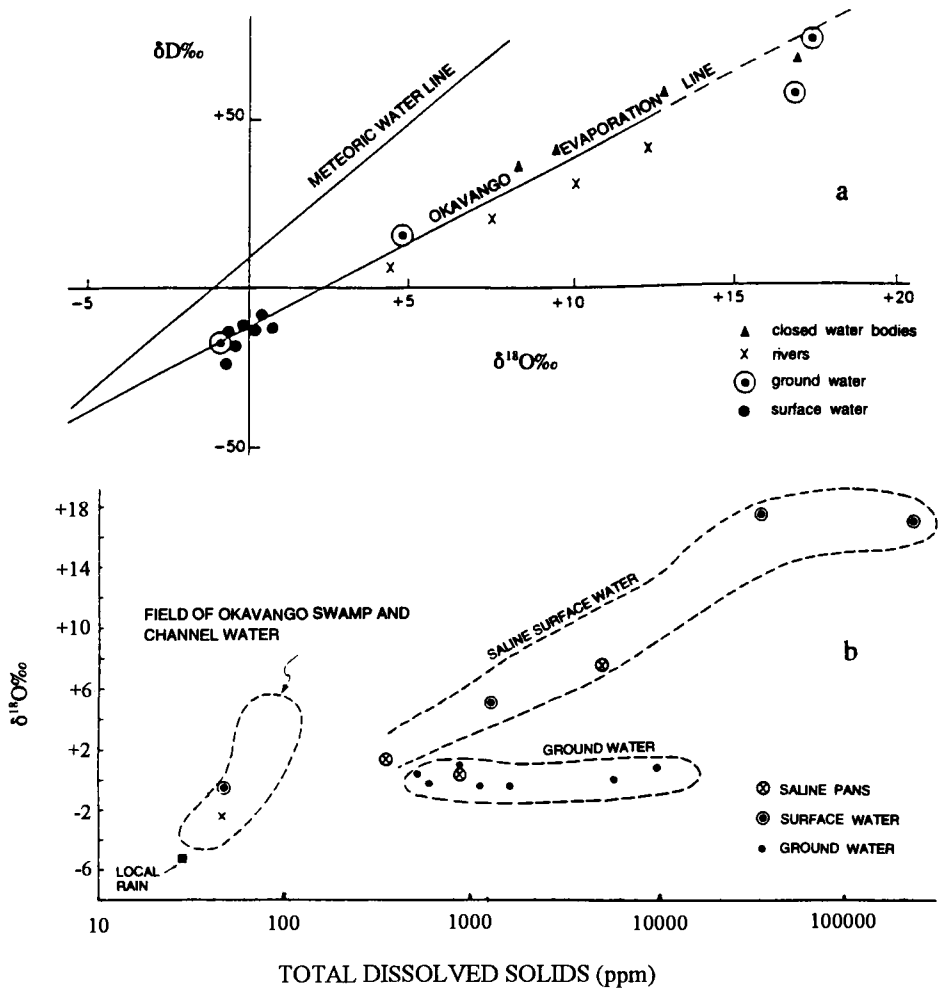


Figure 13.2. Stable isotopic composition of surface water, and of groundwater below an island, in the Okavango Delta of northern Botswana. (a) A δD - $\delta^{18}O$ (SMOW) diagram showing the MWL and an evaporation line for surface water. Ground water below the island resembles surface water of the main channel in which the island is situated. Surface water in a hypersaline evaporation pond on the island reaches extreme positive δD and $\delta^{18}O$ values. (b) A $\delta^{18}O$ vs. total dissolved solids plot for the Okavango showing surface water, evaporation from the saline pond and groundwater on the island. The considerable increase in salinity of groundwater without concomitant isotopic enrichment shows the effect of transpiration of dense vegetation on the island's periphery (McCarthy et al., 1991).

Two possible scenarios exist in establishing the stable isotopic composition of river water flowing through arid regions. One is that the river retains a depleted isotopic composition compared to local arid surface and groundwaters. In this scenario, the compositions reflect the headwaters of the drainage basin and the river water remains relatively unaffected by evaporation during transportation through the arid region. Second, the river may become isotopically more enriched by continued evaporation in the arid catchment basin. Isotopic

enrichment of river water may result from the returnflow of evaporated irrigation water, by natural or man-made impoundments, or from the contribution of tributary water enriched by evaporation, or derived from local precipitation reflecting the local environment.

13.2.4 Rivers displaying isotopic enrichment

The River Murray in Australia is an example where the river water is considerably more enriched than the local meteoric water by the process of evaporation. It drains about 14% of the Australian continent including about 75% of the irrigated land that is critical for the country's agricultural production. An increase of nearly 50‰ in δD is observed over the 2,300 km stretch of the River Murray (Figure 13.3). Only a small fraction of the isotopic enrichment observed along the river (Hughes and Allison, 1984) can be attributed to the geographic variations in the weighted stable isotopic composition of precipitation, as measured over the entire basin. Most of the isotopic enrichment observed along the river must be produced by evaporation, exclusive of transpiration, by either the influx of tributary water already enriched by evaporation, irrigation drainage return flows to the Murray, or direct evaporation from the river.

Having developed a ratio of 0.62‰ enrichment in D for every 1% of water loss by evaporation of the river, and knowing the stable isotopic effect that tributaries have on the river, Simpson and Herczeg (1991) developed a mass balance between direct river evaporation and agriculture return flow. These researchers demonstrated that because of minimal variation in the isotopic composition of precipitation over the basin, tributary input had only a minor effect in enriching the stable hydrogen isotopic composition of the river. Water losses by evaporation from the river surface and irrigation diversion represent approximately 40% of the total water loss to the atmosphere, an amount almost as large as losses by transpiration through plants.

The enrichment rate in Australia was similar to the 0.65‰ enrichment identified by Simpson et al. (1987) that was determined during studies of evaporation from pans in Egypt. The mean stable hydrogen and oxygen isotopic compositions of the White and Blue Niles near their confluence at Khartoum are enriched compared to local waters yet they plot on the GMWL. The Blue Nile has mean stable isotopic (δD , $\delta^{18}O$) values of 0 and -1.5‰, while the White Nile has mean values of +18 and +1.3‰, respectively (Malberg and Abd el Shafi, 1975). The mean stable isotopic compositions of the Nile at Cairo are reported as +28.3‰ in δD and +3.8‰ in $\delta^{18}O$ (Simpson et al., 1987), and resembles compositions of agricultural drainage water. Nile River samples have been reported to be as enriched as +34 and +4.7‰, respectively, after the confluence. These most enriched samples plot on an evaporation slope of about 4.3 (Verhagen et al., 1991). However, the local meteoric water (IAEA, 1992) line does not fall far below this slope, rendering ambiguous the interpretation of the stable isotopic signal in terms of origin of some of the groundwater east of the river.

The enriched stable isotopic nature of the Nile is no doubt a result of evaporation, either from the river surface or from irrigation drainage return flows evaporated during agricultural practices. In either case, evaporation renders the river water more enriched than local meteoric water and provides a method by which to trace the interaction between the river water and local groundwater. The deep groundwater in the Nubian sandstone aquifer of the Sahara Desert has a stable isotopic composition between -80 and -90‰ in δD and between -10 and -11‰ in $\delta^{18}O$, considerably more depleted than the Nile River water. This deep groundwater is thought

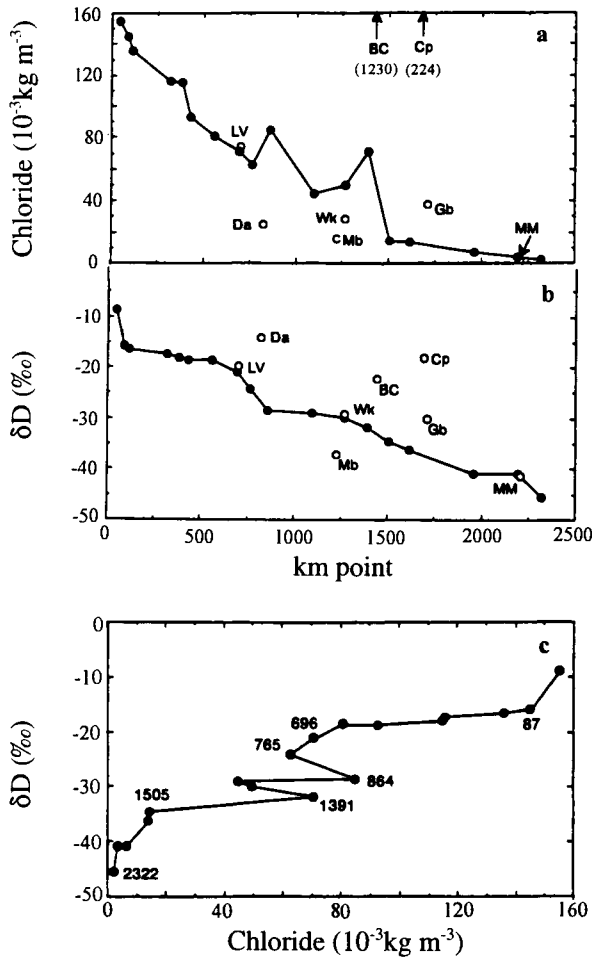


Figure 13.3. Deuterium and salinity values of water in the River Murray, Australia. The effect of evaporation, surface and groundwater inflows is shown (closed circles) in (a) chloride concentrations and (b) δD (SMOW) plotted against distance of river bed measured inland from the estuary. Values for tributaries are shown as open circles. An increase of 1‰ in δD is estimated for every 1% loss due to evaporation. The fluctuations in chloride concentration between 750 and 1,500 km with no concomitant fluctuations in δD (c) are ascribed to the influx of saline groundwater with isotopic values similar to that of the river (Simpson and Herczeg, 1991).

to have been recharged during different climatic conditions, 50,000 to 20,000 years B.P. (Sonntag et al., 1980). This marked isotopic contrast between local groundwater and imported river water allows the use of stable isotopes to study the effects of naturally imported water of a different isotopic composition in arid catchment basins. For example, Verhagen et al. (1991) studied the tritium content in groundwater from the Nubian sandstone, east of the Nile River at Khartoum, Sudan. They demonstrated that although the stable isotopic contrast between river water and local rain is not pronounced, apparent recharge through bank infiltration to groundwater within a few km from the river is derived from infiltration of agricultural irrigation

waters derived from the river. In the southern Kalahari, South Africa, the isotopic contrast between river water and local groundwater was used to show that infiltration of the ephemeral Kuruman River is restricted to a fairly narrow band along the river bank (Verhagen, 1984).

Another example discussed previously is the Truckee River in the Great Basin, which downstream from Lake Tahoe is isotopically more enriched than most of the local water in the arid environment. McKenna et al. (1992) determined that the isotopic composition of the Truckee River is directly controlled by Lake Tahoe discharge. However, even in times of drought when the river receives no water from the lake, the discharge of the river still displays isotopic compositions similar to Lake Tahoe. This similarity was attributed to discharge of bank stored water along the river, as shown in Figure 13.4.

The stable isotopic enrichment due to the evaporation of an upper basin lake has also been used to determine the water budget of a river diverted for electric power generation (Space et al., 1991). The stable isotopic composition of upper basin lake water on the Bishop Creek watershed draining the east slope of the Sierra Nevada, California is enriched by evaporation.

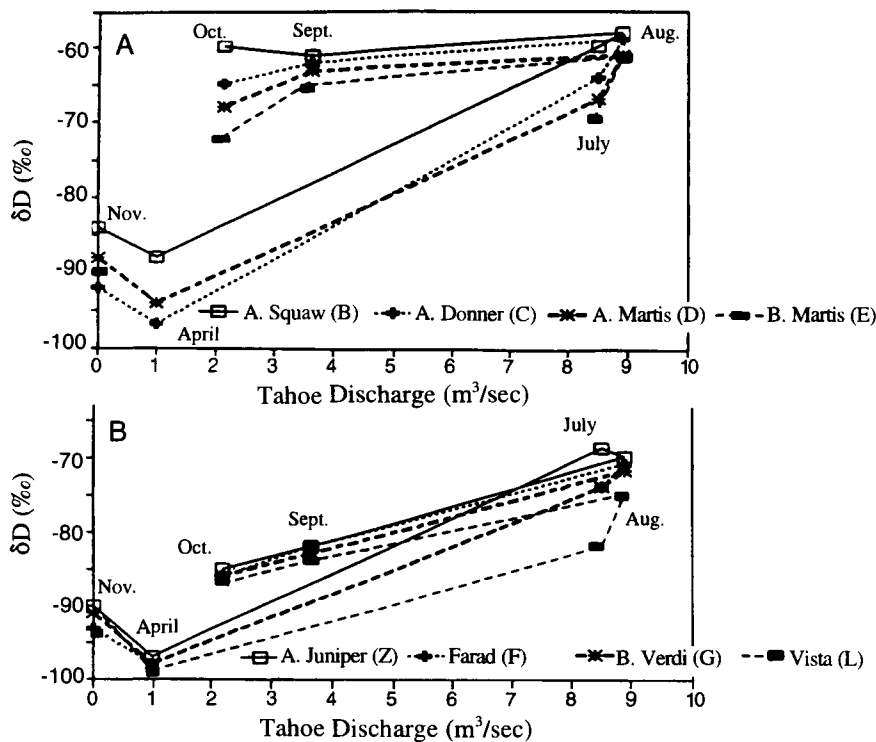


Figure 13.4. Variations in δD for the Truckee River (northern California and Nevada, USA), which drains isotopically enriched Lake Tahoe. δD values in river water are plotted against Lake Tahoe discharge for different sampling stations in the (A) upper and (B) lower reaches of the river, and for different months of the year. In the upper reaches, which during July and August conduct mainly lake water enriched in δD , enriched values are maintained up to September/October, when the discharge of storage of Lake Tahoe water, which predominates over tributary inflow. In the lower reaches, δD values drop almost immediately with a decline in lake discharge (McKenna, et al., 1992).

The lake water is withdrawn and returned at a much lower elevation downstream after being used for power generation. Influx of isotopically depleted tributary water and groundwater therefore has a proportionately greater effect on the river, reduced in flow due to the diversions draining the lake. The diverted water is then returned to the river, thus enriching the isotopic composition of the river. The river water is again diverted and the process is repeated. The return of the depleted diverted water prevents the river from attaining isotopic equilibrium with local groundwater and thus afforded an excellent opportunity to study the isotopic effects of a gaining river by mass balance. The several withdrawal and return cycles resulted in the ability to determine, by mass balance, the amount of groundwater influx and the effect of diversion for power generation.

13.2.5 Rivers without isotopic enrichment

Some large rivers flowing through arid catchment basins have headwaters either at large distances away or at significantly higher elevation than the arid region. If the flow rate of the river, lack of impoundments and diversions for irrigation are such that evaporation does not significantly enrich the stable isotopic composition, such rivers are isotopically more depleted than the local groundwater.

The Colorado River, U.S.A., retains the depleted isotopic composition of the headwater area while flowing through arid catchment basins. The stable isotopic composition of the Colorado River reflects isotopically light precipitation falling outside the arid catchment basin (Friedman et al., 1992). Moreover, the stable isotopic composition of groundwater immediately along the large perennial river (bank storage) matches the river water and is dissimilar to local precipitation. Imported water is bank stored along the river but also flows to man-made extensions into irrigated areas surrounding the river. The ability to distinguish between the imported Colorado River water and groundwater of local origin indicates a lack of large scale migration of Colorado River water far away from the channel and a natural static hydrologic equilibrium between the transient river water and the local groundwater. Considering the minimal rainfall and recharge observed in arid regions, the natural static hydrologic equilibrium between naturally imported surface water and groundwater of local origin is a somewhat surprising condition. This condition is observable for rivers that both retain their stable isotopic composition as well as those that have their isotopic compositions enriched due to evaporation.

13.2.6 Soil water

Unlike in humid regions, evaporation is a major factor controlling the stable isotopic composition of soil water in arid catchment basins. The resultant stable isotopic composition of soil water in arid regions is a function of the composition of the input (which is most commonly rainfall) and losses by evaporation. Much work on the stable isotopic compositions of soil water has been performed by Allison et al. (1983), Barnes and Allison (1983, 1984), Allison and Barnes (1985, 1990) and Walker et al., (1988), and is discussed in detail in Chapter 5. Evaporation imparts a unique isotopic composition on water remaining after evaporative loss in the soil. The resultant curve of the stable isotopic compositions with soil depth is a balance between the diffusive upward vapor flux and the downward convective liquid flux (Figure 5.3 of Chapter 5).

There are three regions in a soil that may be considered with respect to water movement (Shimojima et al., 1990). The first region at the surface is where the isotopic compositions increase from a depleted value down to a maximum enrichment at some depth. Water movement in this surface layer is predominantly in the vapor phase; the maximum enrichment in isotopic composition is observed at the bottom of this layer, which is the depth of the evaporation front. The thickness of the surface region yields an independent estimate of the evaporation rate (Barnes and Allison, 1983). Below the evaporation front, there is a middle region (Shimojima et al., 1990) where the upward evaporation flux changes from predominantly vapor phase movement to a combination of liquid and vapor phase movement, and the resultant isotopic composition is dependent on the relative magnitude of each contributing phase. Most of the soil evaporation occurs in this middle region where the water is in both liquid and vapor phase; thus this is the location of maximum isotopic enrichment. Below this middle region, the isotopic composition becomes more depleted in an exponential fashion until it reaches a constant isotopic composition that is similar to groundwater at depth. In the third region, the relative humidity is 100% and water moves predominantly in the liquid phase. The shape of a plot of stable isotopic composition in soil losing water by evaporation (Munnich et al., 1980) is different than that of free water in lakes. In lakes, convection produces mixing and isotopic homogenization, processes which are prevented in soil by adhesive forces.

Infiltration of rainwater will alter or obliterate the pre-existing curve of stable isotopic composition with depth as well as alter the slope of the evaporation line (the ratio of δD vs. $\delta^{18}O$) in soil moisture. Because evaporation in the soil atmosphere primarily occurs below saturation (100% humidity), the slope of the δD vs. $\delta^{18}O$ will be somewhat less than the 8 observed for equilibrium. Moreover, a minimum slope for kinetic evaporation has been reported to be 2.7 (Fontes et al., 1986). Thus the (δD vs. $\delta^{18}O$) slope of the line of an evaporating soil water should be between 2.7 and 8 depending upon relative humidity and the rate of evaporation. Soil profiles that show alternating δD - $\delta^{18}O$ slopes just below the evaporation front suggest alternating cycles of evaporation and infiltration. In the deepest region of the soil zone where water movement is predominantly in the liquid phase, the slope will be closer to that of the GMWL of 8 (Fontes et al., 1986).

13.2.7 Infiltration and recharge in arid regions

Determining the amount of infiltration and recharge is a critical concern in arid regions. Lysimeter soil physics and time-domain reflectometry (TDR) probes have been used to quantify infiltration. However, these methods are geographically and temporally specific. Therefore, data obtained may have limited applications and may require many measurements over a span of several years to document natural variability. Isotopic studies may provide both qualitative and quantitative information concerning current recharge to deep groundwater. Observations on the saturated zone produce a more integrated picture of the recharge process.

Soil water losses by transpiration

Plants are unable to distinguish between the heavy and light stable isotopes of hydrogen or oxygen during the uptake of soil water or groundwater. And because water movement to the plant root is predominantly in the liquid phase, water loss due to transpiration has minimal effect on the isotopic composition of the remaining soil water or groundwater. The actual process of transpiration, which is simply evaporation from a plant surface, indeed renders water

remaining in the plant leaves isotopically more enriched than the water obtained by the plant, but the effect is limited to the leaf. Thus, water vapor returned to the atmosphere by transpiration may be considered virtually identical to the soil water available to the plant (see Chapter 6).

Transpiration constitutes a substantial proportion of water loss to agricultural areas. By using water budget calculations and measured enrichment of return water used for irrigation in the Nile River Basin in the Eastern Delta agricultural region of Egypt near Cairo, Simpson et al. (1987) estimated that the fraction of original irrigation water lost by evaporation was on the order of 5% while that lost by transpiration was on the order of 60%. This estimate was accomplished by measuring the pumpage rate and return flow rate and observing that the return water is only slightly (about 3‰ in δD) enriched compared to the original Nile water. Assuming little groundwater recharge, the difference must be attributed to transpiration, which as taken in bulk, is a non-fractionating process.

Soil water losses by evaporation

Stable isotopic profiles of soil water have been used to demonstrate groundwater loss by evaporation through the soil column as well as the occurrence of infiltration events (Fontes et al., 1986). Losses of groundwater and soil water by evaporation may occur through the unsaturated zone if the water table is within 20 m of the surface. Losses within these depths may be small, on the order of only 1 mm/yr. However, in terms of regional balance, the total amount of groundwater and soil water lost in this manner may become significant when the large areal extent affected and the small amount of average annual precipitation in arid regions are considered. Evapo-transpirative losses from depths greater than 20 m (Verhagen, 1991; Ndiaye et al., 1993) have been inferred, although the rates involved may be lower.

The profile of the stable isotopic composition of soil water with depth may be simplistically divided into two transport regions, that dominated by vapor-transport and that dominated by liquid-transport. The typical average time required for the isotopic profile to attain equilibrium in the vapor-transport region is about 5 days, whereas the characteristic time required for the liquid-transport region is 1,500 years (Fontes et al., 1986). Thus, the isotopic profile in the vapor-transport region can provide nearly an instantaneous estimate of evaporation and qualitative measurement of episodic cycles of rainfall, whereas the liquid-dominated profile responds with longer time constraints and may contain information on climate change.

Fontes et al. (1986) observed episodic cycles of infiltration from rainfall and evaporation in soil cores from northern Sahara, as shown in Figures 13.5a,b. In one core, all stable isotopic data beneath the evaporating front plotted on a $\delta D - \delta^{18}O$ slope of about 2.9, which is consistent with kinetic enrichment by evaporation through a dry surface layer (minimum slope of 2.7). In contrast, a second profile displayed a more scattered profile of the $\delta D - \delta^{18}O$ relationship, with a similar slope, which was taken as being indicative of episodic cycles of deep infiltration water mixing with the already present soil water and water vapor. This new and old water would then undergo kinetic enrichment by evaporation. Fontes et al., however, could not determine the frequency of the infiltration events by the distortion of the $\delta D - \delta^{18}O$ profile. In the region sampled, the water table is shallow and the evaporation rate is high. The shorter re-equilibration time of the stable isotopic profile in the vapor-dominated region enables frequent infiltration cycles to be observed from the interruption of the typical $\delta D - \delta^{18}O$ slope.

Diffuse infiltration and recharge

Diffuse infiltration occurs when precipitation falls and infiltrates at the same location and thus sub-evenly over major portions of the landscape, before the remaining water is evaporated or collected in catchments. The seasonal and geographic variations in the stable isotopic composition of precipitation (see Chapter 3) may be used to determine (a) whether infiltration is diffuse, (b) the season most conducive to recharge, and (c) the conditions required for infiltration. The seasonal and geographic variation in the isotopic composition of precipitation was compared to the stable isotopic composition of local groundwater in the arid catchments of the Southwest of the United States (Ingraham et al., 1991). This analysis demonstrated that winter precipitation is clearly most responsible for infiltration and recharge in that region. The cooler temperatures, more continual influx of rain, and delayed slow melting of the snow pack on the high peaks, all appear most conducive for infiltration.

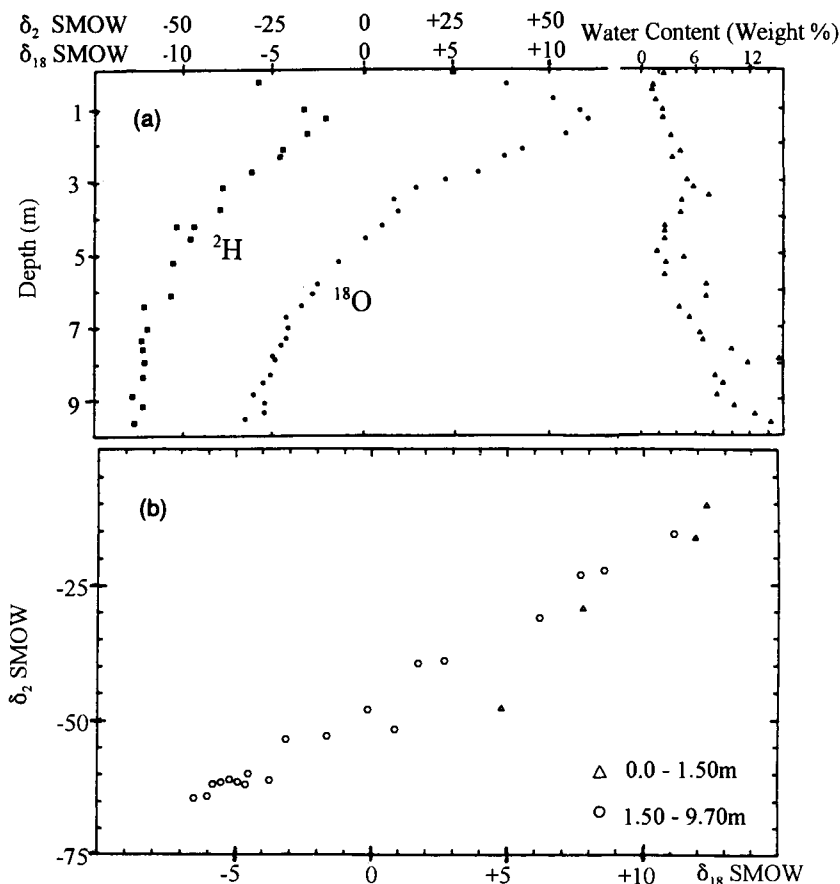


Figure 13.5. δD and $\delta^{18}O$ data for soil moisture in the Wadi Saoura, northern Sahara. (a) Depth profiles of δD , $\delta^{18}O$ and water content. The plots for δD and $\delta^{18}O$ show an increase from the surface to a maximum at 1.5 meters, followed by a monotonic decline to a near-constant value at depth. This is characteristic of water loss by evaporation through unsaturated soils. The maximum marks the evaporation front, where the upward flux of water changes from predominantly liquid phase movement to predominantly vapor phase movement. (b) A δD - $\delta^{18}O$ plot for the same depth profile. The slope of the line (2.9) is compatible with the minimum slope for kinetic enrichment (~ 2.7) (Fontes, et al., 1986).

However, diffuse infiltration may be episodic (Sami, 1992) or seasonal (Liu et al., 1995). Precipitation events below some minimum threshold amount or during certain soil conditions may be completely lost to evaporation, and only events above this amount may be involved in recharge, albeit ephemeral and localized. In addition, perhaps only certain air mass trajectories produce precipitation over the threshold amount to induce infiltration (Benson and Klieforth, 1989). Ingraham et al. (1991) observed ground-water recharge from episodic summer thunderstorm activity in southern Nevada. The summer rains occur primarily as localized high intensity convective storms that are a result of subtropical disturbances moving northward from the Gulf of California. The winter precipitation occurs as low intensity extensions of frontal driven systems off of the Pacific Coast. Average differences between summer and winter precipitation were observed to be as great as 13‰ in $\delta^{18}\text{O}$, and the composition of the groundwater more closely matched that of winter precipitation, suggesting recharge from snowmelt. However, large summer precipitation events from thunderstorms may also have contributed to the groundwater in southern Nevada (Ingraham et al., 1991) as the unique stable isotopic composition of individual summer storm events were traced to a perched groundwater system.

Focused infiltration in arid regions

A common mode of infiltration in arid regions may be described as localized or focused infiltration, which is the infiltration of either ephemeral or perennial surface water as opposed to areal, or diffuse, infiltration of precipitation. In this case, the stable isotopic ratios of the infiltrating water will reflect that of the recharging surface water, which may not be from local precipitation. Localized recharge occurs along perennial rivers such as the Colorado River or the Nile. Whereas the Colorado River retains the depleted isotopic composition of its headwater precipitation (as discussed in Section 13.2.5), the stable isotopic composition of groundwater along the Colorado River matches the depleted nature of the river rather than of the local precipitation (Friedman et al., 1992), indicating that the naturally imported water is an important source for the water budget of the arid catchments along the river.

Intermittent flow in ephemeral river beds, washes, or wadis may also play an important role in localized infiltration and recharge in arid catchment basins. The stable isotopic composition of water in ephemeral washes reflects that of recent local precipitation rather than local groundwater as is the case in more humid environments (Rhode, 1981; Bottomley et al., 1986). The stable isotopic composition of shallow groundwater along 40-Mile Wash near Yucca Mountain in southern Nevada suggests that focused infiltration of ephemeral runoff is an important mechanism of recharge, and that the stable isotopic composition of the groundwater matched that of local precipitation (Benson and Klieforth, 1989; Sadler, 1990). Focused infiltration may also occur through playa lakes (as discussed in Section 13.2.2).

Stable isotopes have also been useful in distinguishing between focused and diffuse groundwater recharge and perhaps assessing the relative contributions of each. Groundwater recharge has been studied using stable isotopes in the Gordonia district of South Africa, the southernmost reach of the Kalahari Basin (Figure 13.6). The ephemeral Kuruman River, which rises outside the area and flows for a few months every 10 - 12 years was thought to be a major source of recharge to the area's groundwater. Stable and radioactive isotopes demonstrated that the influence of the river was confined to a band of at most a few kilometers from its banks. The stable isotopic contrast with actively recharged groundwater in the rest of the area was explained (Verhagen, 1984) by recharge occurring only when the river flows consistently, which occurs only when rainfall is considerably above average for two or more successive

seasons. The stable isotopic compositions of the river, as well as of recent groundwater along the river bed is much lighter than the long-term average at Pretoria (IAEA, 1992), and shows no evaporation. Alternatively, the recharge may be the result of localized convective rainfall events of extreme intensity during generally drier periods. Such events may produce local surface ponding and bring the unsaturated zone to above field capacity. Integrated over decades, or even centuries, such random events would produce the equivalent of aerially spread, diffuse recharge. Although only scant information is available on such events, it is thought that their stable isotopic values may aid in evaluating the importance of focussed and diffuse recharge in the region.

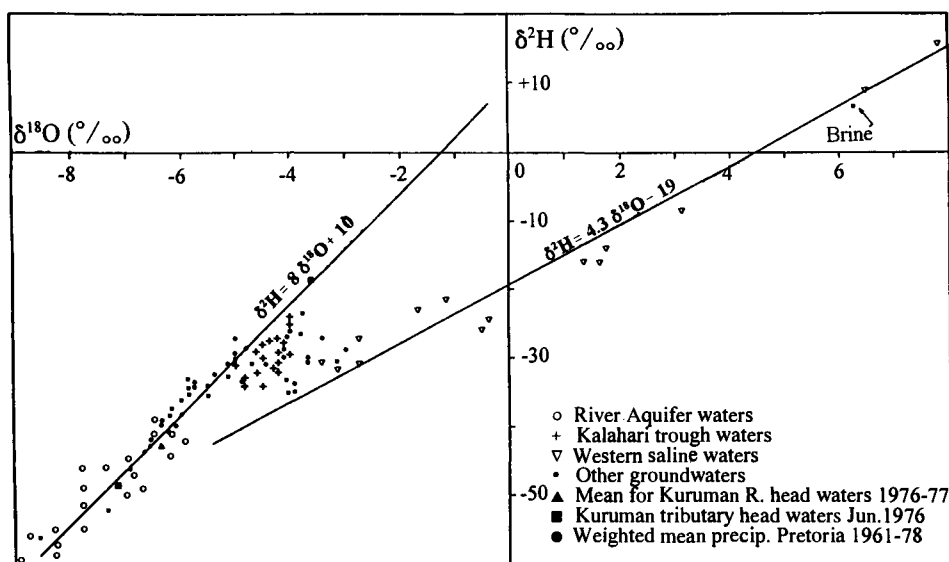


Figure 13.6. A δD - $\delta^{18}O$ diagram for groundwater in Gordonia, in the NW of South Africa. Most of the results cluster around the MWL, but some trend towards an evaporation line characterizing saline groundwater found in the western region. Groundwater close to the ephemeral Kuruman River bed (up to 1 km; open circles) plots in the group largely distinct from groundwater further away from the river (closed circles, crosses). Also shown are δD - $\delta^{18}O$ values for the river and mean rainfall for Pretoria. It is concluded that bank water infiltrated during occasional flooding does not contribute significantly to the regional groundwater inventory (Verhagen, 1984).

13.2.8 Groundwater

Groundwater in arid regions is often isotopically depleted compared to local winter precipitation. Differences between precipitation and deep groundwater are commonly on the order of 10 to 15 ‰ in δD . However, Smith et al. (1992) observed differences of up to 29‰ in δD between the most depleted local winter precipitation in southeast California, U.S.A., and deep groundwater in the area. Deep groundwater in arid regions has commonly been recharged during a cooler and more humid climate or from weather systems travelling a different atmospheric trajectories. The result is a greater amount of recharge water and a more depleted hydrogen isotope composition than present day values. The residence time of deep groundwater in arid region catchment basins can be long, as groundwater movement and discharge is

generally slow. The depth of groundwater (commonly as much as 100s of meters) precludes surface contact, and the present-day recharge is not sufficient to flush away the older groundwater or to significantly alter its composition through admixture.

Environmental isotopes have also been used to understand the complex origins of groundwater of some other arid to semi-arid basins in Africa. The Kalahari, a major arid to semi-arid basin of southern Africa, has been under hydrogeological investigation for several decades. The Upper Carboniferous to Jurassic aquifers are often capped by basalt. There is a blanket of unconsolidated to semi-consolidated aeolian sand, and a flat topography with poorly-developed surface drainage systems. Groundwater quality is usually good, with some localized areas of high salinity. The premise that groundwater was fossil, the remnant of recharge during 'pluvial' periods, was challenged by a series of isotopic studies (Verhagen et al., 1973; Mazor et al., 1977), demonstrating ongoing diffuse rain recharge. Recharge estimates obtained from chloride balance, soil profiling, GIS-soil salinity, and isotopic observations range from 3 to 6 mm/yr (Verhagen et al., 1995). Recharge in the unsaturated zone of the Sahel was estimated by analyzing tritium and chloride concentrations (Gaye and Edmunds, 1996).

Contrary to other arid environments, there is no clear isotopic contrast between shallow (recent) and deep (old) groundwater in the Kalahari. Verhagen (1992) attributed this to (1) vegetal development during protracted periods of lighter rainfall, that increased evapo-transpiration and suppressed recharge, and (2) extremely slow flushing of deep groundwater, maintaining a secular average isotopic composition close to present-day arid to semi-arid values.

The immense Makgadigadi playa lake in northern Botswana constitutes a surface hydrological baseline, but fresh groundwater levels, at a regional low, lie far below the playa floor. The only balancing mechanism to the generally proven present-day recharge to the basin must be regional evapotranspiration from deep (tens of meters) groundwater levels. The absence of hypersalinity in most of the Kalahari basin is ascribed to raised groundwater levels during pluvial periods, when the salinity is flushed out of the aquifers and into fossil drainages and the Makgadigadi (Verhagen, 1991). This concept of salinity build-up and secular flushing processes helps explain why deep-seated, semi-confined older groundwater is sometimes fresher than overlying, younger groundwater (Verhagen, 1992). The deeper groundwater should be partially mobilized only during pluvial episodes, which cleanse the shallower aquifers.

These considerations lead to the concept that structure plays an important role in the development of groundwater salinization (Verhagen, 1995). In an example from north-central Botswana, radiocarbon measurements show most of the groundwater to be actively recharged, and stable isotopes indicate some surface evaporation due to ponding of rainwater before infiltration. In this case there is no correlation between salinization and groundwater residence times. The terrain is exceedingly flat and groundwater levels show no consistent regional gradients. Recharge can only be balanced by evapotranspiration. It was concluded that structure limits lateral groundwater mobility to the extent that even during pluvial periods, and a general rise in groundwater levels, the sub-basin cannot be completely flushed of its paleo-salinity.

13.2.9 The 'd' value in arid groundwater

Deep groundwater in arid regions is also commonly observed to have a lower deuterium excess or 'd' value (see Chapter 3) than the GMWL, thus plotting below the line. The 'd' values in

arid basins have been observed to be on the order of between +5 and +6 (Sami, 1992; Margaritz et al., 1989) as compared to the +10 of the GMWL. There are two possible causes for these low 'd' values: (1) evaporation and (2) the meteoric water was initially evaporated from the ocean under more humid conditions than present day. Evaporation may occur during rainfall through an atmosphere of lower humidity (a process discussed in Chapter 3) prior to infiltration (Yurtsever and Gat, 1981), or in the soil zone prior to deep infiltration or recharge to the deep groundwater system. Additionally, more humid conditions during evaporation may also affect the deuterium excess of meteoric water.

Water may experience significant evaporation and isotopic enrichment after reaching the ground, but prior to infiltration. In southeast California, Smith et al. (1992) found that evaporation occurred during surface flow or from near surface soil moisture. In some topographically flat areas, with little or no surface runoff, rain water may collect in smaller or larger surface depressions or playas, and undergo significant evaporation before infiltration (Verhagen, 1995).

As described in Chapter 5, evaporation of soil water has a significant impact on the stable isotopic composition of recharging soil water. When evaporation is the cause of a low 'd' value, deep groundwaters may be observed to fall on an evaporation line similar to the one found by Sami (1992) for the arid eastern Cape in South Africa with a 'd' value of ~ 6 in deep groundwater and an evaporation line with a slope of ~ 5.4. Commonly, however, groundwater in arid regions does not display significant effects of evaporation as compared to soil water. In this case, groundwater must be replenished by infiltrating water which has not been significantly affected by evaporation. This may be accomplished in arid regions by infiltration occurring from large events above some threshold value of precipitation amount or soil condition. In this way, the infiltration water would not remain in the soil horizon long enough to be isotopically affected by evaporation, and recharge must occur when the soil is wetter than field capacity for longer periods than typical.

Meteoric waters evaporated from the ocean under more humid conditions than present day reflect smaller isotopic kinetic effects (Merlivat and Jouzel, 1979). The +10 intercept of the present day GMWL has been shown by Merlivat and Jouzel (1979) to be the result of kinetic effects representing an average relative humidity of about 80%. As the effects of kinetic processes are inversely related to relative humidity, an increase of relative humidity to about 90% would result in meteoric water line intercepts ('d' values) of about 5. These effects do not, however, influence the slope of the line. Deuterium excess values >10 are also possible. Precipitation in the Middle East derived from the evaporation of water from the Mediterranean Sea has 'd' values of about 20 (Gat and Carmi, 1970).

The stable isotopic composition of groundwater alone does not allow for a unique solution for determining the cause of lower 'd' values than the current GMWL value. Other information such as the age of the groundwater, recharge area and presumed climate at the time of recharge are required to ascertain the cause of the lower 'd' value.

13.3 Sampling

The act of sampling involves collecting a representative aliquot of the natural reservoir of water whether the reservoir be precipitation, surface water, groundwater, or soil water. Each of the

various occurrences of meteoric water may present a unique situation where choosing the timing, location, and sampling method becomes important. Sampling water for stable isotopic analysis in arid catchment basins may present particular problems due to the scarcity of water as well as the possibility of the sampled water being evaporated and thus not representative of the desired reservoir. Taking samples at more than one point in the reservoir will increase confidence in the observed values and potentially reveal hydrological discontinuities. Clearly, an understanding of hydrology of arid catchments is necessary for proper sampling. More importantly, the sampling design should be defined by the hypothesis being tested.

13.3.1 Precipitation

Precipitation sampling requires particular attention in arid catchments; the amount, intensity and stable isotopic composition of precipitation are highly variable in time and space (see Chapter 3). Great care has to be exercised in the design of rainfall collectors to prevent evaporation from the collected rain water. Stable isotopic variation has been observed during storms and between different storms, and is related to the type of atmospheric disturbance and season, as well as the atmospheric flow paths of the storms. Additional stable isotopic modification by evaporation occurs regularly in arid catchments during the fall of rain to the ground. Thus, the collection of samples from only one storm, or series of storms, or even an entire year's worth of precipitation, is not adequate to ascertain the average stable isotopic compositions of precipitation in arid catchment basins. The large temporal variations in precipitation are clearly illustrated in the results of the Global Network for Isotopes in Precipitation (IAEA, 1992) for numerous collection stations in all possible climatic zones worldwide.

13.3.2 Surface water

The major caveat of sampling surface water in arid regions is to be aware that consideration of the origin and spatial representation of the water is more important than occurrence. Streamflow water in arid catchment basins can be ephemeral and only representative of recent precipitation, or could represent groundwater at considerable distance and elevation removed from the arid catchment basin and not interact with the local hydrology. Large containments of surface water in arid regions may not be in hydrologic connection with the groundwater and thus not representative of local base flow. Ephemeral playa lakes are most commonly discharging catchments of ephemeral or seasonal runoff where the water evaporates and does not recharge the groundwater system (Ingraham and Taylor, 1989). In this case the water will simply become isotopically enriched by evaporation. In other cases (i.e., Nativ and Riggio, 1989), however, ephemeral playa lakes may indeed be in hydrologic connection with the groundwater system and recharging. In these cases, lake samples may provide valuable information concerning infiltration and groundwater recharge.

However, playa lakes have also been observed to be both discharging and recharging systems as observed for the ephemeral playa lakes in the North-West Province of South Africa. Water samples collected from these playa lakes indicate that the lake water is a combination of local precipitation and that from the hydrostatic rise of brine from the playa floor during recharge events in the surrounding dune fields.

13.3.3 Soil water

Sampling of soil water in arid catchment basins also requires particular attention in order to obtain a representative sample of hydrologically active soil water. The water contents of soils in arid catchment basins are commonly less than 5% by weight, and extracting such small amounts of water requires either non-fractionating methods, or methods where efficiency allows the complete extraction of the aliquot.

One method of soil water extraction is the use of vacuum distillation under heat. The soil is placed in a vacuum-tight globe and heated with a heating mantle while the globe is attached to low vacuum. The water is simply evaporated from the soil under vacuum and heat and the vapor frozen in a collection tube. Evaporation is an isotopically fractionating process; thus, this method must proceed to at least 98% completion (Araguas-Araguas et al., 1995) in order to obtain a sample isotopically representative of the original soil water. The combined process of heating and vacuum imparts thermal gradients within the soil sample in the extraction globe between the heat on the sides of the globe and the associated reduction of temperature in the center of the globe caused by loss of heat to vaporization during evaporation (Ingraham and Shadel, 1992).

Soil water extraction by distillation using organics is also common practice in liberating water from relatively dry soil. The soil is placed in a boiling chamber with an organic compound, and boiled. The vapors condense in a condensing tube and the immiscible liquids are trapped in a collection vessel, and then separated such that the water can be drained off (Revesz and Woods, 1990). Several organic compounds have been used, including kerosene and toluene, that liberate the soil water but do not isotopically exchange with the water even at the elevated temperatures. The different organic compounds used afford different boiling temperatures and thus extraction temperatures. The advantage of these methods over the heating/vacuum method is the more uniform temperature of extraction; however, each organic compound has a different temperature of extraction. The choice of organic compound, and thus extraction temperature, is important to obtain the desired water sample. Soils containing clay have some water that is weakly bound, such as labile water (crystalline water, as described by Walker and Woods, 1991), with an associated isotopic fractionation, and may not be liberated at lower boiling temperatures as those observed for toluene. This water however, because of its bound nature, albeit weak, and fractionated composition, may not represent hydrologically active water, and thus may not represent the isotopic composition of the soil water as desired as first suggested by Ingraham and Shadel (1992) and later confirmed by Araguas-Araguas et al. (1995).

13.4 Non-Traditional Techniques

Most of the recently developed isotope techniques are aimed at determining the 'age' of water, that is, the time since the water was in equilibrium with the atmosphere. New methods of dating young infiltrating and recharging water may yield information concerning rates of infiltration. The classical methods of dating waters by tritium and ^{14}C have a limit of detectable age or a window of time not covered: the time since infiltration is longer than the effective half-life, or the elapsed time is not long enough for decay to be measurable. Several methods are discussed here including ^3He /tritium, ^{36}Cl , and noble gases, which are designed to extend the presently available ranges and fill the window of time. But first, we present an overview of the use of strontium isotopes to provide hydrogeologic information about water-rock interactions within arid and semi-arid regions.

13.4.1 Strontium

Strontium isotopes (^{87}Sr and ^{86}Sr in particular) have been found to have important applications in arid and semi-arid catchment hydrology. In contrast to ^{18}O and D, Sr isotopes do not undergo significant mass fractionation during phase separation regardless of temperature, chemical speciation, or biological processes, and Sr isotope ratios are not complicated by variations in atmospheric sources because the atmospheric content of Sr is low. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of groundwater at any particular location is a useful tracer because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is mainly controlled by water-rock interactions. Sr derived from mineral weathering reactions will have the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the mineral, and consequently $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of groundwater will reflect previous interaction with source soil and rock minerals along the flow path. A detailed review of Sr systematics is given in Chapter 18.

Strontium isotopes have been used in arid and semi-arid regions to determine the sources of Sr to individual water masses, the geochemical histories of these waters through assessing the degree and extent of water-rock interactions, and source and mixing of isotopically distinct water masses. Recent work by Lyons et al. (1995) in the semi-arid Lake Tyrrell region of northwest Victoria, Australia, was focused on the use of strontium isotopes to study the dynamics and geochemistry of surface water/groundwater interactions. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of regional groundwater indicate two distinct water masses contributing to spring discharge along the western edge of the Lake Tyrrell playa. Shallow groundwater strontium profiles within the discharge area show significant vertical variations in $^{87}\text{Sr}/^{86}\text{Sr}$ in the regional groundwaters. Lyons et al. concluded that the spring water is evapo-concentrated into a brine, which infiltrates through the playa sediments as a dense convective plume, resulting in vertical brine fingering. The observed variations in $^{87}\text{Sr}/^{86}\text{Sr}$ are believed to be in response to varying climatic and hydrologic conditions not previously indicated by traditional isotope and hydrogeochemical data.

Peterman et al. (1992) used strontium isotopes in groundwater to build upon existing traditional isotope data in the Armargosa Desert and Death Valley, U.S.A., to help identify major sources of groundwater recharge (Figure 13.7). It is believed that the Spring Mountains to the southeast are a major contributor of groundwater recharge to the Ash Meadows flow system. If the Spring Mountains are the sole source of recharge to the area, the $\delta^{87}\text{Sr}$ of the groundwater at the Ash Meadows discharge area would be the same as the Spring Mountain recharge values, assuming this recharge water did not come into contact with other rock types or mix with other waters during subsequent flow (closed system). However, this was shown to *not* be the case because most springs in the Ash Meadows discharge area have much larger $\delta^{87}\text{Sr}$ than recharge waters in the Spring Mountains (4.43 to 4.99 and -1.06 to 0.79, respectively). Simple mixing models indicate that the small $\delta^{87}\text{Sr}$ for recharge in the Spring Mountains is balanced by the admixture of a lesser proportion of the large $\delta^{87}\text{Sr}$ values from groundwater in the west-central part of the flow system that produces the observed intermediate $\delta^{87}\text{Sr}$ value of the Ash Meadows discharge. On the basis of deuterium data, Winograd and Friedman (1972) estimated that approximately 65% of recharge to the Ash Meadows flow system occurs in the Spring Mountains with as much as 35% being supplied by underflow from the Pahrangat Valley to the northeast. Thus, the regional $\delta^{87}\text{Sr}$ distribution in spring discharge at Ash Meadows, Nevada, and surrounding recharge areas is consistent with deuterium data previously collected by Winograd and Friedman who identified the Spring Mountains as a major recharge area.

Contrary to the Ash Meadows flow system, chemistry and isotope data indicate that the Sr isotope chemistry of the Great Artesian Basin, Australia, is unlikely to be explained by simple two-component mixing. Groundwater collected by Collerson et al. (1988) from the major Jurassic aquifer shows systematic decrease in Ca^{2+} , Sr^{2+} , and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with increasing age and distance from the recharge area. Groundwater near the recharge area of the basin appears to be relatively unradiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$ ratios = 0.7045 to 0.7054) and becomes more radiogenic (0.7060 to 0.7118) in the central and discharge regions of the basin. Collerson et al. suggest that this may be the result of the addition of continental Sr through dissolution of aquifer silicates.

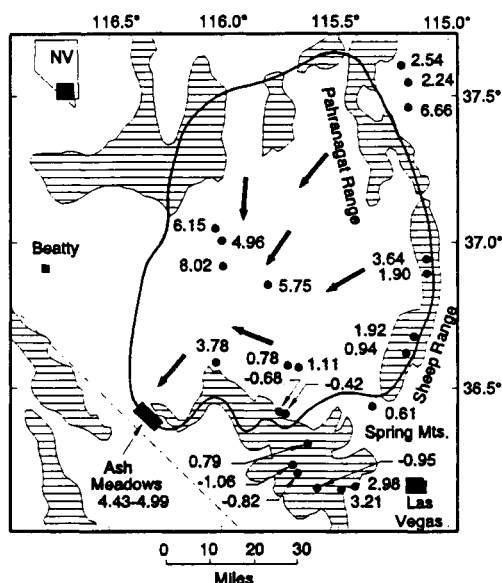


Figure 13.7. $^{87}\text{Sr}/^{86}\text{Sr}$ values for groundwater in the Ash Meadows flow system and adjacent areas. $^{87}\text{Sr}/^{86}\text{Sr}$ values for the Ash Meadows discharge area identify the Spring Mountains as a major recharge area, with a smaller contribution from the west-central part of the flow system (Pahranaag Valley) (Peterman et al., 1992).

Airey et al. (1978) have demonstrated (using $\delta^{18}\text{O}$ and δD data) that waters from the Great Artesian Basin appear to be exclusively of meteoric origin. Therefore, water with unradiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios most likely reflects interaction between recharge water in the aquifer and igneous lithologies of short crustal residence time or allochthonous material derived by dissolution of rocks having low Rb/Sr ratios. These studies clearly demonstrate that the use of Sr isotope geochemistry is an important hydrologic tool in arid and semi-arid environments, providing valuable information about aquifer mineral compositions and sources of Sr to groundwater, and about geochemical and mixing processes in groundwater systems.

13.4.2 ^3He /Tritium

Tritium has been commonly used for the determination of the age of water where the ages are on the order of several decades (see Chapter 3 for a detailed discussion). Because tritium

decays to the noble gas ^3He , this unique decay product is also available for the dating of water. Combined measurement of tritium and ^3He allows estimate of the time elapsed since the water was in equilibrium with the tritium concentration in the atmosphere. This method was first introduced by Jenkins and Clark (1976) in oceanographic studies and was soon applied to groundwater (see Chapter 7 for a more complete discussion).

The apparent ^3He /tritium age can be determined if the tritiogenic ^3He can be separated from other sources of ^3He , which include the ^3He originally in equilibrium with the atmosphere, crust, and mantle. An advantage of this method is that the ^3He /tritium age is independent of initial tritium concentration of the water sample, thus the method circumvents the problem of not knowing the initial input rate of tritium to the water. However, the age is only an apparent age and can only be taken as a true age if all sources of ^3He are known and if mixing of waters of different ^3He /tritium ratios can be quantified. The ^3He /tritium age is non linear with respect to the mixing of water of different ages because of the logarithmic function of the decay of tritium to ^3He . This is a different concept than isotope hydrologists commonly deal with in terms of delta values or tritium units which are linearly additive. The use of ^3He /tritium ratios as a tool for dating water is obviously complicated and the reader is referred to Schlosser (1992) and Chapter 19 for more complete discussions.

13.4.3 Chlorine-36

Chlorine is most commonly found as a chloride anion, as it has an exceptionally high electron affinity, and thus has minimal chemical interaction in the hydrogeologic environment. In addition, it is also hydrophilic and once dissolved in water may be considered close to a conservative tracer. Chlorine has only one unstable isotope of significant half-life, ^{36}Cl . The half-life of ^{36}Cl is 301,000 years (Browne and Firestone, 1986), considerably long in hydrologic terms, and the signal has not been attenuated by radioactive decay as is the case with tritium. Thus ^{36}Cl may be a powerful dating tool in studies assessing water infiltration through the unsaturated zone in arid and semi-arid catchments.

As with tritium (see Chapter 3), nuclear weapons testing has also resulted in a significant atmospheric input of ^{36}Cl . Chlorine-36 concentrations have been measured to be 1,000 times greater than natural background (Bentley et al., 1986). Because ^{36}Cl is not evapotranspired, as is the case with tritium, its accumulation in the soil column renders it useful to determine the downward flux of soil water in arid regions. Particular problems in arid regions are that residence times of the tracers are long where downward percolation rates are low, and in most cases bomb-produced ^{36}Cl has not been observed to penetrate lower than about 2 m.

Recent work by Cook et al. (1994) in a semi-arid region of southern Australia was centered on tritium and ^{36}Cl in the unsaturated zone below the root zone. The ^{36}Cl and tritium peaks appear to coincide; however, because the ^{36}Cl -release peak in rainfall occurred earlier than tritium, the ^{36}Cl would be expected to be deeper in the soil profile. The fact that tritium also moves in the vapor phase may explain the similar depth of the two tracers (Phillips et al., 1988; Scanlon, 1992). Similar infiltration studies in Nevada (Norris et al., 1987), New Mexico (Phillips et al., 1988) and southern Arizona (Liu et al., 1995) have shown that more than one ^{36}Cl peak is possible within the upper few meters of a soil column. These multiple peaks may be the result of a change in hydraulic characteristics and zones of lateral water flow, or a response to the

capillary pressure gradient during the dry season. Chapter 8 provides additional discussion on the use of ^{36}Cl in arid and semi-arid regions.

Chlorine-36 has become a useful tracer because of the development over the past decade of the new isotopic measurement technique of accelerator mass spectrometry. This method has enabled the measurement of extremely small amounts of a range of isotopic species potentially relevant to hydrology such as ^{26}Al , ^{32}Si , ^{41}Ca , ^{81}Kr , and ^{129}I . It has furthermore enabled the analysis of small water samples for ^{14}C , which facilitates dating small quantities of water in pores and fractures.

13.4.4 Noble Gases

Isotopes and activities of noble gases (^3He and ^4He , ^{39}Ar , ^{81}Kr and ^{85}Kr , ^{222}Rn , and Ne/Xe) are being investigated as possible new techniques to be used to solve some of the questions not answered by traditional isotope work. Many advancements have been made in the determination of groundwater ages; recent research trends suggest that noble gases may be useful in determining past recharge temperatures.

Radiogenic stable ^4He is common in high concentrations in deep groundwaters as a result of α -decay of natural U- and Th-series elements in subsurface matrix materials. Solid-to-liquid mass transfer of ^4He from aquifer matrix material to groundwater results in a relationship between the ^4He concentration in groundwater and its age (or travel time). Hence, ^4He has been applied in arid catchment hydrology as a quantitative tracer of groundwater movement to locate areas of deep groundwater discharge (e.g. Marine, 1979; Torgersen, 1980; Stute et al., 1992b). The solubility of dissolved ^4He is temperature dependent, thus making it possible to estimate recharge temperatures (the temperature at which groundwater equilibrates with ^4He) on the basis of ^4He measurements in groundwater, and paleotemperatures have been derived from ^4He concentrations in deep groundwater in the semi-arid southwestern United States (Stute and Sonntag, 1992; Stute et al., 1992a). In addition, these estimates of recharge temperature provide insight into infiltration mechanisms at the time of recharge. For example, as with most arid regions, recharge temperatures similar to wet season or peak snow melt temperatures may indicate conduit controlled groundwater recharge, whereas recharge temperatures similar to mean annual temperatures may indicate infiltration through porous media. Chapter 9 provides a summary of ^4He systematics in groundwater.

Concentrations of ^{85}Kr in groundwater have been used as a dating tool for very young waters (Rozanski and Florkowski, 1979; Loosli, 1992). Krypton-85, a radioactive noble gas with a half-life of 10.7 years, is produced by the fission of uranium and plutonium in nuclear reactors. Although ^{85}Kr has a half-life similar to ^3H , ^{85}Kr is being continuously released into the atmosphere, resulting in an increase of ^{85}Kr activity in precipitation since the 1950's, whereas ^3H activity has been decreasing since the ban on nuclear testing in 1963. ^{85}Kr enters the groundwater system by equilibration of the infiltration water with air in the unsaturated zone, defining the time since the infiltration water was isolated from the atmosphere. The ratio of the two activities, $^3\text{H}/^{85}\text{Kr}$, is a powerful tool not only for dating groundwaters less than 50 years old, but also provides evidence for determining mixing components of different water reservoirs. The application of ^{85}Kr has been limited in hydrologic studies because of the very

large amounts of water required for analysis (at least 100 L). Chapter 9 provides a good overview of sampling procedures and analytical methods for ^{85}Kr .

Although ^{39}Ar , ^{81}Kr and ^{222}Rn have found practical application in catchment hydrology, their use in arid and semi-arid regions has been limited and are discussed elsewhere (see Chapters 8, 9 and 20).

13.4.5 Chlorofluorocarbons

Chlorofluorocarbons (CFCs) have recently been applied in catchment hydrology studies as a tool for dating very young groundwaters. CFCs are stable, anthropogenic organic compounds that have been produced since the 1930's for aerosol propellants and refrigerants. Once released to the atmosphere, chlorofluorocarbons CFCl_3 , CF_2Cl_2 and $\text{C}_2\text{F}_3\text{Cl}_3$ have relatively long residence times (44, 180, and 85 yrs, respectively), where they undergo equilibration with surface waters as a function of temperature. As a result, groundwater containing CFCs must have a component of modern recharge water. Therefore, by measuring CFC concentrations and estimating the recharge temperature in a groundwater sample, a CFC-model age can be determined. CFCs have been used as tracers and as age-dating tools by Thompson et al. (1974), Randall and Schultz (1976), Schultz et al. (1976), Thompson and Hayes (1979), Busenberg and Plummer (1992), Dunkle et al. (1993), Ekwurzel et al. (1994), Reilly et al. (1994), and Hinkle and Snyder (1997).

Tritium and CFCs can be used in a similar manner for detecting modern water, where measurements of CFCs allow estimate of the time elapsed since the water was in equilibrium with the CFC concentration in the atmosphere. However, advantages of CFCs over tritium include lower detectable concentrations than tritium, suggesting CFCs are more sensitive indicators of modern water where modern and old waters mix. In addition to acting as tracers of modern water, CFCs can yield actual recharge ages when mixing and environmental contamination are significant (Hinkle and Snyder, 1997).

Although CFCs have been underutilized in arid regions, CFCs have the potential to be very beneficial in arid regions where large recharge components from bank storage and rivers have equilibrated with CFC concentrations in the atmosphere. However, one assumption of groundwater dating with CFCs is that concentrations in the soil gas immediately above the water table are also in equilibrium with the atmosphere. Unfortunately, in arid regions (where the unsaturated zone may be very thick) soil gas may not be in equilibrium with the atmosphere. Recent studies have shown that there is a time lag associated with diffusion of these gases through the unsaturated zone (Weeks et al., 1982; Severinghaus et al., 1994; Cook and Solomon, 1995), which is strongly dependent on soil water content, CFC solubility, and recharge rate. A more detailed discussion of the physical transport and biochemical processes of chlorofluorocarbons can be found in Chapter 9.

13.5 Future Directions

Isotope techniques are increasingly seen as indispensable tools in resource evaluation when groundwater is to be developed and managed in arid zone catchment basins. The processes

underlying isotope fractionation in the hydrological environment are now sufficiently well understood, including the strengths and weaknesses of individual isotope techniques, such that environmental isotope hydrology is state of the art in arid zone hydrology. It is no exaggeration to claim that isotope techniques have clarified many aspects of, and dispelled many misconceptions about arid zone hydrology. In order to unfold their full potential as practical tools, both stable and relevant radioactive isotope techniques should be employed holistically, along with standard hydrogeological and hydrochemical methods.

Directions of future research concerning the use of isotopes in arid catchment studies will probably be two-fold. One major focus will be on attempts to determine the amount, mode, and rate of infiltration. Major concerns might be the threshold value of the amount of precipitation required to initiate infiltration, and the soil conditions that might lower the threshold value. Another major focus should be on determining and protecting the quality and quantity of the fresh water reservoir. These studies may include attempts at amelioration of the salinity build up due to agricultural use.

Additional uses of isotopes studies that lend themselves to arid catchment basins are studies of climate change. Arid regions are generally the most sensitive to climate change. The Great Basin in western North America, the most arid region in the United States, has been identified as being more sensitive to climate change than any other region (Maggs, 1989). Minor changes in the amount of rainfall can produce changes in runoff, infiltration, and evaporation, and significant changes in vegetation, which would produce additional changes in transpiration and deep infiltration (Verhagen, 1984). An increase in mean annual temperature of only a few degrees Centigrade may be amplified into significant changes of seasonal variations in infiltration as well as evapotranspiration. Controversy exists in the scientific community concerning the cause of climate change, the required degree of perturbation of the forcing mechanisms causing climate change, and the significance of anthropogenic climate change. Many of these questions can be studied and insight gained into these question using isotopic techniques and arid catchment basins afford an excellent natural laboratory for doing so.

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Chapter 14

Groundwater and Surface-Water Interactions in Riparian and Lake-Dominated Systems

John F. Walker and David P. Krabbenhoft

14.1 Introduction

This chapter presents an overview of the application of isotope tracers (primarily the isotopes of water) to further the understanding of hydrologic processes occurring in riparian areas contiguous with stream systems and in hydrologic systems dominated by lakes. The chapter begins with a discussion of the spatial distribution of lake-dominated systems and a general discussion of the dominant hydrological processes occurring in these systems. Next, a brief overview of previous research in this area is presented, which focuses on investigations of recharge processes in riparian areas and studies examining the hydrologic components of lake systems. A more detailed quantitative discussion of groundwater/lake interactions follows, including the application of stable isotopes for estimating groundwater/lake exchange and the development of an index-lake method for simplifying estimates of groundwater/lake exchange. Finally, we present a case study describing qualitatively the current research being conducted in a small forested catchment in northern Wisconsin. This work focuses on the use of multiple isotopic tracers to examine hydrologic processes as the stream flows from the headwaters to its confluence with a large lake. We conclude with suggestions for future directions in applying stable-isotope tracers to understanding hydrologic processes in riparian areas and lake-dominated systems, including the importance of spatial and temporal heterogeneity, the importance of groundwater flow and reaction paths for understanding these complex systems, and the use of multiple isotopic tracers.

14.1.1 Importance of lake-dominated systems

Lakes and wetlands comprise a significant portion of the catchment land surface and cause modifications to the quantity and quality of water as it flows through a catchment. Lakes occupy nearly 8% of the surface area of Canada; in the United States, the total surface area of lakes has not been determined, and although it is certainly less than 8%, it is nonetheless an important portion of the landscape for water supply, recreation, fisheries, and wildlife. Thus, to adequately preserve these important landscape features, an improved understanding of their controlling processes is necessary.

14.1.2 Dominant hydrological processes

The general hydrologic budget for a lake system (similar to the catchment water balance

presented in Chapter 1) is shown schematically in Figure 14.1. The budget is stated mathematically as:

$$\Delta V = P + S_i + G_i - ET - S_o - G_o \quad (14.1)$$

where ΔV is the change in storage, P is precipitation, S_i is surface inflow, including any overland runoff, G_i is groundwater inflow, ET is evapotranspiration, S_o is surface outflow, and G_o is groundwater outflow. In the regions where lakes are most abundant (northeastern and north-central United States, low Arctic, Canadian Shield, and Atlantic provinces of Canada), the dominant budget components are precipitation, evapotranspiration, and groundwater inflow and outflow. Due to the pervasive permeable soils, overland flows are generally small or nonexistent, and if tributary streams exist at all, the flows are small in comparison with precipitation and evapotranspiration. Across the northern portion of North America, snowmelt is the dominant precipitation event, and provides a substantial portion of the input to the lake directly and indirectly through recharge to the groundwater system.

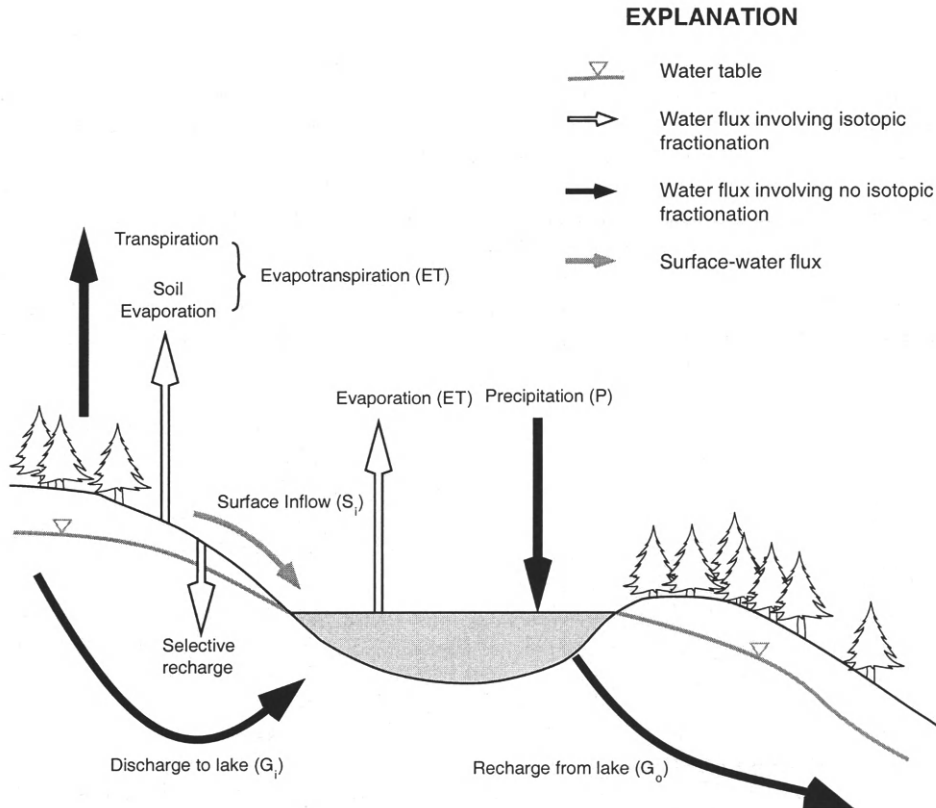


Figure 14.1. Schematic diagram depicting components of the hydrologic budget for a lake system. Modified from Krabbenhoft et al., 1994.

Depending on the spatial and temporal distribution of hydraulic heads surrounding a lake, groundwater/lake systems can be described as one of the following types: (1) recharge systems where the lake surface is higher than the surrounding water table and where water flows to the groundwater system; (2) flow-through systems, where the lake gains water from the groundwater system in some parts of the lake and loses water to the groundwater system in other parts of the lake; and (3) discharge systems, where the lake level is lower than the surrounding water table and where water flows to the lake. Further classification of lakes relates to their position within the regional groundwater-flow system. Terminal-lake systems are defined as lakes that function as the discharge point of the regional groundwater-flow system. For terminal lakes, water is removed by evaporation and through surface outflow.

14.2 Previous Studies in Lake Systems

In this section, previous studies applying stable isotopes to the characterization of hydrologic budgets are examined, specifically for lake-dominated systems. Note that the fundamental concepts of the use of isotopic tracers to separate flow components were presented in Chapter 1, and will not be repeated here.

Numerous researchers have applied isotopic tracers to estimate the components of the hydrologic budget for lake systems. The literature can be divided into three groups based on the general objectives and approach of the isotopic analysis. In the first group, isotopic and mass balance analysis is used to explain the isotopic composition of the lake in general terms of bulk inflow and outflow or mixing processes within the lake. In the second group, isotopic and mass-balance analysis is used to estimate a particular term in the hydrologic budget, typically either groundwater inflow or outflow. In the third group, detailed analyses are used to describe processes occurring in the hydrologic system.

Among the first group, several studies have used detailed isotopic samples within a lake along with assumptions about the isotopic content of various components of the hydrologic budget to "explain" the isotopic content of the lake and hence make general inferences about the hydrologic budget of the lake. For example, water samples along depth profiles in Lake Titicaca were analyzed for $\delta^{18}\text{O}$ and compared to theoretical plots of steady-state lake isotopic content versus relative humidity for assumed ranges of the isotopic content of air moisture and the ratio of evaporation to total input to the lake (Fontes et al., 1979a). Based on the observed range of $\delta^{18}\text{O}$ and relative humidity, the authors concluded that there are relatively small net losses of lake water from the system. The authors indicated that further sampling of rain water and atmospheric vapor is needed to further refine the results. A similar approach applied to Lake Asal found the most plausible model indicates a steady lake level and net loss through evaporation ranging from 20 - 40% of the total inflow (Fontes et al., 1979b). Further refinement of the isotopic composition of atmospheric moisture is needed to give a better estimate of the net loss from the lake. Based on δD and $\delta^{18}\text{O}$ profiles in saline and fresh-water lakes in Antarctica and companion samples from surrounding glaciers, researchers used theoretical scenarios from an isotopic mixing model plotted as δD versus $\delta^{18}\text{O}$ to explain the isotopic content of the lakes (Matsubaya et al., 1979). The authors conclude that saline lakes near the coast are still receiving sea-water inflow, whereas other lakes in the region are isolated from sea water--their isotopic content is controlled by the mixing of lake water with inflow from glacial melt water or precipitation.

The second group of papers use isotopic and hydrologic mass balances to solve for a particular term in the hydrologic budget of a lake. In a seminal paper, the use of δD and $\delta^{18}O$ was demonstrated to be effective in separating bulk inflow from bulk outflow for a lake's hydrologic budget (Dincer, 1968). Likewise, Allison et al. (1979) and Turner et al. (1984) used single inflow and outflow terms and tritium data to quantify the hydrologic budget of two lakes in Australia. Unfortunately, individual inflow and outflow terms were not distinguished from one another in these studies, limiting the practical application of the results. Zimmermann (1979) used δD samples collected over a 4-year period and isotopic mass balance to estimate evaporation and bulk inflow for two lakes; groundwater inflow was inferred as the difference between total inflow and precipitation. These researchers found that results based on $\delta^{18}O$ were less accurate than those based on δD because $\delta^{18}O$ is more sensitive to relative errors in the kinetic separation term.

The third group of studies use lake and adjacent groundwater samples to describe interaction between the groundwater system and the lake. For example, researchers used δD and $\delta^{18}O$ to argue that Lake Chala was not a significant source of water to springs that were previously thought to be in direct connection with the lake (Payne, 1970). In a similar investigation, δD , $\delta^{18}O$ and tritium samples were used to demonstrate that Lake Schwerin, Germany, loses some water to the groundwater system, but that lake-derived groundwater does not enter a nearby lake (Hübner et al., 1979). Based on rainfall, lake and groundwater samples near Lake George in New South Wales, investigators demonstrated that deep groundwater samples beneath the lake originated from distant recharge areas, whereas shallow samples beneath the lake exhibited evidence of a mixing of lake water and deeper groundwater (Jacobson et al., 1991). Likewise, precipitation, lake and groundwater samples in four transects moving away from each "side" of the lake were collected near an artificial lake in Germany (Stichler and Moser, 1979). The authors found that flow directions could be deduced from the δD and $\delta^{18}O$ content in the wells in relation to the lake content and local meteoric water line (LMWL), and that wells down-gradient of the lake showed seasonal patterns corresponding to seasonal lake water variations. Finally, an investigation of Lake Barco in Florida, U.S.A. utilized samples from wet/dry collectors, the lake, and nested piezometers beneath and adjacent to the lake to describe interactions between the lake and groundwater system (Katz et al., 1995). The authors were able to put together a detailed description of the complex flow patterns around the lake, and found that isotopic analyses provided insight into transient mounding beneath the lake that would not have been discovered using synoptic water-level measurements and steady-state modeling.

14.3 Estimating Groundwater Exchange with Lakes

Groundwater components of water budgets for lakes commonly are calculated as the residual of average precipitation and evaporation fluxes and changes in lake storage, leading to considerable uncertainty in calculated values (Winter, 1981). This type of budget calculation only provides an estimate for net groundwater flow because the calculation never separates the inflow and outflow components. Such budgets combine the net groundwater fraction (inflow-outflow) of the lake budget with the errors associated with other components of the lake budget. In many cases, these errors are comparable in magnitude to the individual groundwater-flow components; relative errors greater than 100% are possible. For solute-loading estimates, errors of this magnitude are unacceptable and prevent further understanding of groundwater/lake systems.

14.3.1 Stable-isotope mass-balance method

Equations presented in this section apply to groundwater/lake systems that are in hydrologic and isotopic steady states and were published by Krabbenhoft et al. (1994). Equations that describe isotopic mass balances for nonsteady state systems and mathematical forms that pertain to the estimation of evaporation from lakes can be found in Chapters 5 and 7; Gilath and Gonfiantini, 1983; and Gonfiantini, 1986.

For the purposes of this chapter, the isotope mass-balance method is applied to several seepage lakes in northern Wisconsin, U.S.A. where streamflows and overland flows are insignificant. Such lakes are typical of the poorly integrated drainage of glaciated regions that are underlain by moderate to thick glacial deposits. Under these conditions, the hydrologic budget can be simplified to include only terms for precipitation, evaporation, and groundwater. By restricting the analysis to lakes that are in isotopic steady state and by assuming that groundwater outflow is isotopically the same as lake water, Krabbenhoft et al. (1990b) combined expressions for the hydrologic budget and the isotopic mass balance to derive the following expression for the groundwater-inflow rate:

$$G_i = \frac{P(\delta_L - \delta_P) + E(\delta_E - \delta_L)}{\delta_{G_i} - \delta_L} \quad (14.2)$$

where G_i is the groundwater-inflow rate, δ_L is the isotopic composition of the lake, P is the precipitation rate, δ_P is the isotopic composition of the precipitation, δ_{G_i} is the isotopic composition of the groundwater inflow, E is the evaporation rate, and δ_E is the isotopic composition of the evaporate. In this expression, all of the terms except the isotopic composition of the lake evaporate (δ_E) are directly measurable. The average isotopic composition of the lake evaporate can be calculated from the relation formulated by Craig and Gordon (1965):

$$\delta_E = \frac{(\alpha^* \delta_L - h \delta_A - \epsilon)}{[1 - h + 10^{-3} K(1 - h)]} \quad (14.3)$$

where δ_A is the isotopic composition of local atmospheric moisture, h is the relative humidity normalized to the surface temperature of the lake, α^* is the equilibrium isotope fractionation factor at the temperature of the air-water interface, ϵ is the total fractionation factor, K is an empirical constant relating the kinetic fractionation factor and relative humidity, and all δ and ϵ values are in permil (‰).

Sparkling Lake, a groundwater flow-through lake in northern Wisconsin (Figure 14.2), was used to test the isotope mass-balance method for estimating the groundwater component of a lake's hydrologic budget. Both the isotope mass-balance method and a numerical groundwater-transport model were used (Krabbenhoft et al., 1990b); rates calculated by the two methods were comparable. The major results of the isotope mass-balance study are summarized here.

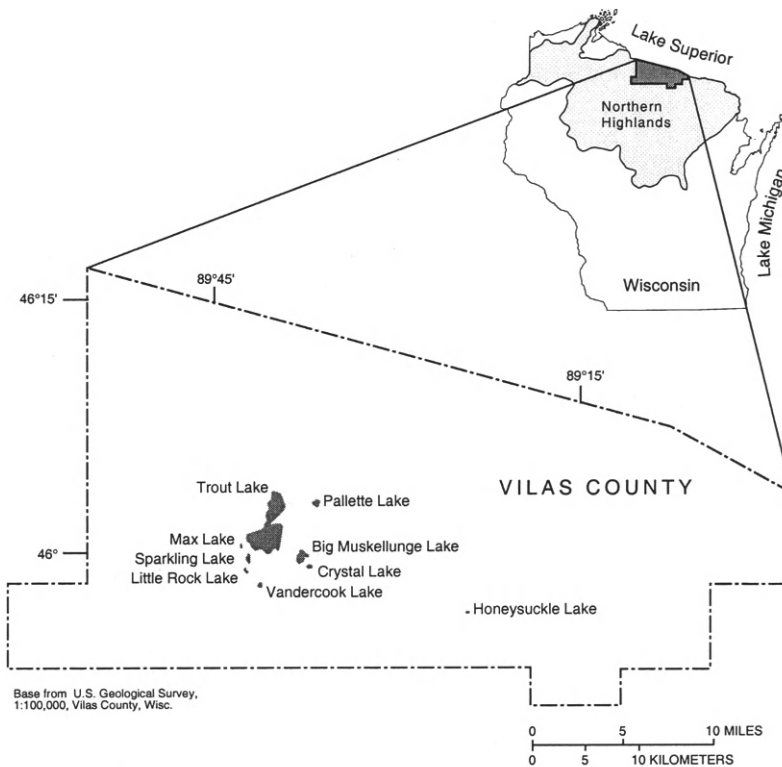


Figure 14.2. Location of lakes sampled for groundwater-component investigations (Trout Lake was not sampled). Little Rock Lake was artificially divided and sampled as two separate lakes (North and South). Modified from Krabbenhoft et al., 1994.

In the sandy outwash area of northern Wisconsin, high hydraulic conductivity promotes the exchange of water between groundwater systems and lakes. Sparkling Lake occupies a topographically low position in the local groundwater system; thus, it receives a consistent flow of groundwater, which constitutes a substantial part of the lake's hydrologic budget. The average depth of the lake is 10 m (lake volume/surface area), and the hydraulic residence time (lake volume/total outflow rate) is relatively long (calculated to be about 10 years). These characteristics of Sparkling Lake satisfy the assumptions for use of Equation 14.2 and increase the accuracy of groundwater-flow estimates.

In the mass-balance study, the isotopic composition of precipitation at Sparkling Lake was shown to vary sinusoidally, with nearly a 17‰ difference in $\delta^{18}\text{O}$ between summer precipitation and the winter snowpack (-5 to -22‰, respectively; see Figure 14.3). The average volume-weighted $\delta^{18}\text{O}$ of precipitation was estimated to be -10.9‰. Several atmospheric moisture samples were collected during the ice-free periods. Analysis of these samples showed that local atmospheric moisture is in isotopic equilibrium with precipitation, except during July and August, the warmest months. The disequilibrium during these 2 months is believed to be the result of water-vapor contributions from the many nearby lakes and (or) Lake Superior.

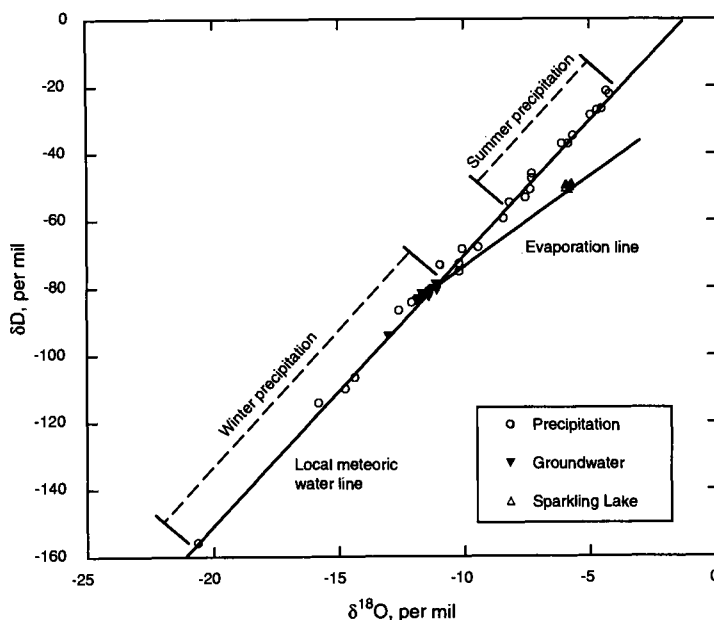


Figure 14.3. Isotopic compositions (δD versus $\delta^{18}O$) of precipitation, groundwater, and Sparkling Lake water. Modified from Krabbenhoft et al., 1994.

The $\delta^{18}O$ composition of the lake water was virtually invariant during the 2-year sampling period: the average $\delta^{18}O$ value was -5.75‰ , and the standard deviation was 0.1‰ , which is roughly equal to the analytical error expected for $\delta^{18}O$ determination. These values were obtained from samples collected during semi-annual turnover periods when the lake was thermally and chemically homogeneous. During maximum summer and winter thermal stratification, however, epilimnetic waters were observed to be slightly fractionated; the summer $\delta^{18}O$ value was -5.6‰ , and the winter $\delta^{18}O$ value was -5.9‰ . The monthly isotopic composition ($\delta^{18}O$) of lake evaporate from Sparkling Lake was estimated by using Equation 14.3. Monthly evaporation-rate estimates were used to calculate the weighted average annual $\delta^{18}O$ of lake evaporate (-16.9‰).

Ambient groundwater in the Sparkling Lake area is isotopically homogeneous; average $\delta^{18}O$ is $-11.5 \pm 0.3\text{‰}$. Downgradient from the lake, however, an easily identifiable plume of isotopically enriched lake water provided substantiating evidence for assumed flow paths based on hydraulic-head measurements. The 0.6‰ difference between average precipitation and groundwater was attributed to the selective recharge of isotopically depleted spring snowmelt compared to isotopically enriched summer precipitation.

By use of Equation 14.2, the isotopic information described above, and the average annual precipitation and evaporation rates (0.79 and 0.52 m/year, respectively), the average annual groundwater inflow rate to Sparkling Lake was estimated to be 0.27 m/year (expressed as the volumetric flow rate divided by the surface area of the lake). Because Sparkling Lake has no surface-water inflows, the groundwater-outflow rate could be estimated as the residual in the

hydrologic budget, 0.50 m/year. These results were consistent with the results from a three-dimensional groundwater-flow and solute-transport model of the Sparkling Lake system, from which the groundwater-inflow and outflow rates were estimated to be 0.20 and 0.52 m/year, respectively (Krabbenhoft et al., 1990a).

14.3.2 Index-lake method

The most difficult aspect of using stable isotopes for estimating hydrologic-budget components of lakes is determining the evaporation rate (E) and the weighted average isotopic composition of the lake evaporate (δ_E) (Webster et al., 1990). The isotopic composition of water vapor that evaporates from the surface of a lake can be estimated by use of Equation 14.3. This expression shows that the isotopic composition of lake evaporate is controlled by the interactions of the lake with the overlying atmosphere. Measurements of air and water temperatures, relative humidity, and the isotopic composition of ambient atmospheric moisture are needed. Sampling of ambient atmospheric moisture is a tedious and time-consuming process and is rarely done. When atmospheric-moisture measurements have been made, as they were at Sparkling Lake (Webster et al., 1990), it is theoretically possible to extrapolate the results for use on nearby lake systems and to assume that these lakes are affected by the same atmosphere. This kind of extrapolation is referred to as the "index-lake method" (Dincer, 1968; Gat, 1971); whereby the results from a lake whose isotopic balance has been carefully determined are used to estimate hydrologic-budget components of nearby lakes.

The lake district of northern Wisconsin is a particularly appropriate area for applying the index-lake method. This area contains more than 3,000 lakes situated in sandy, glacial outwash soils (Frey, 1966; Attig, 1985). The region is topographically homogeneous, consisting of a mosaic of similar low-relief watersheds that yield little or no overland runoff to lakes and streams. Therefore, recharge on a regional scale should be relatively uniform, resulting in a groundwater system with a uniform isotopic composition; this uniformity is an underlying assumption of the index-lake method.

The application of the index-lake method presented here is only for lakes that are in hydraulic and isotopic steady states. A lake's steady-state isotopic composition is determined by the long-term averages of δ_A , δ_P , h , P , E , and water and air temperatures, which can vary greatly daily and seasonally and to some degree annually. Therefore, it is only proper to apply the index-lake method to lakes of similar hydraulic residence time, during which time the averages of these controlling factors are determined.

The isotopic composition of evaporating water bodies on plots of $\delta^{18}\text{O}$ versus δD lie on evaporation lines. The intersection of any evaporation line with the local meteoric water line (LMWL) corresponds to the average composition of all water entering the lake. Geographically clustered lakes that meet the requirement of being in isotopic steady state should plot along the same evaporation line, provided they are indeed affected by the same atmospheric conditions and have about the same hydraulic-residence times. Groundwater-rich lakes should fall along the line closer to the meteoric water line, whereas groundwater-poor lakes containing highly evaporated water should plot farther from the LMWL. The isotopic compositions of four lakes (see Figure 14.2 for lake locations) in northern Wisconsin that are within 10 km of each other and that have hydraulic residence times of about 10 years are plotted on Figure 14.4. The four lakes (Crystal, Palette, Big Muskellunge, and Sparkling) are groundwater flow-through lakes

and have no surface inflows or outflows; thus, they have the same hydrologic-budget components (they receive water from precipitation and groundwater inflow and lose water to evaporation and groundwater outflow). A best-fit evaporation line for these four lakes has an $R^2 = 0.997$ and intersects the LMWL at $\delta^{18}\text{O} = -11.0\text{‰}$, a value close to the measured input-water composition for the index lake (Sparkling Lake), -11.1‰ . This close agreement indicates that the hydrologic budgets of the lakes chosen for this application can be determined by the index-lake method.

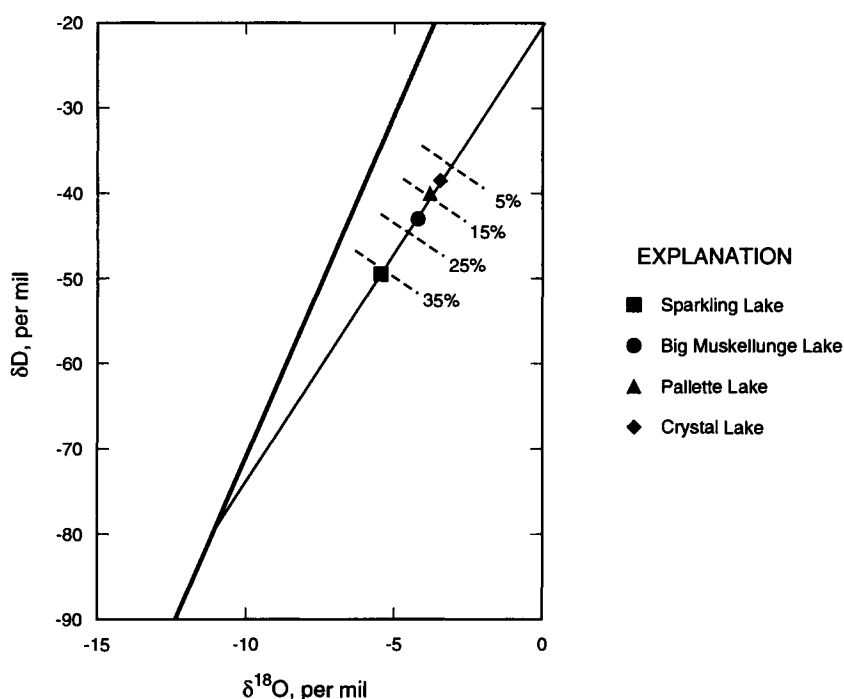


Figure 14.4. Isotopic compositions (δD versus $\delta^{18}\text{O}$) of four lakes in Vilas County, Wisconsin. The heavy line is the local meteoric water line based on data shown in Figure 14.3; the light line is the evaporation line determined by best fit for the four lakes shown. Dashed lines represent specified ratios of G_i/P calculated from Equation 14.4. Modified from Krabbenhoft et al., 1994.

Under the assumption of isotopic steady state and for the case where there are no surface inflows and outflows, the hydrologic budget and isotopic mass balance equations can be combined and solved for the groundwater outflow rate (G_o) relative to the evaporation rate (E), as follows:

$$\frac{G_o}{E} = \frac{\left[\left(\frac{P}{E} \right) (\delta_{G_i} - \delta_P) + \delta_E - \delta_{G_i} \right]}{\delta_{G_i} - \delta_L} \quad (14.4)$$

If long-term averages of P and E for the index lake are assumed to be the same for those of the other lakes, groundwater outflow can be estimated by Equation 14.4, and the only remaining unknown in each lake's hydrologic budget, G_p , can be determined easily as the residual of the hydrologic budget. In the same manner, one can specify a groundwater-inflow rate and solve Equation 14.4 for δ_L to estimate the steady-state isotopic composition of a lake. Specified ratios of annual groundwater inflow to annual precipitation rates (G_i/P) that approximately bracket the compositions of the three lakes and Sparkling Lake are plotted on the evaporation line in Figure 14.4. Groundwater-inflow rates for these lakes were estimated by use of Equation 14.2 and are listed in Table 14.1. The accuracy of the estimates for Big Muskellunge, Palette, and Crystal Lakes depends on the accuracy of the groundwater inflow estimate for Sparkling Lake (the index lake) and on the validity of the assumptions for the index-lake method. The estimated error for groundwater inflow to Sparkling Lake is ± 7 cm/year (Krabbenhoft et al., 1990b), which then represents a minimum error for the estimates of the other lakes. Therefore, for lakes that receive relatively small amounts of estimated groundwater inflow, the relative error associated with the estimate increases, and the utility of the index-lake method is reduced.

Table 14.1. Comparison of groundwater-inflow rates (m/year) for several Wisconsin lakes.

Lake	Isotope method	Solute method
Sparkling	0.29	0.24
Big Muskellunge	0.15	0.14
Palette	0.10	0.13
Crystal	0.07	0.03

Isotopic compositions of lakes whose hydraulic-residence times are relatively short (about 2 years or less) vary seasonally (Gat, 1995). Seasonal response occurs whenever a significant mass of water of a different isotopic composition either is added to or removed from the lake. Seasonal variations in P , E , G_p , δ_p , δ_A , and δ_E cause variations in δ_L for isotopically nonsteady-state systems. In northern Wisconsin, many shallow lakes are isotopically nonsteady state. Observed $\delta^{18}\text{O}$ variations for several shallow lakes in northern Wisconsin are shown in Figure 14.5; Sparkling Lake is shown for comparison. The isotopically-light value for each of these lakes represents an early spring water sample, whereas the enriched value represents late fall. These data demonstrate the substantial seasonal variations in isotopic composition that may arise in relatively shallow lakes when compared to isotopically invariant (deeper) lakes such as Sparkling Lake. Attempts to apply the isotope mass-balance method for estimating annual groundwater exchange rates for these lakes would be challenging because determination of the average annual δ_L would be difficult. On the other hand, seasonal variations in the isotopic compositions of lakes can provide valuable insight into processes (such as exchanges of water with atmosphere) that otherwise would be imperceptible in isotopically steady-state systems.

In some situations, natural-solute tracers can be used in the same manner as stable-isotope tracers to estimate hydrologic-budget components for lakes (Stauffer, 1985). As dilute recharge waters from precipitation enter the aquifer, dissolution reactions result in net additions of dissolved solids. In northern Wisconsin where glacial-outwash sediments are deficient in

carbonate minerals, silicate hydrolysis is the dominant dissolution reaction (Kenoyer and Bowser, 1992; Bullen et al., 1996). These reactions result in net additions of major cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and bicarbonate (HCO_3^-) to water. Through this process, groundwater discharge becomes the dominant source of cations and alkalinity for northern Wisconsin lakes (Kenoyer and Anderson, 1989). Therefore, by measuring solute concentrations in precipitation, groundwater, and lake water, an expression for groundwater inflow can be derived that is directly analogous to Equation 14.2:

$$G_i = \frac{P(C_L - C_P) - E(C_L)}{C_{G_i} - C_L} \quad (14.5)$$

where C_P , C_{G_i} , and C_L are the solute concentrations in precipitation, groundwater inflow, and the lake, respectively. This relation is applicable only for systems that are compositionally in steady state and where the solute acts conservatively within the lake.

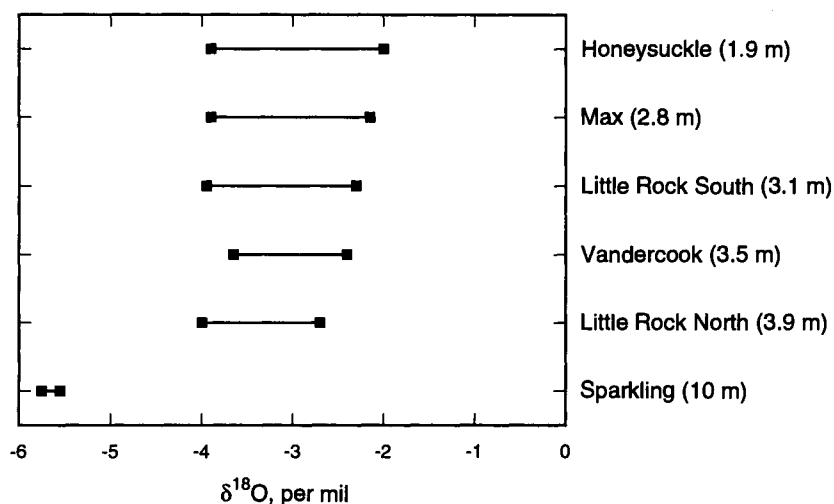


Figure 14.5. Observed range of $\delta^{18}\text{O}$ values for five nonsteady-state lake systems and the steady-state Sparkling Lake system. The mean depth of each lake is shown in parentheses. Modified from Krabbenhoft et al., 1994.

Use of solute tracers has one particular advantage over use of stable isotopes in that the solute concentrations in lake evaporate are assumed to be equal to zero. This assumption means that the errors associated with estimating the isotopic composition of lake evaporate do not apply to the solute tracer method. On the other hand, the chemistry of groundwater is often much more heterogeneous than the isotopic composition of the water (Krabbenhoft et al., 1990b). In addition, contamination problems can be a concern for solutes at low concentrations, but isotope samples are unaffected by contamination. Thus, estimates of average isotopic composition of a groundwater system are more accurate than are average chemical compositions. Therefore the two methods have different degrees of appropriateness depending on the site.

Groundwater-inflow rates as calculated by the solute and isotope mass-balance methods (Equations 14.5 and 14.2, respectively) for several northern Wisconsin lakes are listed in Table 14.1. Dissolved calcium was used as the solute tracer because it is the constituent whose concentration differs the most between groundwater and precipitation—the two input components to be separated by the solute mass-balance method. In addition, calcium is nearly conservative in the soft water and moderately acidic to circum-neutral lakes of northern Wisconsin. Results from the solute and isotope methods agree relatively well, except for Crystal Lake, where groundwater flow reversals are frequent. In this case, the isotope method is unable to discern groundwater discharge, which is isotopically equivalent to the lake water that had previously recharged from the lake prior to the flow reversal. Equation 14.5 can be set equal to zero (i.e., no groundwater inflow) and solved for C_L , as follows:

$$C_L^0 = \frac{PC_P}{P - E} \quad (14.6)$$

where C_L^0 is the solute concentration for a lake with no groundwater inflow. Substitution of values for northern Wisconsin ($P = 0.79$ m, $E = 0.52$ m, and $C_P = 0.2$ mg Ca/L (Krabbenhoft et al., 1990b)) in Equation 14.6 yields a dissolved-calcium concentration of 0.7 mg/L. This value is close to that of Honeysuckle Lake (0.6 mg Ca/L), a nearby lake that is known to have no groundwater inflow (William Rose, U.S. Geological Survey, oral commun., 1991). The close agreement between the calculated and the measured values also increases confidence in the values of P , E , and C_P used in the solute mass-balance method.

14.4 Wisconsin WEBB Case Study

In this section preliminary research findings are presented for an ongoing study in a small forested catchment in northern Wisconsin. The research is being conducted under the auspices of the Water, Energy, and Biogeochemical Budgets (WEBB) program, which is a portion of the Global Climate Change research initiative of the U.S. Geological Survey. The study area coincides approximately with one of the Long Term Ecological Research (LTER) sites funded by the United States National Science Foundation, the North Temperate Lakes LTER. After a brief description of the study area, the overall study design will be discussed. Next, an overview of the progression of the flow system will be presented, followed by a more detailed examination of the data from three hillslope sites. We conclude this section with implications concerning use of isotopes to discern groundwater/surface-water interactions.

14.4.1 Study area

Thousands of kettle lakes, formed at the end of the last continental glaciation about 10,000 years ago, are concentrated in the Northern Highlands Lake District of north-central Wisconsin. The lakes range in size from 0.1 to more than 1,500 hectares, in depth from 1 to 33 m, and in fertility from oligotrophic to eutrophic. Sparsely settled by humans, the lake district lies within two state forests that protect 80% of the land area and 60% of the lake frontage. Many lakes have totally forested watersheds and no private frontage. The forest vegetation consists of a mixture of coniferous and deciduous species.

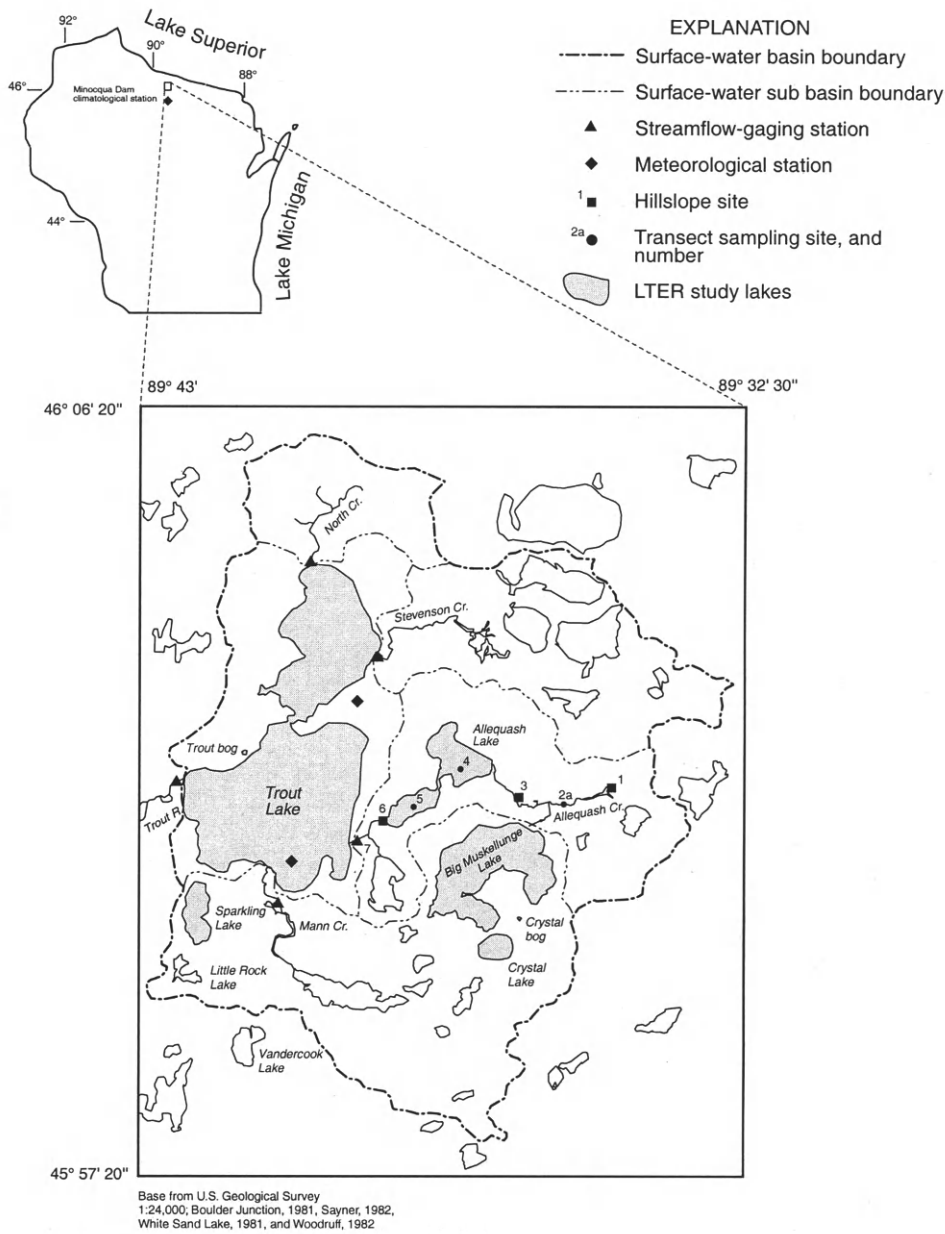


Figure 14.6. Location of Wisconsin WEBB project and LTER study lakes.

Geologic features of the area are dominated by a sandy outwash plain consisting of 30-50 m of unconsolidated sand and coarser till overlying Precambrian igneous bedrock. The predominant soils are thin, poorly developed forest soils with high organic content in the upper horizon. The area is representative of the glacial lake districts common to the upper Midwest and Canada but has some individual characteristics that distinguish it from other nearby lake areas. Among the most important of these features is the fact that the glacial drift is essentially carbonate free, with the result that the groundwater chemistry is almost entirely controlled by silicate hydrolysis.

The seven study lakes of the LTER project (Figure 14.6) are within 10 km of each other, range in elevation from 492 to 502 m a.s.l., and are exposed to almost identical climate. Mean monthly temperatures are minimum in January, ranging from -17 to -6 °C, and are maximum in August, ranging from +13 to +26 °C. Precipitation averages 76 cm/year. The lakes are ice free about 7 months each year. The climate at the project site is affected by air masses from the North Pacific, the North Atlantic, the Gulf of Mexico, the Arctic, the High Plains, and the Ohio Valley. Located about 70 km southeast of Lake Superior, and 200 km northwest Lake Michigan, the LTER site is also under strong climatic influence from the Great Lakes.

Most of the lakes in the area are seepage lakes—they have no surface-water inlets or outlets. Thus water budgets are dominated by direct precipitation, groundwater flow, and evapotranspiration. The seven LTER study lakes, five of which are seepage lakes, are all in the same groundwater flow system (Figure 14.6). There are strong chemical gradients among them that reflect increasing proportions of groundwater inputs. Those that are situated high on the landscape, such as the two bog lakes and Crystal Lake, receive little groundwater flow and no streamflow. Their ionic concentrations are low, with specific conductance ranging from 10-20 $\mu\text{S}/\text{cm}$. Other lakes that are low on the landscape, such as Trout Lake, are dominated by groundwater and stream inputs, as reflected by greater specific conductance (70-90 $\mu\text{S}/\text{cm}$).

Several single-lake basin hydrogeologic studies recently conducted in the North Temperate Lakes (NTL) area (Kenoyer, 1986; Marin, 1986; Krabbenhoft, 1988; Wentz and Rose, 1989; Krabbenhoft and Babiarz, 1992; Rose, 1993) have led to detailed descriptions of the groundwater flow network around three of the LTER lakes (Sparkling Lake, Crystal Lake, and Crystal Bog) and three non-LTER lakes in the area (Little Rock Lake, Palette Lake, and Vandercook Lake). All of these studies concluded that the unconsolidated aquifer is hydraulically very conductive, providing for good connection between the aquifer and the lakes. Because the precipitation readily percolates into the sandy soils of the region, surface-water runoff is negligible as a hydrologic input to the lakes.

14.4.2 Study design

One objective of the WEBB study is to examine processes at several spatial scales to explore possible predictive capabilities of scaling up from smaller to larger catchments. Therefore, sampling and data collection is being carried out at two spatial scales. The large-scale sampling is conducted at 10 discrete points on Allequash Creek and two tributaries from the headwaters to the confluence with Trout Lake (Figure 14.6; some sampling sites not shown for clarity). Samples were collected in fall 1991 and monthly from May through October for 1992 and 1993. The samples were analyzed for major cations and anions, nutrients (total, ammonia and nitrate nitrogen, total phosphorus, and orthophosphorus), total organic and inorganic carbon,

pH, alkalinity, and several stable isotopes (D , ^{18}O , $^{87}Sr/^{86}Sr$, and ^{13}C). Associated with the large-scale sampling, a continuous record of discharge of all four streams tributary to Trout Lake is being collected at their confluence with Trout Lake and at the outlet from Trout Lake (Figure 14.6). Additionally, samples were collected periodically from the other streams tributary to Trout Lake and at the outlet from Trout Lake (monthly from October 1991 through June 1993 and during six sampling trips per year).

At the smaller spatial scale, detailed monitoring sites have been installed on three hillslopes starting at the headwaters and ending at the outlet from Allequash Lake (Figure 14.6, sites 1, 3 and 6). At each of the three sites, transects of nested piezometers were installed from near the top of the hillslope to the base of each hill. Additional nested sampling points extend from the base of the hill to the other side of the stream, including a group of three well nests under the streambed. Samples were collected from all the nested wells in the fall of 1992, and monthly from June 1993 through October 1993. The samples were analyzed for major cations and stable isotopes (D , ^{18}O , and $^{87}Sr/^{86}Sr$); a subset of the well samples were analyzed for dissolved organic and inorganic carbon, pH, alkalinity, dissolved carbon gases (CO_2 and CH_4) and ^{13}C . Two sets of nested gravity and suction lysimeters were used to sample the vadose zone. At each site, bulk collectors are used to obtain precipitation and throughfall samples, which are analyzed for stable isotopes (D , ^{18}O , and $^{87}Sr/^{86}Sr$). Associated with the small-scale sampling, continuous records of instantaneous throughfall, stream discharge, water levels in the hillslope piezometer nests, and tension in the vadose zone at six locations are collected. A general schematic diagram depicting the instrumentation and groundwater-sampling sites for the hillslope sites is presented in Figure 14.7.

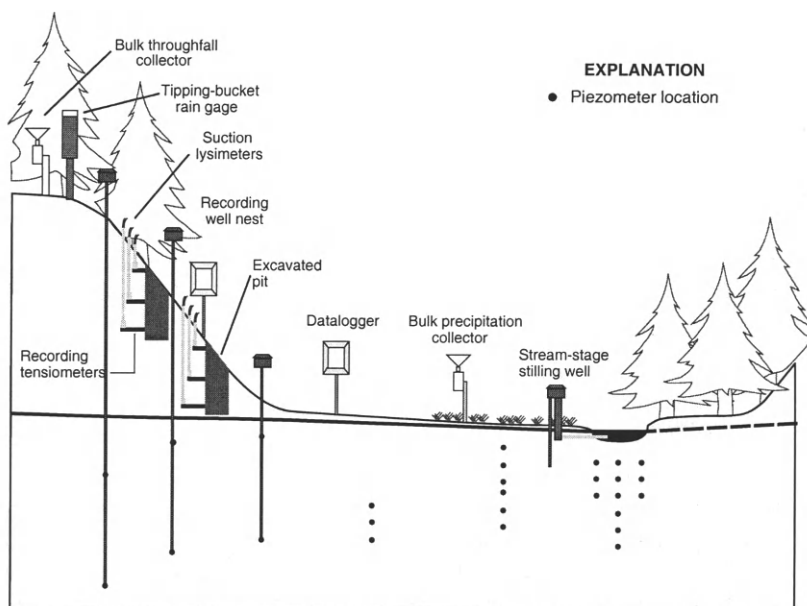


Figure 14.7. Schematic diagram depicting instrumentation and sampling points on hillslope sites at the Wisconsin WEBB research site.

14.4.3 Isotopic flow-system progression

As discussed previously, a plot of the isotopic composition (δD versus $\delta^{18}O$) can reveal differences between meteoric sources of water and evaporative sources of water. For the case at Allequash Creek, this amounts to a distinction between groundwater and more local surface water (i.e., lake water). Results for stream-transect samples collected from October 1991 through February 1992 are shown in Figure 14.8. As one moves from the headwaters (site 1) to the confluence with Trout Lake (site 7), the flow system progresses from a more or less homogeneous meteoric source (groundwater and local recharge) to a mixture of groundwater, precipitation, and evaporated surface sources. The general trend for $\delta^{18}O$ samples collected through time is the same (Figure 14.9a); stream water at the headwaters is close to the average groundwater composition for the area (-11‰), and the $\delta^{18}O$ composition becomes progressively enriched along the transect, indicating evaporation along the stream course and mixing with other evaporated waters.

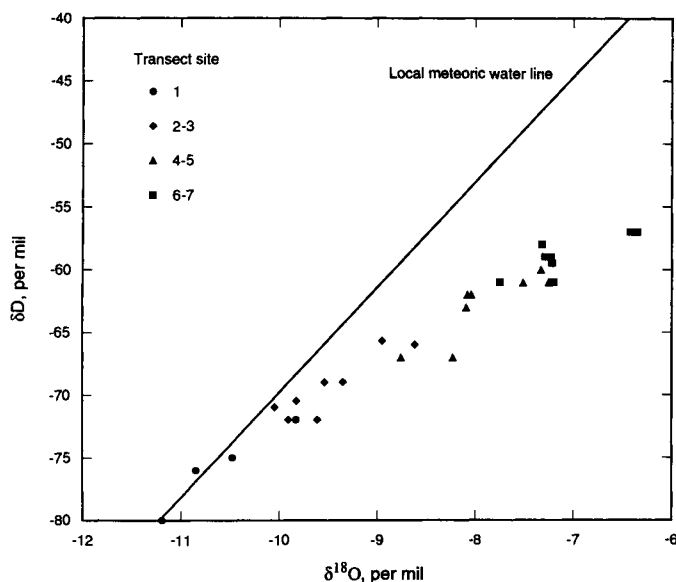


Figure 14.8. Isotopic compositions (δD versus $\delta^{18}O$) of samples collected along the Allequash Creek transect from October 1991 through February 1992. The local meteoric water line was established in a previous study (Krabbenhoft et al., 1990a).

In many cases, use of additional isotopes can provide further information to improve understanding of a flow system. The stable-isotope pair $^{87}Sr/^{86}Sr$ can be used to discern subtle differences in the contact of water with different mineral matrices or the amount of contact time with similar mineral matrices (Bullen et al., 1996), thus further distinguishing the origin of the groundwater source water. In the case of the Allequash Creek catchment where the aquifer mineral composition is believed to be relatively homogeneous, slower flow rates or longer contact time result in a more radiogenic signal (enriched in ^{87}Sr), whereas faster flow rates give

a depleted ^{87}Sr signal. The general trend for $\delta^{87}\text{Sr}/^{86}\text{Sr}$ samples collected through time at the stream transect sites would indicate groundwater discharge from relatively long flow paths at the headwaters, inclusion of relatively shallow flow paths from sites 1 to 3, interception of more distant flow paths to the lake (sites 4 and 5), and then a further progression toward mixing with shallow flow paths from sites 6 to 7 (Figure 14.9b). Although the $\delta^{87}\text{Sr}/^{86}\text{Sr}$ results indicate relatively shallow and thus local flow paths, periodic sampling of the hillslope piezometers shows values that are not sufficiently radiogenic to explain the water in the stream, which indicates that the “shallow” flow paths are still quite distant from the stream and do not predominantly originate as recharge on the adjacent hillslopes.

The overall picture of the Allequash Creek flow system is a progression from a pure groundwater source to a mixture of relatively deep groundwater, relatively shallow groundwater, and evaporative (surface) water. Further examination of the flow system comes from a detailed look at the isotopic compositions at a smaller spatial scale.

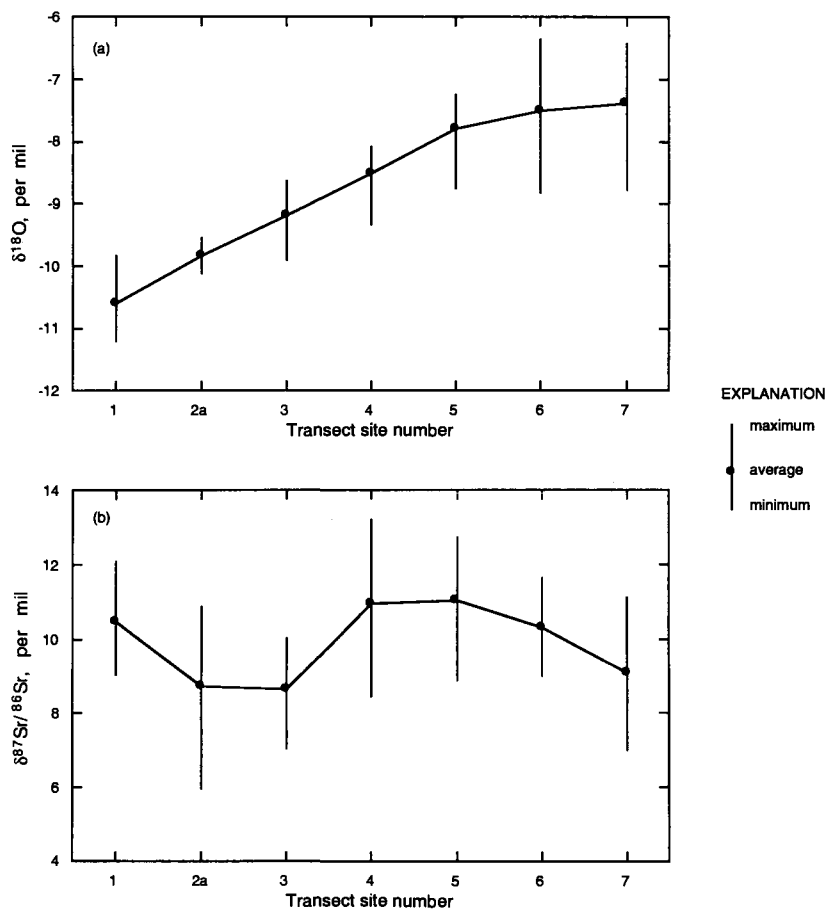


Figure 14.9. Allequash Creek transect sampling results for (a) $\delta^{18}\text{O}$ and (b) $\delta^{87}\text{Sr}/^{86}\text{Sr}$. Results show the range of values at each transect site for samples collected from October 1991 through October 1992.

14.4.4 Isotopic complexity

In this section, data collected during the spring of 1993 at each of the three detailed hillslope sites will be presented. The original sampling in the fall revealed several places where additional piezometers were needed to adequately define spatial trends. The piezometers were installed the following spring, and all subsequent sampling was from the more complete set of piezometers.

The values of $\delta^{18}\text{O}$ collected from wells at the headwaters of Allequash Creek (hillslope site 1) plot near the LMWL, clustering around the average composition of well-mixed groundwater ($\delta\text{D} \approx -81\text{‰}$, $\delta^{18}\text{O} \approx -11.3\text{‰}$). The small degree of variation does not exhibit any spatial structure in the hillslope cross section. The isotopic composition (δD versus $\delta^{18}\text{O}$) of the piezometer samples shows the relatively homogeneous groundwater noted by Krabbenhoft et al. (1990b). This is consistent with the general description presented earlier, with the headwaters receiving well-mixed groundwater and the homogeneity in part due to relatively long flow paths.

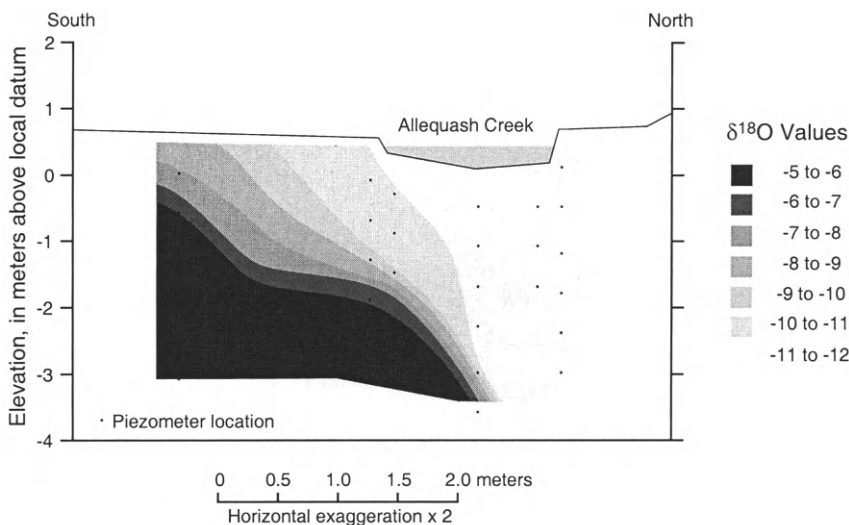


Figure 14.10. Cross section depicting shaded regions between isopleths of $\delta^{18}\text{O}$ from piezometer samples collected at hillslope site 3 during June 1993.

A cross section with shading between isopleths of $\delta^{18}\text{O}$ for hillslope site 3 shows the degree of spatial variability ($\delta^{18}\text{O}$ ranges from -5 to -11‰) present in a relatively confined area near the stream (Figure 14.10). Perhaps the most prominent feature is the presence of a “plume” of water that is very enriched in $\delta^{18}\text{O}$ (values from -5 to -6‰). The near vertical orientation of the contours indicates that the source of enriched water is flowing upward from depth and is contributing more flow than the recharge water from the hillslope. The isotopic composition (δD versus $\delta^{18}\text{O}$) of the piezometer samples from hillslope site 3 indicates that the water in the “plume” originates from an evaporative source (Figure 14.11a). The most likely source for this water is Big Muskellunge Lake (average $\delta^{18}\text{O}$ composition of -4.5‰), which is nearly 1 km away in another surface-water catchment (Figure 14.6). The average $\delta^{18}\text{O}$ composition of the

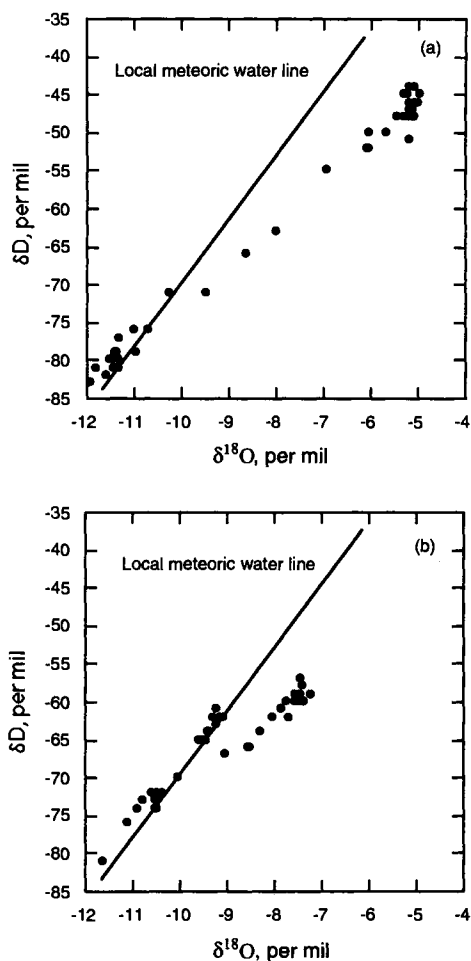


Figure 14.11. Isotopic compositions (δD versus $\delta^{18}O$) of samples collected from piezometers at hillslope site 3 (a) and hillslope site 6 (b) during June 1993. The local meteoric water line was established in a previous study (Krabbenhoft et al., 1990a), and is extended to cover the range observed at all hillslope sites.

stream (-9.5‰) would indicate that the stream either may receive water from a mixture of locally-derived groundwater and the plume of water from Big Muskellunge Lake or is simply an evaporative evolution of water from the pond at the headwaters as it moves through the stream system. Experiments to test these hypotheses are ongoing at the present time.

A cross section with shading between isopleths of $\delta^{18}O$ for hillslope site 6 is presented in Figure 14.12. Again there is a high degree of spatial variability present in a relatively small area near the stream. The isopleths of $\delta^{18}O$ suggest local recharge water getting to the stream from the hillslope, and perhaps a deeper source of water flowing toward the stream originating from below the southern bank. The -8‰ contour dipping away from the north side of the stream channel indicates that the stream probably is receiving groundwater on the southern side and

recharging water to the groundwater system on the north side of the creek. This interpretation is consistent with periodic head measurements made in selected piezometers in the vicinity of the creek. The isotopic composition (δD versus $\delta^{18}O$) of groundwater samples from below the stream (Figure 14.11b) indicate that the water under the middle and north side of the stream is derived from stream or lake recharge, which is consistent with the measured flow direction. Indeed, site 6 is directly downstream from Allequash Lake, hence the stream water will contain a high percentage of lake water.

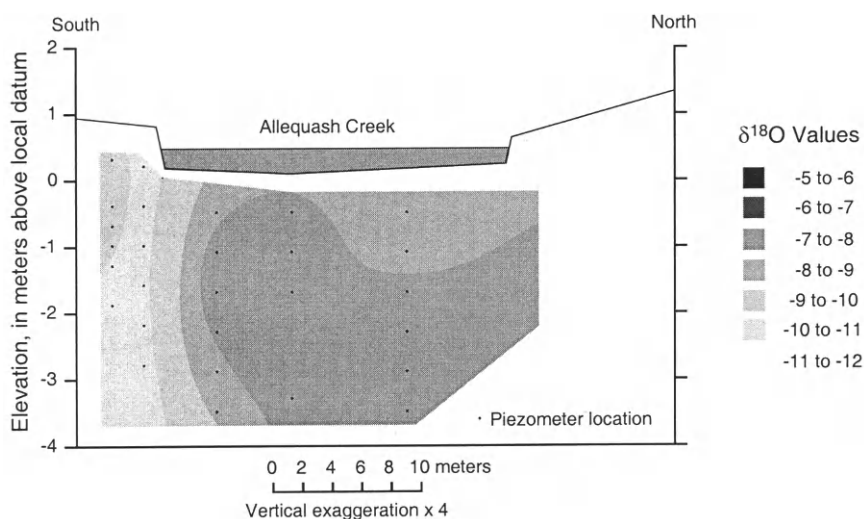


Figure 14.12. Cross section depicting shaded regions between isopleths of $\delta^{18}O$ from piezometer samples collected at hillslope site 6 during June 1993.

In summary, the overall stream system appears to move from a well-mixed groundwater-dominated system at the headwaters to a flow system with complex flow directions and sources. Midway through the stream system (site 3) the flows appear to come from both shallow and deep sources. At the outlet of the system shallow and deep sources also appear to contribute to the stream, with the added complexity of groundwater recharge as well as discharge across the stream channel. The spatial variability of the observed groundwater isotope values at the individual cross sections is verification of the complex nature of the flow system. This combination of multiple isotope sampling from the lakes, the stream, and the groundwater system has provided a powerful tool to augment more traditional hydrologic approaches.

14.5 Concluding Remarks

In this section, several observations are made based on the results of our case study. First, the importance of spatial and temporal heterogeneity is discussed in the context of using stable isotopes to distinguish components of the hydrologic budget. Next, the importance of groundwater flow and reaction paths is discussed. Finally, a case is made for the use of multiple isotopes and other environmental tracers.

Based on the results presented in Figures 14.10 and 14.12, it is clear that significant spatial heterogeneity of isotopic tracers exists (as shown in other hydrologic systems in Chapters 10, 11 and 12). Even if one could derive a single representative value, use of a single concentration to represent all groundwater would result in misleading conclusions. Under no circumstances could one have inferred the complex pattern of flow and multiple sources present in the hillslope/Allequash Creek system by just sampling the surface water. Thus, traditional streamflow separation techniques, with intensive stream sampling and limited groundwater sampling, may not have the appropriate sampling focus.

As is true in streamflow separation, a single groundwater term may not be appropriate for assessing stream water quality. For studies attempting to understand the geochemical interactions of surface water and groundwater, a more detailed analysis of flow paths is necessary. For the study presented in Section 14.4, there appear to be at least two distinct groundwater-flow sources contributing to the stream. These sources may have substantially different geochemical compositions. Likewise, the geochemical evolution depends not only on the flow paths but on the mineral composition of the matrix the water is flowing through, and the amount of contact time with the minerals. Thus, techniques to examine reaction paths are necessary for a more thorough understanding of the geochemical interactions.

The understanding of flow and reaction paths is increased by the use of multiple isotopic tracers. In the example presented in Section 14.4, the natural isotopes of water (δD and $\delta^{18}O$) were used to identify sources of water, whereas a lithogenic isotope ($\delta^{87}Sr/\delta^{86}Sr$) helped to distinguish between flow-path depths, and can be used to elucidate reaction paths. While these new tools are powerful, traditional hydrologic monitoring is crucial for corroborating isotopic results and for quantifying rates of surface water/groundwater interactions. Through a combination of multiple isotopic tracers, intensive small-scale groundwater sampling, vadose-zone sampling, precipitation sampling, and stream sampling, a more complete understanding of the interactions between surface water and groundwater can be gained.

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Use of Stable Isotopes in Evaluating Sulfur Biogeochemistry of Forest Ecosystems

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15.1 Introduction: Forest Ecosystem Sulfur Dynamics

Over the past decade there have been intensive investigations on the sulfur dynamics of forest ecosystems and surface waters. Much of this research activity has focused on temperate forests of North America and Europe. The major impetus for these studies can be attributed to the dominant role of sulfur as a component of "acidic deposition" in these regions. The dynamics of sulfur in forest ecosystems including catchments has been discussed extensively (e.g., Hultberg et al., 1994; Johnson, 1984; Johnson et al., 1986; Mitchell et al., 1992b; Mitchell and Lindberg, 1992) and thus the major aspects of sulfur dynamics will be reviewed only briefly. The major pools and fluxes of sulfur within forest ecosystems are depicted in Figure 15.1.

Atmospheric deposition is the major source of sulfur inputs for many forest ecosystems. For highly polluted areas such as Central and Eastern Europe, these atmospheric inputs can approach 80 kg S/ha/yr, but for less polluted sites inputs are generally less than 20 kg S/ha/yr, and for remote sites as little as 2 kg S/ha/yr (Mitchell et al., 1992b). Mineral weathering is generally a minor source of sulfur for most forests, especially for those underlain by soils derived from glacial till and bedrock of siliceous igneous rocks, since granite contains less than 100 µg S/g (Murphy, 1980). However, for some forest catchments in which sedimentary materials such as shales (average concentration of 2400 µg S/g) are prevalent, weathering inputs can exceed those from the atmosphere (e.g., Gibson et al., 1983; Krouse and Case, 1981; Mitchell et al., 1986).

Within forest ecosystems, both inorganic and organic forms of sulfur are found. The determination of sulfur constituents, especially organic forms, has often been defined operationally with the analytical procedures reviewed elsewhere (Tabatabai, 1992). The major organic sulfur constituents are carbon-bonded sulfur, including some amino acids, and ester sulfates such as choline sulfates and sulfated thioglycides. Carbon-bonded sulfur is generally the dominant organic form. There is often a close correspondence between organic carbon and organic sulfur concentrations in soils (Mitchell et al., 1992b). Thus on a content basis, most of the sulfur in forest ecosystems is organic (generally more than 80%) with major pools in the forest floor and mineral soil due to their respective large amounts of organic matter.

The dominant form of inorganic sulfur is sulfate for most forest ecosystems. The actual form of sulfate may vary, thus affecting the lability of various sulfate pools in the soil. The lability

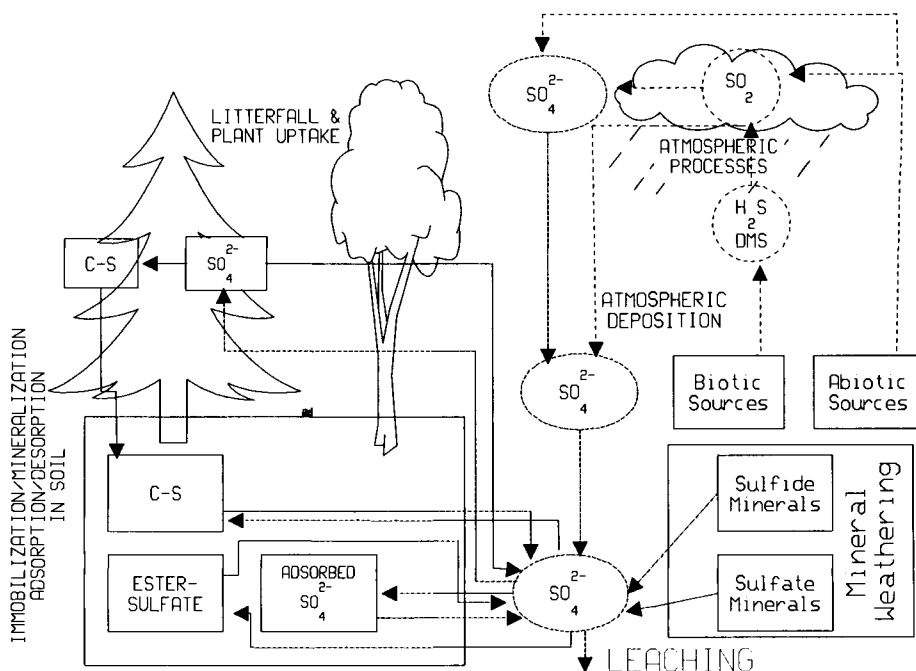


Figure 15.1. Sulfur cycle in a forest ecosystem.

ranges from: 1) highly mobile sulfate in the soil water, to 2) adsorbed sulfate, which can be desorbed, to 3) sulfate minerals, which may precipitate and redissolve, and to 4) sulfate which is irreversibly retained. The capacity for sulfate retention varies among soils, but highly weathered soils with high concentrations of iron and aluminum sesquioxides are notable for their capacity to retain sulfate (Mitchell et al., 1992b).

There has been considerable conjecture on the relative importance of organic and inorganic processes in regulating sulfate flux in forest ecosystems, but in general it appears that the organic forms (especially in the mineral soil) are quite recalcitrant and thus the short term dynamics (annual and seasonal changes) are primarily regulated by inorganic sulfate adsorption-desorption processes (Mitchell et al., 1992a, 1994). In some soils, especially those with high aluminum and sulfate concentrations, sulfate minerals such as jurbanite (AlOHSO_4) and basaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 5\text{H}_2\text{O}$) may also form. The retention of sulfate, whether adsorbed or as a mineral, is important in regulating the response of forest ecosystems to changes in sulfur inputs and thus affecting sulfate concentrations in associated surface and ground waters.

The two important pathways for sulfur loss from forest catchments are gaseous outputs and transport in water percolating through the system (Figure 15.1). It is generally believed that gaseous outputs are rather small, typically accounting for only 0.2 to 0.5 kg S/ha/yr although for tropical forests these fluxes may be greater (Andreae and Jaeschke, 1992). In contrast, losses via drainage waters may be greater than 60 kg S/ha/yr at highly polluted sites and can

even exceed current atmospheric inputs (Mitchell et al., 1992b). High removal rates by leaching are especially prevalent in soils with low sulfate adsorption capacities and high atmospheric inputs (derived from anthropogenic pollution).

15.2 Controls on Sulfur Isotope Composition

The radioactive isotope of sulfur (^{35}S) with a half-life of 87.4 days has been used extensively as a tracer and also forms naturally in the atmosphere (Cooper et al., 1991; Michel, 1993; Michel and Turk, 1995). A lack of ^{35}S in runoff is evidence that the residence time of atmospherically derived sulfate exceeds 1 year. The use of ^{35}S in forest soils has recently been reviewed by Dhamala and Mitchell (1992) and will not be discussed in this chapter. Sulfur has four stable isotopes (^{32}S , ^{33}S , ^{34}S and ^{36}S) with relative natural abundances averaging about 95.02, 0.75, 4.21 and 0.017%, respectively. Due to the higher abundances of ^{32}S and ^{34}S , mass spectrometric analyses are usually restricted to these isotopes. Generally, the sulfur is analyzed by mass spectrometry after conversion to SO_2 or SF_6 . The isotopic composition of samples is expressed using the $\delta^{34}\text{S}$ notation defined as:

$$\delta^{34}\text{S}(\text{‰}) = \left[\frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}} - 1 \right] \times 10^3 \quad (15.1)$$

where ‰ (per mil) is parts per thousand and $^{34}\text{S}/^{32}\text{S}$ is the ratio of the number of ^{34}S atoms to the number of ^{32}S atoms in the sample or standard. The historical international standard is troilite (FeS) from the Cañon Diablo meteorite. Although it is believed that the sulfur isotopic composition of the meteoritic troilite represents the primordial value of the solar system (Thode, 1991), the small isotopic variability in this standard prompted the International Atomic Energy Agency to define a Ag_2S standard (IAEA-S1) which has a $\delta^{34}\text{S}$ value of -0.30‰.

In addition to $\delta^{34}\text{S}$ measurements, $\delta^{18}\text{O}$ determinations of sulfate have also been used. The analytical procedures (Rees and Holt, 1991) and the rationale for these measurements has been reviewed elsewhere (Holt and Kumar, 1991). The isotopic compositions of both the sulfur and oxygen of sulfate have been most commonly used in examining sources of ground water sulfate. More recently, this two-element isotopic approach has been extended to ascertain the relative contributions of atmospheric inputs, organic sulfur mineralization and/or mineral weathering to sulfate in drainage waters. The use of $\delta^{18}\text{O}$ analyses in evaluating sulfur dynamics is aided by the following phenomena: 1) the rate of oxygen isotopic exchange between water and sulfate is extremely slow at low temperatures and moderate pH ranges; 2) the rate of oxygen isotopic exchange between sulfur dioxide and water is very large; and 3) the difference between $\delta^{18}\text{O}$ values in surface and ground water and ambient oxygen is usually large. As a result, sulfate is formed with distinctive $\delta^{18}\text{O}$ values. When this information is combined with $\delta^{34}\text{S}$ data, information may be obtained on the pathways and their relative contributions to sulfate formation and fluxes. Examples of such applications are described later in this chapter.

The sulfur isotopic composition of an ecosystem component is controlled by essentially two factors: the isotopic composition of sources (in combination with mixing ratios) and isotopic

discrimination during sulfur transformations. These factors result in substantial variation in natural abundances of sulfur isotopes with $\delta^{34}\text{S}$ values typically ranging from -40 to +40‰ although more extreme values may be found (Figure 15.2). Much of the differences in sulfur isotopic compositions among materials can be attributed to large kinetic isotope effects in microbially mediated sulfur transformations of which the dissimilatory sulfate reduction ($2\text{H}^+ + \text{SO}_4^{2-} + 4\text{H}_2 \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$) is most important. During this process, anaerobic bacteria of the *Desulfovibrio* and *Desulfotomaculum* genera can generate H_2S with $\delta^{34}\text{S}$ values substantially lower than that of the SO_4^{2-} reactant, which consequently becomes relatively enriched in ^{34}S .

The utilization of stable sulfur isotopes in environmental research has been recently reviewed by Krouse and Grinenko (1991). The present chapter will examine their use in conjunction with hydrological analysis focusing on forest catchments. Most of this work has concentrated on sulfur fluxes and transformations, with hydrological data being included to aid the interpretation of the sulfur isotope data. In hydrological evaluations such as discerning water flow paths, the oxygen and hydrogen isotopic composition of the water has been analyzed rather than the isotope composition of dissolved sulfate. The use of sulfur isotopes in forest ecosystems has taken two approaches: natural tracer studies where sulfur with a distinctive isotope composition has been used to identify pollutant sources or experimental tracer studies where isotopically distinctive S has been added to the system under investigation. This former approach has been employed in some detail to study the impact of sulfur dioxide emissions and dust produced from elemental sulfur blocks as products of sour gas processing plants in Alberta, Canada (Krouse et al., 1984, 1991). Information was obtained not only on the contribution of pollutants to the sulfur budgets of forests, but also to ascertain the importance of some fluxes of sulfur within the system. It is also possible to use isotopically distinct sulfur sources as tracers in ecosystem studies examining sulfur transformations and pathways. Examples of such studies are described later in this chapter.

Differences in natural stable isotope abundances have also been used to ascertain the flux pathways and transformation rates of sulfur. This natural abundance approach necessitates that sulfur components within the system have significant variation in their $\delta^{34}\text{S}$ values. These differences may be due to isotopic fractionation or the mixing of sulfur with distinctive isotopic signatures (e.g., atmospheric and mineral sulfur sources).

15.2.1 Isotope fractionation

The isotopic composition of sulfur within a forest catchment is dependent upon both the sources of sulfur (Figure 15.1) as well as any fractionation which may occur within the watershed itself. Isotopic fractionation (see Chapter 2) can be due to either isotopic exchange reactions or kinetic processes (unidirectional sulfur transformation). During bacterial sulfate reduction reactions, the overall kinetic isotope fractionation tends to increase with lower conversion rates (Chambers and Trudinger, 1979; Kaplan and Rittenberg, 1964). For simple isotopic exchange reactions (e.g., $\text{H}_2^{32}\text{S} + ^{34}\text{SO}_2 \rightleftharpoons \text{H}_2^{34}\text{S} + ^{32}\text{SO}_2$) the isotopic equilibrium constants between chemical species can be calculated. However, isotope exchange will only take place (i.e., the isotopic composition of the compounds will be altered) if local conditions provide the high activation energy required for the exchange reaction. These isotopic exchange reactions are probably less important than kinetic effects due to biotic processes in affecting *in situ* changes of the natural isotopic composition of sulfur pools within catchments.

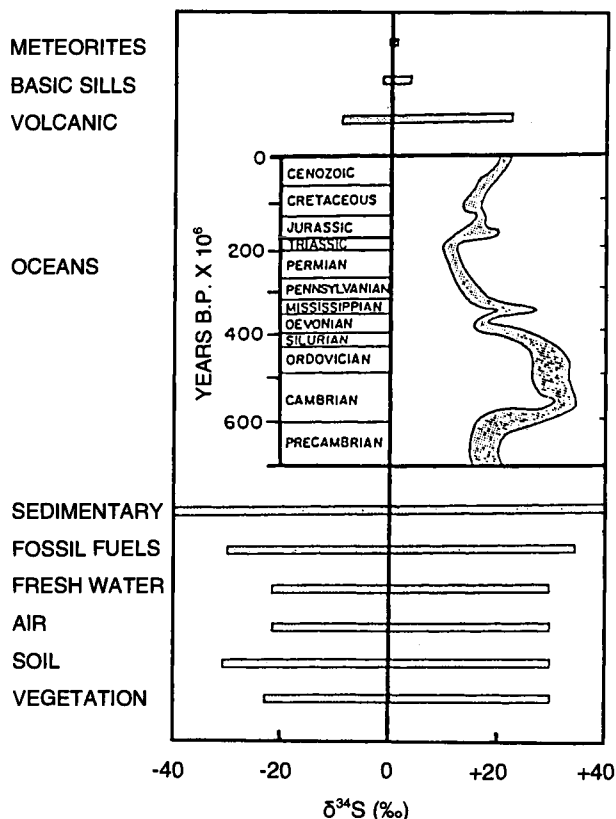


Figure 15.2. Natural variation in sulfur isotopes. From Krouse (1989).

Adsorption/desorption

The adsorption-desorption of sulfate is one of the most important processes affecting net sulfur retention or loss in catchments. It has been shown that the capacity of some watersheds to retain excess sulfur derived from acidic deposition may be explained by their soil properties. In general, older, more weathered soils have higher capacities for sulfate adsorption than younger, unweathered soils (Rochelle et al., 1987). Although there has been some attempt to relate sulfate adsorption to specific soil properties such as the presence of iron and aluminum sesquioxides, there is considerable variation in the predictive values of these characteristics among soils (Harrison et al., 1989; Mitchell et al., 1992b).

Few studies have examined isotopic fractionation associated with adsorption. Van Stempvoort et al. (1990) have shown for the Plastic Lake watershed in Ontario, Canada using both laboratory and field analyses that isotopic fractionation due to sulfate adsorption-desorption was of minor importance. They used both sulfur and oxygen isotopes to estimate a mean fractionation between dissolved and adsorbed sulfate of only -0.3‰ for $\delta^{34}\text{S}$ and $+0.1\text{‰}$ for $\delta^{18}\text{O}$ (Van Stempvoort et al., 1990; Van Stempvoort and Krouse, 1994). Mayer et al. (1992,

1993, 1995b) also found that there was little isotopic difference between sulfate in solution and adsorbed sulfate and thus concluded that adsorption plays a minor role in isotopic discrimination. Such minor fractionation needs to be clearly distinguished from the more significant fractionation due to dissimilatory sulfate reduction which has been shown in anaerobic environments (e.g., Fry, 1989; Nriagu, 1974).

Biotic processes

There is some potential for isotopic discrimination by plants especially under elevated conditions of sulfur loading (Winner et al., 1989). Although the movement of sulfur within forest vegetation and volatilization of sulfur have not been intensively investigated (Garten, 1988), these processes should not have a major effect on the isotopic composition of sulfur constituents (especially dissolved sulfate) in most forest catchments, especially in temperate regions affected by acidic deposition. As described previously, the amount of sulfur volatilized is small compared to sulfur inputs through atmospheric deposition and losses through other pathways, especially soil leaching. In temperate regions, the amount of sulfur cycling through the vegetation, as measured by requirement, is about 10 kg S/ha/yr. This amount is often less than atmospheric inputs which may range from less than 1 to more than 80 kg S/ha/yr (Mitchell et al., 1992b; Mitchell and Lindberg, 1992). There is some evidence that assimilation by some plants discriminates against ^{34}S , resulting in lower $\delta^{34}\text{S}$ values (~ -1 to -2‰) (Krouse et al., 1991). However, it is generally believed that most biological assimilation of sulfate results in little isotopic fractionation (Kusakabe et al., 1976). The vegetation is a relatively minor pool compared to the forest floor and mineral soil which together generally constitute more than 90% of the sulfur within forest catchments. It has been suggested that microbial mineralization and immobilization processes may be important in affecting the isotopic composition of organic sulfur, resulting in high ($+3.6\text{‰}$ enrichment) and low (-1‰ depletion) $\delta^{34}\text{S}$ values for ester sulfates and carbon-bonded sulfur, respectively (Mayer et al., 1992). Thus, atmospheric inputs and soil processes may be of greater importance than plant uptake in affecting the sulfur isotopic flux and content of these systems. Sulfur pools in tropical areas might show some interesting sulfur isotopic compositions due to the high volatilization rates of sulfur from vegetation and low atmospheric sulfur inputs (Andreae and Jaeschke, 1992), but no such studies have yet been performed.

Microbial processes may play a role in affecting the isotopic composition of sulfur within a watershed, especially if there are micro-sites which are oxygen depleted and thus would be subject to dissimilatory sulfate reduction. Although this process generally does not have a major impact on the overall cycling of sulfur within forest watersheds (Mitchell et al., 1992b) because oxygen depletion is not typical, there are likely to be temporal and spatial differences in $\delta^{34}\text{S}$ values in some portions of watersheds (e.g., wetlands and hyporheic zones) caused by oxidation-reduction gradients, as will be discussed later for specific studies.

To ascertain the potential role of microbial processes in affecting the isotopic composition of sulfur within the watershed, the relative importances of abiotic versus biotic transformations on sulfur need to be considered. An examination of pool sizes within forest catchments shows that the organic sulfur forms (mostly carbon-bonded sulfur and ester sulfates) generally dominate the sulfur pools. For temperate forests, organic sulfur compounds generally account from 80 to 99% of the total sulfur, except for a few sites with very high deposition rates of sulfate and either high sulfate adsorption capacities or conditions favoring the formation of sulfate minerals (Mitchell et al., 1992b; Mitchell and Lindberg, 1992). Although organic pools

dominate the overall mass of sulfur within these systems, they appear to be fairly recalcitrant even under experimental alterations such as whole-tree harvesting (Mitchell et al., 1989) or acidic additions (Mitchell et al., 1994). In contrast, significant changes in absorbed sulfate pools have been found after these same experiments. Such manipulation studies thus suggest that microbial processes mediating the immobilization of sulfate or mineralization of organic sulfur pools would not have a marked effect on the isotopic composition of sulfate in soil solution or surface waters especially in those systems with high atmospheric inputs and high leaching rates of sulfur. However, forest ecosystems, which have low inputs and substantial sulfur recycling by the biota, may develop distinctive isotopic compositions within the various sulfur pools of vegetation and soil. There are indications that dissimilatory sulfate reduction within saturated zones may be a significant source of isotopic alteration in some catchments.

15.2.2 Atmospheric sources of sulfur

Factors regulating the isotopic composition of sulfur in the atmosphere (Table 15.1) have been reviewed by Newman et al. (1991). Oceanic sources may have an important role in affecting $\delta^{34}\text{S}$ values in coastal areas since marine aerosols have a reported $\delta^{34}\text{S}$ value of +21.0‰ that reflects the present, very uniform oceanic sulfate isotopic composition (Thode, 1991). Anthropogenic emissions such as those from the combustion of fossil fuels may affect the $\delta^{34}\text{S}$ values of atmospheric sulfur even if the sources are distant (Krouse, 1989; Newman et al., 1991; Nriagu and Coker, 1978; Nriagu et al., 1991a). These anthropogenic inputs can cause considerable variation in $\delta^{34}\text{S}$ values of precipitation due to the relative contributions from various sources with different isotopic signatures (Figure 15.3). Fossil fuels and sulfide ores exhibit a wide range of isotopic compositions ($\delta^{34}\text{S}$ coal, -30 to +30‰; gas and oil, -5 to +30‰; and sulfide ores, -25 to +25‰; Newman et al., 1991). However, the observed range of $\delta^{34}\text{S}$ values from various anthropogenic emissions is often small and overlapping, making it difficult to determine sulfur sources using only $\delta^{34}\text{S}$ values.

Biogenic emissions of sulfur may also influence the isotopic composition of atmospheric sulfur. Biogenic gases such as H_2S and DMS (dimethyl sulfide) may be substantially depleted in ^{34}S as a result of kinetic isotope effects during dissimilatory sulfate reduction. For example, it has been estimated that the average $\delta^{34}\text{S}$ of volatile sulfur from marine systems is about +10‰ (Newman et al., 1991). In some localized continental locations, biogenic H_2S with very negative $\delta^{34}\text{S}$ values has been incorporated into soil and vegetation (e.g., Krouse and Van Everdingen, 1984). The role of biogenic sulfur in affecting the isotopic composition of the atmosphere has generally focused on H_2S and organic sulfur gases, especially DMS from marine and freshwater sources. It has also been shown that terrestrial plants under conditions of sulfur stress may release H_2S with a lower $\delta^{34}\text{S}$ value (difference up to 15‰) compared with that of foliar sulfate (Winner et al., 1981). Variations in anthropogenic (i.e., fossil fuel combustion) and biogenic sulfur $\delta^{34}\text{S}$ have been used to ascertain their relative contributions to atmospheric sulfur (Nriagu et al., 1987; Nriagu and Krouse, 1992).

15.2.3 Geological sources of sulfur

There is considerable variation in the $\delta^{34}\text{S}$ composition of various mineral sources (e.g., Nielsen et al., 1991). As indicated previously, a major reason for this difference is due to the

Table 15.1. Isotopic composition of atmospheric sulfur.

Location	Type of Sample	$\delta^{34}\text{S}$ mean, range (‰)	Reference
Oceanic atmosphere	SO_4^{2-} aerosols, SO_2 , particulate S, H_2S	+3.5, -21.9 to +16.2 (SD=6.24)	Newman et al. (1991, Table 5.3) ¹
Italy	Precip.	+2.1, -2.5 to +8.3	Newman et al. (1991, Table 5.4) ²
Israel	"	+6.5, +4.5 to +14.3	"
Japan	"	+7.3, -1.3 to +15.6	"
Czechoslovakia	"	+6.0, +0.4 to +9.7	"
Poland	"	+3.7, +2 to +8	"
Sweden	"	+5.9, +3.2 to +8.2	"
USSR	"	+5.8, +0.7 to +12.9 (SD=2.6, N=14)	"
USA	"	+5.6, -1.5 to +8.0	"
New Zealand	"	+10.9, 0 to +19.4	"
Canada	"	+4.9, +2 to +9.4	"
Arctic	"	+10.7, +9.2 to +11.9	"
Antarctica	"	+17, +9 to +22	"
Atlantic Ocean	"	+13.7, +12.1 to +15	"
Pacific Ocean	"	+13.1, +9.4 to +16.3	"
Bear Brook Watershed, Maine (40 km from Atlantic coast)	Precip.	+4.2 to +7.6	Stam et al. (1992)
Hubbard Brook Experimental Forest, White Mountains, New Hampshire	Precip.	+5.17, +1.68 to +8.24	Zhang (1994)
"	Precip.	+2.3 to +3.0	Saltzman et al. (1983)
"	Aerosols	+0.8 to +3.5	"
Mountains of Colorado and Wyoming	Snow Pack	+3.8 to +8.4	Turk et al., 1993; Finley et al., 1995
Mt. Evans, Colorado	Precip. (snow)	+3.5 to +4.4	Turk et al., 1993
Northwest Ontario	Precip.	+4.44 to +5.93	Hesslein et al., 1988
Central Ontario	Precip.	+2.9 to +5.6	Van Stempvoort, 1989
Canadian Arctic	Aerosols	+9.5 to +4.8	Nriagu et al., 1991a
Scandinavia	Aerosols	+4.4 to +7.6	"
Germany near Munich	Precip.	-3.9 to +3.5	Mayer et al., 1995b
Germany, Black Forest	Precip.	+0.5 to +3.6	Mayer et al., 1995a
"	SO_2	+1.0 to +6.0	"

¹Summarized from 14 means of 9 studies.²Data summarized by region from cited sources.

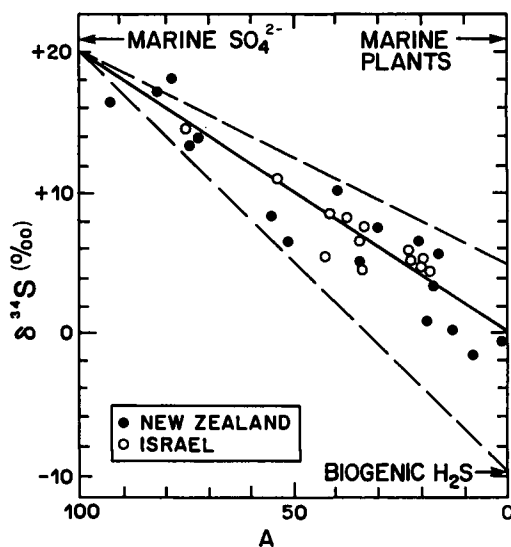


Figure 15.3. Relationship between $\delta^{34}\text{S}$ of rainwater SO_4^{2-} and percentage of seawater SO_4^{2-} near coastal areas of Israel and New Zealand. $A=100$ corresponds to 100% seawater. From Newman et al. (1991).

dissimilatory reduction of sulfate to sulfide which discriminates in favor of ^{32}S . In the formation of sulfide minerals, the isotopic difference between residual sulfate and the formed sulfide depends on whether the system is open with an unlimited supply of sulfate, or closed in which sulfate supply is restricted (see Chapter 2). In the former case, the sulfide may be highly depleted in ^{34}S . Within marine sediments, pyritic sulfides have $\delta^{34}\text{S}$ values ranging from -49.6 up to $+5.2\text{‰}$, with an average of -27.5‰ ; whereas sulfate in these sediments has a much higher average $\delta^{34}\text{S}$ value of $+20.0\text{‰}$ (Lein et al., 1983). Within different rocks, the isotopic composition of sulfur varies due to mineral composition with rocks dominated by sulfides such as pyrite generally having substantially lower $\delta^{34}\text{S}$ values than those dominated by sulfate minerals (Table 15.2). For example, within clayey rocks from Russia dominated by pyrite, $\delta^{34}\text{S}$ values ranged from -26.7 to $+1.8\text{‰}$ (with 24 out of 26 rocks being less than -3.8‰) while rocks dominated by carbonate and sulfate minerals had $\delta^{34}\text{S}$ values ranging from $+4.9$ to $+24.2\text{‰}$ (Migdisov et al., 1983). Although the actual sulfur isotopic composition of any specific rock type is a function of various geological processes, there appears to be spatial consistency of the isotopic composition of sediments formed at similar times and conditions throughout the Earth's history (Figure 15.2). Sulfur isotope data for the lithosphere have been used in evaluating sulfur residence time in the Earth's crust (Migdisov et al., 1983).

15.2.4 Sulfur isotopes in the hydrosphere

The $\delta^{34}\text{S}$ composition of waters are controlled by differences in the $\delta^{34}\text{S}$ values of atmospheric and mineral weathering inputs in conjunction with various fractionation processes (Nriagu et al., 1991b). There have been extensive studies of sulfur isotopes in marine systems. The $\delta^{34}\text{S}$ value of oceanic sulfate is $+21.0\text{‰}$ (Rees et al., 1978) and marine sulfate can have a major

influence on the isotopic composition of atmospheric inputs in watersheds near marine sources as discussed previously. Oceans as well as freshwaters can contribute biogenic inputs of reduced sulfur gases which affect the isotopic composition of atmospheric deposition (Nriagu et al., 1991b).

Reviews of limnetic $\delta^{34}\text{S}$ information have been provided by Ivanov et al. (1983) and Nriagu et al. (1991b). Based on a summary of 58 measurements from diverse lakes, Nriagu et al. (1991b) found the $\delta^{34}\text{S}$ values of sulfate were always positive, but varied from +3.5 to +87‰ while H_2S $\delta^{34}\text{S}$ values in the lakes were negative (-32 to -11‰). The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values for sulfate have been used together to evaluate both inputs to lakes, especially anthropogenic sources, as well as *in situ* processing. There is less information on lotic systems, but some patterns have been found. For example, rivers in Australia have elevated $\delta^{34}\text{S}$ values of +12‰ for sulfate due to mineralogical sources (i.e., evaporites). More typically, $\delta^{34}\text{S}$ values are lower with approximate means for rivers in Europe, North America and the entire Earth being +6, +4 and +7‰, respectively (Nriagu et al., 1991b).

Table 15.2. Mass and $\delta^{34}\text{S}$ on major sedimentary envelope of the Earth. Derived from Migdisov (1983).

Source	Sulfate		Pyrite		Total Sulfur	
	% S	$\delta^{34}\text{S}$ (‰)	% S	$\delta^{34}\text{S}$ (‰)	% S	$\delta^{34}\text{S}$ (‰)
Continents as a whole	0.105	+7.6	0.169	-8.7	0.274	-2.5
Ocean sediments, seismic layer	0.126	+19.4	0.038	-43.6	0.165	+4.8
Sedimentary envelope of Earth	0.106	+8.7	0.159	-9.3	0.265	-2.2

For studies of groundwaters, the concomitant examination of both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ has been especially useful in looking at sources and pathways of sulfur. It has been shown that the $\delta^{34}\text{S}$ values show less variability of sulfate in precipitation, soil waters, and surface waters than $\delta^{18}\text{O}$ values of sulfate from these same sources. Some of this increased variability in $\delta^{18}\text{O}$ is likely due to the large range of $\delta^{18}\text{O}$ values of water from the atmosphere to the subsurface (Hendry et al., 1986). However, the higher variability of $\delta^{18}\text{O}$ values than $\delta^{34}\text{S}$ values is largely due to bacterial mediated processes because during sulfide oxidation to sulfate, variable portions of oxygen is added from both water and oxygen; in contrast, the $\delta^{34}\text{S}$ value is conserved if all the dissolved sulfide is oxidized to sulfate (Van Stempvoort and Krouse, 1994). Analysis of both $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ has been used to trace the contribution of anthropogenic sulfate to ground waters (Van Donkelaar et al., 1995). An example of how isotope analysis of groundwater sulfate was applied to ascertain the relative contribution of bedrock gypsum in an aquifer in Ontario is shown in Figure 15.4.

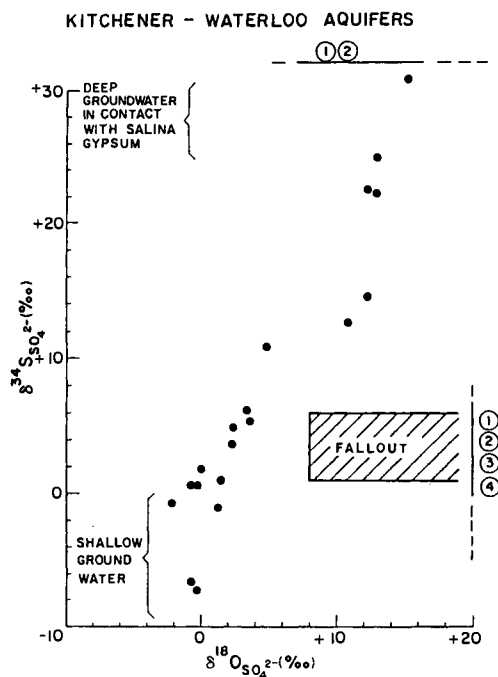


Figure 15.4. The oxygen and sulfur isotopic composition of sulfate in the Kitchener and Waterloo aquifers, Ontario. Circled numbers refer to ranges of values in the fallout area. Salina gypsum has a $\delta^{34}\text{S}$ value of +28‰. From Nriagu et al. (1991b).

15.2.5 Sulfur isotopes in soil and terrestrial vegetation

The $\delta^{34}\text{S}$ values of soils and vegetation have been reviewed by Krouse et al. (1991) and the results summarized in Figures 15.5 and 15.6. For soils the differences in $\delta^{34}\text{S}$ values among sites have been attributed to atmospheric inputs, local mineral sources and reduction processes in anaerobic environments. For example, soils in New Zealand have $\delta^{34}\text{S}$ values approaching that of seawater, suggesting the oceanic spray is the primary sulfur source (Kusakabe et al., 1976). The importance of atmospheric inputs, especially those with distinctive isotopic signatures, in affecting soil $\delta^{34}\text{S}$ values has also been demonstrated (Krouse et al., 1984). Some soils in Alberta and California with low $\delta^{34}\text{S}$ values ($\sim -30\text{‰}$) have been encountered (Figure 15.5) and it has been suggested that the sulfur was derived from the weathering of sulfide minerals and/or organic sulfur in shales (Krouse et al., 1991). For vegetation growing in areas with low atmospheric inputs of sulfur, the $\delta^{34}\text{S}$ values of vegetation generally reflect those of the soil sulfate. However, in those areas with high atmospheric inputs, the $\delta^{34}\text{S}$ composition of vegetation may also reflect direct incorporation of sulfur as sulfur dioxide through the stomata as well as possible enrichment of ^{34}S due to biogenic emission of reduced sulfur gases which may be depleted in ^{34}S (Krouse et al., 1991). However, in most cases there does not appear to be a marked difference between the $\delta^{34}\text{S}$ values in wet and dry deposited sulfur since precipitation and throughfall $\delta^{34}\text{S}$ values are similar (Mayer et al., 1995a; Mörh and Torssander, 1995; Stam et al., 1992; Van Stempvoort and Krouse, 1994).

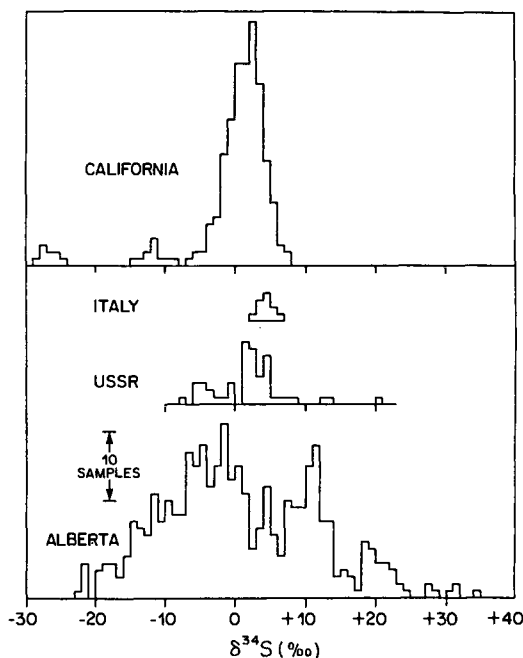


Figure 15.5. Natural sulfur isotopic abundances in various soils. From Krouse et al. (1991).

15.3 Natural Abundance Studies

There have been relatively few studies which have examined the natural isotopic composition of sulfur compounds in forest catchments. Most of these studies have focused on the use of the stable isotopes of sulfur, although some attention has also been given to analyses of oxygen isotopes in evaluating sources and sinks of sulfate. Some of these studies are described below.

15.3.1 Hubbard Brook Experimental Forest, New Hampshire

The Hubbard Brook Experimental Forest (HBEF) in the White Mountains has been a focal point of watershed biogeochemical research in the United States. Fuller et al. (1986) examined the isotopic composition of sulfur, including both organic and inorganic fractions in the soil as well as sulfate in soil water and surface waters (Figure 15.7). This analysis was done in Watershed 5 prior to whole tree harvesting in the winter of 1983-1984 (Mitchell et al., 1989). The isotopic composition of sulfate extracted from the soil (both adsorbed and soluble forms) generally corresponded to that of sulfate in soil solutions obtained by lysimeters. These inorganic soil sulfate pools tended to have higher $\delta^{34}\text{S}$ values than those of organic sulfur. The reason for the lower $\delta^{34}\text{S}$ in the organic constituents was not known, but it has been suggested that the formation of the organic sulfur occurred over a longer period dating from the last glaciation (see also Mitchell et al., 1989). Low $\delta^{34}\text{S}$ values of organic sulfur have also been documented for other sites as discussed previously.

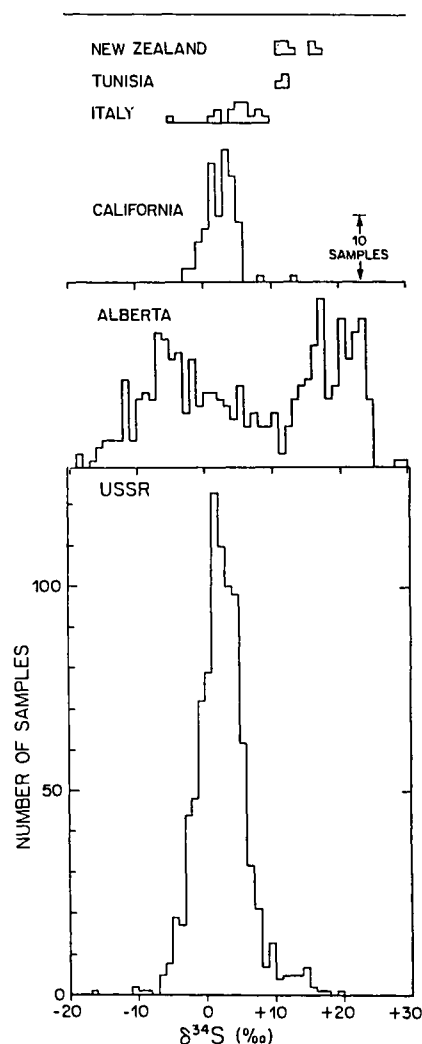


Figure 15.6. The $\delta^{34}\text{S}$ values for vegetation from various locations in the world. From Krouse et al. (1991).

Concentrations of sulfate and $\delta^{34}\text{S}$ values were also measured along an elevational gradient in soil and stream water during a one year period. Sulfate concentrations and $\delta^{34}\text{S}$ values both decreased at lower elevations (Figure 15.8). The higher sulfate concentrations in the upper elevations may have been due to a greater abundance of conifers, which are effective collectors of dry deposited sulfur (Hultberg et al., 1994). The reason for the change in $\delta^{34}\text{S}$ values was not known, but Fuller et al. (1986) suggested that it might have been due to (1) differential contributions of sulfur from weathering of minerals with distinctive $\delta^{34}\text{S}$ compositions, (2) isotopic fractionation between SO_2 and HSO_3^- in the atmosphere and differences in the relative contribution of dry and wet deposition with elevation, and (3) different contributions of sulfate reduction processes in the saturated zones at different elevations.

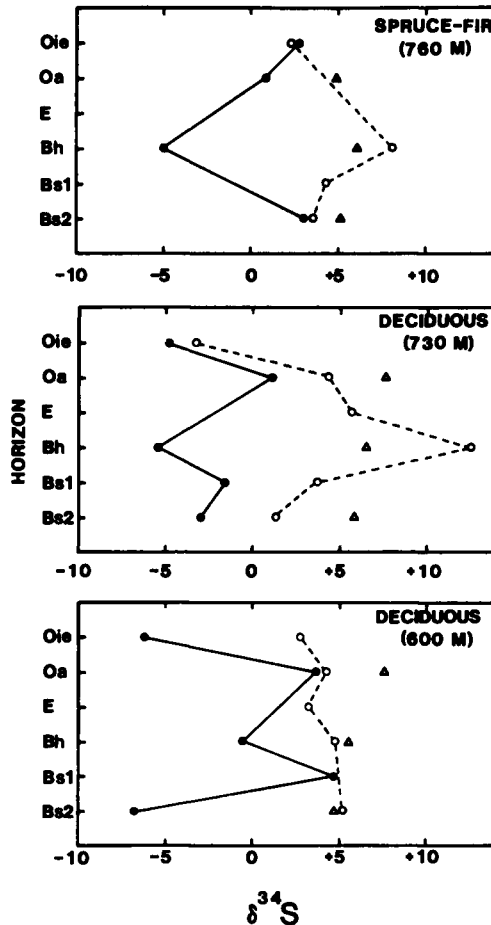


Figure 15.7. Values of $\delta^{34}\text{S}$ for both organic and inorganic fractions in the soil as well as sulfate in soil water at HBEF. From Fuller et al. (1986).

Zhang (1994), also working at HBEF, examined the isotopic composition of streams. In these streams the $\delta^{34}\text{S}$ values ranged from +0.5 to +6.4‰, with lowest values being found during the winter of 1991 which had low flow rates (Figure 15.9). A similar pattern was also exhibited in lysimeter solutions taken from the Bs horizon (Zhang, 1994). The reason for this temporal difference within the streams was not known, but it may have been partly due to the lower contribution during low flow periods of sulfate from higher elevation with its higher $\delta^{34}\text{S}$ values (Fuller et al., 1986).

15.3.2 Bear Brook Watershed, Maine

Bear Brook Watershed (BBW) is on the south-facing slope of Lead Mountain in eastern Maine and is about 40 km from the Atlantic coast. This site has been the location of various studies

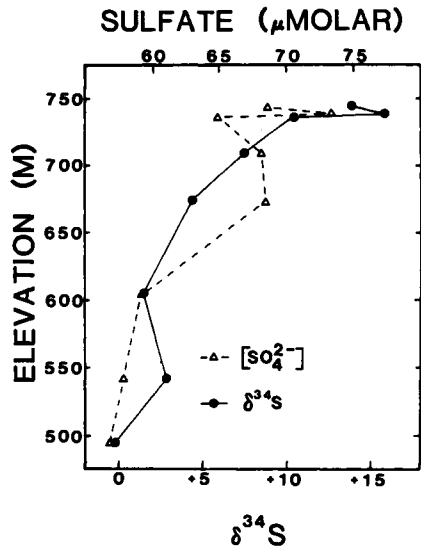


Figure 15.8. Values of $\delta^{34}\text{S}$ along elevational gradient at HBEF. From Fuller et al. (1986). Soil organic sulfur (solid circles); soil sulfate (open circles); soil solution (open triangles).

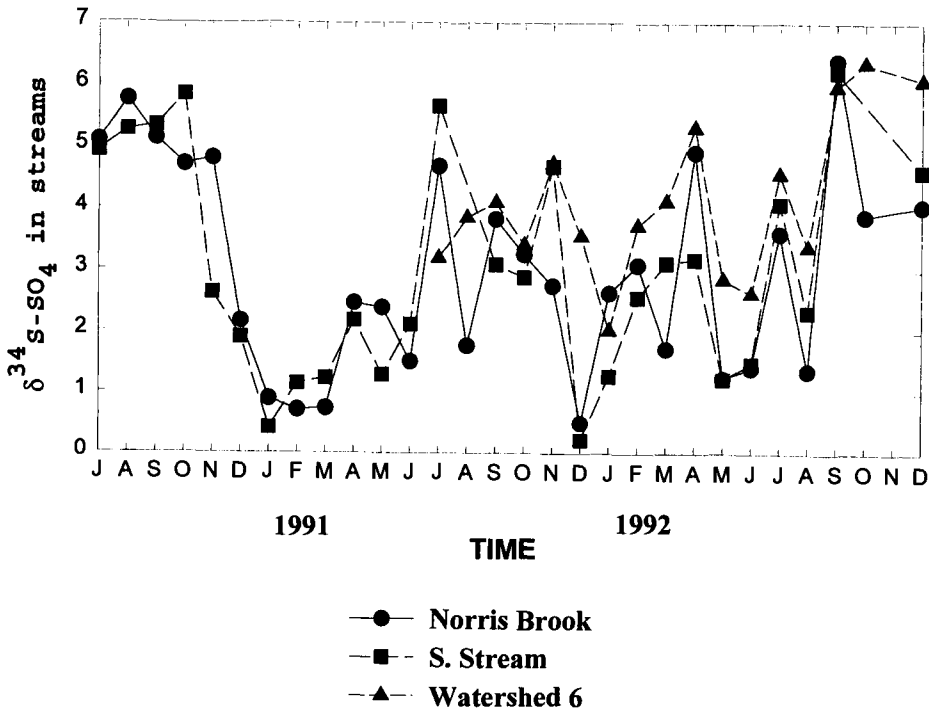


Figure 15.9. Values of $\delta^{34}\text{S}$ for streams at HBEF. Modified from Zhang (1994).

on biogeochemistry including experimental chemical additions which will be described later. Precipitation and stream $\delta^{34}\text{S}$ measurements from 1989 through 1990 were reported by Stam et al. (1992). An update through 1992 is reported below.

Sulfur isotope compositions of sulfate of precipitation (range: $\delta^{34}\text{S}$ -1.6 to +7.6‰) and throughfall (range: -0.7 to +7.5‰) varied considerably while exhibiting a general decline over time (Figure 15.10). From July 1987 to the commencement of $(\text{NH}_4)_2\text{SO}_4$ manipulation of the West Bear Brook (WBB) watershed in November 1989, $\delta^{34}\text{S}$ values of stream sulfate were very closely matched to those of East Bear Brook (EBB) (Figure 15.11). Over the five and one-half years of monitoring, $\delta^{34}\text{S}$ values of stream sulfate in East Bear Brook (EBB, non-manipulated watershed) decreased at a rate similar to that of precipitation and throughfall. In addition to this general decrease over the course of the study, $\delta^{34}\text{S}$ values of stream sulfate for both East and West Bear Brooks fluctuated among years, as well as among and within seasons of a single year. Often there was a decrease in $\delta^{34}\text{S}$ values of stream sulfate during the first major late winter/early spring snowmelt. This decrease was followed by a general increasing trend in $\delta^{34}\text{S}$ values until the following late winter/early spring snowmelt period. Shorter-term fluctuations in $\delta^{34}\text{S}$ values modified this general post-snowmelt increase. The shorter-term fluctuations corresponded with the $[\text{SO}_4^{2-}\text{-marine}]/[\text{SO}_4^{2-}\text{-total}]$ of stream solutions. This relationship supported the interpretation that the isotopic composition of stream sulfate was controlled by the relative concentrations of marine versus non-marine sulfate.

At BBW, $\delta^{34}\text{S}$ values of stream sulfate were sometimes controlled by inputs from atmospheric deposition. When fresh precipitation and throughfall were not stored in the snowpack, $\delta^{34}\text{S}$ values of contemporaneous stream and precipitation and/or throughfall samples tended to be similar. The similar rates of decrease in $\delta^{34}\text{S}$ values of stream sulfate with those of precipitation and throughfall further support this interpretation.

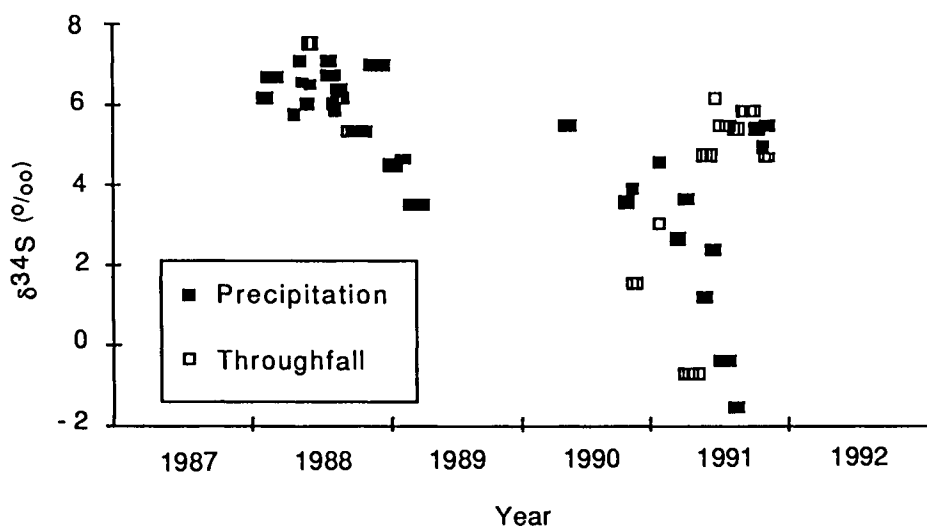


Figure 15.10. Values of $\delta^{34}\text{S}$ of precipitation and throughfall at BBWM from 1988 through 1992. From Stam et al. (1992) and unpublished data.

An absence of any significant change in $\delta^{34}\text{S}$ values of sulfate with elevation along either East or West Bear Brook may indicate the lack of any elevationally dependent processes (e.g., biological isotopic fractionation, mineral weathering, or scavenging of sulfur dioxide aerosols) that could produce such a change. This absence of elevation differences in $\delta^{34}\text{S}$ values of SO_4^{2-} differs from the pattern noted previously for HBEF, emphasizing the importance of monitoring site specific characteristics. Given the relatively small size and steep terrain of the catchment, water residence time within the watershed may be of such short duration that fractionation of sulfur isotopes is minimized by mixing. Increases in $\delta^{34}\text{S}$ values of stream sulfate during snowpack, however, may have reflected fractionating processes and/or the increased influence of another sulfur source (e.g., soil compartment) within the watershed.

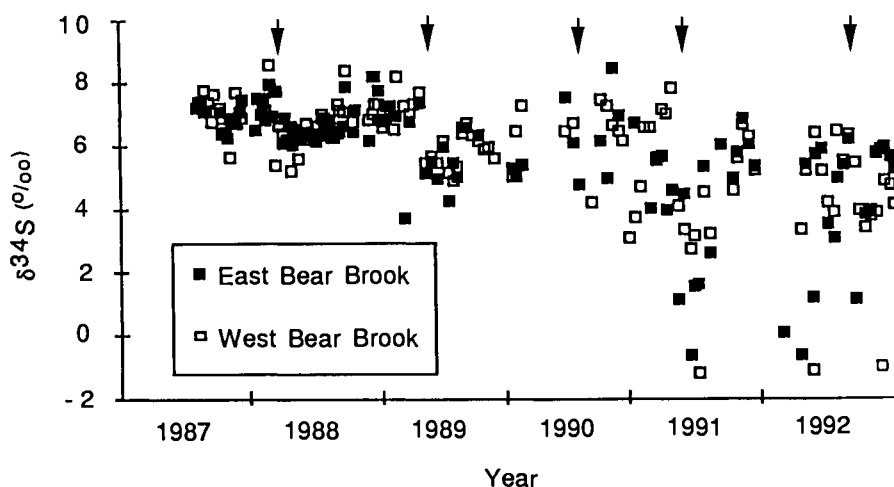


Figure 15.11. Values of $\delta^{34}\text{S}$ of East and West Bear Brook at Maine from 1987 through 1992. From Stam et al., 1992 and unpublished data. Arrows indicate the first major late winter/early spring snowmelt.

15.3.3 Experimental Lakes Area, Ontario, Canada

Hesslein et al. (1988) monitored $\delta^{34}\text{S}$ values in stream inflows and outflow of Lake 239. The $\delta^{34}\text{S}$ in precipitation sulfate ranged from +3 to +9‰ with a mean of +4.8‰. Within the streams, the $\delta^{34}\text{S}$ values ranged from +5 to +15‰ and showed pronounced variation with both stream flow and sulfate concentration (Figure 15.12). Hesslein et al. (1988) suggested that this relationship might be due to greater dissimilatory sulfate reduction rates from inlet streams during low flow periods, resulting in lower sulfate concentrations and higher $\delta^{34}\text{S}$ values. They also used the isotopic data to calculate sulfur retention within the lake and found that the isotopic balances were in general agreement with those obtained by elemental mass balances.

15.3.4 Rocky Mountains, Colorado and Wyoming

Turk et al. (1993) reported on the $\delta^{34}\text{S}$ values (range -4.1 to +6.7‰) of high altitude lakes (elevation 3,002 to 3,993 m) in Colorado. For those lakes with positive $\delta^{34}\text{S}$ values (+4.4 to

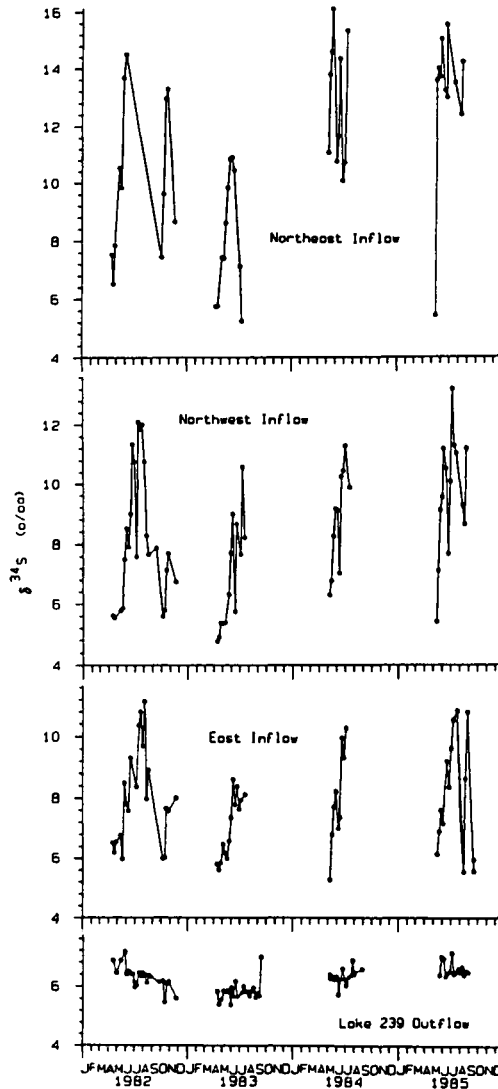


Figure 15.12. Values of $\delta^{34}\text{S}$ for Lake 239 at ELA in Ontario. From Hesslein et al. (1988).

+6.7‰), the isotopic composition was similar to that of precipitation inputs and associated snow packs (Table 15.1). For the lakes with negative $\delta^{34}\text{S}$ values (-3.5 to -4.5‰), Turk et al. (1993) suggested that there were significant sources of mineral sulfur (i.e., pyrite), the weathering of which would contribute to these lower values. A pyrite sample obtained within the vicinity of one lake had a $\delta^{34}\text{S}$ value of -7‰. The differences in isotopic composition of atmospheric versus mineral sulfur were used in estimating the relative contribution of these two sources to the lakes. For three lakes with high sulfur inputs from mineral weathering, atmospheric sulfur contributed from 17 to 43% of the sulfate within the lake.

Finley et al. (1995) used $\delta^{34}\text{S}$ determinations to ascertain the sources of sulfur for a catchment at West Glacier Lake, Wyoming (elevation 3,270 to 3,500 m) in which $\delta^{34}\text{S}$ runoff values of sulfate ranged from -1.8 to +4.9‰. Concentrations of sulfate were inversely related to discharge rates and $\delta^{34}\text{S}$ values. Atmospheric sulfur (determined from snow pack samples) had a $\delta^{34}\text{S}$ value of +5.6‰ that was higher than the $\delta^{34}\text{S}$ values of pyrite samples (range +0.7 to +4.1‰) from bedrock. It was concluded that these pyrite samples were not representative of the sulfur from mineral weathering because a two component mixing model would predict lower $\delta^{34}\text{S}$ values from mineral weathering. Other factors that were considered were the effects of preferential dilution of sulfate from the snowpack and microbial processes in affecting the resultant $\delta^{34}\text{S}$ values, but the quantitative importance of these processes was not known.

15.3.5 Black Forest, Germany

The $\delta^{34}\text{S}$ values of sulfate (in precipitation, throughfall, soil water, stream water, and groundwater), SO_2 in the air, and sulfur in the soil and bedrock were studied in the Black Forest by Mayer et al. (1995a). The $\delta^{34}\text{S}$ values show that atmospheric deposition, not mineral weathering, was the major source of sulfur to these systems. However, $\delta^{18}\text{O}$ values of soil water sulfate indicate that a considerable proportion of the sulfate was derived from the mineralization of the carbon-bonded sulfur, suggesting that atmospherically derived sulfur was cycling through the organic soil pool. Results from this study showed that in precipitation, $\delta^{18}\text{O}$ values of sulfate and water were positively related (Figure 15.13). Previous studies have also reported a marked depletion of $\delta^{18}\text{O}$ values of sulfate between precipitation and runoff in forested catchments (e.g., Caron et al., 1986). For the Black Forest site, positive relationships between $\delta^{18}\text{O}$ values of sulfate and water were found for soil solutions taken at 10 and 30 cm depths, but not at 80 cm (Figure 15.13). There was also a trend of decreasing $\delta^{18}\text{O}$ values of sulfate as precipitation water passed down through the first meter of soil. The only process that could explain these differences in the pattern of $\delta^{18}\text{O}$ values of sulfate in soil solution would be the mineralization of carbon-bonded sulfur.

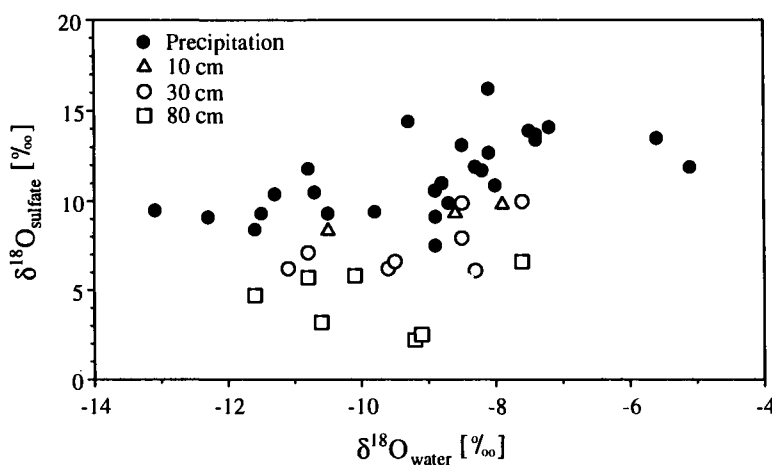


Figure 15.13. Relationship between $\delta^{18}\text{O}$ values in water and sulfate in precipitation and soil solution taken from 1989 and 1992 in two forested catchments in the Black Forest of Germany (Mayer, 1993).

The $\delta^{34}\text{S}$ values varied with depth and among the sulfur fractions (i.e., organic sulfur and inorganic sulfate). Mayer et al. (1995a) suggested that these differences were due to isotopic fractionation in which the forest vegetation and microbes show small accumulations of the heavier $^{34}\text{SO}_4^{2-}$, whereas during mineralization of organic sulfur to sulfate the lighter ^{32}S reacts preferentially. They also found that sulfate adsorption/desorption had a negligible effect on isotope fractionation.

15.4 Applied Tracer Studies

The availability of sulfur minerals with a wide range of $\delta^{34}\text{S}$ values makes it possible to use them as tracers in evaluating sulfur cycling.

15.4.1 Hubbard Brook Experimental Forest, New Hampshire

Fourteen plots were established in 1988 within Norris Brook Watershed at HBEF (Zhang, 1994). Zero tension lysimeters were installed under the Oa, Bh, and Bs horizons. Three treatment levels were used: low, medium, and high (46, 183 and 594 kg S/ha/yr, respectively) with three replicates and five plots as control. Ammonium sulfate ($\delta^{34}\text{S} = -3\text{‰}$) was added monthly on 12 subplots (4 m²) for two years starting June 1990. Lysimeter solutions were collected monthly and analyzed for sulfate and $\delta^{34}\text{S}$. Soil samples were collected in May 1991 and June 1992. The soil samples were analyzed for sulfur constituents and their respective isotope compositions. There was a distinct treatment effect on sulfur isotopic ratios in both lysimeter solutions (Figure 15.14) and soils (Figure 15.15). In general, the higher the dosage, the lower the $\delta^{34}\text{S}$ values of solution and soil due to the contribution of the $(\text{NH}_4)_2\text{SO}_4$.

It was assumed that sulfate in solution came only from soil and fertilizer, with atmospheric contributions being negligible since the fertilizer loading rates generally far exceeded atmospheric inputs (11 to 28 kg S/ha/yr; Likens et al., 1990). A model was developed which used these isotopic data to estimate how much of the sulfate in solution was derived from $(\text{NH}_4)_2\text{SO}_4$:

$$(\delta^{34}\text{S}_w \cdot [\text{SO}_4^{2-}]_w) = (\delta^{34}\text{S}_f \cdot [\text{SO}_4^{2-}]_f) + (\delta^{34}\text{S}_s \cdot [\text{SO}_4^{2-}]_s) \quad (15.2)$$

where $\delta^{34}\text{S}_w$, $\delta^{34}\text{S}_f$ and $\delta^{34}\text{S}_s$ refer to lysimeter solution, fertilizer (-3‰), and soil, respectively. $[\text{SO}_4^{2-}]_w$, $[\text{SO}_4^{2-}]_f$ and $[\text{SO}_4^{2-}]_s$ refer to sulfate concentration in lysimeter solution, fertilizer, and soil, respectively. This equation can be rearranged to:

$$[\text{SO}_4^{2-}]_f = \left\{ [\text{SO}_4^{2-}]_w \cdot (\delta^{34}\text{S}_w - \delta^{34}\text{S}_s) \right\} / \left\{ \delta^{34}\text{S}_f - \delta^{34}\text{S}_s \right\} \quad (15.3)$$

As expected the model calculations demonstrated that the amount and proportion of sulfate from $(\text{NH}_4)_2\text{SO}_4$ increased with loading (Figure 15.16). It was also found that the increased retention with loading was caused mainly by a decreased solution pH, which increased soil adsorption of sulfate, and may have possibly contributed to the formation of sulfate minerals (Zhang, 1994).

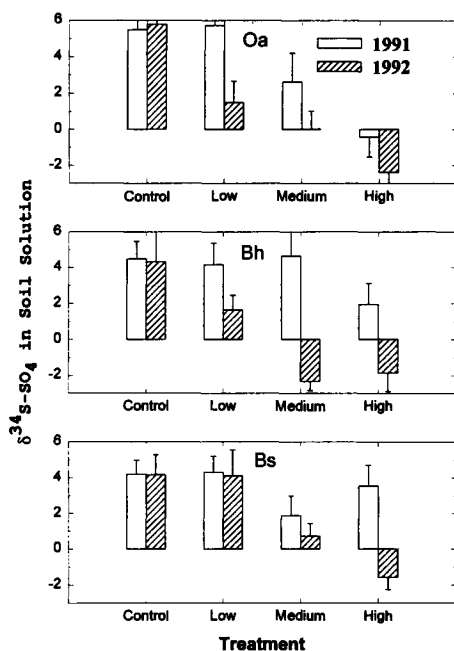


Figure 15.14. Values of $\delta^{34}\text{S}$ in soil water with different application rates of ammonium sulfate at HBEF. Modified from Zhang (1994).

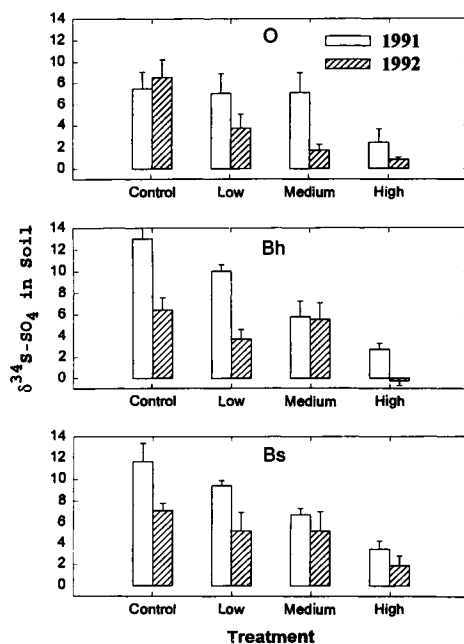


Figure 15.15. Values of $\delta^{34}\text{S}$ in soil sulfur with different application rates of ammonium sulfate at HBEF. Modified from Zhang (1994).

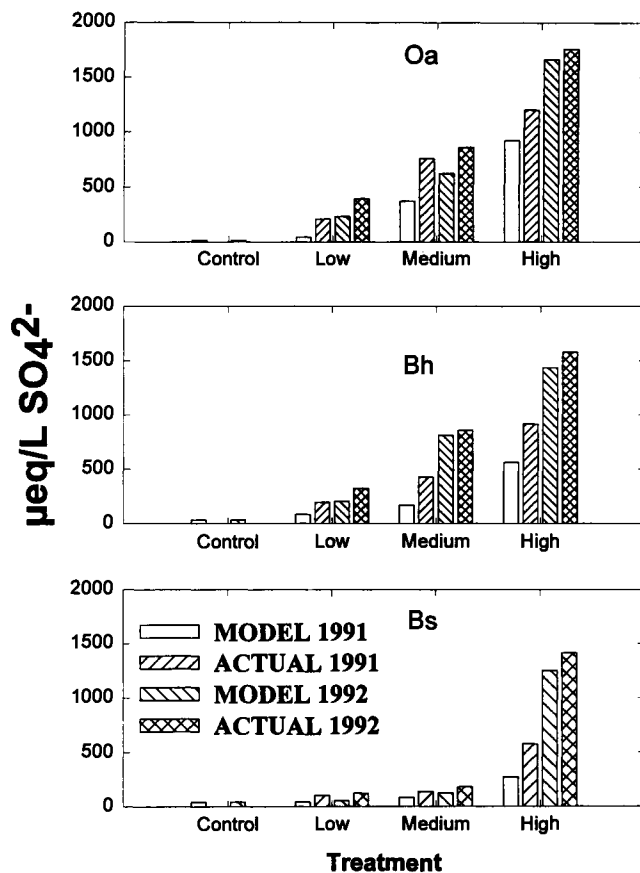


Figure 15.16. Mass balance calculations using isotopic data at HBEF using model described in text. Modified from Zhang (1994).

15.4.2 Bear Brook Watershed, Maine

Addition of $(\text{NH}_4)_2\text{SO}_4$ (29 kg S/ha/yr; $\delta^{34}\text{S} = -3.0\text{‰}$) to the West Bear Brook watershed increased concentrations and altered $\delta^{34}\text{S}$ values of stream sulfate in West Bear Brook (WBB) within two weeks following the first watershed treatment on November 1989. For the first two years of watershed treatment, the effects of $(\text{NH}_4)_2\text{SO}_4$ on $\delta^{34}\text{S}$ of stream sulfate values were variable, and it was not until the third year of watershed treatment that the $\delta^{34}\text{S}$ of stream sulfate was affected in a consistent manner by treatment.

Ammonium sulfate influenced $\delta^{34}\text{S}$ values of WBB stream sulfate in two distinctly different ways depending on the season during the first two years of watershed manipulation. For example, during the summers of 1990 and 1991, added sulfate lowered the $\delta^{34}\text{S}$ values of WBB stream sulfate with respect to that of East Bear Brook (EBB) (Figure 15.11). This indicates the transfer of the treatment sulfate through the watershed to the stream without marked interactions which alter isotopic abundances.

In the second pattern, which is indicative of more complex sulfur dynamics, the $\delta^{34}\text{S}$ values of stream sulfate in WBB were influenced in a manner opposite to the isotopic composition of treatment sulfate. For example, during the first four months of watershed manipulation, ^{34}S -enriched sulfate (initial watershed treatment sulfate was $+11.9\text{‰}$ $\delta^{34}\text{S}$) caused a decrease, rather than an increase in $\delta^{34}\text{S}$ values of WBB stream sulfate with respect to those of EBB. It is hypothesized that isotopic exchange of ^{34}S -enriched treatment sulfate with comparatively ^{34}S -depleted sulfate which was present on the anion exchange complex within the watershed caused the retention of ^{34}S -enriched treatment sulfate and mobilization of the ^{34}S -depleted sulfate.

In a manner which was also inconsistent with the isotopic composition of treatment sulfate, the two summer periods (1990 and 1991) of similarity between $\delta^{34}\text{S}$ values of treatment sulfate and stream sulfate were each followed by an autumn-through-spring-snowmelt period during which $\delta^{34}\text{S}$ values of WBB stream sulfate was increased relative to that of EBB even though the $\delta^{34}\text{S}$ value of treatment sulfate was -3.0‰ . The increases from 1991-1992 of $\delta^{34}\text{S}$ values in stream sulfate occurred even after the WBB watershed had received ten treatments of $(\text{NH}_4)_2\text{SO}_4$ with a low $\delta^{34}\text{S}$ value. These results also suggest that significant amounts of the added sulfate were being held within the watershed and the sulfate in drainage waters from WBB contained substantial amounts of sulfur previously retained in the soil. These results differ from that obtained from the natural abundance studies (see Section 15.3.2) which suggested rapid loss of sulfate from some precipitation events and snowmelt. Such differences might be due to differences in hydrologic pathways during periods of short water residence times such as during snowmelt compared to base flow conditions.

During autumn, elevated $\delta^{34}\text{S}$ values of stream sulfate coincided with increases in precipitation and stream flow. Elevated stream concentrations of nitrate and sulfate also occurred during this time. This coupled with the ^{34}S -enriched nature of ester sulfate ($+5$ to $+16\text{‰}$ $\delta^{34}\text{S}$ versus $+3.5$ to $+5.2\text{‰}$ $\delta^{34}\text{S}$ for inorganic sulfate) within watershed soils support the hypothesis that mineralization of ester sulfate was the cause of elevated $\delta^{34}\text{S}$ values of WBB stream sulfate during these periods. The absence of such a pattern during the third year of watershed manipulation is interpreted as indicating that this labile soil pool of ester sulfate had equilibrated with the treatment sulfate.

15.4.3 West Whitecourt, Alberta, Canada

In Alberta sour (H_2S rich) gas processing has presented the opportunity for large scale isotope tracer experiments. Sulfur dioxide emissions and sulfur dust with $\delta^{34}\text{S}$ values around $+20\text{‰}$ were added to boreal forest ecosystems with background $\delta^{34}\text{S}$ values ranging from 0 down to -30‰ . At West Whitecourt, penetration of the technogenic sulfur into the subsoil has been determined very effectively with sulfur isotopes (Legge and Krouse, 1992). The proportions and concentrations of sulfate attributable to the industrial operation have also been determined by isotope balance calculations for surface waters. A correlation was also found between the concentration of dissolved organic sulfur and the $\delta^{34}\text{S}$ values of sulfate attesting to the reaction of pollutant sulfur with natural organic compounds (Krouse et al., 1984). More recently, sulfur isotope data have identified sulfate reduction in some groundwater at relatively shallow depths, probably promoted in localized organic-rich waterlogged environments.

15.4.4 Bavaria, Germany

Mayer et al. (1992, 1993, 1995b) and Prietzel et al. (1995) studied the effects of elevated sulfur inputs to forest soils in Bavaria, Southern Germany. They used sulfate, which was derived from Silurian gypsum of the Salina Formation from Ontario, Canada, as a tracer for sulfur cycling. This sulfate had a high $\delta^{34}\text{S}$ value of +28‰ which differs by more than 25‰ from the natural and anthropogenic sulfur sources at their five study sites. This isotopically labeled sulfur was added into forest soil cores taken from each site as a mixture of calcium sulfate, ammonium sulfate and sulfuric acid that approximated throughfall chemistry for German forest ecosystems. Sulfur fractions and their respective isotopic compositions in the soil and leachates were analyzed (Figure 15.17). These data were used to calculate the amount of sulfate which was retained. After 89 weeks the maximum amount of sulfate throughput in seepage water was only 34% of the input. From 36 to 74% of the sulfur added was retained as inorganic sulfur with the remainder being incorporated into organic sulfur (Mayer et al., 1993, 1995b). The magnitude of incorporation into organic forms was greater than that generally found for forest soils (Mitchell et al., 1992b), although some investigations have suggested that incorporation of sulfur into organic sulfur may be an important factor for sulfur retention in some forest watersheds (Fitzgerald et al., 1983; Swank et al., 1984). For this same experiment, however, Prietzel et al. (1995) reported that the sulfate adsorption was the major factor affecting the retention of sulfur in these soils and that adsorption and possibly formation of sulfate minerals exceeded microbial immobilization by a factor from two to four.

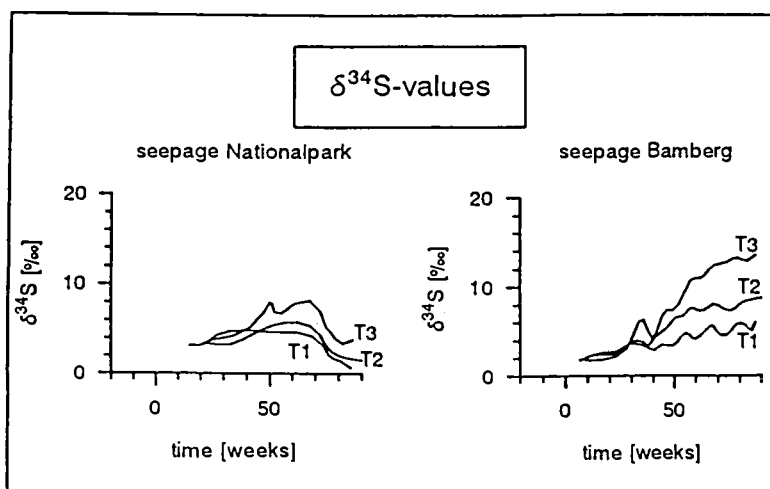


Figure 15.17. Values of $\delta^{34}\text{S}$ in soil leachates (seepage) from soil column experiments in Germany. From Mayer et al. (1993).

15.4.5 Höglwald, Germany

The environmental consequences of K_2SO_4 application were evaluated in a Norway spruce forest at the Höglwald site near Munich, Germany. A solution of K_2SO_4 (70 kg S/ha) was added

in July 1990. The sulfur was derived from Silurian gypsum and had a $\delta^{34}\text{S}$ value of +26‰. Before application of the experimental solution, the soil and drainage water had $\delta^{34}\text{S}$ values near 0‰. Drainage water was sampled beneath the forest floor and at 20 and 100 cm soil depths. Sulfur isotopic data indicated that the sulfate passed through the forest floor within the first four months of application. At 20 cm depth, the $\delta^{34}\text{S}$ values increased to +14‰ during the first six months of the experiment, accounting for approximately 50% of the added sulfur. Thereafter, the $\delta^{34}\text{S}$ values decreased gradually, suggesting that the sulfur had been retained in the upper portion of the soil. No isotopically labeled sulfate could be detected at 100 cm soil depth even 2.5 years after application. Within the A horizon at the surface of the mineral soil total $\delta^{34}\text{S}$ values of total sulfur in soil increased 5‰ confirming that most of the added sulfur was being retained in the top of the soil profile. Total sulfur in the soil below 40 cm showed no evidence of isotopic enrichment. Analyses of sulfur constituents suggested that the added sulfur was being retained as either adsorbed sulfate or sulfate minerals (Figure 15.18).

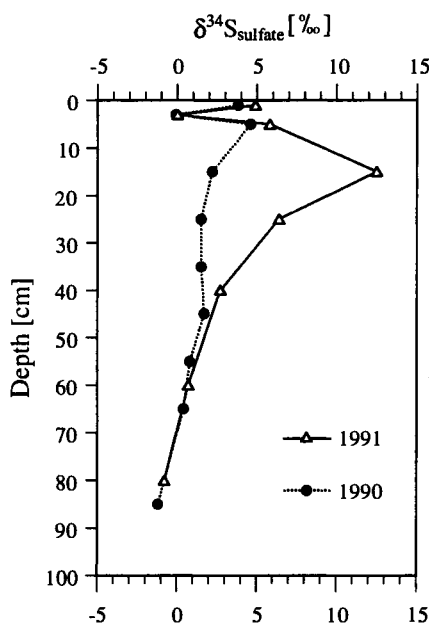


Figure 15.18. Effects of K_2SO_4 ($\delta^{34}\text{S}$ value of +26‰) additions on LiCl-extractable soil sulfate $\delta^{34}\text{S}$ values taken before (1990) and 11 months (1991) after treatment at Höglwald, Germany.

15.4.6 Black Forest, Germany

Two catchments with Norway spruce forests were treated in 1988 with MgSO_4 and $(\text{NH}_4)_2\text{SO}_4$ (170 kg S/ha). The $\delta^{34}\text{S}$ values of the fertilizer were 8 and 12‰ higher, respectively, than those values of the foliage, soil and seepage water in the catchments (Giesemann et al., 1995). There was a maximum increase of 2‰ in $\delta^{34}\text{S}$ in foliage 6 to 18 months after application suggesting some uptake of the added sulfur by the forest stand. Changes in $\delta^{34}\text{S}$ values of total sulfur in soil were <2‰, but $\delta^{34}\text{S}$ values for phosphate extractable sulfate increased up to 4‰.

15.4.7 Skjervatjern Catchment, Norway

The HUMEX (Humic Lake Acidification Project) program used experimental additions of sulfuric acid in a small catchment (8.9 ha) on granitic bedrock which is covered primarily with organic rich soils up to 2 m in depth. The added sulfate was depleted in ^{34}S ($\delta^{34}\text{S}$ value $\sim 0\text{‰}$) compared to the $\delta^{34}\text{S}$ values in the non-sulfate component of peat and the sulfate within the lake which were $+13.7$ and $+12.3\text{‰}$, respectively (Morgan, 1992). Peat was sampled at a controlled portion of the watershed as well as at two sites (lower and upper bog) which were experimentally acidified. At all sites Cr-reducible sulfur (iron sulfide compounds) had lower $\delta^{34}\text{S}$ values than the total sulfur pool which was dominated by carbon-bonded sulfur. The lower $\delta^{34}\text{S}$ for the Cr-reducible sulfur reflects its formation by dissimilatory sulfate reduction. For $8\frac{1}{2}$ months after the initiation of acidification, there was no detectable change in either sulfur pools or $\delta^{34}\text{S}$ values of peat. The lack of response was not unexpected due to the short duration of the experiment. Also, the addition rate of sulfuric acid was lower than originally planned due to mechanical problems. However, it was found that the $\delta^{34}\text{S}$ values were consistent among sites and with peat depth, suggesting that changes in sulfur pools may be detected in the future.

15.4.8 Lake Gårdsjön Catchment, Sweden

The reversibility of acidification was investigated using a roof enclosure (6300 m^2) over a catchment at Lake Gårdsjön. Values of $\delta^{34}\text{S}$ were ascertained for bulk deposition, throughfall, soil water, groundwater and drainage one year prior and two years after the roof was erected (Mörth and Torssander, 1995). Before the roof was erected, soil sulfate had a uniform $\delta^{34}\text{S}$ value of $+5.5\text{‰}$. After the roof was erected, water which contained marine derived sulfate ($+19.5\text{‰}$ $\delta^{34}\text{S}$ and $+9.3\text{‰}$ $\delta^{18}\text{O}$) was sprinkled on the catchment at a rate of 2.2 kg S/ha/yr versus a previous input of 14.2 kg S/ha/yr . Although the sulfate concentration in drainage decreased by about 30%, the $\delta^{34}\text{S}$ value of sulfate changed only 0.5‰ suggesting substantial mixing of the added sulfate with sulfur in the catchment. The $\delta^{18}\text{O}$ values of sulfate indicate that from 17 to 26% of the sulfate was derived from oxidation of sulfur (e.g., mineralization of carbon-bonded sulfur) although no net mineralization of sulfur was detected. For this roof experiment mass chemical balances concluded that 25% of the sulfate lost in drainage was from sulfate added by sprinkling, but the isotopic information indicated that only a small portion of this added sulfate was actually being lost with the remainder of the sulfur being derived from native sulfur pools. These results agree with other studies (e.g., Mayer et al., 1995a,b) which have also shown that there is considerable recycling of sulfur in forest ecosystems although mass balances may suggest that there is little net retention of sulfur.

15.5 New Research Directions

1) Further application of the combined use of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ analyses may help to differentiate the various sources of sulfate in catchments. Such analyses can be applied to various sources and sulfur pools. These analyses could be combined with isotopic determinations of water to evaluate both hydrological and biogeochemical processes concomitantly.

2) Further development of techniques which allow for determination of $\delta^{34}\text{S}$ in small ($<20\mu\text{g S}$) samples (e.g., Giesemann et al., 1994; Pichlmayer and Blochberger, 1988; Wachsmann and Heumann, 1992) will permit greater refinement of S isotopic distributions both among S constituents as well as better delineation of temporal and spatial variability of S fluxes and pools.

3) Because the dynamics of sulfur and nitrogen are inextricably linked in forest watersheds and both sulfur and nitrogen are important constituents of acidic deposition, concomitant studies of $\delta^{34}\text{S}$ and $\delta^{15}\text{N}$ in conjunction with chemical mass balances would be useful.

4) The production of inexpensive isotopically distinct S compounds would make experimental studies on sulfur dynamics more cost effective, especially at the whole catchment scale. Currently enrichment studies are limited to compounds which differ in $\delta^{34}\text{S}$ values by only 10 to 30‰ from typical natural abundances. Using such small enrichments makes it difficult to detect changes in the sulfur isotopic composition especially when natural pool sizes are large compared to the experimental additions.

5) More detailed studies *in situ* are needed on isotopic discrimination processes especially those associated with microbial mineralization and immobilization in forest soils.

6) Studies of tropical forest catchments are needed and may present unique opportunities for examining sulfur isotopic relationships.

15.6 Summary

The understanding of the sulfur dynamics of forest catchments has advanced considerably during the past decade. General background information has been obtained on the stable sulfur isotopic composition of various constituents of these ecosystems. Some of this information has aided in the interpretation of sulfur dynamics for studies using natural abundance measurements and experimental additions of isotopically distinct sulfur compounds. In a few cases these "experimental" additions have been the direct result of anthropogenic pollution from fossil fuel processing or utilization.

Studies of forest watersheds using a combination of elemental and isotopic mass balances have produced new insights on sulfur dynamics. To date, however, there has yet to be completed a thorough study on stable sulfur isotopes within a catchment that quantifies all sources, sinks and pools. Such a study may be especially useful if a system can be found in which the constituents have distinctive isotopic compositions. Further information is also required on basic processes affecting the flux and distribution of sulfur isotopes within the system. Although there have been some studies which have combined the use of both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values to evaluate sources of sulfate to the drainage waters of forested catchments, these studies have generally lacked *in situ* measurements of isotopic discrimination that may be associated with some biotic and abiotic processes. Combined approaches using isotopic measurements of other system components including nitrogen ($\delta^{15}\text{N}$) and water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) may be especially useful in evaluating flowpaths and their relationship to sulfur dynamics.

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Tracing Nitrogen Sources and Cycling in Catchments

Carol Kendall

16.1 Introduction

Recent concern about the potential danger to water supplies posed by the use of agricultural chemicals has focused attention on the mobility of various solutes, especially nitrate and pesticides, in shallow hydrologic systems. Nitrate concentrations in public water supplies have risen above acceptable levels in many areas of the world, largely as a result of overuse of fertilizers and contamination by human and animal waste. The World Health Organization and the United States Environmental Protection Agency have set a limit of 10 mg/L nitrate (as N) for drinking water because high-nitrate water poses a health risk, especially for children, who can contract methemoglobinemia (blue-baby disease). High concentrations of nitrate in rivers and lakes can cause eutrophication, often followed by fish-kills due to oxygen depletion. Increased atmospheric loads of anthropogenic nitric and sulfuric acids have caused many sensitive, low-alkalinity streams in North America and Europe to become acidified. Still more streams that are not yet chronically acidic could undergo acidic episodes in response to large rain storms and/or spring snowmelt. These acidic "events" can seriously damage sensitive local ecosystems. Future climate changes may exacerbate the situation by affecting biogeochemical controls on the transport of water, nutrients, and other materials from land to freshwater ecosystems.

The development of effective management practices to preserve water quality, and remediation plans for sites that are already polluted, requires identification of the actual sources and understanding of the processes affecting local nitrate concentrations. In particular, a better understanding of hydrologic flowpaths and solute sources is required to determine the potential impact of contaminants on water supplies. Determination of the relation between nitrate concentrations in groundwater and surface water and the quantity of nitrate introduced from a particular source is complicated by (1) the occurrence of multiple possible sources of nitrate in many areas, (2) the presence of overlapping point and non-point sources, and (3) the co-existence of several biogeochemical processes that alter nitrate and other chemical concentrations. In many circumstances, isotopes offer a direct means of source identification because different sources of nitrate often have isotopically distinct nitrogen and oxygen isotopic compositions. In addition, biological cycling of nitrogen often changes isotopic ratios in predictable and recognizable directions that can be reconstructed from the isotopic compositions.

The main emphasis of the chapter will be on uses of isotopes in tracing sources and cycling of nitrogen in the *water-component* of forested catchments. However, the author has become convinced that watershed hydrologists not only have to look beyond hydrology to biogeochemistry, but must work towards an *ecosystem* or *landscape* approach to watershed processes. This kind of broad, interdisciplinary approach acknowledges that soil processes, deep

groundwater reservoirs, agricultural and urban activities, and plant/animal functions all may have interacting roles in the watershed. Therefore, although the chapter focuses on dissolved nitrate in shallow waters, there will be brief mention of related subjects such as nutrient uptake studies in agricultural areas, large-scale tracer experiments, groundwater contamination studies, food-web investigations, and uses of compound-specific stable isotope techniques. This is *not* a chapter on environmental controls on nitrogen cycling in catchments; for good recent reviews of this topic see Cirino and McDonnell (1997) and Stoddard (1994). And this is *not* a chapter on ^{15}N -tracer approaches; for a good review of tracer methods, see Knowles and Blackburn (1993).

16.1.1 Fundamentals of nitrogen isotopes

The whole-earth abundance of N is 0.03%, with 97.76% of the total N located in rocks, 2.01% in the atmosphere, and the remainder in the hydrosphere and biosphere (Hübner, 1986; from various sources). There are two stable isotopes of N: ^{14}N and ^{15}N . The wide range of oxidation numbers exhibited by nitrogen compounds, ranging from +5 (NO_3^-) to -3 (NH_4^+), results in a wide natural range of isotopic compositions.

The average abundance of ^{15}N in air is constant (Junk and Svec, 1958), with $^{15}\text{N}/^{14}\text{N} = 1/272$. Nitrogen isotope ratios are generally reported in permil (‰) relative to N_2 in atmospheric air, using the standard definition of δ (which is properly spelled and pronounced "delta" *not* "del"):

$$\delta^{15}\text{N}_{\text{AIR}} = \{[(^{15}\text{N}/^{14}\text{N})_{\text{x}} / (^{15}\text{N}/^{14}\text{N})_{\text{AIR}}] - 1\} \cdot 1000 \quad (16.1)$$

where x = sample and AIR = the reference standard gas. Analytical precisions of 0.1‰ or better are common. To improve interlaboratory comparisons, $\delta^{15}\text{N}$ values should be normalized to the compositions of reference materials with widely different $\delta^{15}\text{N}$ values (Böhlke and Coplen, 1995). For example, $\delta^{15}\text{N}$ values can be normalized to the values of the IAEA ammonium sulfate reference materials N-1 and N-2, which we found to have compositions of +0.45‰ and +20.35‰, respectively (Kendall and Grim, 1990). Some additional reference materials are available for interlaboratory comparisons (Böhlke et al., 1993; Böhlke and Coplen, 1995).

16.1.2 Methods

Below is a brief description of how various N-bearing materials can be collected and analyzed for *natural abundance* isotopic composition, focused mainly on dissolved species. This is a rapidly evolving field with new methods being published every month. For up-to-date information, consult your library or the Web (see Chapter 2 for information about useful WEB sites and other analytical details). "Nitrogen Isotope Techniques" edited by Knowles and Blackburn (1993) provides a detailed, practical description of field and laboratory methods for N-related biological studies, mostly focusing on ^{15}N tracer approaches, not the natural abundance applications that are the focus of this book. The chapter by Shearer and Kohl (1993) provides a description of natural abundance $\delta^{15}\text{N}$ applications, including a rebuttal to the skepticism of some ecologists about natural abundance applications of N isotopes. On the other hand, a recent review by Handley and Scrimgeour (1997) concluded that "the use of $\delta^{15}\text{N}$ is a powerful tool for obtaining insights through $\delta^{15}\text{N}$ pattern analysis, and for deriving new questions to be tested, but it is not a reliable tracer of nitrogen fluxes in soils or plants growing in soils."

Although this chapter focuses on uses of N isotopes to understand water chemistry, isotopic compositions generally cannot be interpreted successfully in the absence of other chemical and

hydrologic data. In particular, since redox reactions have such a profound impact on isotope fractionations, information on pH and dissolved oxygen concentrations are especially critical. A multi-isotope approach using the C, O, and S isotopic compositions of other organic and inorganic components will also aid interpretation of $\delta^{15}\text{N}$ variations in the ecosystem.

How and where the samples are collected is as least as important as how and where they are analyzed. Adequate assessment of the temporal and spatial variability in potential endmembers is essential. In particular, sampling during fertilizer or manure application should be avoided because of rapid fractionations in the soil soon after application (i.e., ammonia volatilization and nitrification). Also, the nitrate- $\delta^{15}\text{N}$ values of materials applied at the surface (e.g., fertilizer, manure, treated waste) are best sampled beneath the application sites, after the N-bearing materials have been nitrified during downwards transport through the soil zone.

Dissolved N-species

There are several methods in current use for collecting dissolved inorganic and organic nitrogen (DIN and DON) species from natural waters and preparing them for $\delta^{15}\text{N}$ analysis. Since these species are biologically labile, samples should be filtered immediately after collection, using 0.45 μ or finer filters; 0.1 μ filters will markedly increase shelf-life (Patton, 1995). Use of silver filters for DON samples can aid preservation efforts. Samples should be kept chilled until analyzed. Water samples are commonly preserved with sulfuric acid, mercuric chloride (note: this is a hazardous material), chloroform, or by freezing. It is advisable to check with the lab that will be analyzing the samples to learn how they recommend samples should be preserved.

One method for collecting DIN from fresh waters for isotopic analysis is to use ion exchange resins (Hoering, 1957; Moore, 1977; Garten, 1992; Silva et al., in review; Chang et al., in review). Ammonium and nitrate are collected on cation and anion resins, respectively, in the field and the samples are sent to the lab for processing and analysis. The benefits of using exchange resins are: (1) elimination of the need to transport large volumes of water to the laboratory for processing, (2) elimination of the need for hazardous preservatives (e.g., HgCl_2), and (3) ability to concentrate nitrogen from very dilute waters. Other anions and cations can successfully compete for exchange sites on resins, so such techniques are NOT suitable for saline or brackish waters; one must know something about water chemistry before using these techniques.

Ammonium can be removed from the sample and converted to N_2 gas for mass spectrometric analysis by (1) steam distillation of ammonium followed by oxidation with a hypobromite solution, and purification of N_2 in a Cu/CuO furnace (Bremner, 1965; Bremner and Edwards, 1965); (2) distillation followed by collection of ammonium on an ammonium-specific zeolite (Velinsky et al., 1989) and sealed-tube combustion using Cu/CuO and CaO to produce pure N_2 (Kendall and Grim, 1990); or (3) the so-called "micro-diffusion method" where ammonium is slowly diffused into an acid solution or onto acidified filter paper to produce ammonium sulfate, and combusted or reacted as above to form N_2 (MacKown et al., 1987; Sigman et al., 1997; Downs et al., in press). Automated combustion of solid samples for C, N, and S (and now pyrolysis of samples for O and H) isotopes and elemental percentages on an elemental analyzer connected to a continuous-flow mass spectrometer has recently become a very popular method for analyzing more than 100 samples per day with analytical precisions of about 0.2‰ (except for $\delta^2\text{H}$). This automated method can be applied to any of the methods below that produce solids (e.g., silver nitrate, ammonium sulfate, DON, etc), and to some liquids.

Nitrate has conventionally been prepared by distilling off any existing ammonium, reducing nitrate to ammonium by a Kjeldahl reaction (Bremner, 1965; Bremner and Edwards, 1965), and

then converting the ammonium to N_2 using any of the above methods. Sigman et al. (1997) have adapted the micro-diffusion method for the analysis of seawater nitrate. A simple method, suitable for samples with negligible organic N, is to freeze-dry filtered samples, and then combust the resulting nitrate and other salts using Cu/CuO and CaO to produce pure N_2 (Kendall and Grim, 1990).

Using an ion exchange method to collect nitrate (Silva et al., in review), the nitrate is later eluted with HCl, neutralized with Ag_2O , filtered to remove the AgCl precipitate, freeze-dried, and the remaining $AgNO_3$ combusted to N_2 . This method is only suitable for fresh waters because high concentrations of anions in solution can interfere with nitrate absorption, causing a depletion of ^{15}N in the sample. Samples can be archived, refrigerated on the column, for up to 2 years with minimal fractionation. Our group has used this method for over a thousand samples since 1991, and various modifications of it are being used by several other groups (e.g., Wassenaar, 1995; Aravena and Robertson, 1998; Harrington et al., 1998).

Nitrate can also be analyzed for $\delta^{18}O$. Amberger and Schmidt (1987) described a method whereby the sample was converted to KNO_3 , combusted with $Hg(CN)_2$ to produce CO_2 that was purified and analyzed for $\delta^{18}O$. A modification of the method (Silva et al., in review) eliminates the need for hazardous materials such as mercuric cyanide by converting the sample to $AgNO_3$ and combusting it with graphite to produce quantitative yields of CO_2 . Using this method to collect and process nitrate samples for $\delta^{15}N$ and $\delta^{18}O$, analytical precisions for the laboratory standards put through the entire procedure are better than $\pm 0.1\text{‰}$ for $\delta^{15}N$, and $\pm 0.5\text{‰}$ for $\delta^{18}O$. For "real" samples, the error bars are about twice the size. An alternative laboratory combustion method (Revesz et al., 1997) that reacts samples in the form of KNO_3 with catalyzed graphite gives excellent precision. Analysis on the automated pyrolysis system (Farquhar et al., 1997; Kornexl et al., in press) discussed above will probably soon become the preferred analytical method.

Dissolved organic nitrogen (DON) is usually operationally defined as the N in dissolved organic matter (DOM) or dissolved organic carbon (DOC). Fractions of DOM rich in N include amino acids, proteins, and phenols. Because a wide variety of dissolved organic molecules contain nitrogen, exactly what is analyzed for DON- $\delta^{15}N$ depends primarily on how the water sample is processed after particulate N is removed. Methods for isolating the DOM for later combustion to N_2 and analysis for $\delta^{15}N$ range from the very simple freeze-drying of the sample, to the addition of several possible methods prior to freeze-drying, including removal of DIN by ion chromatography, ultrafiltration to isolate a specific molecular weight fraction followed by ion chromatography (Bronk and Glibert, 1991), roto-evaporation followed by dialysis to remove DIN (Feuerstein et al., 1997), and passage through various resins to separate different fractions by their chemical properties (Aiken et al., 1979; Thurman and Malcolm, 1981).

Other N-bearing species

Particulate organic nitrogen (PON) is operationally defined as the nitrogen in particulate organic matter (POM). POM is usually collected on precombusted glass-fiber filters (GF/F), and combusted to N_2 to determine the $\delta^{15}N$; it can also be analyzed for C, S, O, and H isotopes.

Plants and animals are extremely simple to analyze for bulk isotopic composition, especially for $\delta^{15}N$, $\delta^{13}C$, and $\delta^{34}S$. The samples are dried, ground, combusted, and analyzed -- generally using an automated system as described above.

Gases can also be collected and analyzed for $\delta^{15}\text{N}$ (see Knowles and Blackburn, 1993), $\delta^{18}\text{O}$, and other isotopes of interest. Gases are usually collected in a gas-tight syringes, bottles with septa-caps, or specially designed evacuated sample vessels. The samples may need to be combusted, and are then purified on a vacuum line or by passage through a gas chromatograph before analysis. An automated head-space sampler connected to the mass spectrometer can greatly reduce the manpower required for analysis.

16.2 The Nitrogen Cycle

A schematic diagram of the nitrogen cycle in forest ecosystems is shown in Figure 16.1. Biologically-mediated reactions (e.g., assimilation, nitrification, and denitrification) strongly control nitrogen dynamics in the soil. These reactions commonly result in increases in the $\delta^{15}\text{N}$ of the substrate and decreases in the $\delta^{15}\text{N}$ of the product. Attempts to trace fixed N through the ecosystem are hampered by the complex fractionations caused by multiple cycles of mineralization, nitrification, immobilization, plant uptake, and denitrification within the soil (Lajtha and Schlesinger, 1986). Before describing some of these processes, we will briefly review some isotope geochemistry.

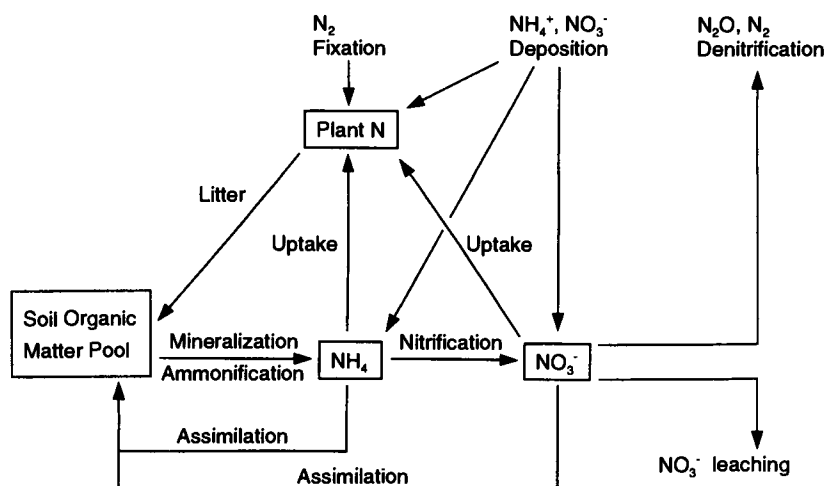


Figure 16.1. Nitrogen transformations and processes affecting $\delta^{15}\text{N}$ values in forest ecosystems. Modified from Nadelhoffer and Fry (1994).

16.2.1 Isotopic fractionations

Chemical, physical, and biological processes can be viewed as either reversible *equilibrium* reactions or irreversible unidirectional *kinetic* reactions; both kinds can have significant isotope fractionations. The processes are commonly modeled using Rayleigh equations (see below). This subject is discussed in detail in Chapter 2, and will be only briefly summarized here.

The fractionation factor associated with the equilibrium exchange reaction $A \leftrightarrow B$ is defined as:

$$\alpha = R_A/R_B \quad (16.2)$$

where R is $^{15}\text{N}/^{14}\text{N}$. Irreversible (unidirectional) kinetic fractionation effects involving metabolic nitrogen transformations are generally more important than equilibrium fractionation effects in low temperature environments. Kinetic fractionation factors are highly variable, depending on reaction rates, concentrations of products and reactants, environmental conditions, and species of the organism. In general, the lighter isotope reacts more readily, resulting in products that are lighter than the reactants. In contrast, reversible equilibrium reactions can produce products heavier or lighter than the original reactants.

Kinetic fractionation factors can be defined as:

$$\alpha_{p-s} = R_p/R_s \quad (16.3)$$

where R_p and R_s are the $^{15}\text{N}/^{14}\text{N}$ ratios of the product and substrate (reactant), respectively. An isotope enrichment factor, ϵ , can be defined as:

$$\epsilon_{p-s} = 1000 \cdot (\alpha - 1) \quad (16.4)$$

If the reactant concentration is large and fractionations are small:

$$\epsilon_{p-s} \approx \Delta = \delta_p - \delta_s \quad (16.5)$$

where Δ (del) is another term for the enrichment factor. Del (or "big del" as it is sometimes called) is the *apparent* fractionation; it is the difference in the $\delta^{15}\text{N}$ values that are actually measured in the field and laboratory.

Readers of this book and articles dealing with isotope fractionations must be careful: both α and ϵ values are defined in various ways by different authors. This chapter attempts to use the terms as "normally defined" for equilibrium systems (i.e., if $s \rightarrow p$, $\alpha_{p-s} = R_p/R_s$). However, these terms are commonly defined "in reverse" of normal usage in papers aimed at a biological audience to avoid using values of $\epsilon < 0$, or α values < 1 . For example, the enrichment factor is sometimes defined in reverse (i.e., ϵ_{s-p}), fractionation factors are commonly defined in reverse (i.e., $\alpha = R_s/R_p$), many use the relation $\beta = 1/\alpha$ so that $\beta > 1$ (e.g., Figure 16.2), and some workers define a "discrimination factor" $D_{s/p} = (\alpha_{s/p} - 1) \cdot 1000$ where s/p denotes substrate relative to products. Good discussions of fractionations associated with biological processes include Hübner (1986) and Fogel and Cifuentes (1993). Readers should also keep in mind that the fractionation and enrichment factors determined in any particular study cannot readily be extrapolated to other studies because the degree of fractionation is strongly dependent on local conditions. Hence, the literature (including this chapter) contain a wide variety of ϵ_{p-s} values for any particular reaction.

The Rayleigh equation describes the evolution of the isotopic composition of the residual reactant (substrate) during both kinetic and equilibrium processes (see Chapter 2). A commonly used formulation of the Rayleigh equation for systems with a constant fractionation factor is:

$$\delta \approx \delta_o + \epsilon_{p-s} \ln(f) \quad (16.6)$$

where δ_o is the initial composition of the substrate, f is the remaining fraction of the substrate, and $\epsilon_{p-s} < 0$. If ϵ is defined to be > 0 , then the "+" in the equation should be replaced with a "-".

After all these equations, the reader might well have concluded that isotope fractionation is a very confusing concept. Not so! The idea is very simple: organisms preferentially use the *light* isotope (^{14}N) over the *heavy* isotope (^{15}N) so that almost anything created by the organism (the

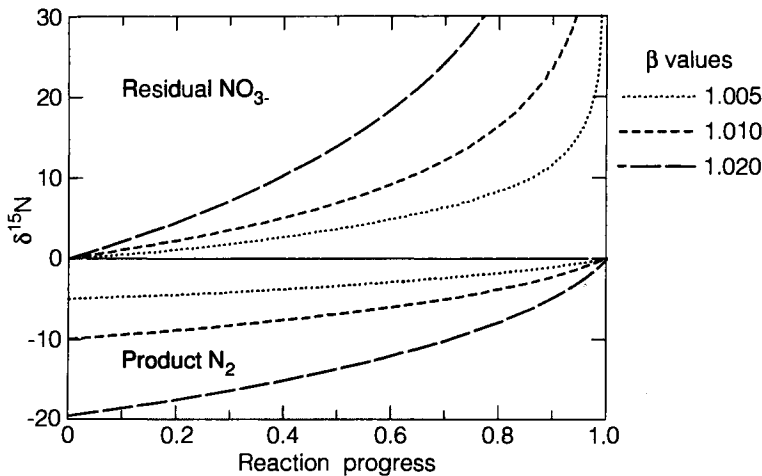


Figure 16.2. Reaction progress vs. the $\delta^{15}\text{N}$ values of residual reactant (NO_3^-) and cumulative product (N_2) resulting from denitrification; calculated using the Rayleigh equation for fractionation factors (β) of 1.005, 1.010, and 1.020. The higher the β value, the higher the $\delta^{15}\text{N}$ of the NO_3^- and the lower the $\delta^{15}\text{N}$ of the N_2 .

product) is isotopically lighter than the material not used (the reactant or substrate). For example, when microbes convert ammonium to nitrate (nitrification), the nitrate being formed is lighter (lower $\delta^{15}\text{N}$ value) than the ammonium being left behind. And as organisms use up the reactant, the $\delta^{15}\text{N}$ values of the product and left-over reactant change in predictable manner.

As shown schematically in Figure 16.2, the $\delta^{15}\text{N}$ of the cumulative product N_2 is always lighter than that of the residual reactant NO_3^- . At the start of the reaction (reaction progress = 0), the $\delta^{15}\text{N}$ of the reactant is 0‰, and the $\delta^{15}\text{N}$ of the first bit of product is lighter than the reactant (by -5, -10, or -20‰, depending on which fractionation factor (β) is being considered). As the reaction progresses, the $\delta^{15}\text{N}$ of the reactant and the product both get heavier, and when all the reactant is used up (reaction progress = 1), the $\delta^{15}\text{N}$ of the cumulative product is equal to the starting composition of the reactant ($\delta^{15}\text{N} = 0$) but the last bit of remaining reactant can have a very high $\delta^{15}\text{N}$ value. Therefore, the isotopic compositions of materials are highly dependent on the value of the fractionation factor and the size of the remaining reservoir of reactants.

Many biological processes consist of a number of steps (e.g., nitrification: $\text{organic-N} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$). Each step has the potential for fractionation, and the overall fractionation for the reaction is highly dependent on environmental conditions including the number and type of intermediate steps, sizes of reservoirs (pools) of various compounds involved in the reactions (e.g., O_2 , NH_4^+), soil pH, species of the organism, etc. Hence, estimation of fractionations in natural systems is very complex.

A useful "rule of thumb" is that most of the fractionation is caused by the so-called "rate-determining step" -- which is the slowest step. This step is commonly one involving a large pool of substrate where the amount of material actually used is small compared to the size of the reservoir. In contrast, a step that is not rate-determining generally involves a small pool of some compound that is rapidly converted from reactant to product; because the compound is converted to product as soon as it appears, there is no fractionation at this step. The isotopic compositions

of reactant and product during a multi-step reaction where the net fractionation is controlled by a single rate-determining step can be successfully modeled with Rayleigh equations.

16.2.2 Processes affecting N isotopic compositions

It is impossible to do justice to this complex topic in the space allowed. This section will highlight some of the major points of particular relevance to studying watersheds, with an emphasis on *nitrate in waters*. For an excellent review of nitrogen isotopes in soil-plant systems, see Högborg (1997). A monograph by Handley and Scrimgeour (1997), describing their many years of experience in studying nitrogen cycling in an abandoned field with isotopic techniques, provides a fascinating critique of $\delta^{15}\text{N}$ studies. Handley and Raven (1992) provides a general review of $\delta^{15}\text{N}$ applications in ecosystem studies. Griffiths (1998) contains many pertinent short articles on biological and ecological applications of isotopes.

Fixation

The term *N-fixation* refers to processes that convert unreactive atmospheric N_2 into other forms of nitrogen (Figure 16.1). Although the term is usually used to mean fixation by bacteria, it has also been used to include fixation by lightning and, more importantly, by human activities (energy production, fertilizer production, and crop cultivation) that produce reactive N (NO_x , NH_3 , and organic N). Biotic fixation in the absence of human activities provides about 90-130 Tg N per year (Tg = teragram, or a trillion grams); human activities have added an additional load of ≈ 140 Tg N per year (Galloway et al., 1995). These authors predict that the anthropogenic fixation rate will increase by 60% by the year 2020, mainly due to increased fossil-fuel combustion and fertilizer use, especially in Asia. This increase in N loading is causing critical ecosystem changes on both the local and global scale (Galloway et al., 1995); concern about the impact of these changes on human activities is the main reason for the increased interest in uses of nitrogen isotopes in environmental studies.

Fixation of atmospheric N_2 by blue-green and other bacteria (including those in N_2 -fixing root nodules, e.g., in legumes and alders) by the enzyme nitrogenase commonly produces organic materials with $\delta^{15}\text{N}$ values slightly less than 0‰. A compilation by Fogel and Cifuentes (1993) indicates measured fractionations ($\epsilon_{\text{p-s}}$) ranging from -3 to +1‰. Because these values are generally lower than the values for organic materials produced by other mechanisms, low $\delta^{15}\text{N}$ values in organic matter are often cited as evidence for N_2 fixation. The isotopic compositions of N-bearing materials produced by anthropogenic fixation (atmospheric gases produced during fossil fuel combustion, and artificial fertilizers produced from atmospheric gases) are discussed in Section 16.3.1.

Common methods for quantifying biological fixation include the acetylene block technique and two isotopic methods: the ^{15}N tracer dilution method (Warembourg, 1993; Watanabe and Wada, 1993) and the ^{15}N natural abundance method (Shearer and Kohl, 1988). Perhaps the main benefit of the isotope methods is that the fixation estimate integrates over the entire life of the leaf analyzed instead of being an instantaneous rate. The natural abundance method has the further advantage that nothing has to be added and the disturbance to the ecosystem is limited to the sampling of leaves, soils, fertilizer, and air for isotopic measurement (Shearer and Kohl, 1988; 1993). A recent discussion of the topic (Högborg, 1997) notes that it is sometimes possible to obtain quantitative fixation-N data using the natural abundance method under carefully chosen conditions, and that sometimes this technique is the only practical method for assessing whether fixation is occurring.

Assimilation

Assimilation generally refers to the incorporation of N-bearing compounds into organisms; although some workers view N_2 fixation as a special form of assimilation, the term *assimilation* will be used here to refer only to incorporation (uptake) of ammonium, nitrate, or nitrite (Figure 16.1). Oxidized forms of N are initially reduced by nitrate or nitrite reductases to ammonium, that is eventually assimilated into organic matter. Assimilation, like other biological reactions, discriminates between isotopes and generally favors the incorporation of ^{14}N over ^{15}N . In a recent review of natural abundance ^{15}N uptake studies, Högberg (1997) concluded that while evaluations of the potential contribution of a specific N source that had a unique isotopic signature were often successful (e.g., foodweb studies), interpretations of the contributions of different N sources to plants based on natural abundance measurements generally needed confirmation by some independent non-isotopic method, or by ^{15}N tracer methods (e.g., Powlson and Barraclough, 1993; Glibert and Capone, 1993).

Measured values for apparent fractionations caused by assimilation by microorganisms in soils show a range of -1.6 to +1‰, with an average of -0.52‰ (compilation by Hübner, 1986). Fractionations by vascular plants show a range of -2.2 to +0.5‰ and an average of -0.25‰, relative to soil organic matter (Mariotti et al., 1980). N uptake by plants in soils causes only a small fractionation and hence, only slightly alters the isotopic composition of the residual fertilizer or soil organic matter.

Fogel and Cifuentes (1993) present an elegant model for ammonium assimilation in aquatic algae that predicts total fractionations of -4, -14, or -27‰ depending on whether algae cells are nitrogen limited, enzyme limited, or diffusion limited, respectively. However, for the low pH values and low ammonium concentrations common to soils, the model predicts that availability of N is the limiting condition and the transport of ammonia across cell walls is probably rapid, resulting in a small (< -4‰) overall fractionation.

A large range of fractionations (-27 to 0‰) has been measured in field and laboratory experiments for nitrate and ammonium assimilation by algae in aquatic environments (compiled by Fogel and Cifuentes, 1993). The much larger range of fractionations observed in aquatic environments vs. soil environments reflects the interplay of several possible kinetic and equilibrium isotope effects as a function of environmental conditions. In general, smaller fractionations are observed for higher growth rates and for lower NO_3 and NH_4 concentrations.

The term *dissimilation* has been used to refer to N-metabolism because it can be viewed as the opposite of *assimilation* (Hübner, 1986). In metabolic reactions, the N compound is used as a supplier of energy by being either an electron donor (e.g., in redox reactions by nitrifying bacteria) or an electron acceptor (e.g., in the oxidation of organic compounds by denitrifiers).

Mineralization

Mineralization is usually defined as the production of ammonium from soil organic matter. This is sometimes called *ammonification*, which is a less confusing term (Figure 16.1):



Mineralization usually causes only a small fractionation ($\pm 1‰$) between soil organic matter and soil ammonium.

The reader should note that many other workers use the term *mineralization* for the overall production of nitrate from organic matter by several reaction steps. This usage results in literature that gives fractionations for mineralization that can range from -35 to $\approx 0\%$, depending on which step is rate limiting (Delwiche and Steyn, 1970; Feigin et al., 1974; Letolle, 1980). The large fractionations are caused by the nitrification of ammonium, not the conversion of organic N to ammonium. In general, the $\delta^{15}\text{N}$ of soil ammonium is usually within a few permil of the composition of total organic N in the soil. Reviews of ^{15}N tracer methods for determining mineralization and nitrification rates in soils and waters include: Mosier and Schimel, 1993; Powlson and Barraclough, 1993; and Glibert and Capone, 1993.

Nitrification

Nitrification is a multi-step oxidation process mediated by several different autotrophic organisms for the purpose of deriving metabolic energy; the reactions produce acidity. Nitrate is not the only product of nitrification; different reactions produce various nitrogen oxides as intermediate species (e.g., NO_2^- , NO, N_2O). Nitrification can be described as two partial oxidation reactions, each of which proceeds separately:

oxidation by *Nitrosomonas*,



followed by oxidation by *Nitrobacter*,



A detailed discussion of the nitrogen fractionations involved in these reactions can be found in Hübner (1986). Several workers have investigated the source of the oxygen in these reactions (Hollocher et al., 1981; Andersson and Hooper, 1983; Kumar et al., 1983; and Hollocher, 1984), and current understanding is that two of the oxygens in NO_3^- derive from H_2O and one derives from O_2 , and there may be further O exchange between nitrite and water (see Section 16.4.3).

The total fractionation associated with nitrification depends on which step is rate determining: one of the nitrification reactions listed above or the earlier production of ammonium from organic matter. Because the oxidation of nitrite to nitrate (Equation 16.10) is generally quantitative (rapid) in natural systems, this is generally not the rate determining step, and most of the N fractionation is probably caused by the slow oxidation of ammonium by *Nitrosomonas*. In soils, overall nitrification fractionations (β) have been estimated to range between 1.012 and 1.029 (Shearer and Kohl, 1986); i.e., the enrichment factors are -12 to -29‰ ($\delta^{15}\text{N}_{\text{NO}_3} < \delta^{15}\text{N}_{\text{NH}_4}$).

In general, the extent of fractionation is dependent on the size of the substrate pool (reservoir). In N-limited systems, the fractionations are minimal. Hence, the $\delta^{15}\text{N}$ of soil nitrate is usually within a few permil of the composition of total organic N in the soil. If there is a large amount of ammonium available (e.g., artificial fertilizer has been applied), nitrification is stimulated, and the oxidation of the fertilizer ammonium is the rate-determining step; this would likely cause a large fractionation. The $\delta^{15}\text{N}$ value of the first-formed nitrate is relatively low (Figure 16.3), but as the ammonium pool is used up, the nitrification rate decreases, oxidation of ammonium

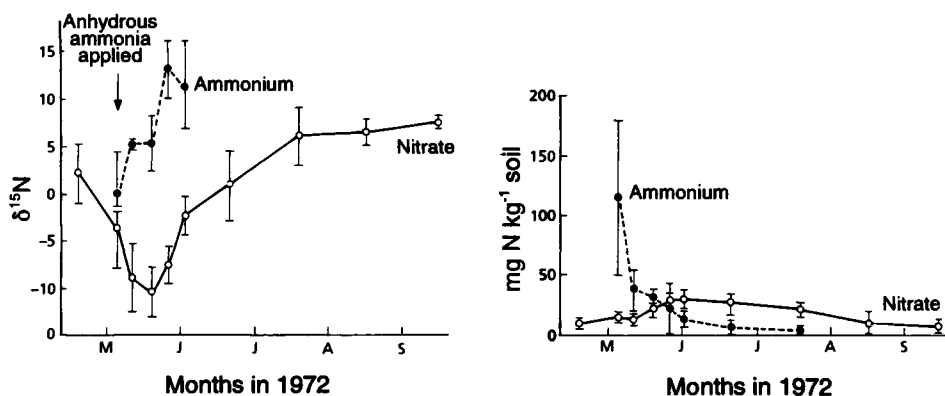


Figure 16.3. The conversion of NH_4 to NO_3 and changes in their $\delta^{15}\text{N}$ values resulting from application of anhydrous NH_3 fertilizer to an agricultural field, volatilization of ammonia, and nitrification of the ammonium. Modified from Feigin et. al (1974).

is no longer the rate-determining step, the overall nitrification fractionation decreases, and the $\delta^{15}\text{N}$ value of the total nitrate increases towards pre-fertilization values (Feigin et al., 1974).

Therefore, one cannot accurately predict the $\delta^{15}\text{N}$ value of nitrate being leaked to surface water or groundwater from an agricultural field from simple measurement of the average $\delta^{15}\text{N}$ of ammonium fertilizers. The $\delta^{15}\text{N}$ of soil nitrate is commonly a few permil lighter (and sometimes heavier) than that of soil N because of fractionations associated with mineralization and/or nitrification. And even if the fertilizer applied were 100% synthetic KNO_3 or guano, there would still be a possibility of post-depositional increases in $\delta^{15}\text{N}$ caused by denitrification as the nitrate was slowly transported to the sampling point. Increases in $\delta^{15}\text{N}$ of nitrate caused by denitrification are less likely in coarse-grained soils where waters percolate rapidly (and have higher concentrations of dissolved oxygen) than in finer-grained soils (Gormly and Spalding, 1979). Hence, the best way to assess the “effective” $\delta^{15}\text{N}$ value of the fertilizer or manure *endmember* is to collect samples from beneath the field where the materials are applied, avoiding sample collection soon after application since the fractionations are greatest then.

Volatilization

Volatilization is the term commonly used for the loss of ammonia gas from surficial soils to the atmosphere; the ammonia gas produced has a lower $\delta^{15}\text{N}$ value than the residual ammonium in the soil. Volatilization involves several steps that can cause fractionation, including (1) the equilibrium fractionations between ammonium and ammonia in solution, and between aqueous and gaseous ammonia, and (2) the kinetic fractionation caused by the diffusive loss of ^{15}N -depleted ammonia. The overall process can cause large isotopic enrichments since the fractionations of the equilibrium and kinetic steps are each reported to be >1.02 (Hübner, 1986); the actual fractionation depends on the pH and other factors. Volatilization in farmlands results from applications of urea and manure to fields, and occurs within piles of manure; the resulting organic matter may have $\delta^{15}\text{N}$ values $>20\text{‰}$ because of ammonia losses.

Animal waste contains a wide variety of N-bearing compounds, both aqueous and solid, but most of the N is in the form of urea. The urea may be hydrolyzed to ammonia, and later oxidized (nitrified) to nitrate (Kreitler, 1975; Heaton, 1986):



Note that the above reaction consists of both reversible (equilibrium) reactions and irreversible (kinetic) reactions, but the overall reaction is unidirectional in that urea is irreversibly oxidized to nitrate. The hydrolysis of urea or ammonium fertilizer results in a temporary increase in pH, that favors the loss of ammonia gas by *volatilization*. The overall unidirectional reaction causes a preferential loss of ammonia depleted in ^{15}N relative to the ammonium in solution (Figure 16.3). The loss of ammonia restores acidity and the remaining ammonium, now enriched in ^{15}N , remains in solution. Much of the enriched ammonium is later nitrified to ^{15}N -enriched nitrate (Figure 16.3). The degree of enrichment is determined by a variety of environmental factors that influence the rate of volatilization (eg., soil pH, windspeed, moisture, temperature, etc). In a survey of fertilized soils in Texas, Kreitler (1975) attributed a 2-3‰ increase in $\delta^{15}\text{N}$ in underlying groundwater relative to the applied fertilizer to volatilization, and noted that losses of ammonia in alkaline soils can be very large and cause dramatic shifts in $\delta^{15}\text{N}$.

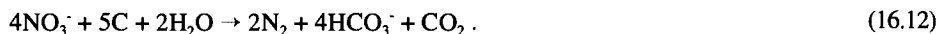
Sorption/desorption

Sorption/desorption reactions can cause small isotope fractionations as a result of isotope exchange on the charged surfaces of clays and other material. However, there is little evidence for nitrate sorption in soils. Cation exchange resins and kaolinitic clays favor the retention of the heavier isotope in the adsorbed fraction of NH_4^+ ; anion resins favor the retention of the lighter isotope of NO_3^- (Delwiche and Steyn, 1970). Hence, chromatographic (retardation) processes in soil profiles could cause the more "mobile" ammonium that is available for uptake by roots or oxidation by nitrifiers to have a lower $\delta^{15}\text{N}$ value. A compilation by Hübner (1986) shows that ion-exchange fractionations are commonly in the range of 1 to 8‰. The actual fractionation observed is dependent on concentration and the fractionation factor (distribution coefficient) for the exchange with the clay material (Hübner, 1986). The fractionation factor will probably vary with depth in the soil because of changes in clay composition and water chemistry.

Denitrification

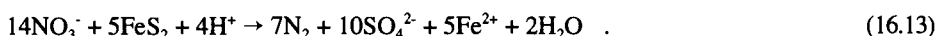
Denitrification is a multi-step process with various nitrogen oxides (e.g., N_2O , NO) as intermediate compounds resulting from the chemical or biologically mediated reduction of nitrate to N_2 . Depending on the redox conditions, organisms will utilize different oxidized materials as electron acceptors in the general order: O_2 , NO_3^- , SO_4^{2-} . Although microbial denitrification does not occur in the presence of significant amounts of oxygen, it can occur in anaerobic pockets within an otherwise oxygenated sediment or water body (Koba et al., 1997).

Nitrate reduction by the heterotroph *Pseudomonas denitrificans* and the simultaneous respiration of CO_2 from the oxidation of organic matter is the major cause of denitrification in soils:



However, denitrification during the chemo-autotrophic respiration of *Thiobacillus denitrificans*, which oxidizes sulfur, can also be important in sewage purification systems (Batchelor and Lawrence, 1978). *Pseudomonas denitrificans* is a facultative (capable of heterotrophic and

autotrophic metabolic activity) anaerobic microorganism that switches to nitrate reduction at O_2 levels of less than about 0.5mg/L (Hübner, 1986); other facultative denitrifiers make this "switch" at different O_2 levels. The stoichiometry of the denitrification reaction mediated by *Thiobacillus denitrificans* is:



Denitrification causes the $\delta^{15}N$ of the residual nitrate to increase exponentially as nitrate concentrations decrease (Figure 16.2), and causes the acidity of the system to decrease. For example, denitrification of fertilizer nitrate that originally had a distinctive $\delta^{15}N$ value of +0‰ can yield residual nitrate with much higher $\delta^{15}N$ values (e.g., +15 to +30‰) that are within the range of compositions expected for nitrate from a manure or septic-tank source (Figure 16.4). Measured enrichment factors (apparent fractionations) associated with denitrification ($\epsilon_{N_2-NO_3}$) range from -40 to -5‰; hence, the $\delta^{15}N$ of the N_2 is lower than that of the nitrate by about these values. The N_2 produced by denitrification results in *excess N_2 contents* in groundwater; the $\delta^{15}N$ of this N_2 can provide useful information about sources and processes (Section 16.5.2).

There are several methods for determining the presence or extent of denitrification, including various enzyme-blockage methods (e.g., the acetylene blockage method) and ^{15}N tracer methods (Mosier and Schimel, 1993). Natural abundance isotope methods include comparison of the increases in the (1) $\delta^{15}N$ of nitrate, (2) concentration and $\delta^{15}N$ of total N_2 , or (3) relative $\delta^{15}N$ and $\delta^{18}O$ of nitrate, with decreasing nitrate concentrations (see Section 16.5.2).

The greenhouse gas N_2O can be produced and released to the atmosphere by various mechanisms including denitrification in boggy soils and in aquatic systems near the sediment/water interface (e.g., Duff and Triska, 1990), and nitrification in soils. These two processes should be distinguishable isotopically because of differences in reaction mechanisms and kinetic fractionations. Further support for the source of the N_2O can be gained by analyzing the $\delta^{15}N$ (and $\delta^{18}O$) of other N-bearing compounds affected by the production of N_2O . The N_2O produced by nitrification is not likely to be metabolized in oxygenated waters, and will maintain its characteristic $\delta^{15}N$ and $\delta^{18}O$ values; in contrast, the $\delta^{18}O$ and $\delta^{15}N$ of N_2O in anoxic conditions will increase because of consumption by denitrifiers (Yoshinari and Koike, 1994).

16.3 $\delta^{15}N$ Values of Nitrogen Sources and Reservoirs

Most terrestrial materials have $\delta^{15}N$ compositions between -20 and +30‰. Although a recent compilation noted that the extreme $\delta^{15}N$ values for "natural" terrestrial substances reported thus far were -49 to +102‰ (Böhlke et al., 1993), these extreme values are the products of fairly unusual recycling of N; more typical ranges of major reservoirs are shown in Figure 16.4. The dominant source of nitrogen in most forested ecosystems is the atmosphere ($\delta^{15}N = 0‰$); many plants fix nitrogen and organisms cycle this nitrogen into the soil. Other sources of nitrogen to watersheds include fertilizers produced from atmospheric nitrogen with compositions of $0 \pm 3‰$ and animal manure with nitrate $\delta^{15}N$ values generally in the range of +10 to +25‰; rock contributions of N to waters are almost always negligible. Note that fertilizer and animal waste have generally distinctive $\delta^{15}N$ values; however, the compositions of atmospheric and soil nitrate are not distinctive and overlap the compositions of fertilizer and animal waste. The $\delta^{15}N$ ranges of these N reservoirs at any single site are usually much less than shown on the figure.

Two factors control the $\delta^{15}N$ values of any N-bearing compound in the subsurface (1) variations in the $\delta^{15}N$ values of *inputs* (sources) and *outputs* (sinks) of the compound in the subsurface,

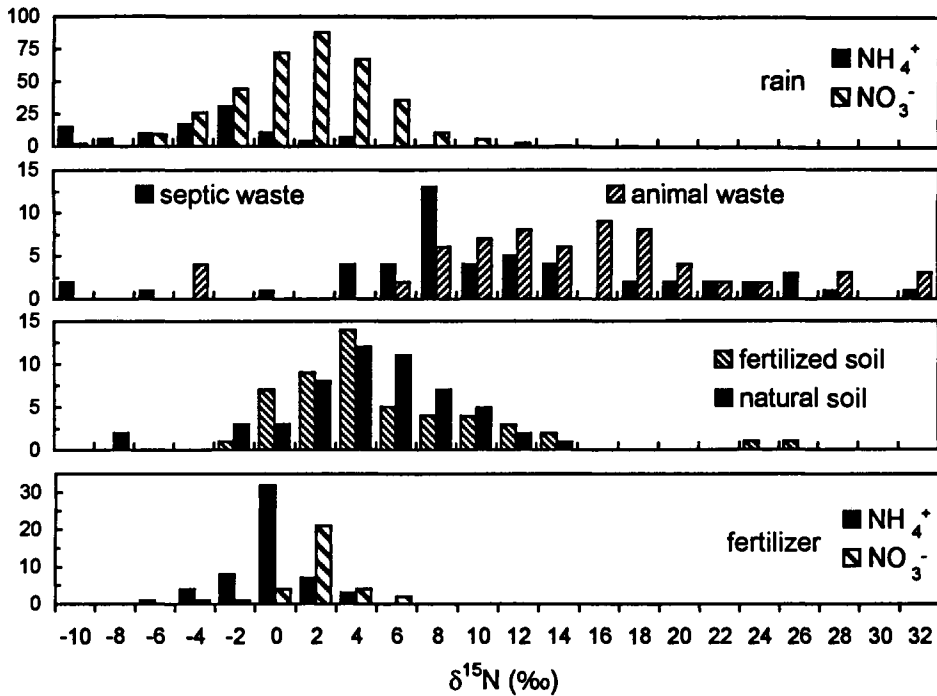


Figure 16.4. Summary of the range of $\delta^{15}\text{N}$ values for the major sources of nitrogen in the hydrosphere. The labels on the x-axis are for the high-end of the range plotted within the cell. Precipitation data from: Hoering (1957), Moore (1977), Heaton, (1986, 1987), Freyer (1978, 1991), Garten (1992, 1995), Paerl and Fogel (1994), Heaton et al. (1997), and the other sources listed in caption of Figure 16.8. Soil nitrate data from the compilation of Fogg et al. (1998) from the following sources: Bremner and Tabatabai (1973), Kreitler (1975, 1979), Rennie et al. (1976), Black and Waring (1977), Shearer et al. (1978), Gormly and Spalding (1979), and Wolterink et al. (1979). Fertilizer data are from: Kohl et al. (1971), Aly et al. (1981), Shearer et al. (1974b), and Rennie et al. (1976).

and (2) chemical, physical, and biological transformations of materials within the soil or groundwater that produce or remove the compound. Good reviews of the topic from different perspectives are given in Hübner (1986) and Högberg (1997). The sections below are intended to give the reader some general information about the isotopic compositions of various N sources or reservoirs, and how the N-cycling processes described in Section 16.2.2 affect these compositions. The discussion necessarily deals in generalizations derived at a limited number of sites, but the reader must not deduce from this that all ecosystems are alike, and the $\delta^{15}\text{N}$ values measured at one site cannot be blithely extrapolated to another.

16.3.1 Atmospheric sources

Complex chemical reactions in the atmosphere result in a large range of $\delta^{15}\text{N}$ values of N-bearing gases and solutes depending on the compound involved, the season, meteorological conditions, ratio of NH_4 to NO_3 in the precipitation, types of anthropogenic inputs, proximity to pollution sources, distance from ocean, etc. (Hübner, 1986). Natural atmospheric sources of these gases and solutes include volatilization of ammonia from soils and animal waste (with

fractionations as large as -40‰), nitrification and denitrification in soils and surface waters, and production in thunderstorms from atmospheric N_2 . Anthropogenic sources include chemical processing and combustion of fossil fuels in automobiles and power plants. The $\delta^{15}\text{N}$ values of atmospheric NO_3 and NH_4 are usually in the range of -15 to $+15\text{‰}$ (Figure 16.4). Extremely low $\delta^{15}\text{N}$ values for NO_3 can be expected near chemical plants because of sorption of NO_x gases (with high $\delta^{15}\text{N}$ values) in exhaust scrubbers (Hübner, 1986).

There have been few comprehensive studies of $\delta^{15}\text{N}$ of precipitation, in part because of the difficulty of analyzing such dilute waters. Isotope shifts of several permil can occur between and within storms because of selective washout of N-bearing materials (Heaton, 1986), and the total range observed at any single location can be as large as 20‰ . Studies in Germany (Freyer, 1978; 1991) and South Africa (Heaton, 1986; 1987) have found that $\delta^{15}\text{N}$ values of NO_3 show a seasonal cycle of low $\delta^{15}\text{N}$ values in spring and summer rain and higher values in the winter. Freyer (1978) attributed this cycle to the release of depleted nitrogen oxides from soils (including nitrification of fertilizers) during the warm and moist growing season, and attributed the production of enriched NO_x during colder seasons to the increased combustion of fossil fuels. Later work showed that variations in the $\delta^{15}\text{N}$ of NO_x (i.e., its source) were not necessarily the main control on $\delta^{15}\text{N}$ of NO_3 because of the large fractionation ($\approx +18\text{‰}$) associated with the conversion of NO to NO_2 in the atmosphere (Freyer et al., 1993).

In general, the NO_3 in rain appears to have a higher $\delta^{15}\text{N}$ value than the co-existing NH_4 (Figure 16.4). For example, the average $\delta^{15}\text{N}$ values of NO_3 and NH_4 in Germany were $-2.5 \pm 3.0\text{‰}$ and $-12.0 \pm 1.9\text{‰}$, respectively; the lower NH_4 values were explained by washout of ^{15}N -depleted atmospheric NH_3 , and the higher NO_3 values by washout of NO and NO_2 (Freyer, 1978). Over a 1-year study at Walker Branch watershed (Tennessee, USA), the mean $\delta^{15}\text{N}$ values of NO_3 and NH_4 in precipitation (rain and throughfall) were $+2.3 \pm 2.4\text{‰}$ and $-3.4 \pm 2.1\text{‰}$, respectively (Garten, 1992); the lower NH_4 values were again explained by washout of atmospheric NH_3 . Equilibrium exchange reaction of gaseous NO or NO_2 with dissolved NO_3 would result in ^{15}N enrichment of the NO_3 . However, other studies have illustrated various complicated relations (Moore, 1977; Heaton, 1987), and there is considerable inter-storm and seasonal variability.

The concentrations of N-bearing materials in precipitation are highly variable and often site-specific. Although precipitation in the eastern parts of the USA often contains subequal quantities of NH_4 and NO_3 , NH_4 is preferentially retained (utilized) in the tree canopy relative to atmospheric NO_3 (Garten and Hanson, 1990), so that a larger proportion of the atmospheric nitrogen that reaches the soil surface is in the form of NO_3 . The mean $\delta^{15}\text{N}$ of red maple leaves in N-deficient ridges and slopes at the Walker Branch watershed is $-3.2 \pm 1.2\text{‰}$, similar to the composition of NH_4 in bulk precipitation (Garten, 1992). This suggests that atmospheric NH_4 might be a significant source of N for the trees, but further work is needed to verify this.

Considerable attention has been given to nitrogen oxides (and sulfur oxides) in the atmosphere because of their contributions to *acid rain*. This is discussed in more detail in Chapter 22 (also see Heaton et al., 1997). Despite the complications of the atmospheric N cycle, isotope tracing of sources has been successful in some local studies. For example, there is some evidence that NO_x emitted from coal combustion has a markedly different $\delta^{15}\text{N}$ value ($+6$ to $+9\text{‰}$) than NO_x emitted from automobiles (-13 to -2‰), at least at the study area in South Africa (Heaton, 1990). The low values were attributed to kinetic fractionations in the formation of NO from atmospheric N_2 and O_2 , and the high values to the $\delta^{15}\text{N}$ value of the coal (usually $> 0\text{‰}$) plus kinetic fractionations related to the breakdown of NO back to N_2 and O_2 . Estimates for the $\delta^{15}\text{N}$ value of nitric acid vapor from anthropogenic sources range from -2.7‰ in Germany (Freyer, 1991), to $+6.0 \pm 2.3\text{‰}$ in Tennessee where 75-90% of the NO_3 in dry deposition to an artificial

tree was believed to be HNO_3 vapor derived from coal combustion (Garten, 1995). The $\delta^{15}\text{N}$ of NO_3 in dry deposition in Tennessee was about 6‰ heavier than in rain, close to the composition of soil nitrate. Hence, it is not surprising that throughfall, which contains dry deposition on the tree canopy, has a higher $\delta^{15}\text{N}$ value than rain. For example, the $\delta^{15}\text{N}$ value of NO_3 in throughfall was found to be higher than in open-air rain, whereas the $\delta^{15}\text{N}$ of NH_4 in throughfall had a variable composition relative to rain, in studies in Tennessee (Garten, 1992) and Yorkshire (UK) (Heaton et al., 1997). These findings suggests that throughfall- $\delta^{15}\text{N}$ is a better integrator of atmospheric N inputs to forested catchments than rain- $\delta^{15}\text{N}$.

Combined use of the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate (Section 16.4) may allow better separation of atmospheric and terrestrial nitrate sources (Amberger and Schmidt, 1987; Durka et al., 1994; Kendall et al., 1995b; in review; Böhlke et al., 1997), including the possible separation of different anthropogenic sources. Oxygen isotope ratios have proved useful for distinguishing N_2O from nitrification and denitrification (Wahlen and Yoshinari, 1985).

16.3.2 Fertilizers

Use of N-bearing fertilizers has a great impact on crop productivity, the $\delta^{15}\text{N}$ values of farmland plants, and on the N contents and $\delta^{15}\text{N}$ values of farmland soils. Overuse of fertilizers has resulted in high concentrations of nitrate, and significant changes in the $\delta^{15}\text{N}$ of the nitrate, in the surface waters and groundwaters issuing from farmland soils. Artificial (inorganic) fertilizers produced by the fixation of atmospheric N_2 include the commonly-applied urea, ammonium nitrate, and potassium nitrate. These *anthropogenic* fertilizers have $\delta^{15}\text{N}$ values that are uniformly low reflecting their atmospheric source (Figure 16.4), generally in the range of -4 to +4‰; however, some fertilizer samples have shown a total range of -8 to +7‰ (see compilations by Hübner, 1986; Macko and Ostrom, 1994). Mean $\delta^{15}\text{N}$ values are (1) urea = $+0.18 \pm 1.27\text{‰}$, (2) NH_4 = $-0.91 \pm 1.88\text{‰}$, and (3) NO_3 = $+2.75 \pm .76\text{‰}$ (Hübner, 1986). Organic fertilizers (which include so-called "green" fertilizers such as cover crops and plant composts, and liquid and solid animal waste) generally have higher $\delta^{15}\text{N}$ values and a much wider range of compositions (generally +2 to +30‰) than inorganic fertilizers because of their more diverse origins. Note that the $\delta^{15}\text{N}$ of nitrate in fertilized soils may not be the same as the fertilizer.

16.3.3 Animal waste

It has often been observed that animals (microbes to invertebrates) are slightly enriched in ^{15}N relative to their diet, which is sometimes expressed as the isotope in-joke "you are what you eat plus 3‰" (or thereabouts). The increases in $\delta^{15}\text{N}$ in animal tissue and solid waste relative to diet are due mainly to the excretion of isotopically light N in urine or its equivalent (Wolterink et al., 1979). Animal waste products may be further enriched in ^{15}N because of volatilization of ^{15}N -depleted ammonia, and subsequent oxidation of much of the residual waste material may result in nitrate with a high $\delta^{15}\text{N}$ (Figure 16.4). By this process, animal waste with a typical $\delta^{15}\text{N}$ value of about +5‰ is converted to nitrate with $\delta^{15}\text{N}$ values generally in the range of +10 to +20‰ (Kreidler, 1975; 1979), and human and other animal waste become isotopically indistinguishable under most circumstances (an exception is Fogg et al., 1998).

16.3.4 Plants

N-autotrophs can utilize a variety of materials from purely inorganic compounds (NH_4 , NO_3 , N_2 , NO_2) to amino acids, and can have a wide range in $\delta^{15}\text{N}$ values depending on environmental

conditions. However, most plants have $\delta^{15}\text{N}$ values in the range of -5 to $+2\text{‰}$ (Fry, 1991). Plants fixing N_2 from the atmosphere have $\delta^{15}\text{N}$ values of about 0 to $+2\text{‰}$, close to the $\delta^{15}\text{N}$ value of atmospheric N_2 . N-heterotrophs (e.g., fungi) that utilize organically fixed N in the form of amino acids, have $\delta^{15}\text{N}$ values that are generally higher than soil N (Högberg, 1997). Recent investigations have concluded that there is negligible fractionation during plant uptake in most natural N-limited systems (Nadelhoffer and Fry, 1994; Högberg, 1997); nevertheless, tree tissues and litter have slightly lower $\delta^{15}\text{N}$ values than soil. Under higher nutrient conditions, preferential uptake of ^{14}N by plants results in a few permil fractionation between plants and DIN. Whereas, in general, microorganisms and plants preferentially uptake ammonium, soil nitrate is preferentially assimilated by tree roots relative to soil ammonium (Nadelhoffer and Fry, 1988).

Spatial variability in foliar $\delta^{15}\text{N}$ is commonly observed within forested catchments. A compilation of data for non-fixing trees by Garten (1993) shows as much as a $3\text{--}15\text{‰}$ range in $\delta^{15}\text{N}$ values among the same species in small geographic areas. The large range reflects spatial variability in the relative amounts, $\delta^{15}\text{N}$ values, and bioavailability of atmospheric versus various soil sources of N; some examples of processes affecting variability are described below. The $\delta^{15}\text{N}$ values of non-fixing plants from a chronosequence in Hawaii (USA) increased substantially (-5.9 to $+0.7\text{‰}$) with age; soils showed a similar increase but were about 4‰ heavier (Vitousek et al., 1989). This increase with age was attributed to less reliance on ^{15}N -depleted precipitation sources, higher rates of N cycling, more fixation and assimilation of N, and greater leaching losses in more mature soils. Foliar $\delta^{15}\text{N}$ values were higher on valley bottoms than on ridgetops in Tennessee (USA), reflecting the greater uptake of high- $\delta^{15}\text{N}$ soil DIN by plants in the valleys and greater uptake of low- $\delta^{15}\text{N}$ atmospheric ammonium on ridges where soil DIN is more limited (Garten, 1993). The ^{15}N -enrichment of trees closer to the ocean relative to ones at higher elevations or at greater distances from the ocean perhaps reflects input of sea spray enriched in ^{15}N (Virginia and Delwiche, 1982; Heaton, 1987).

16.3.5 Soils

Nitrogen is recycled continuously between the atmosphere, soil, and the biosphere. The $\delta^{15}\text{N}$ of total soil N ranges from about -10 to $+15\text{‰}$, with most soils having $\delta^{15}\text{N}$ values in the range of $+2$ to 5‰ . Cultivated soils had slightly lower $\delta^{15}\text{N}$ values ($+0.65 \pm 2.6\text{‰}$) than uncultivated soils ($+2.73 \pm 3.4\text{‰}$), according to a major soil survey by Broadbent et al. (1980). The $\delta^{15}\text{N}$ is affected by many factors including soil depth, vegetation, climate, cultural history, etc. Most of the N in soils is bound in forms not readily available to plants; hence, the $\delta^{15}\text{N}$ of total soil N is generally not a good approximation of the $\delta^{15}\text{N}$ of N available for plant growth.

Soluble DIN (mainly NO_3) constitutes about 1% of the N in soils, and hence is a very small pool whose $\delta^{15}\text{N}$ is much more sensitive to change than the larger organic pool. Turnover times of DIN in various soils are on the order of days (Davidson et al., 1990, 1992; Högberg, 1997). Because nitrate is more mobile in soils than ammonium, it is less likely to accumulate and, hence, readily leaches from soils. Although it has often been assumed that nitrate is the most abundant N solute in catchment waters, several recent studies have found that DON is actually the dominant N solute (Hedin et al., 1995; Gorham et al., 1998). The few DON- $\delta^{15}\text{N}$ values available for catchment waters are described in Section 16.7.2.

There have been several investigations of the $\delta^{15}\text{N}$ values for soil nitrate from different environments (i.e., “natural” soils (tilled and untilled), soils fertilized with synthetic fertilizers or manure, soils contaminated with septic waste, etc). The data generated by a number of studies are summarized in Figure 16.4. In general, the soil nitrate produced from fertilizer

(average $\delta^{15}\text{N}$ value = $+4.7 \pm 5.4\text{‰}$) and animal waste (average $\delta^{15}\text{N} = +14.0 \pm 8.8\text{‰}$) are isotopically distinguishable but they both overlap with the compositions of nitrate in precipitation and natural soils. However, given the large range of $\delta^{15}\text{N}$ values of the nitrate sources, the average values of sources from one site cannot be automatically applied to another; this is vividly illustrated by a recent compilation of nitrate $\delta^{15}\text{N}$ data (Fogg et al., 1998).

Two factors, drainage and influence of litter, have a consistent and major influence on the $\delta^{15}\text{N}$ values of soil DIN (Shearer and Kohl, 1988). Nitrate in soils on lower slopes and near saline seeps has a higher $\delta^{15}\text{N}$ value than nitrate in well-drained soils (Karamanos et al., 1981), perhaps because the greater denitrification in more boggy areas results in ^{15}N -enriched residual nitrate. The $\delta^{15}\text{N}$ values of nitrate in soils from valley bottoms at the Walker Branch watershed are higher than for soils from ridges and slopes, consistent with a theoretical model that explains the increase in the $\delta^{15}\text{N}$ of inorganic N in soil as a function of the higher relative rates of immobilization and nitrification in these bottom soils (Shearer et al., 1974). There is also greater uptake of atmospheric ammonium (which generally has a low $\delta^{15}\text{N}$ value) on the ridges because the limited availability of soil DIN there (Garten, 1993). It has recently been proposed that the release (drainage) of N from catchment soils can be explained by a flushing of the high-N upper layers of the soil during snowmelt or autumn storms, combined with a draining mechanism during snowmelt where recharge of the groundwater transports N from the upper soil layers into deeper flowpaths that contribute to baseflow throughout the year (Creed et al., 1996).

Areas with abundant litter deposition (e.g., under trees and bushes) commonly have lower total $\delta^{15}\text{N}$ values than open areas (Shearer and Kohl, 1988; Nadelhoffer and Fry, 1988), presumably because losses of ^{14}N to plant uptake during mineralization and nitrification in the open-area soil (i.e., natural soil processes) were not "offset" by the recycling of N from decaying litter. Discrimination against ^{15}N during decomposition of litter (Melillo et al., 1989) results in the gradual ^{15}N -enrichment of the residual organic material. Finer grained organic matter is generally enriched in ^{15}N relative to coarser material (Tiessen et al., 1984).

Well-drained soils typically show an increase in total soil- $\delta^{15}\text{N}$ with soil depth or with decreasing organic N content (Shearer et al., 1978; Shearer and Kohl, 1986). Nadelhoffer and Fry (1988) concluded that this increase in forests was due solely to fractionation during net mineralization, and not to differential preservation of components of litter with greater $\delta^{15}\text{N}$ values. Surficial soil organic matter $\delta^{15}\text{N}$ values are generally similar to or slightly greater than the values for plant litter; these values increase to about $+8 \pm 2\text{‰}$ at depths of 20-40 cm (Nadelhoffer and Fry, 1994). This increase in $\delta^{15}\text{N}$ with depth and age can be viewed as mainly the result of the metabolism of microbial heterotrophs that produce ^{15}N -enriched biomass as a result of excreting ^{15}N -depleted waste (Nadelhoffer and Fry, 1994). The loss of the bio-available, ^{15}N -depleted ammonium to plant uptake, nitrification, and leaching coupled by recycling of the ^{15}N -enriched biomass, will inevitably lead to increases in $\delta^{15}\text{N}$ of the total soil N. Accumulation of ^{15}N -enriched, recalcitrant, mycorrhizal N with depth has also been suggested as an explanation for the increases in $\delta^{15}\text{N}$ (Gebauer and Dietrich, 1993). And there is some evidence that the $\delta^{15}\text{N}$ of DON also increases with depth (Sherry Schiff, pers. comm., 1998).

Several investigators have reported that although nitrate $\delta^{15}\text{N}$ values usually increase with depth in surface soils, values can decrease below the rooting zone (50-500 cm) where N concentrations are low and N pools are mainly derived from leaching from above. Delwiche and Steyn (1970) noted that where there is a significant change in texture in the profile (e.g. a point where sand content is unusually high), there is a significant enrichment in ^{15}N . But they could not demonstrate a consistent relationship between ^{15}N content of N and soil particle size

or total N content to the soil. Shearer et al. (1974) developed a theoretical model to explain the $\delta^{15}\text{N}$ of soil DIN as a function of the relative rates of N immobilization and nitrification.

Although mineralization followed by nitrification and leaching are probably major causes of enrichments in total soils, other processes can also produce increases in $\delta^{15}\text{N}$ of nitrate with depth. For example, the inverse correlation of nitrate- $\delta^{15}\text{N}$ and nitrate concentration beneath agricultural fields (Gormly and Spalding, 1979; Böttcher et al., 1990) and in a forest (Koba et al., 1997) were attributed to increasing denitrification with depth. Seasonal changes in soil temperature may also affect the $\delta^{15}\text{N}$ of nitrate, resulting in higher values in the summer in unfertilized fields (Ostrom et al., 1998). In well-oxygenated vadose zones, there may be little or no change in the $\delta^{15}\text{N}$ of nitrate past the root zone, indicating little denitrification or other nitrogen cycling reactions during transport (Gormly and Spalding, 1979; Fogg et al., 1998).

The complexity of the soil makes detailed studies of the different soil DIN pools difficult. For example, soil extractions using different soil:extractant ratios (Lindau and Spalding, 1984) and extractant chemical type (Burns and Kendall, in review; using DI, KCl and NH_4Cl extractants) can cause more than a 6‰ range in nitrate $\delta^{15}\text{N}$. Three possible explanations of these data have been proposed: (1) these values are artifacts caused by disturbance of the small, biologically active pools of N, (2) different pools of nitrate may have different $\delta^{15}\text{N}$ values, or (3) different pools are differentially available to flushing, perhaps because the nitrate pools are associated with different pore sizes or types of grain surfaces. Plants are integrators of the $\delta^{15}\text{N}$ of available N sources, and although there are complexities caused by storage effects, perhaps plants – especially fine roots – would provide the simplest and best estimate of the $\delta^{15}\text{N}$ value of available N in the soil (Högberg, 1997).

16.3.6 Groundwater

In the last decade as nitrate concentrations in public supply wells have reached unacceptable levels in many parts of the world, it has become obvious that more attention needs to be paid to linkages between human activities on the surface and groundwater quality (Follett, 1989; Spalding and Exner, 1993). Nevertheless, groundwater is an often forgotten reservoir of nitrate in catchments. This is because many *catchment hydrologists* have not realized that there might be significant amounts of groundwater stored within the bedrock of the catchment, and many *forest and agricultural biologists* have paid little attention to processes below the root zone. All too often the bedrock is erroneously regarded as being impermeable and thus of little relevance to surface water hydrology, and to ecosystem processes on the landsurface and in streams. In fact, not only is groundwater the major source of water to streams in almost all catchments (see Chapters 1, 10-14, and 20-21), but because deep groundwater systems often extend beyond the catchment “boundaries” assigned from surface topography, these leakages can have a significant effect on catchment water and solute budgets. For more information on assessing the hydrologic properties of shallow and deep groundwater reservoirs, see Chapters 7 and 9.

The main N-related processes in groundwater that affect catchment hydrology are probably denitrification, temporary storage, and transport to streams. How the nitrate-containing waters are transported to the stream has a dramatic effect on nitrate concentrations in streamwater (Böhlke and Denver, 1995). If waters containing high concentrations of nitrate that “escaped” below the rootzone are intercepted by tile drains or if these waters travel along deep flowpaths in oxidized aquifers before discharging vertically upwards directly beneath the streambed, the nitrate-rich waters could be discharged unchanged into the stream. On the other hand, if these groundwaters flow laterally through anoxic zones in adjacent riparian areas or through deeper

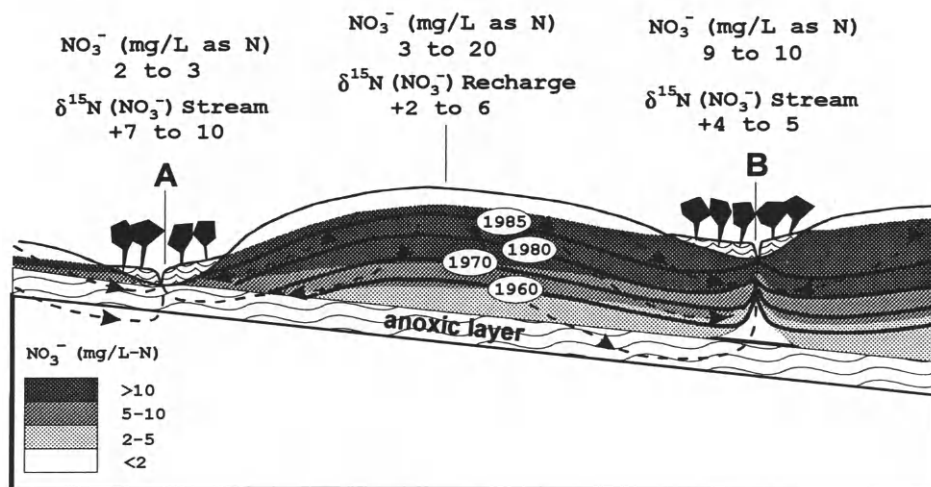


Figure 16.5. Schematic cross-section through an agricultural catchment in the Delmarva Peninsula, Maryland (USA) showing the increase in age of waters (solid lines, based on CFC data) and decrease in nitrate concentration with depth (shaded zones). Flowlines (dashed) to stream A are more shallow than the flowlines to stream B, intersect the riparian zone, and many flowlines are within the anoxic bedrock unit; hence, enhanced denitrification along the flowlines contributing to stream A results in lower nitrate concentrations and higher $\delta^{15}\text{N}$ values than in stream B. Modified from Böhlke and Denver (1995).

unoxidized units where denitrification and other processes reduce the DIN contents, the groundwaters may be a significant sink for nitrate in catchments. This is illustrated by Figure 16.5 where the nitrate concentrations and $\delta^{15}\text{N}$ values in two adjacent streams are largely a function of the different flowpaths utilized. In this case, storage time was less important than the geochemistry of the geologic unit; the age ranges of waters discharging to both streams were similar. Several recent studies have found larger groundwater nitrate reservoirs in catchments than previously suspected (Kendall et al., 1995b; Williams et al., 1997; Burns et al., 1998).

16.4 $\delta^{18}\text{O}$ Values of Nitrate Sources and Reservoirs

The $\delta^{18}\text{O}$ of nitrate is a promising new tool for determining nitrate sources and reactions. Because much less is known about the $\delta^{18}\text{O}$ of various nitrate sources and the fractionations associated with different nitrogen cycling mechanisms, this discussion is separate from the discussion of $\delta^{15}\text{N}$ reservoirs (Section 16.3). Although several techniques have been developed since the 1980's for analysis of nitrate for $\delta^{18}\text{O}$ (Amberger and Schmidt, 1987; Kendall et al., 1996; Revesz et al., 1997; Silva et al., in review), there have been few applications of these methods, probably because all the methods are labor intensive and the first involves hazardous materials.

Fundamentals: Oxygen has three stable isotopes: ^{16}O , ^{17}O , and ^{18}O . Stable oxygen isotopic compositions are given in terms of $^{18}\text{O}/^{16}\text{O}$ ratios using the δ definition given above. The $\delta^{18}\text{O}$ values of nitrate are reported in ‰ relative to the standard V-SMOW. Figure 16.6 is a

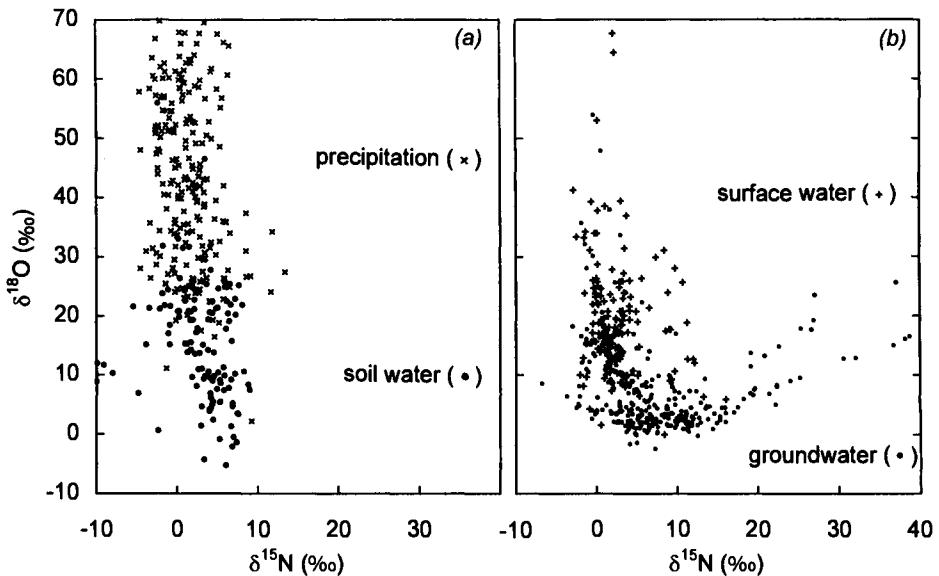


Figure 16.6. Compilation of nitrate $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ data from the following sources: Amberger and Schmidt (1987), Voerkelius (1990), Böttcher et al. (1990), Aravena et al. (1993), Durka et al. (1994), Wassenaar (1995), Kendall et al. (1995b), Ging et al. (1996), Böhlke et al. (1997), Aravena and Robertson (1998), Kendall et al. (in review), Bollwerk et al., (in preparation), unpublished data from S. Schiff (pers. comm., 1998), unpublished data B. Mayer (pers. comm., 1998), and unpublished U.S. Geological Survey data. A colored version of this and other plots in this chapter are located at URL <http://wwwrcamnl.wr.usgs.gov/isoig/isopubs/>.

compilation of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of nitrate. Surprisingly, there is almost an 80‰ range in $\delta^{18}\text{O}$ values, corresponding to a 30‰ range in $\delta^{15}\text{N}$ values. Most of the spread in $\delta^{18}\text{O}$ values is caused by precipitation samples, but there is also considerable variability in nitrate- $\delta^{18}\text{O}$ values in streams and soils. Although the oxygens in nitrate are thought to be derived from atmospheric O_2 (about +23‰; Kroopnick and Craig, 1972) and environmental H_2O (normal range: -30 to +5‰), the larger range of nitrate- $\delta^{18}\text{O}$ values indicates that oxygen isotopes in nitrate are fractionated from their source compositions during atmospheric processes.

16.4.1 Atmospheric nitrate

There are limited data on the $\delta^{18}\text{O}$ of nitrate in atmospheric deposition, with almost nothing known about possible spatial or temporal variability, or their causes. The first published data on the $\delta^{18}\text{O}$ of nitrate in precipitation were from forests in Bavaria, in Germany (Voerkelius, 1990; Durka et al., 1994), and showed a relatively tight cluster of $\delta^{18}\text{O}$ values in the range of +55 to +75‰. A much larger range of values (+18 to +70‰) was observed for some 110 rain, throughfall, snow, and snowmelt samples from three forested USGS research sites in the USA (Loch Vale, CO; Catskills, NY; and Sleepers River, VT), with an average of $+45 \pm 15\%$ (Kendall et al., in review). A set of data ($n = 62$) from forests in north-western Germany (Muensterland, near Dortmund) show a range of about +23 to +58‰, with an average of about $+36 \pm 9\%$ (Bernhard Mayer, pers. comm. 1998), and a set from sites in east-central Canada show a range of about +28 to +51 (Sherry Schiff, pers. comm. 1998).

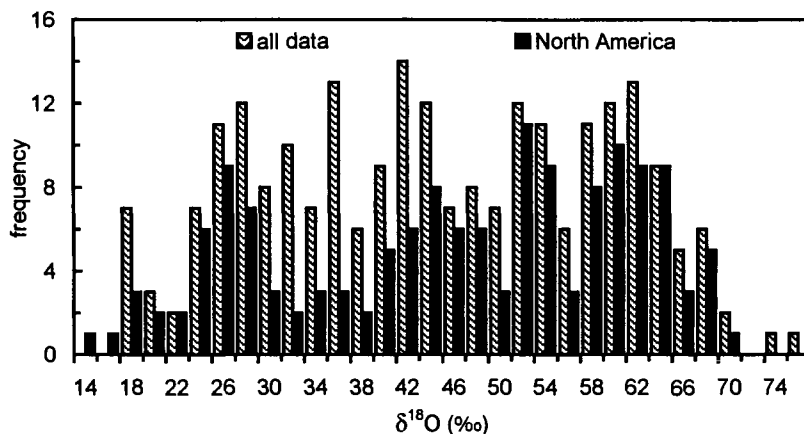


Figure 16.7. The $\delta^{18}\text{O}$ of nitrate in precipitation samples (rain, throughfall, snow, and snowmelt) collected over various time intervals. Separate histograms show all available nitrate- $\delta^{18}\text{O}$ data, and just data from sites in North America. North American data were compiled from: Kendall et al. (1996), Kendall et al. (in review), unpublished data from S. Schiff (pers. comm., 1998), and unpublished USGS data from collaborations with J. Sueker, M. Williams, L. Pardo, and J. Sickman. German data were compiled from: Voerkelius (1990), Durka et al. (1994), and unpublished data from B. Mayer (pers. comm., 1998). The labels on the x-axis are for the high-end of the range plotted within the cell.

Figure 16.7 shows all available nitrate- $\delta^{18}\text{O}$ values for precipitation (which includes values for rain, throughfall, snow, and snowmelt). Two different histograms are shown: (1) all data, and (2) only data from North America, most of which is from the three USGS sites mentioned above. The average nitrate- $\delta^{18}\text{O}$ value for the entire precipitation data set is $+43.6 \pm 14.6\text{‰}$ ($n=232$). There are no statistically significant differences among different types of precipitation for the data set as a whole; however, there often are consistent differences for sample types at an individual site (e.g., nitrate- $\delta^{18}\text{O}$ values in snowmelt at Loch Vale are usually lower than the values in snow, perhaps because of infiltration by rain with lower nitrate- $\delta^{18}\text{O}$ values).

Possible explanations for the large range in $\delta^{18}\text{O}$ values include fractionations associated with nitrate formation in thunderstorms, incomplete combustion of fossil fuels in power plants and vehicle exhaust, and photochemical reactions in the atmosphere. Some of these processes have been shown to fractionate nitrogen isotopes (Heaton, 1990). Given the large $\delta^{15}\text{N}$ range of nitrate and ammonium produced by different reactions and degrees of equilibration in the atmosphere (Heaton, 1987; Freyer, 1991), and the high $\delta^{18}\text{O}$ values reported for ozone and other nitrogen and carbon oxides in the atmosphere (Wahlen and Yoshinari, 1985; Krankowsky et al., 1995; Röckmann et al., 1998), it is likely that "natural" atmospheric nitrate has a wide range of $\delta^{18}\text{O}$ values too. Furthermore, since Heaton (1990) reported that the $\delta^{15}\text{N}$ of NO_x from coal exhaust was about 10‰ heavier than NO_x from automobile exhaust, it is possible that these different anthropogenic sources of atmospheric nitrate may also have characteristic $\delta^{18}\text{O}$ values. Heaton (1990) attributed the different $\delta^{15}\text{N}$ values to kinetic fractionations associated with the reversible reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons \text{NO}_x + \text{N}$; these reactions probably would cause similar kinetic fractionations of the O isotopes. Hence, the combined use O and N isotopes is likely to be useful for tracking different kinds of pollutants -- if not on a global scale than perhaps on a regional scale.

What evidence is there that different natural and/or anthropogenic atmospheric nitrate sources might have different $\delta^{18}\text{O}$ values? The bimodal distribution of North American data in Figure

16.7 (and perhaps the non-normal distribution of the entire data set) show moderate evidence of at least 2 sources and/or processes affecting the compositions. The lower mode is centered around values of +22 to +28‰, and the higher mode (or modes) has values centering around +56 to +64‰. Prior to the first reported analyses from Bavaria, it had been speculated that “natural” atmospheric nitrate $\delta^{18}\text{O}$ values might be around +23‰, the $\delta^{18}\text{O}$ value of atmospheric O_2 . However, given the large $\delta^{15}\text{N}$ range of nitrate and ammonium produced by different reactions and degrees of equilibration in the atmosphere (Heaton, 1987; Freyer, 1991), and the high $\delta^{18}\text{O}$ values reported for ozone and other nitrogen oxides in the atmosphere, it is likely that “natural” atmospheric nitrate has a wide range of $\delta^{18}\text{O}$ values. More recently, some nitrate-rich salts from deserts in northern Chile and southern California (USA) that have $\delta^{15}\text{N}$ values near 0‰ and $\delta^{18}\text{O}$ values between +30 and +50‰ have been tentatively interpreted as evidence for long-term accumulation of atmospheric N deposition in hyper-arid environments (Böhlke et al., 1997). The best way to determine the pre-industrial atmospheric nitrate isotopic composition is by analysis of NO_3 in ice cores. Until this is accomplished, all we have are speculations. However, it appears likely that the O in nitrate with $\delta^{18}\text{O}$ values close to that of atmospheric O_2 is probably derived from the atmospheric O_2 , with the slight enrichments in ^{18}O perhaps caused by kinetic fractionations during “back reaction” of NO_x to O_2 .

All the data reported for precipitation in Bavaria (+50 to +70‰) plot within the high- $\delta^{18}\text{O}$ mode. This part of Europe has high concentrations of nitrate in precipitation, many acid-rain damaged forests, and is downwind of highly industrialized parts of central Europe. Hence, one possible explanation for the high $\delta^{18}\text{O}$ values of nitrate in precipitation in Bavaria is that the values may reflect an anthropogenic pollution source, perhaps derived from fossil fuel burning. The samples from Muensterland, further from coal-burning centers of central Europe, have considerably lower $\delta^{18}\text{O}$ values. Although there is no obvious correlation between nitrate loading and the $\delta^{18}\text{O}$ values of nitrate among the three well-studied USA catchments, the lower values from sites in less-densely inhabited and industrialized Canada provide some support of this hypothesis. It should be noted that the bimodal distribution seen in North American samples is not apparent in the entire data set. In fact, there is even some evidence that there may be another “source” around +45‰ in the North American data set. The lack of a bimodal distribution in Europe may indicate that the sources are more interspersed or that there is better atmospheric mixing.

It is possible that methodological problems are causing some of the variations seen in Figure 16.7. Analysis of nitrate for $\delta^{18}\text{O}$ is both time-consuming and analytically difficult, which is why there are so few data available. It should be noted that the Bavarian samples were all analyzed using the Amberger and Schmidt (1987) mercury cyanide method whereas all the other samples were analyzed using various modifications of the silver nitrate method of Silva et al. (in review). Furthermore, incomplete removal of DOC, a problem that has plagued users of both methods, can have a significant effect on the $\delta^{18}\text{O}$ of the nitrate, with some samples (e.g., throughfall and snowmelt) having probably higher concentrations than other forms of precipitation; contamination by DOC-oxygen probably results in mid-range $\delta^{18}\text{O}$ values. In our lab, “blanks” have $\delta^{18}\text{O}$ values in the range of +20 to +30‰ and we have noticed that small samples often have lower-than-expected $\delta^{18}\text{O}$ values, possibly because of contamination.

Given the international interest in solving acid-rain problems, it is surprising that so little attention has been focused on the possibility of tracking different sources of atmospheric nitrate by its O and N isotopic composition. From the data presented above, it is not unreasonable to speculate that processes in coal-fired power plants may produce nitrate with high $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, car-combustion processes may produce nitrate with low $\delta^{15}\text{N}$ (and perhaps low $\delta^{18}\text{O}$) values, and natural atmospheric processes appear to produce nitrate with low to intermediate $\delta^{18}\text{O}$ values and intermediate $\delta^{15}\text{N}$ values. More data are certainly needed to assess processes

controlling the spatial and temporal ranges in isotopic composition. For example, because the $\delta^{18}\text{O}$ of the precipitation reflects changes in air-mass sources, there may be a correlation between water $\delta^{18}\text{O}$ and nitrate $\delta^{18}\text{O}$ values in precipitation samples.

16.4.2 Synthetic fertilizers and reagents

Amberger and Schmidt (1987) analyzed a number of types of anthropogenic nitrates and determined that synthetic nitrate formed from atmospheric oxygen has a distinctive $\delta^{18}\text{O}$ value (+18 to +22‰). All three oxygens in this nitrate are derived from atmospheric O_2 (+23‰), and hence the $\delta^{18}\text{O}$ values are similar to that of O_2 .

16.4.3 Microbial nitrate

Biochemical and bacteriological literature to date indicates that nitrate produced by microbial nitrification in laboratory cultures derives two oxygens from the oxygen in water molecules and one oxygen from O_2 (Kumar et al., 1983; Andersson and Hooper, 1983; Hollocher, 1984); see Equations 16.8 to 16.10. If the oxygens are incorporated without any fractionation, then the $\delta^{18}\text{O}$ of microbial nitrate can be calculated if the $\delta^{18}\text{O}$ of water and O_2 are known, as shown below:

$$\delta^{18}\text{O}_{(\text{NO}_3)} = \frac{2}{3} \delta^{18}\text{O}_{(\text{H}_2\text{O})} + \frac{1}{3} \delta^{18}\text{O}_{(\text{O}_2)} \quad (16.14)$$

For waters with $\delta^{18}\text{O}$ values in the normal range of -25 to +4‰ (see Chapter 3), the $\delta^{18}\text{O}$ of soil nitrate formed from *in situ* nitrification of ammonium, should be in the range of -10 to +10‰, respectively (Figure 16.8a). For highly evaporated water (+20‰), the $\delta^{18}\text{O}$ of nitrate could be as high as about +21‰ (Böhlke et al., 1997). The above model makes four critical assumptions: (1) the proportions of oxygen from water and O_2 are the same in soils as observed in laboratory cultures, (2) there are no fractionations resulting from the incorporation of oxygen from water or O_2 , (3) the $\delta^{18}\text{O}$ of water used by the microbes is identical to that of the bulk soil water, and (4) the $\delta^{18}\text{O}$ of the O_2 used by the microbes is identical to that of atmospheric O_2 .

There have been few *dual isotope* tests of the validity of this simple model for microbial nitrification in soils. A few groundwater studies (e.g., Böttcher et al., 1990) show nitrate data that appear to fit the model, but several other studies have reported groundwater nitrate with "higher than expected" $\delta^{18}\text{O}$ values (i.e., values that were 5-10‰ higher than predicted based on the ambient water- $\delta^{18}\text{O}$ values). Only the one experiment conducted under saturated, flowing conditions (Voerkelius, 1990) clearly supports the model. Other experiments (Amberger, 1987; Kendall et al., 1995a; Kendall et al., in review; B. Mayer, pers. comm., 1998), conducted in moist but not saturated soils, produced anomalies that suggest that one or more assumptions of the model may not be valid. Our lab and field studies suggest that the $\delta^{18}\text{O}$ of microbial nitrate commonly may be as high as +16‰ in shallow soils with water- $\delta^{18}\text{O}$ values of -5 to -20‰.

A variety of explanations have been offered for these high nitrate- $\delta^{18}\text{O}$ values. Amberger and Schmidt (1987) and Böhlke et al. (1997) speculated that the nitrate may have formed in soil waters that had higher-than-expected $\delta^{18}\text{O}$ values because of evaporation. Wassenaar (1995) attributed the higher values to nitrification during the summer when soil water $\delta^{18}\text{O}$ values were higher, with perhaps minor denitrification. Aravena et al. (1993) hypothesized that the high values might be caused by changes in the proportion of O from water and O_2 sources. Based on lab incubation and extraction experiments, Kendall et al. (1995a) speculated that the cause might

be heavier than expected $\delta^{18}\text{O}$ values of O_2 and/or H_2O within semi-isolated soil pores. Exchange of O in nitrate with O in water can be ruled out as an explanation because this would make the $\delta^{18}\text{O}$ of nitrate lower, not higher. And there is virtually no O exchange between O_2 and other species because of the stability of diatomic oxygen. Nevertheless, minor exchange with O_2 during the formation of nitrite or nitrate would could cause the appropriate enrichment in nitrate- $\delta^{18}\text{O}$, if there was some *biochemical* explanation for why the organism would spend the energy to break apart diatomic oxygen. Episodic denitrification in isolated pores that temporarily go anoxic could also be responsible for the heavy values. Lastly, in analogy to the variable proportions of O from different sources observed in sulfates (van Everdingen and Krouse, 1985), it may be found that there is more than one nitrification pathway, causing different intermediate species to have different compositions, and resulting in a large range of nitrate $\delta^{18}\text{O}$ values.

The speculation that nitrate in different soil pores might have different isotopic compositions because of different degrees of nitrogen cycling in the pores (Kendall et al., 1995a) is supported by the range in nitrate $\delta^{15}\text{N}$ found by using different extractants (see Section 16.3.5). Interestingly, although we observed a 6‰ range in $\delta^{15}\text{N}$, there was no change in the $\delta^{18}\text{O}$ of the soil nitrate removed with different extractant types (Kendall et al., in review). The lack of variability in $\delta^{18}\text{O}$ makes sense when one considers the relative "mobility" of the N compared to the O in pores (i.e., H_2O and O_2 move more easily between pores, thus homogenizing their compositions). Furthermore, whereas N cycling reactions (e.g., denitrification) leave an "imprint" in the $\delta^{15}\text{N}$ of residual N, the $\delta^{18}\text{O}$ of new nitrate is controlled solely by the $\delta^{18}\text{O}$ of local water and O_2 and is completely reset when the nitrate is reduced to ammonium or is incorporated into biomass. For example, if snow NO_3 ($\delta^{18}\text{O} \approx +50\text{‰}$) is completely assimilated and later the same N is nitrified, the nitrate would no longer have a $\delta^{18}\text{O}$ value recognizable as atmospheric NO_3 .

Figure 16.8a shows how the $\delta^{18}\text{O}$ value of nitrate could be affected by changes in the $\delta^{18}\text{O}$ values of water and O_2 . It is likely that the O_2 (and perhaps the H_2O) available to nitrifiers in the small soil pores has been significantly affected by microbial processes, and is commonly enriched in ^{18}O relative to "bulk" compositions. For example, the oxygen isotope fractionation associated with bacterial respiration (conversion of O_2 to CO_2) is 1.015 (Lane and Dole, 1956; Guy et al., 1993), which means that the residual O_2 becomes heavier over time. When ^{18}O -enriched sources of O are utilized by microorganisms, the resulting nitrate is also enriched in ^{18}O . More research on this topic is clearly indicated, but ^{18}O enrichment in O_2 rather than H_2O is probably a more likely explanation for the high $\delta^{18}\text{O}$ values of microbial nitrate because it is much easier to change the $\delta^{18}\text{O}$ value of the small amounts of O_2 in soil water than the $\delta^{18}\text{O}$ value of the much larger amounts of H_2O in soils. Soils frequently go anoxic, especially in microsites (Koba et al., 1997), demonstrating the minute amounts of O_2 involved; such large changes in O_2 caused by microbial reactions would cause large kinetic fractionations and high $\delta^{18}\text{O}$ values of residual O_2 .

If microbial nitrate is "labeled" by the $\delta^{18}\text{O}$ value of ambient water, the seasonal change in the $\delta^{18}\text{O}$ of water might cause a seasonal change in soil nitrate $\delta^{18}\text{O}$ (Figure 16.8a). Alternatively, if fields are irrigated with evaporated water at the same time that ammonium fertilizer is applied, the nitrate formed might reflect the evaporated signature of the water $\delta^{18}\text{O}$. Hence, it is possible that relative contributions of nitrate from the nitrification of fertilizer and soil N can be estimated by analyzing both isotopes of nitrate in samples suspected to be derived from these sources.

Microbial nitrification can produce a variety of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values depending on several factors, including reservoir sizes, initial δ values (of NH_4 , O_2 , and H_2O), fractionation factors, and whether there are episodic additions of NH_4 and O_2 from the surface (i.e., from rainfall or fertilizer application). The δ values of microbial nitrate will change over time as these factors

change. Figure 16.8b shows several hypothetical examples of the ^{15}N and ^{18}O enrichments that might be produced by progressive nitrification of ammonium under various conditions, ranging from the large ($\epsilon = -10\text{‰}$) fractionations that can be produced immediately after fertilizer application (see Figure 16.3), to the small ones usually observed in soils ($\epsilon = -2\text{‰}$). The three nitrification curves on Figure 16.8b were calculated by assuming that the ammonium and O_2 reservoirs were being depleted at the same rate (i.e., using equivalent values of *reaction progress* (f) for nitrification and respiration; see Equation 16.6).

Infiltration of fertilizer during irrigation or of snow NH_4 during melting would add both N and O_2 to deeper soil pores. However, because of the large possible differences in O and N reservoir sizes (and other factors), there are no necessary linkages between the O and N fractionations except that nitrification uses O from O_2 and ceases when O_2 is depleted. Depending on the relative fractionations caused by nitrification and respiration, progressive nitrification could produce δ values plotting along lines of different slopes (the curves on Figure 16.8b) or could produce increases in either the $\delta^{18}\text{O}$ or $\delta^{15}\text{N}$ of nitrate over time (the striped areas). Periodic additions of ammonium and O_2 from the surface, followed by alternating episodes of nitrification and denitrification, could result in a soil nitrate pool that has fairly constant, but somewhat heavier, δ values compared to the sources.

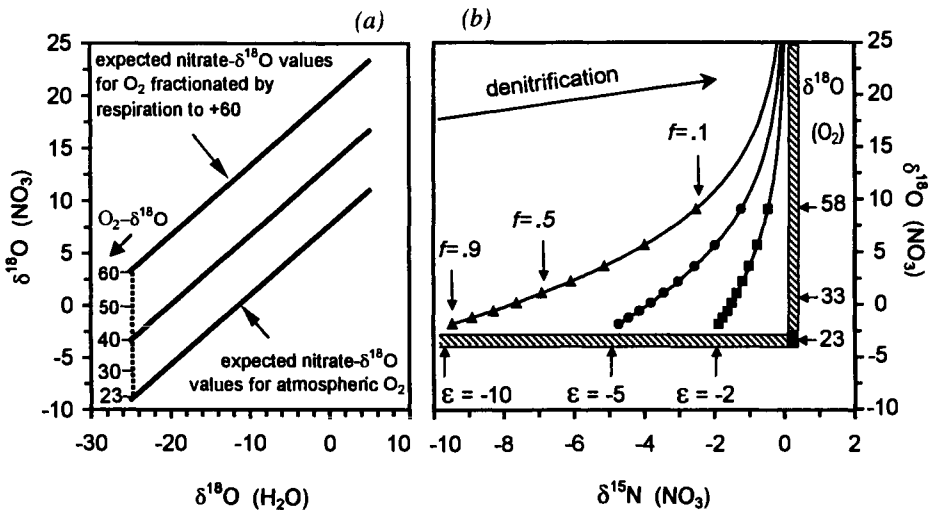


Figure 16.8. (a) The range of nitrate- $\delta^{18}\text{O}$ values expected for microbial nitrification with ambient H_2O - $\delta^{18}\text{O}$ values ranging from -25 to $+4\text{‰}$ (winter to summer values), and O_2 - $\delta^{18}\text{O}$ values ranging from that of the atmosphere ($+23\text{‰}$) to $+60\text{‰}$ for soil O_2 fractionated by respiration. (b) Microbial nitrification can produce a wide range of nitrate- $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values; several scenarios for how these values might evolve over time are shown. The three curves show the changes in δ values of nitrate during nitrification and respiration, with nitrification $\epsilon_{15\text{N}}$ values of -10 , -5 , and -2‰ ; a respiration $\epsilon_{18\text{O}}$ value of -15‰ ; and f = fraction of NH_4 and O_2 remaining. The values of O_2 - $\delta^{18}\text{O}$ for various f values are shown to the left, with arrows pointing to the respective f values. The initial conditions are: H_2O - $\delta^{18}\text{O} = -15\text{‰}$, O_2 - $\delta^{18}\text{O}_{(\text{initial})} = +23\text{‰}$, NH_4 - $\delta^{15}\text{N}_{(\text{initial})} = 0\text{‰}$, and that nitrification of NH_4 and respiration loss of O_2 occurred at the same rate (i.e., with the same f values for both). The striped zones show the δ values produced for conditions where nitrification and respiration are completely disconnected. For example, if the NH_4 and O_2 reservoir sizes were greatly different and only one was significantly depleted over time, the nitrate formed might only show variation in either $\delta^{18}\text{O}$ or $\delta^{15}\text{N}$. The slopes of the three nitrification lines range from about 1.5 to 8, which is readily distinguishable from the denitrification slope of about 0.5.

16.4.4 Other processes affecting nitrate $\delta^{18}\text{O}$ values

Any process that uses or produces any nitrogen oxide (including nitrate) will probably fractionate the oxygen isotopes in addition to the nitrogen isotopes. Furthermore, most biological processes are likely to discriminate against ^{18}O and favor the reaction of ^{16}O relative to ^{18}O in the same way that ^{14}N is utilized in preference to ^{15}N . Hence, we can expect that changes in $\delta^{18}\text{O}$ of the nitrogen oxide during a process will often be proportional to changes in $\delta^{15}\text{N}$, keeping in mind that the mass difference between the two oxygen isotopes is roughly twice that of the two nitrogen isotopes.

Common microbial processes that may be expected to fractionate oxygen isotopes in NO_3 , leaving the residual NO_3 enriched in ^{15}N and ^{18}O , include: assimilation (uptake), absorption/desorption, and denitrification. Of these three, there are limited data only on denitrification. Denitrification along a flowpath changes the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of residual nitrate in a distinctive manner, making the combined analysis of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate a powerful tool for recognizing denitrification. This topic is discussed in detail in Section 16.5.2.

There seems to be little information about possible O isotope exchange between water and nitrate. Many have speculated that NO_3 might behave somewhat like SO_4 , with slow exchange rates with water except at high temperatures and low pH values. Since our nitrate collection method (Silva et al., in review) extracts nitrate from resins with HCl, we were concerned that this might cause fractionation. However, we could see no exchange between nitrate and low-pH, high- $\delta^{18}\text{O}$ water over timescales of a couple weeks. This needs further testing; however, the consistency of data from field areas argues against significant rapid exchange.

Mixing certainly has a significant effect on the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of nitrate in catchment waters. Almost all the surface waters plotted on Figure 16.6 have δ values intermediate between the values of precipitation and those of soil and/or groundwaters. The larger $\delta^{18}\text{O}$ range in soil water than groundwaters is probably caused by infiltration of significant amounts of precipitation into the shallow forest soils where most of the samples were collected. The narrow range of $\delta^{18}\text{O}$ values in groundwaters (except for the samples affected by denitrification) is mostly a function of study location: most of the groundwaters are from agricultural areas and other pollution studies (not forested catchments) where the deeper waters are better mixed than in shallow forest soils, and where a much larger proportion of the nitrate is derived from nitrification of applied fertilizer and manure than from precipitation.

16.5 Tracing Sources and Cycling of Nitrate

Under ideal circumstances, stable nitrogen isotopes offer a direct means of source identification because the two major sources of nitrate in many agricultural areas, fertilizer and manure, generally have isotopically distinct $\delta^{15}\text{N}$ values (Figure 16.4). Hence, under favorable conditions, the relative contributions of these two sources to groundwater or surface water can be estimated by simple mass balance. Soil-derived nitrate and fertilizer nitrate commonly have overlapping $\delta^{15}\text{N}$ values, preventing their separation using $\delta^{15}\text{N}$ alone (Figure 16.4).

An early attempt to use *natural* $\delta^{15}\text{N}$ values to determine sources of nitrate in surface waters (Kohl et al., 1971) received a highly critical response (Hauck et al., 1972). This was partly because the use of the $\delta^{15}\text{N}$ values of fertilizer and animal waste to trace their relative contributions to groundwater is complicated by several reactions (e.g., ammonia volatilization, nitrification, denitrification, ion exchange, and plant uptake) taking place within the hydrologic

system that can significantly modify the $\delta^{15}\text{N}$ values. Furthermore, mixing of point and non-point sources along shallow flowpaths makes determination of sources and extent of denitrification very difficult. Because of all these problems, attempts to use $\delta^{15}\text{N}$ for tracing the source and fate of nitrate in groundwaters and surface waters often have only limited success, despite the moderately good separation of $\delta^{15}\text{N}$ values (Figure 16.4). But it is interesting to note that the many subsequent isotopic studies of nitrate sources in *groundwater* did not elicit much controversy at all, perhaps because they considered in more detail the effects of denitrification and other $\delta^{15}\text{N}$ -altering processes. Many have speculated that analysis of the $\delta^{18}\text{O}$ of nitrate in conjunction with $\delta^{15}\text{N}$ would significantly improve our ability to trace nitrate sources and cycling.

Figure 16.9 is a "simplified" version of Figure 16.6 and shows the normal range of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values for the dominant sources of nitrate. Nitrate derived from ammonium fertilizer, soil organic matter, and animal manure have overlapping $\delta^{18}\text{O}$ values; for these sources, $\delta^{15}\text{N}$ is a better discriminator. In contrast, nitrate derived from nitrate fertilizer or atmospheric sources are readily separable from microbial nitrate using $\delta^{18}\text{O}$, even though the $\delta^{15}\text{N}$ values are overlapping. From the few dual-isotope studies of groundwater nitrate that have been conducted thus far (Böttcher et al., 1990; Aravena et al., 1993; Wassenaar, 1995), it is not yet clear how useful $\delta^{18}\text{O}$ will be in **source** characterization in *groundwater*. However, the dual isotope method has proved quite useful for source identification in some *surface-water* studies (Ging et al., 1996; Kendall et al., 1995b, 1996), as described in Sections 16.6.1 and 16.6.2.

The following sections discuss various isotopic techniques for determining the relative contributions of different sources of nitrate (i.e., how to resolve *mixing* problems), and several different methods for recognizing and accounting for the impact of denitrification on isotopic compositions and water chemistry. Section 16.6 presents several case studies in more detail. But the reader must not be misled into thinking that the successful solution of the mixing algebra insures that the source determinations are accurate.

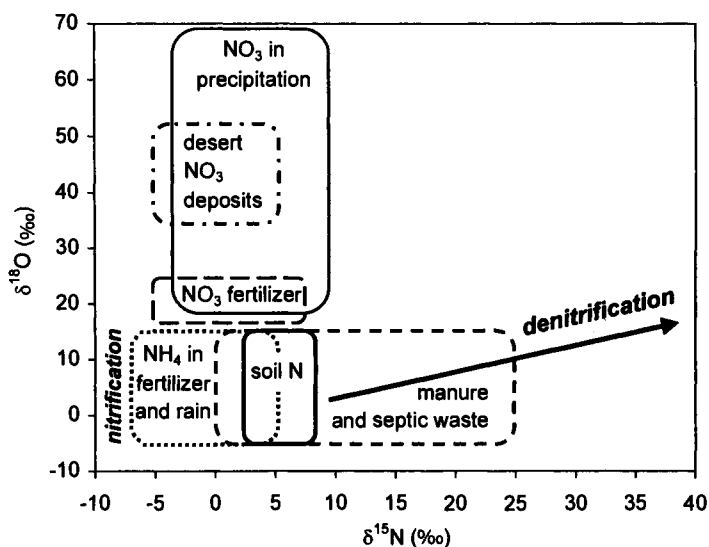


Figure 16.9. Schematic of typical ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of nitrate from various sources, simplified from data presented in Figure 16.6. Nitrification of ammonium and/or organic-N in fertilizer, precipitation, and organic waste can produce a large range of δ values, as shown. Soil waters tend to have higher NO_3 - $\delta^{18}\text{O}$ values, and a larger range of NO_3 - $\delta^{18}\text{O}$ values, than groundwaters because of the higher $\delta^{18}\text{O}$ values of O_2 and/or H_2O in soils.

It is difficult to determine realistic isotopic compositions of proposed endmembers and assumptions of conservative mixing are always dubious when biologically labile materials are concerned. On a similar theme, Handley and Scrimgeour (1997) concluded their monograph on the application of $\delta^{15}\text{N}$ to ecosystem studies with several “words to the wise” about successful uses of $\delta^{15}\text{N}$, including (1) don’t overinterpret the data, and (2) be careful about attempting to apply “univariate isotope theory to multivariate field problems.”

16.5.1 Mixing

If nitrate in groundwater or surface water derives from the mixing of two different sources that are known to have distinctive $\delta^{15}\text{N}$ values, in the absence of any subsequent fractionations, the relative contributions of each can readily be calculated. Many articles have illustrated this point on $\delta^{15}\text{N}$ versus NO_3 concentration plots, showing that mixtures must plot on a line between the two “endmember” compositions. However, such mixing lines are truly *straight* only when $\delta^{15}\text{N}$ values are plotted against $1/\text{NO}_3$ (see Chapter 2). On the standard $\delta^{15}\text{N}$ vs. NO_3 plots, mixing lines are hyperbolic unless the NO_3 contents of the endmembers are identical. An example of this is given in Figure 16.10a (from Mariotti et al., 1988) where two waters with nitrate concentrations of 0.2 and 10 mg/L mix together; note that the curvature of the mixing line is very slight for some mixing proportions.

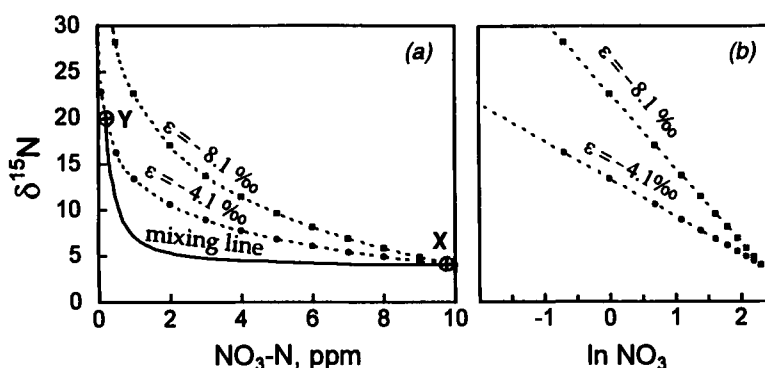


Figure 16.10. (a) Theoretical evolution of the $\delta^{15}\text{N}$ and the nitrate-N concentration during mixing (solid line) of two waters X and Y, and during an isotope fractionating process (e.g., denitrification of water X with a NO_3 concentration of 10 ppm). Denitrification for $\epsilon = -4.1\text{‰}$ results in a curve (dashed line) that ends at Y, one of the mixing endmembers. Two different enrichment factors are compared: $\epsilon = -4.1\text{‰}$ and $\epsilon = -8.1\text{‰}$. The data points represent successive 0.1 increments of mixing or denitrification progress. (b) Plotting the natural log of NO_3 concentration for a fractionation process yields a straight line. Modified from Mariotti et al. (1988).

Unfortunately, life is rarely this simple. There are multiple potential sources of nitrate in various ecosystems, the sources rarely have constant compositions, and even if they did, the initial compositions may have been altered by various fractionating processes before or after mixing. Hence, estimates of relative contributions will often be only qualitative. In particular, denitrification can greatly complicate the interpretation of $\delta^{15}\text{N}$ values because the exponential increase in $\delta^{15}\text{N}$ of residual nitrate with decreasing NO_3 content caused by denitrification can sometimes be confused with mixing of nitrate sources. For example, on Figure 16.10a, all three curves are almost linear for nitrate concentrations of 2 to 10. Hence, an incautious worker could try to interpret all three as mixing lines. However, as shown on Figure 16.10b, two of these curves are exponential relations resulting from denitrification, not mixing lines.

Mixing of sources can sometimes be resolved by analysis of both the $\delta^{18}\text{O}$ and the $\delta^{15}\text{N}$ of nitrate (or other semi-conservative chemical tracers). This dual-isotope approach has three main potential benefits: (1) oxygen isotopic *separation* of some sources is greater than for nitrogen isotopes, allowing better source resolution by having two tracers, (2) some nitrate sources that are presently indistinguishable with $\delta^{15}\text{N}$ alone (e.g., fertilizer vs. soil nitrate, or atmospheric vs. soil nitrate) may be identified only when the $\delta^{18}\text{O}$ of nitrate is analyzed, and (3) oxygen isotopic compositions of nitrate vary systematically with nitrogen isotopic compositions during denitrification (as illustrated in Figure 16.9). Thus, in systems where the dominant sources of nitrate are isotopically distinctive, source contributions can -- in theory -- be determined despite significant denitrification.

16.5.2 Denitrification

Denitrification is the process that poses most difficulties for simple applications of nitrate isotopes. Hence, for successful applications of nitrate isotopes for tracing sources, it is critical to (1) determine if denitrification has occurred, and, if so (2) determine what was the initial isotopic composition of the nitrate (which is a necessary prerequisite for later attempts to define sources). There are many methods for identifying and quantifying denitrification in groundwater; some of these are applicable to soils and aquatic systems too. The following discussion focuses on several of the most commonly applied *field-geochemical* methods for quantifying denitrification. Common *biological* methods for quantifying denitrification, conducted either in the laboratory or in the field -- including ^{15}N tracer additions to chambers (Mosier and Schimel, 1993), acetylene inhibition chamber methods, acetylene inhibition soil-core methods, and denitrification enzyme assay techniques -- will not be discussed here.

Geochemical signature

Denitrification leaves a geochemical *signature* that can be interpreted as evidence for its occurrence and extent. The most obvious evidence for denitrification is the presence of a redox gradient that generates a series of oxidation-reduction reactions, including the reduction of nitrate in the appropriate position in the sequence. Hence, in a closed system, denitrification occurs between the disappearance of dissolved O_2 by aerobic respiration and the appearance of Mn^{2+} and Fe^{2+} , if minerals containing these elements exist in the system (Mariotti et al., 1988). Denitrification and other reduction reactions (i.e., reactions that consume acidity) in groundwater are usually associated with significant increases in alkalinity (mostly bicarbonate) resulting from oxidation of organic matter. The newly formed bicarbonate ($\delta^{13}\text{C} \approx -23\text{‰}$) may be isotopically distinctive relative to original bicarbonate ($\delta^{13}\text{C} \approx -12\text{‰}$). Thus, evaluation of the changes in $\delta^{13}\text{C}$ value with reaction progress can, in theory, provide supporting evidence for denitrification or allow estimation of the extent of denitrification (Aravena and Robertson, 1998; also Chapter 18).

Enrichment in ^{15}N

During denitrification, the $\delta^{15}\text{N}$ value of the residual nitrate increases in proportion to the logarithm of the residual nitrate fraction (Figure 16.3). This can be expressed using the classical Rayleigh equation, that may be approximated in some situations (Mariotti et al., 1982) as:

$$\delta_R = \delta_{R_0} + \epsilon \ln C/C_0 \quad (16.15)$$

where δ_R is the $\delta^{15}\text{N}$ value of the reactant nitrate at time t , δ_{R_0} is the initial $\delta^{15}\text{N}$ value of the nitrate, C is the NO_3 content at time t , C_0 is the initial NO_3 content, and ϵ is the enrichment factor (with $\epsilon < 0$ to make the algebra work). Figure 16.10a shows curves for the $\delta^{15}\text{N}$ values

resulting from denitrification with two different fractionation factors, plus a curve for mixing with a dilute water with a different $\delta^{15}\text{N}$ value. Since mixing and denitrification curves can be similar, data should also be plotted as $\delta^{15}\text{N}$ vs. $1/\text{NO}_3$ (which will yield a straight line for mixtures of two sources), and $\delta^{15}\text{N}$ vs. $\ln \text{NO}_3$ (which will yield a straight line for any process, like denitrification, which can be described using the Rayleigh equation -- i.e., any exponential relation). Under favorable circumstances, plotting data in this way (Figure 16.10b) can provide supporting evidence for the determination of whether mixing or denitrification has occurred (Mariotti et al., 1988), and can be used to estimate the enrichment factor and initial conditions.

A large range of isotopic enrichment factors for denitrification ($\epsilon = -40$ to -5‰) have been calculated (see Hübner, 1986), determined in laboratory experiments (Delwiche and Steyn, 1970), measured in the soil (Mariotti et al., 1982), and observed in marine studies (Cline and Kaplan, 1975). However, Mariotti et al. (1988) noted that at many sites where denitrification in groundwater was identified by the above method, the ϵ values showed a more narrow range of about -5 to -8‰ . What causes this large range of observed enrichment factors? Mariotti et al. (1988) presented two hypotheses.

One explanation is that the denitrification rate is the main control on the enrichment factor. Hence, denitrification is a first-order reaction where slow rates (caused by low temperatures or low quantities of electron donors) result in larger fractionations (Mariotti et al., 1982). Therefore, small ϵ values near -5‰ suggest relatively rapid denitrification, and large fractionations, such as the $-30 \pm 6\text{‰}$ reported by Vogel et al. (1981) for denitrification in groundwater under the Kalahari desert, would indicate a slow denitrification rate. This model is consistent with the $\approx 14,000$ years Vogel et al. (1981) estimated for the time required to account for present conditions in the Kalahari aquifer.

An alternate explanation, elegantly presented by Mariotti et al. (1988), is that relatively impermeable aquifers may provide a sink for nitrate that effectively reduces the enrichment factor. For example, the porosity of chalk can exceed 40% of the total volume, yet 90% of the porosity is dead-end pores where the water is virtually immobile. In these pores, denitrification can proceed to completion, catalyzed by bacteria on the walls of the pores. Consequently, the nitrate concentrations within the pores are lower than in nearby flowpaths where waters travel more rapidly. This concentration gradient between the low-nitrate pores and the high-nitrate flowpaths, causes molecular diffusion of nitrate into the pores, which act as an effective sink for nitrate. Mariotti et al. (1988) further observe that the isotope effect associated with diffusion should be small or nonexistent, resulting in a smaller net enrichment factor. One consequence of this model is that a change in hydrologic conditions (e.g., an increase in pumping rate in the aquifer), should result in a significant decrease in denitrification potential.

Mariotti et al. (1988) conclude that the use of nitrate- $\delta^{15}\text{N}$ to study denitrification processes is well suited to groundwater investigations, and is easier to apply than using the $\delta^{15}\text{N}$ of dissolved N_2 because of (1) the relative ease of collection and preservation of nitrate samples compared to samples of N_2 gas, (2) the complications associated with accurate determination of the fraction of N_2 produced by denitrification, and (3) uncertainty whether there is a simple Rayleigh relation between the N_2 produced by denitrification and reaction progress.

Isotopes can also be used to study denitrification in soils (Delwiche and Steyn, 1970; Mariotti et al., 1981) and the hyporheic zone (McMahon and Böhlke, 1996). As discussed in section 16.3.5, the commonly observed increase in $\delta^{15}\text{N}$ in soils with decreasing nitrate concentration may, in part, be due to denitrification. A study by Koba et al. (1997) uses the relative changes in $\delta^{15}\text{N}$, nitrate concentration, and water chemistry in soils to conclude that intermittent

denitrification is occurring in anaerobic microsites of otherwise aerobic soils as the water table rises in response to storm events and pores become temporarily waterlogged.

Excess N_2

The dominant N-bearing product of denitrification is N_2 ; the intermediate N-bearing byproducts (NO_2 , NO , N_2O) are generally in low abundance. The dissolved N_2 in groundwater consists of atmospheric N_2 incorporated during recharge, plus N_2 produced by denitrification. If the dissolved N_2 in groundwater is measured, the amount of *excess N_2* produced by denitrification can sometimes be estimated. In addition, the dissolved N_2 can be analyzed for $\delta^{15}N$, the $\delta^{15}N$ value of excess N_2 can be estimated, and this information can be used to estimate both the extent of denitrification and initial composition of the nitrate (Vogel et al., 1981; Böhlke and Denver, 1995; McMahon and Böhlke, 1996). Figure 16.3 shows how the $\delta^{15}N$ value of N_2 is affected by the fractionation factor and the extent of denitrification (reaction progress).

Several studies have evaluated the extent of denitrification in aquifers by analysis of the $\delta^{15}N$ of dissolved N_2 , and then calculation of the $\delta^{15}N$ of the excess N_2 (Vogel et al., 1981; Wilson et al., 1990; Böhlke and Denver, 1995; McMahon and Böhlke, 1996; Böhlke et al., in review). The relative contributions of original atmospheric N_2 and excess N_2 can be estimated in several ways. If the atmospheric N_2 content of recharge waters were only a function of temperature, the initial N_2 content could be calculated (1) if the average recharge temperature were known, or (2) from the measurement of the noble gas composition of the sample (i.e., Xe, Ne, Ar, etc.) because these will behave conservatively in groundwater after recharge.

Measurement of the N_2/Ar ratio in groundwater is one way to estimate the excess N_2 produced by denitrification. This ratio varies only slightly with temperature (37.3 at 5°C, to 38.3 at 20°C) in air-equilibrated water. However, solution of small air bubbles (with N_2/Ar ratio of 83.5) during infiltration, because of increases in hydrostatic pressure as waters migrate downwards, causes groundwaters to have higher ratios than expected for the recharge temperature (Wilson et al., 1994). The amount of this entrained air can also be quantified by determining the "neon index" -- the ratio of the measured Ne content and the expected air-equilibrated Ne content at the derived recharge temperature (Wilson et al., 1994). Values greater than 1 indicate supersaturation with entrained air. A study of nitrate in a sandstone aquifer in England, concluded that N_2/Ar ratios higher than 44 were evidence of N_2 from denitrification (Wilson et al., 1994).

Böhlke and Denver (1995) used the difference in the N_2 contents of the suboxic-denitrified waters (NO_3 -free) and air-saturated water samples with the same Ar concentration as an upper limit for the amount of excess N_2 , as shown in Figure 16.11a. The upper limit of 135 μM of excess N_2 is equivalent to 270 μM reduced NO_3 . After adjustment for the small (0.7‰) isotopic enrichment caused by solution (Klots and Benson, 1963), the $\delta^{15}N$ of excess N_2 can be calculated by simple mass balance. Figure 16.11b shows the estimated $\delta^{15}N$ values for the excess N_2 in the samples plotted in Figure 16.11a range from +2 to +5‰. This range is indistinguishable from the range of $\delta^{15}N$ of NO_3 in oxic groundwaters from the same location where no denitrification has occurred; complete denitrification should produce N_2 with the same $\delta^{15}N$ as the initial NO_3 . The negative correlation between the $\delta^{15}N$ values of N_2 and Ar/N_2 ratio indicates that the dissolved N_2 in the denitrified waters was a mixture of atmospheric N_2 and N_2 produced by denitrification.

Enrichment in ^{18}O and ^{15}N of nitrate

Denitrification causes increases in the $\delta^{15}N$ and $\delta^{18}O$ of the residual nitrate (Figure 16.9). Although field and laboratory studies have recorded a wide range of kinetic enrichment factors

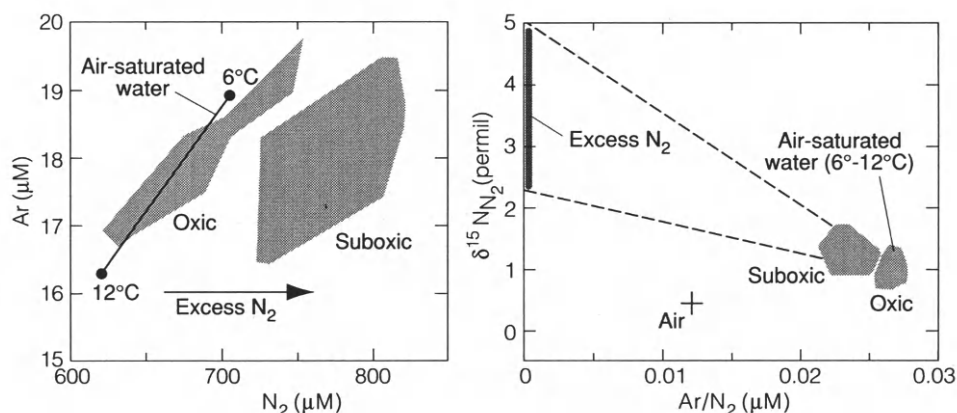


Figure 16.11. $\delta^{15}\text{N}$ values and gas contents of dissolved air in oxic and suboxic waters. Data for oxic waters are consistent with atmospheric equilibration at $9 \pm 3^\circ\text{C}$, and data for suboxic waters indicate the presence of excess N_2 in concentrations up to $135\mu\text{M}$, which is equivalent to $270\mu\text{M}$ of reduced NO_3^- (a). $\delta^{15}\text{N}$ values for oxic waters are consistent with equilibration at $9 \pm 3^\circ\text{C}$, and values for suboxic waters indicate that the excess N_2 has a $\delta^{15}\text{N}$ value between 2 and 5‰ (b). Modified from Böhlke and Denver (1995).

for both isotopes as a function of local conditions, in each case the *ratio* of enrichment of oxygen to nitrogen was close to 1:2 (Olleros, 1983; Amberger and Schmidt, 1987; Böttcher et al., 1990; Voerkelius and Schmidt, 1990; Kendall and McMahon, unpublished data). Therefore, denitrification produces a distinctive isotopic *signature* on $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ plots (i.e., slopes of about 0.5). The two irregular lines of groundwater samples with high $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values on Figure 16.6b are mostly from denitrification studies by Böttcher et al. (1990) and Aravena et al. (1998); these are the upper and lower lines, respectively.

Figure 16.9 can be used to illustrate a useful application of this characteristic enrichment in the $\delta^{18}\text{O}$ of nitrate for a situation where $\delta^{15}\text{N}$ values are ambiguous, based on a true situation. Local water managers were concerned that a public-water supply well downgradient from a heavily fertilized (KNO_3) orchard had elevated NO_3^- contents. Although the managers were convinced that fertilizer was the source of the nitrate, they wanted "proof" and had a few samples analyzed for $\delta^{15}\text{N}$. To their surprise, the $\delta^{15}\text{N}$ values ranged from +5 to +6‰, which did not provide support for their theory because this value is higher than the compositions expected for fertilizer ($0 \pm 2\text{‰}$). Were they wrong about the nitrate source? The measured values *could* indicate mixing with an additional source of nitrate (e.g., leaking septic tanks or local manure sources), that the fertilizer had a higher $\delta^{15}\text{N}$ value than expected (see Figure 16.4), or they could be caused by denitrification. Analysis of a few NO_3^- samples for $\delta^{18}\text{O}$ could have helped resolve this question because significant denitrification of fertilizer results in different $\delta^{18}\text{O}$ values than mixing of fertilizer and manure (Figure 16.9).

Another powerful application of the dual isotope method takes advantage of the apparently constant ratios of ^{18}O and ^{15}N enrichment ($\Delta\delta^{18}\text{O}/\Delta\delta^{15}\text{N}$) factors during denitrification. If the ratio is constant, and the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ compositions of the two potential sources of nitrate contributing to groundwater are known, are distinguishable, and do not show much scatter in composition, *in theory* the "original" relative contributions of these two sources to the nitrate in any sample of groundwater can be estimated from the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of the nitrate (Figure 16.12). Furthermore, if the ratio is consistent over a wide range of field conditions, it

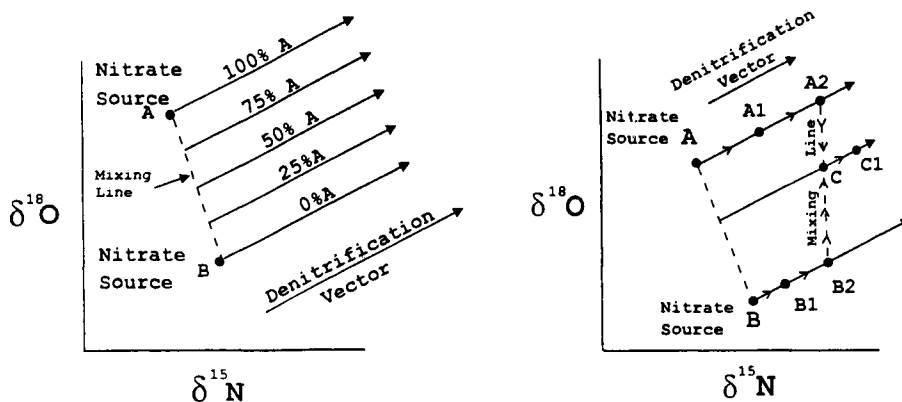


Figure 16.12. Determination of the relative contributions of nitrate to groundwater from two sources: fertilizer (A) and animal manure (B) using $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate. If the sources have distinctive compositions, the effects of mixing can be distinguished from the effects of denitrification. Vectors A → A2 and B → B2 show the compositions of nitrate derived from progressive denitrification of A and B, respectively. All mixtures of waters where one-third of the nitrate was derived from B and two-thirds of the nitrate was derived from A plot along vector C → C1, regardless of the timing of denitrification relative to mixing.

should be possible to determine the source contributions in a two-source situation regardless of the effects of denitrification. Such estimations are not affected by the extent or timing of denitrification and mixing, or the spatial arrangement of the sources (i.e., point versus non-point sources). A more complete description of this model is given by Kendall et al. (1995c).

16.6 Application Studies

The section below describes a number of types of generally successful applications of nitrogen and oxygen isotopes of nitrate at the catchment scale. However, from my perspective as a hydrologist at the USGS, most of the real interest in the uses of N isotopes is in tracing nitrate sources in larger-scale agricultural and urban basins. Hence, this will be discussed first below, followed by additional applications more directly related to smaller, often forested catchments that are the purview of the “traditional” (read: old fashioned) watershed hydrologist or biogeochemist. To get on my soapbox, more watershed biogeochemists need to embrace the challenge of extending what they have learned at the small catchment scale to these larger-scale, human-impacted watersheds and basins. Other reviews of applications of N isotopes in forested ecosystems and polluted environments, respectively, are Nadelhoffer and Fry (1994) and Macko and Ostrom (1994).

16.6.1 Agricultural and urban sources of nitrate

There is a fair amount of isotopic literature on this topic, some of which will be described in detail below. Some relevant groundwater $\delta^{15}\text{N}$ studies include: Kreitler (1975, 1979), Kreitler et al. (1978), Gormly and Spalding (1979), Kreitler and Jones (1975), Vogel et al. (1981), Kreitler and Browning (1983), Mariotti et al. (1988), Wells and Krothe (1989), Wilson et al. (1990), Smith et al. (1991), Spalding et al. (1993), Böhlke and Denver (1995), and McMahon and Böhlke (1996). There have been only a few studies thus far using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ to study nitrate sources and cycling mechanisms in groundwater: Amberger and Schmidt (1987),

Böttcher et al. (1990), Aravena et al. (1993), Wassenaar (1995), and Aravena and Robertson (1998). It is not yet clear whether $\delta^{18}\text{O}$ of nitrate will prove to be the panacea some had hoped for. However, since it is likely that more studies in the future will utilize a multi-isotope approach, the discussion below will concentrate on dual isotope studies.

What sources of nitrate can be distinguished using isotopes?

Most of the interest in uses of nitrate isotopes centers around how to differentiate (1) fertilizer vs. animal waste contributions to groundwater or surface water, (2) septic tank leakages vs. animal waste, and (3) natural soil N from fertilizer and/or wastes. Below is a brief discussion of what works and what does not.

Fertilizer vs. animal waste: These components usually can be separated successfully using $\delta^{15}\text{N}$ alone (see Figure 16.4). Quantification of relative contributions is usually better in well-oxygenated, sandy soils than in clays because of the lesser opportunity for denitrification (Gormly and Spalding, 1979). However, if the effects of denitrification can be estimated by the methods described in Section 16.5.2, then sources can be determined more accurately. Because most applied fertilizer is dominated by ammonium, analysis of $\delta^{18}\text{O}$ of nitrate may not add much additional information; however, this isn't always true (see discussion below of Ging et al., 1996).

Septic tank leakages vs. animal waste: The nitrate derived from these two materials usually have overlapping $\delta^{15}\text{N}$ values and cannot be distinguished using $\delta^{15}\text{N}$ alone; however, see Fogg et al. (1998) for an example where the values are significantly different. It is possible that if the waters in which the waste was nitrified had distinctive $\delta^{18}\text{O}$ values, analysis of nitrate for O and N isotopes might be useful for distinguishing sources (Aravena et al., 1993); see Figure 16.8. It is also possible that these waste sources could be differentiated using a multi-isotope approach, perhaps by analysis of the C, N, and S isotopic compositions of the other dissolved species and DOM that accompanies the nitrate, or in the case of aquatic systems, the isotopic compositions of organisms that utilize the nutrients -- but this is pure speculation at this time. Other possible tracers of these waste sources include: boron isotopes, lithium isotopes, caffeine, and hormones.

Natural soil N from fertilizer and/or wastes: As shown in Figure 16.4, natural soil nitrate has a $\delta^{15}\text{N}$ value that is intermediate between those of fertilizer and waste, and commonly overlaps their compositions. Attempts to distinguish between soil and waste nitrate using $\delta^{15}\text{N}$ are often successful (e.g., Kreitler and Jones, 1975; Kreitler and Browning, 1983), whereas fertilizer and soil nitrate usually cannot be distinguished. Chances of differentiating fertilizer and soil nitrate using $\delta^{15}\text{N}$ would be improved if the waste were very enriched in ^{15}N , and using $\delta^{18}\text{O}$ would be more successful if a significant proportion of the applied fertilizer were nitrate or if the nitrification of waste took place in highly evaporated soil water (Figure 16.8). Contributions from all three sources might be estimated by using other tracers in addition to nitrate isotopes.

Determination of sources of nitrate in groundwater

Nitrate concentrations in municipal wells downgradient from heavily fertilized agricultural areas in the "Fuhrberger Feld" catchment near Hannover (Germany) decreased with distance from the fields. Böttcher et al. (1990) analyzed nitrate in groundwater for $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ to ascertain whether the decreases were caused by microbial denitrification or mixing with more dilute waters from nearby forests. They found that low concentrations of nitrate were associated with high $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values, and vice versa. Furthermore, changes in $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values along the flowpath were linearly related, with a slope of $\Delta\delta^{15}\text{N}/\Delta\delta^{18}\text{O} = 1:2.1$. The linear relation between the isotope values and the logarithm of the fraction of residual nitrate (i.e., the data fit a Rayleigh equation) indicated that denitrification with constant enrichment factors for O and N were

responsible for the increases in $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ (Figure 16.9). The enrichment factors calculated by regression analysis were $\epsilon = -15.9\text{‰}$ for $\delta^{15}\text{N}$ and $\epsilon = -8.0\text{‰}$ for $\delta^{18}\text{O}$. The higher correlation coefficients for $\delta^{18}\text{O}$ than for $\delta^{15}\text{N}$, resulting probably from the large variety of N sources in the area and the greater possibilities for N isotope effects during various transformations, suggest that $\delta^{18}\text{O}$ might be better suited for identifying denitrification than $\delta^{15}\text{N}$ (Böttcher et al., 1990).

The applicability of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate and other tracers to delineate contaminant plumes derived from domestic septic systems was evaluated by Aravena et al. (1993), in a study within an unconfined aquifer beneath an agricultural area in Ontario (Canada). They found that $\delta^{15}\text{N}$ of nitrate, $\delta^{18}\text{O}$ of water, and water chemistry (esp. Na) were effective for differentiating between the plume and native groundwater. The differences in $\delta^{15}\text{N}$ values reflect differences in dominant N sources (human waste vs. mixed fertilizer/manure). There was good delineation of the plume with water- $\delta^{18}\text{O}$ values, reflecting differences in residence time of water within the shallow unconfined aquifer, and the deeper confined aquifer that supplies water to the house and the plume. There was no significant difference between the $\delta^{18}\text{O}$ of nitrate in the plume and in local groundwater; the $\delta^{18}\text{O}$ values suggest that nitrification of ammonium, from either human waste or agricultural sources, is the source of the nitrate. The lack of separation with $\delta^{18}\text{O}$ of nitrate suggests that the $\delta^{18}\text{O}$ of nitrate may not be a useful tracer of nitrate sources except in areas dominated by nitrate fertilizers (Aravena et al., 1993). Another study of a septic plume determined that use of a multi-isotope approach (using $\delta^{13}\text{C}$ of DIC, and $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of sulfate in addition to nitrate $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$) provided valuable insight into the details of the processes affecting nitrate attenuation in groundwater (Aravena and Robertson, 1998).

The high concentrations of NO_3 in shallow groundwater in the Abbotsford aquifer, British Columbia (Canada), are believed to have resulted from nitrification of poultry manure, with lesser amounts of ammonium fertilizers (Wassenaar, 1995). This study found that ammonia volatilization caused the nitrate- $\delta^{15}\text{N}$ values to increase to $+8$ to $+16\text{‰}$. Since local groundwater had a narrow range of $\delta^{18}\text{O}$ values (-10 to -12‰), nitrate formed by nitrification in the aquifer was expected to have $\delta^{15}\text{N}$ values from about -1 to $+1\text{‰}$. However, nitrate- $\delta^{18}\text{O}$ values generally ranged from $+2$ to $+5\text{‰}$, with values as high as $+10\text{‰}$. The higher-than-expected nitrate- $\delta^{18}\text{O}$ values were attributed to either (1) nitrification in the summer when recharge waters have $\delta^{18}\text{O}$ values of -10 to -6‰ , and soil waters are subject to additional evaporative enrichment, or (2) minor denitrification under the manure piles (Wassenaar, 1995).

Determination of sources of nitrate in stream water

There has been a much smaller number of agricultural/urban nitrate isotope studies in rivers, perhaps because of the critical response elicited by the first such study by Kohl et al. (1971). Besides the papers discussed below, other relevant papers include: Cravotta (1994) who used a multi-isotope approach to determining sources of nutrients in the river, and Kendall et al. (1995b, 1996) who used the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate to determine the dominant source of nitrate in early spring runoff in three forested catchments in the USA, and concluded that most of the nitrate in streamflow during the period of potential acidification was apparently derived from pre-melt sources, probably largely composed of precipitation from previous years (see Section 16.6.2).

Kohl et al. (1971) investigated the sources of nitrate in drainage waters of the Sangamon River (Illinois, USA) and concluded that about half the nitrate was derived from soil sources and half from unfractionated fertilizer nitrate. This conclusion was strongly criticized by Hauck et al. (1972) and others because fractionation effects and natural variability in soil systems would make it impossible to apply simple mixing models to the $\delta^{15}\text{N}$ values. A study on the small Yerres River (France) presented a somewhat similar study showing how the stream $\delta^{15}\text{N}$ changed along different segments of the river as three different sources contributed variably

(Mariotti and L  toll  , 1977; L  toll  , 1980). Natural soil nitrate with a steady-state $\delta^{15}\text{N}$ value was the main source of nitrate to baseflow; episodically superimposed on this were high concentrations of unfractionated fertilizer that leached through the soils and into drains during winter and spring storms, and low concentrations of nitrified animal wastes enriched in ^{15}N by volatilization of ammonium that appeared in the stream during small summer storms. H  bner (1986) reanalyzed both sets of stream nitrate data and suggested that a logarithmic relation could be fitted to the data sets, with apparent enrichment factors of 5–6‰, suggesting that denitrification or assimilatory fractionation effects could also be a factor. Because of all these complications (and in the hope of “turning a sow’s ear into a silk purse”), Shearer and Kohl (1993) suggested that perhaps the best use of natural abundance ^{15}N research is not to try to estimate contributions from different sources, but to study N transformations.

In accordance with this suggestion, surface-water nitrate studies by B  hlke and Denver (1995) in an agricultural watershed in Maryland (USA) and McMahon and B  hlke (1996) in the Platte River in Colorado (USA) focused their attention on quantifying the effects of denitrification and mixing between the river and aquifer, and not on trying to assess contributions from specific nitrate sources (although the $\delta^{15}\text{N}$ values did suggest the nitrate derived from animal waste and fertilizer). Denitrification was quantified by measurement of the excess N_2 and the $\delta^{15}\text{N}$ of dissolved N_2 , and flowpaths were established from chlorofluorocarbon (CFC) and hydraulic data. Substantial denitrification was found in reducing zones within the aquifer in Maryland (Figure 16.5), but there probably was limited denitrification in the wetlands and shallow organic soils adjacent to the streams because the deeper groundwater flowpaths avoided these buffer strips and converged directly beneath the streambeds and rapidly discharged upwards (B  hlke and Denver, 1995). The hyporheic zone was found to be a major site for denitrification for the Platte River (McMahon and B  hlke, 1996).

A pilot study by Ging et al. (1996) used $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate to determine the dominant sources of nitrate in storm runoff in suburban watersheds in Austin, Texas (USA). Samples from several suburban creeks were collected three times at baseflow and four times during storms, and analyzed for chemistry and isotopic composition. Figure 16.13 shows that during baseflow (high chloride concentrations), nitrate had high $\delta^{15}\text{N}$ and low $\delta^{18}\text{O}$ values; in contrast, during storms (low chloride concentrations), nitrate had low $\delta^{15}\text{N}$ and high $\delta^{18}\text{O}$ values. The strong correspondence of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values during changing flow conditions suggests that the stream composition can be explained by varying proportions of two endmember compositions, one dominated by nitrate fertilizer ($\delta^{15}\text{N} = +4\text{‰}$, $\delta^{18}\text{O} = +25\text{‰}$) that is the major source of water during storms and the other a well-mixed combination of sewage and fertilizer sources ($\delta^{15}\text{N} = +10\text{‰}$, $\delta^{18}\text{O} = +15\text{‰}$) that contributes to baseflow.

Although almost all the applied fertilizer in the Austin area is believed to be ammonium with only minor amounts of nitrate fertilizer, stormflow waters have nitrate $\delta^{18}\text{O}$ values generally in the range of +15 to +27‰, characteristic of anthropogenic nitrate fertilizer. This is puzzling since the nitrification of a fertilizer composed originally of about 95% ammonium and 5% nitrate should have a $\delta^{18}\text{O}$ of no greater than about +10 to +15‰. Possible explanations are (1) that nitrate fertilizer is a major source of nitrate in the stream (that implies that the ammonium fertilizer is being largely assimilated or otherwise immobilized) so that the isotopic signature of the originally small amount of nitrate is *bio-magnified*, (2) that a significant portion of the nitrate is from atmospheric sources, despite the low concentration of nitrate in rainfall, or (3) the high $\delta^{18}\text{O}$ values reflect contributions of natural soil nitrate produced under highly evaporated conditions (see B  hlke et al., 1997).

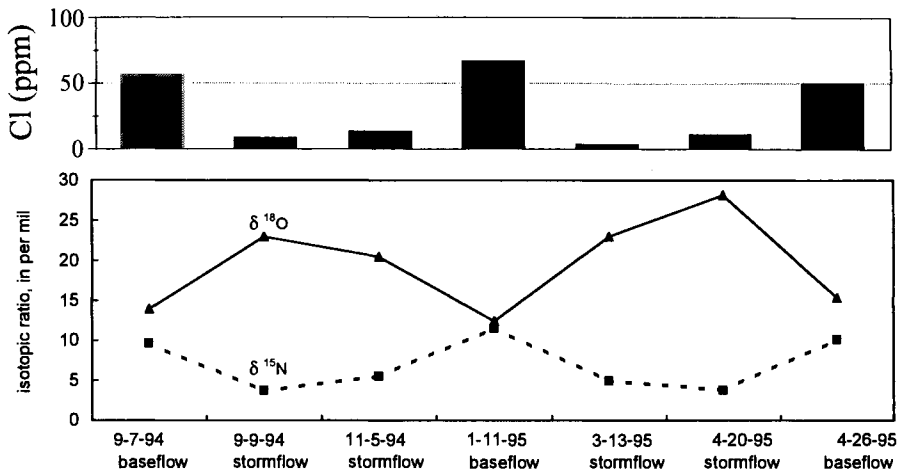


Figure 16.13. Average $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of NO_3 during stormflow (low Cl) and baseflow (high Cl) conditions in urban streams in Austin, Texas (USA). Modified from Ging et al. (1996).

Age-dating pollution changes

By combining nitrogen isotope analyses with ground-water dating, it is possible to estimate the timing of nitrate-related events including (1) the rate of natural denitrification, (2) when contaminated or remediated groundwaters will reach the streams (Böhlke et al., 1992; Böhlke and Denver, 1995), and (3) changes in contamination loads in the recharge zone over time (Böhlke and Denver, 1995; Böhlke et al., in review). Böhlke and Denver (1995) showed that in places where the extent of denitrification can be quantified, analyses of dated, denitrification-corrected groundwaters can provide a valuable record of past contamination loads in the recharge zone. This type of record can be valuable in localities where long-term fertilizer-use data are missing or unreliable. The study showed that nitrate concentrations in recharge increased by about a factor of 5 between 1950 and 1990, at about the same time the amount of applied fertilizer increased by about a factor of 5.

16.6.2 Sources of N in acid-rain affected forested catchments

Another useful application of the dual isotope approach is for determination of the relative contributions of atmospheric and soil-derived sources of nitrate in shallow groundwater. This problem is intractable using just $\delta^{15}\text{N}$ because of overlapping compositions of soil and atmospherically derived nitrate (Figure 16.4). However, data from several German forests (Voerkelius, 1990; Durka et al., 1994) and three catchments in the USA (Kendall et al., 1995b, 1996) indicate that the $\delta^{18}\text{O}$ of nitrate in precipitation is in the range of +25 to +75‰ (Figure 16.7), easily distinguishable from microbial nitrate with $\delta^{15}\text{N}$ values in the range of -10 to +15‰. If such heavy $\delta^{18}\text{O}$ values are typical of atmospherically derived nitrate elsewhere, or at least in places where there are significant anthropogenic sources of atmospheric nitrogen, contributions from precipitation and soil nitrate should be distinguishable, as illustrated in the examples below.

Nitrate in snowmelt runoff

During early spring melt, many small catchments experience episodic acidification because of large pulses of nitrate and hydrogen ions being flushed into the streams. There has been some

controversy over the source of this nitrate. Microbially produced soil nitrate and atmospheric nitrate are the main sources of nitrate in stream water. Mineralization of N in leaf litter and in the organic layer of the soil, followed by nitrification while the soils are covered with a thermally insulating layer of snow, may be an important source of nitrate to surface waters during snowmelt (Rascher et al., 1987); this nitrate is then flushed into the stream during snowmelt.

Three studies were initiated during the 1994 snowmelt season (and continued through 1997) in watersheds in forested catchments in Colorado, Vermont, and New York (USA) to test hypotheses about nitrate sources during snowmelt and storm runoff. Snow, rain, snowmelt, soil waters, groundwaters, and stream waters collected before, during, and after the acidic snowmelt pulse were analyzed for water- $\delta^{18}\text{O}$, nitrate- $\delta^{18}\text{O}$, nitrate- $\delta^{15}\text{N}$, and major ions (Kendall et al., 1995b, 1996, in review). Hydrograph separations using water- $\delta^{18}\text{O}$ showed that almost all of the water in the streams during snowmelt was derived from snowmelt. In contrast, the nitrate- $\delta^{18}\text{O}$ of stream water in the Loch Vale watershed (Colorado) during the melt period in 1994 had increased only slightly from the pre-melt baseflow value of $\approx +15\text{‰}$ and showed little change over time (Figure 16.14a), suggesting that the nitrate was largely derived from pre-melt sources. The one stream sample with a high $\delta^{18}\text{O}$ value was collected from meltwater flowing off the snowpack, so this nitrate was clearly derived almost exclusively from atmospheric sources. During subsequent years of sampling (Figure 16.14b), the nitrate- $\delta^{18}\text{O}$ in streamwater during the snowmelt was significantly higher than the pre-melt $\delta^{18}\text{O}$ value, suggesting larger contributions of nitrate from precipitation (Campbell et al., in review).

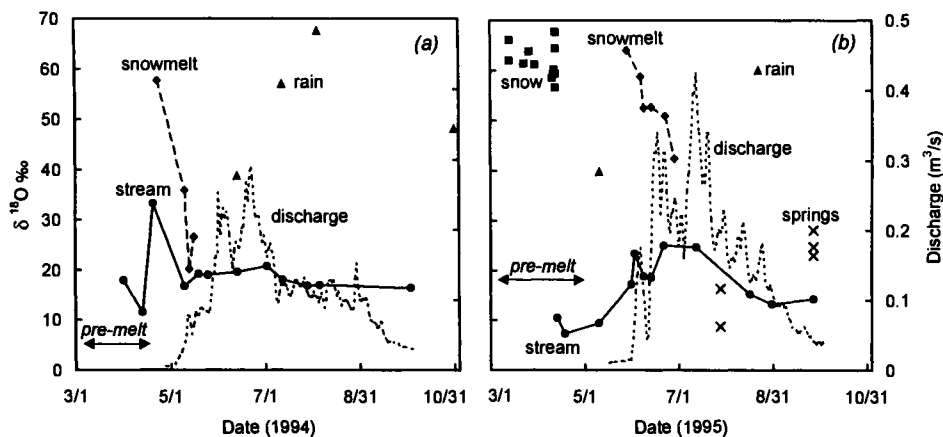


Figure 16.14. $\delta^{18}\text{O}$ of NO_3 in streamwater and discharge at Andrews Creek, at Loch Vale watershed, Colorado (USA) in 1994 and 1995. (a) The $\delta^{18}\text{O}$ of nitrate in the stream during snowmelt 1994 were only slightly greater than values for samples collected during pre-melt baseflow, except for the high value during overland flow from the snowpack; from Kendall et al. (1996). (b) Many of the stream samples in 1995 had higher nitrate $\delta^{18}\text{O}$ values, suggestive of significant contributions from atmospheric nitrate; from Kendall et al. (in review).

Almost all the stream nitrate samples from the seven different tributaries in the three catchments plot within a relatively narrow 20‰ range of $\delta^{18}\text{O}$ values, with a 7‰ range in $\delta^{15}\text{N}$ values (Figure 16.15). This range is identical to the range of values for soil waters and groundwaters from the catchments and is outside the $\delta^{18}\text{O}$ range of almost all the precipitation and melt samples. Furthermore, the overlapping compositions of streamwater and subsurface waters strongly

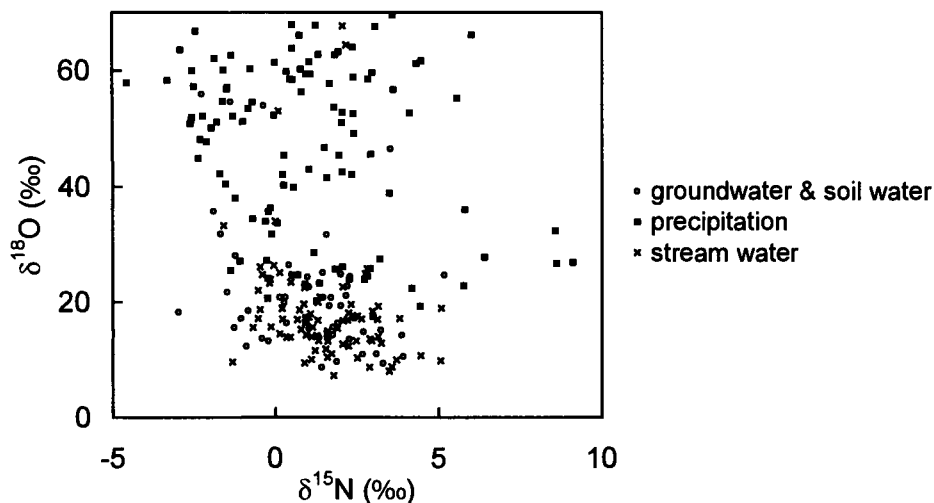


Figure 16.15. $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of nitrate from precipitation, streams, groundwater, and soil water from three forested catchments in the USA, 1994-96. From Kendall et al. (in review).

suggests that the nitrate in streamwaters was largely derived from subsurface sources. Hence, atmospheric nitrate from the melting snowpack was not a significant source of nitrate in early runoff in these catchments. The nitrate eluted from the snowpack appeared to go into temporary storage, to perhaps leak into the streams later in the season. Most of the nitrate in streamflow during the period of potential acidification was apparently derived from pre-melt sources, probably a mixture of mixture of atmospheric nitrate from previous years and microbial nitrate (Kendall et al., 1995b, in review).

The main sources of uncertainty in calculating the relative contributions from the two nitrate sources are (1) the ranges in the end member compositions, especially for atmospheric nitrate, and (2) uncertainty about whether snow ammonium is retained in the soil or is nitrified to nitrate (Kendall et al., 1995b), resulting in a third potential source of nitrate to the system. A further complication is that nitrification of snow ammonium would produce new nitrate with a $\delta^{18}\text{O}$ value very similar to microbially produced soil nitrate, causing the atmospheric *signal* to be less distinctive. ^{15}N -labeled ammonium added to the surface of the snowpack in 1994 at a nearby watershed in Colorado (Niwot Ridge) was not nitrified in the snowpack or in the soils during the snowmelt period, indicating that snow ammonium was probably not a significant source of nitrate to the stream in the early spring in 1994 (Williams et al., 1996). Therefore, snow ammonium can perhaps be ignored in isotope mass balance calculations, at least during snowmelt at Loch Vale.

These pilot studies have clearly indicated that careful sampling of potential sources will be required for accurate estimates of their relative contributions to streamflow. In particular, the observed variability in the $\delta^{18}\text{O}$ of atmospherically derived nitrate makes it vital that snow lysimeters be positioned at several elevations, and that adequate samples be collected to assess temporal and spatial variability in the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of newly eluted nitrate from the snowpack. The nitrate-rich reservoirs in the catchments need to be located and the soil and shallow ground water in these zones must be sampled several times in early winter, prior to any thaws. It is unclear how much variability might be found in these reservoirs because of seasonal changes

in microbial processes and chemical fluxes. The effect of nitrification of snow and soil ammonium on N budgets is unknown, and will require careful sampling combined with field experiments with ^{15}N -labeled ammonium to decipher.

Forest decline

Isotopes have been used to explain N-dynamics in forests impacted by acid rain. In these systems, the supply of atmospherically derived nitrogen exceeds the demand by plants and soil microbes; the situation has been termed *nitrogen saturation* (Aber et al., 1989). Early stages of nitrogen saturation are characterized by frequent high-nitrate pulses in stream water; later stages result in elevated concentrations of nitrate in baseflow year round (Aber et al., 1989). High levels of nitrogen deposition are correlated with forest declines.

Isotopic methods can sometimes be used to study changes in forest health; such studies are a main element of the NITREX program in Europe (Sullivan, 1991). For example, the $\delta^{15}\text{N}$ of needles or leaves is being used by several groups as an indicator of forest N status, especially for assessing N losses via nitrification followed by leaching (Garten and van Miegrot, 1994; Gebauer et al., 1994; Nasholm et al., 1997). Several studies have suggested that the variations in the $\delta^{15}\text{N}$ of plants might be used as indicators of environmental stresses (Gebauer and Schulze, 1991). Winkler and Gebauer (1993) present a model for N metabolism in forests to explain the N contents and $\delta^{15}\text{N}$ values of damaged plants in ecosystems stressed by acid rain. They suggest that the increases in $\delta^{15}\text{N}$ values of pine needles in damaged pines are due to changes in metabolism (shifts towards degradation of pre-existing organic substances, instead of utilizing DIN). An alternative explanation is that the needles are affected by changes in the $\delta^{15}\text{N}$ values of soil N (i.e., soils are not at steady state). For example, the accumulation of arginine in trees in response to N fertilization may cause a decrease in ammonium-uptake in the soils and a consequent increase in nitrification, resulting in an ^{15}N -enriched ammonium pool that is then utilized for needle formation (Nasholm et al., 1997). The $\delta^{15}\text{N}$ in whole-wood from rings from two trees in New Hampshire (USA) showed a systematic decrease from the 1960's onwards, perhaps because of a decrease in the $\delta^{15}\text{N}$ of available N or isotope fractionation accompanying translocation of N (Poulson et al., 1995).

Research using $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate in several forests in Bavaria (Germany) has concluded that atmospheric deposition is a major source of nitrate to the catchments, and that the $\delta^{18}\text{O}$ of nitrate in springs was correlated with the general health of the forest (Durka et al., 1994). The $\delta^{18}\text{O}$ values of nitrate in springs in limed (buffered) or relatively healthy forests suggested that atmospheric nitrate comprised a small fraction of the nitrate. Although the nitrate output from these forests is high (because of internal nitrification plus atmospheric sources), nitrate consumption by plants and soil microorganisms was apparently sufficient to recycle a large portion of the atmospheric nitrate so that its original atmospheric *signature* was lost. In contrast, sites with declining forests had springs with higher proportions of nitrate derived from the atmosphere, and apparently little recycling of nitrate by the ecosystem. Hence, acid-induced forest decline appears to inhibit nitrate consumption and recycling by soil microorganisms (Durka et al., 1994).

The $\delta^{18}\text{O}$ of nitrate in stream and soil waters in some USA catchments (Figure 16.15) is similar to the compositions seen in German springs. Although all the USA forests are apparently healthy, the data indicate that these forests are leaking nitrate that is derived, in large part, from atmospheric deposition. This may be an early warning sign that these forest ecosystems are being damaged by air pollution and acid rain. However, Kendall et al. (1995b) concluded that there are insufficient data at this time to make any conclusions about the relationships between

$\delta^{18}\text{O}$ of nitrate in storage and the relative rates of nitrate deposition, advection through the soil, and biological consumption. The $\delta^{18}\text{O}$ (and to a lesser/different extent, the $\delta^{15}\text{N}$) of nitrate leaking from forests is controlled by several factors including (1) *relative rates* of atmospheric deposition, microbial production, microbial consumption, and transport of nitrate through the soil; (2) *health of the ecosystem* -- ability of microorganisms to utilize excess nitrate; (3) *spatial distribution* of nitrate deposition and microbial activity -- fraction of total nitrate deposited where the microbes are located; and (4) *hydrology* -- residence time of deposited nitrate along flowpaths through organic-rich horizons where microbes are active.

16.6.3 Nitrogen-limited systems

The widespread occurrence of N limitation in terrestrial ecosystems is a bit surprising considering the omnipresence of N-fixers (Vitousek and Howarth, 1991). Biogeochemical mechanisms that favor N limitation over P limitation include higher mobility and consequent removal of DIN from soils, especially in disturbed systems (cultivated or burned); and greater availability of P relative to N during slow decomposition of organic matter (Vitousek and Howarth, 1991).

The productivity of most agricultural and "natural" terrestrial ecosystems is limited by N availability (Vitousek and Howarth, 1991). Extensive research on the processes affecting the supply of N in fertile ecosystems has resulted in the generalization that the mineralization of organic N to ammonium and its later oxidation to nitrate are the major "bottlenecks" restricting the availability of N to plants (Vitousek and Howarth, 1991). However, research in infertile ecosystems (e.g., the acidic soils typical of pine forests) has shown that plants are tapping some organic N as well as the DIN pool released by mineralization (Northup et al., 1995), hence bypassing the mineralization step that had been viewed as the limiting factor in N cycling in terrestrial ecosystems. Northup et al. (1995) show that the polyphenol concentration of decomposing pine litter controls the relative proportion of N released as DON versus DIN.

In N-limited systems, all the DIN substrate may be converted to organic matter, resulting in little fractionation between DIN and plant. Hence, whereas the low $\delta^{15}\text{N}$ values of N-limited forest soils are generally attributed to the continuous input of litter with low ^{15}N abundance (Shearer and Kohl, 1986), this might be merely a symptom rather than a cause and the low $\delta^{15}\text{N}$ values of the soils might instead be the result of a tightly closed N cycle (Högberg, 1990). The initial response of a N-limited system to increased N loading is a change in $\delta^{15}\text{N}$ towards the composition of the added N. However, large increases in $\delta^{15}\text{N}$ (Figure 16.3) can occur in a variety of environments when ammonium is added (by acidic rain or applied fertilizer) because of volatilization of low- $\delta^{15}\text{N}$ (Meints et al., 1975; Feigin et al., 1974; Högberg, 1990, 1991).

16.6.4 Labeled-tracer studies

Tracer techniques based on the use of ^{15}N have been important in agronomic research for many decades. Most agricultural tracer applications are based on the fact that the $^{15}\text{N}/^{14}\text{N}$ ratios are close to 1/272 in all natural materials, and that biogeochemical and physical processes cause negligible changes in $^{15}\text{N}/^{14}\text{N}$. This fact may seem puzzling following the preceding discussions of the causes of the considerable variability in the $^{15}\text{N}/^{14}\text{N}$ ratios of different compounds. However, it depends on perspective: agronomic tracer studies have typically been conducted by adding fertilizer with unnaturally high (or sometimes low) $^{15}\text{N}/^{14}\text{N}$ ratios to plots, ratios different enough from *natural abundance ratios* that natural variations in the N cycle are insignificant in comparison, and can be ignored. The amount of change in isotope ratio from

the background level (i.e., 1/272) permits calculation of the extent to which the tracer has become part of the ecosystem.

Isotope ratios in such studies are usually reported in terms of atomic weight % ^{15}N (fractional percentages), where ‰ (at natural abundance levels) equals ± 0.00037 at. % ^{15}N . The $\delta^{15}\text{N}$ value of ammonium sulfate that is 10 at. % ^{15}N is calculated as follows:

$$\delta^{15}\text{N}_{\text{AIR}} = \{[(10/90) / (1/272)] - 1\} \cdot 1000 = +29,222\text{‰} . \quad (16.16)$$

For a thorough review of the use of ^{15}N as a tracer in soil studies, see Hauck and Bremner (1976). Knowles and Blackburn (1993) also provides detailed guidelines on how to apply ^{15}N tracer techniques to a variety of ecosystem studies.

Mass-balance calculations can be made using:

$$n_T F_T = n_1 F_1 + n_2 F_2 \quad (16.17)$$

where n represents the molar quantities of the element of interest, and F represents the fractional isotopic abundances (e.g., the fractional abundance of $^{15}\text{N} = ^{15}\text{N}/(^{15}\text{N} + ^{14}\text{N})$). Substitution of δ for F provides only insignificant errors for natural abundance ratios (0.02‰ for ^{13}C), but is inappropriate for isotopically labeled materials.

Many isotopically labeled (spiked) compounds, some with labeling of multiple elements, are commercially available. The costs for microcosm, plot, and field-scale experiments are commonly in the range of \$100 to \$10,000 (USD). Applications of high concentrations of ^{15}N (typically in the range of 10 to 50 at. % ^{15}N) permit the investigator to almost ignore natural variations in ^{15}N abundance within the study area, and use sample collection, preparation, and isotope ratio analysis procedures that are unsuitable (because of lack of precision and accuracy) for the kinds of natural abundance work described elsewhere in this chapter. For this reason, researchers are advised to be exceedingly cautious when considering the use of techniques or laboratories used for labeled tracer (agronomic) studies, for natural abundance samples.

Larger-scale watershed or ecosystem-scale studies can also be conducted within a reasonable budget if the investigator dilutes the applied ^{15}N spike several orders of magnitude so that the study becomes essentially a natural abundance study with an artificially labeled compound. For example, Kling (1994) reports that the amount of ^{15}N -labeled material required to increase the $\delta^{15}\text{N}$ value of lake phytoplankton by 30‰ cost \$300, and the amount to increase the $\delta^{15}\text{N}$ of algae in a whole-river experiment by 850‰ cost less than \$4000 (USD).

In the last decade there have been several long-term watershed manipulation experiments with ^{15}N -labeled tracers. These ecosystem-scale tracer experiments are a relatively unobtrusive means for studying biogeochemical processes in undisturbed systems. These studies are possible because of the relatively small range of natural terrestrial compositions, and because modern mass spectrometers can be used to detect the very small changes in $\delta^{15}\text{N}$ resulting from movement of the diluted labeled tracer into ecosystem pools. Changes in the $\delta^{15}\text{N}$ values of any particular N pool are inversely proportional to the pool size; hence mass balances must be calculated to compare fluxes of labeled N into different pools.

In a study of ecosystem N retention, N-labeled nitric acid (+350‰) was applied on large (15m x 15m) replicated plots in a hardwood forest in the Bear Brook Watershed, Maine (USA). The material was sprayed during the growing seasons over a 4-year period (1988-91). Analyses of

composite samples from a control and treated plot have shown that the amount of *spike* applied is sufficient for tracing movement of the spike through the ecosystem. About 95% of the total nitrate-N applied was retained in the ecosystem, and in the treated plots, 70-92% remained in the soil (Magill et al., 1996).

Williams et al. (1996) applied ^{15}N -labeled ammonium and nitrate to the surface of the snowpack in the Rocky Mountains (USA) in 1993-95 in an attempt to determine the fate of atmospherically derived N. Their data showed no evidence for nitrification within the snowpack. Instead, the isotopically labeled ammonium was quickly immobilized in the underlying soils, where 60% of it was later nitrified. The maximum immobilization occurred after the start of snowmelt but prior to melt-out.

16.6.5 Food web studies

Nitrogen, carbon, and sulfur isotopes can provide critical information about nutrient dynamics and trophic relations in aquatic and terrestrial environments. The isotopic composition of organic matter depends on the isotope ratio of inorganic (source) material in the system, but is also influenced by the enzymatic fractionation, diffusion, and equilibrium effects that occurred during primary production. Interpretation of diet sources is further complicated by temporal variability in the isotopic compositions of nutrient sources and when organisms shift from one source to another (e.g., from NO_3 to NH_4). Hence, accurate analysis of food web dynamics requires measurements of both organic and inorganic pools on the appropriate time-scales. Good reviews include Peterson and Fry (1987), Ehleringer and Osmond (1989), Ostrom and Fry (1993), Boon and Bunn (1994), Michener and Schell (1994), and Kling (1994).

Carbon isotopes show little fractionation between food and consumer, and are commonly used to determine the primary sources of C and energy for aquatic consumers (Peterson and Fry, 1987). Although there are few comparable sulfur isotope data, there appears to be minimal fractionation during plant uptake (Trust and Fry, 1992), and little evidence of fractionation in higher organisms (Peterson and Fry, 1987). However, a recent review of controlled-diet studies found that organisms fed high-protein diets had higher $\delta^{34}\text{S}$ values than when fed low-protein diets, with fractionations ranging from -0.9 to +2‰ (McCutchan, 1998; McCutchan et al., in review). In contrast, the $\delta^{15}\text{N}$ values of consumers tend to be 2-4‰ higher than the $\delta^{15}\text{N}$ values of their diet, making $\delta^{15}\text{N}$ values useful for determining the trophic positions of various consumers (Peterson and Fry, 1987). The N isotope shifts between trophic levels can be used to quantify the bioaccumulation of contaminants like methyl mercury and PCB up the foodchain (Cabana and Rasmussen, 1994, 1996). Although the trophic transfer isotope-shifts are small compared with the large isotopic differences between some important food sources, these shifts may not be insignificant in a multiple-link food chain (Peterson and Howarth, 1987) or where isotope ratios of sources are similar to one another. Figure 16.16 shows an example where the consumers are enriched in ^{15}N relative to their primary food sources, plankton and spartina.

In N-limited systems, all the DIN substrate may be converted to organic matter, resulting in no fractionation between inorganic and organic N. On the other hand, fractionations resulting from nitrification, denitrification, algal uptake, and remineralization all contribute to complexity of using N in food-web studies. For example, nitrification and denitrification may occur at different depths in the soil (and water column), causing *residual* ammonium and nitrate to become heavier, and newly produced nitrate to become lighter; hence, the nitrate and ammonium pools can have distinctive $\delta^{15}\text{N}$ values that later may be incorporated into organisms (Mariotti et al., 1984). Both nitrification and uptake can result in large and dynamic

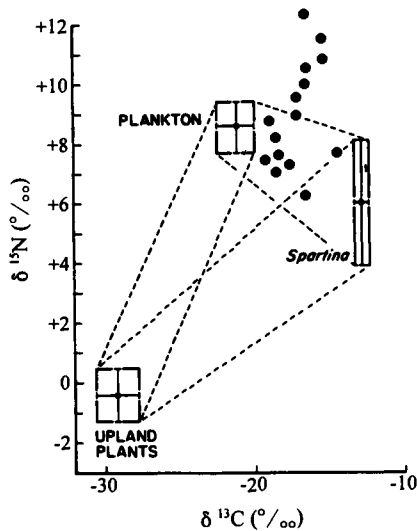


Figure 16.16. Carbon and nitrogen isotopic ratios of consumers (solid dots) relative to the ranges in composition of potential food sources. Note the $\delta^{15}\text{N}$ enrichment for consumers versus food sources. Modified from Peterson and Howarth (1987).

seasonal variations in the $\delta^{15}\text{N}$ of residual ammonium (Cifuentes et al., 1989). As a result of changes in DIN composition and $\delta^{15}\text{N}$, plants can have >10‰ variability in $\delta^{15}\text{N}$ with season (Boon and Bunn, 1994; McCutchan, 1998).

Despite all this complexity, stable isotope ratios do offer an effective tracer for following nutrient flows in ecosystems, although the limitations of the method are not always fully appreciated. It is clear that the isotope values reported in one field study cannot be blindly applied to the next. A careful attempt must be made to sample the spatial and temporal variability in the potential sources and in the organisms of interest. Multiple-element isotope studies often can provide much greater insight into ecosystem processes and source characteristics than single-element studies. Since the mid-1990's, food web studies have become much less expensive because of the increased availability of laboratories with automated preparation systems for C, N, and S isotopic measurements of solid samples. In addition, compound-specific isotope ratio mass spectrometry (Section 16.7.3) has the potential for much more accurate determinations of food web relations than possible with the more conventional analysis of bulk solid samples by tracing specific organic molecules from diet to consumer.

16.7 New Frontiers

From many possible choices, the section below represents my perspective on what are the “hot” frontiers in watershed isotope biogeochemistry. Most of these are broad research topics and approaches, not limited to only nitrogen isotopes. Four of these frontiers are the result of recent technological advances in isotope and other tracer methods (dual isotope method, compound-specific stable isotope techniques, age-dating methods, DON isolation methods), and two are the result of advances in modeling (multi-isotope geochemical and linked geochemical/hydrologic models).

16.7.1 Applications of the dual isotope method

The dual isotope method is in its infancy; there are many potentially powerful applications that have not yet been tested or utilized, including:

1. Atmospheric nitrogen deposition to the ocean is significant: about twice that of natural riverine input and about equal to that of river systems affected by anthropogenic loadings (Fogel and Paerl, 1993; Paerl and Fogel, 1994). The distinctive $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of atmospheric nitrate should assist quantification of atmospheric contributions to productive coastal (estuarine) waters.
2. There is some evidence (Kendall et al., 1995b) that different anthropogenic sources of atmospheric nitrate (e.g., automobile exhaust versus power plant emissions) may have characteristic $\delta^{18}\text{O}$ values that can be used to track different kinds of pollutants. $\delta^{18}\text{O}$ values might also help interpretation of seasonal variation in N deposition and $\delta^{15}\text{N}$.
3. Although all the potential NO_3 sources cannot be distinguished using only $\delta^{18}\text{O}/\delta^{15}\text{N}$ because of substantial overlap of compositions (Figure 16.9), it is likely that atmospheric sources *can* be distinguished from soil sources in pristine catchments unaffected by NO_3 fertilizers. This could be very useful in National Parks and other pristine areas (Lake Tahoe, for example) that are being impacted from air pollution from nearby urban areas. Also, by concentrating efforts on assessing natural variability in *forested* areas of major basins, one can develop estimates of atmospheric sources that can be applied to adjacent areas affected by additional N loads from agricultural and waste pollutants.
4. The $\delta^{15}\text{N}$ values of animal waste (human or farm) and applied fertilizers are distinctive. However, they may not have distinctive $\delta^{18}\text{O}$ values because very little of the N in either applied fertilizers or waste materials is originally in the form of nitrate. Most of the nitrate that is eventually produced by recharge of these sources is produced by nitrification from ammonium or organic N, and hence has a $\delta^{18}\text{O}$ value controlled by the $\delta^{18}\text{O}$ of ambient H_2O and O_2 . Therefore, distinctive $\delta^{18}\text{O}$ values of these two sources of N might only be achieved if the $\delta^{18}\text{O}$ of the waters utilized during nitrification are different (Figure 16.8). Situations that would promote such differences are summer evaporation of soil water in fertilized fields, use of evaporated irrigation return water on fertilized fields, and use of non-native (imported) water for home or animal use (i.e., septic waters would have the $\delta^{18}\text{O}$ value of the imported water; see Aravena et al., 1993).
5. Quantifying relative contributions of two nitrate sources to a simple system that is subsequently affected by denitrification (Figure 16.12).

16.7.2 Tracing sources and sinks for DOM

Researchers are now finding that DON is the dominant source of N exiting many forested systems (Hedin et al., 1995; Gorham et al., 1998). Because DON has not been routinely measured in most streams, this finding may have a profound impact on N budget calculations. Although there is little known about sources and sinks of DON, there is some evidence that DON mobilized from forest litter is retained in the upland mineral soils (Currie et al., 1996) and that wetlands are a major source to streams (Schiff et al., 1990, 1997a,b).

Isotope analyses of DOM from forests are still relatively uncommon, but workers are finding that DOC samples from different positions in the soil and watershed sometimes have distinctive chemical and isotopic compositions that can provide information about their sources (Schiff et al., 1990, 1997a; McKnight et al., 1997). For example, Schiff et al. (1997a,b) have found that most of the DOC exported from wetlands near Ontario (Canada) during high flow periods was recently fixed C whereas the DOC was older during low flow when groundwater sources predominated. In wetlands in Wisconsin (USA), Schindler and Krabbenhoft (1998) have found high rates of DOC production in the hyporheic zone but found little of this DOC in streamwater due to rapid uptake and/or volatilization. There is some evidence (S. Schiff, pers. comm., 1998) that $\delta^{15}\text{N}$ values of DON in forest soils increased with age and depth. A survey of DON from soils and aquatic systems worldwide showed a large range in $\delta^{15}\text{N}$ values, from -4 to +17‰, with the values > +10 generally from human-impacted sites (C. Kendall and G. Aiken, unpublished data); the hydrophilic fraction of the DOM generally had higher N and slightly higher $\delta^{15}\text{N}$ values than the more hydrophobic fraction. In summary, the analysis of DOM for isotopes appears promising and worth further investigation in soils and aquatic systems. Compound-specific isotope techniques should eventually provide new ways of differentiating DON from various sources.

16.7.3 Applications of compound-specific isotope ratio mass spectrometry

Since the mid-1980's, there have been major technological advances in stable isotope geochemistry resulting from the combination of chromatographic techniques with gas-ratio mass spectrometry. This new field is sometimes referred to as *compound-specific* isotope ratio mass spectrometry because specific compounds, not bulk samples containing many different organic compounds, are analyzed for $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, or $\delta^{34}\text{S}$. The new mass spectrometers capable of such analyses are often called "continuous flow" mass spectrometers because compounds separated on the gas chromatograph are carried in a helium flow through combustion furnaces and purification systems directly into the mass spectrometer for isotope analysis (see Chapter 2). Gases and volatile liquids can be injected directly into the new instruments; dense liquids and solids must first be derivatized (chemically degraded to produce a mixture of injectable compounds). Good reviews of this exciting new field are given by Macko (1994) and in Schoell and Hayes (1994).

The analysis of individual molecular components for isotopic composition has great potential as a method for tracing the source, biogeochemistry, and degradation of organic liquids and gases because different materials have characteristic isotope spectrums or biomarkers. Compounds studied thus far include hydrocarbons (mostly by the petrochemical companies), chlorophyll derivatives, fatty acids, amino acids, and carbohydrates. Most compound-specific research has been focused on isotopes (mostly carbon) in petroleum products. Oils from different sources are likely to have characteristic isotope signatures, each a function of the source organic material and the conditions that produced the oil. Thus, oil reservoirs can be matched with host rocks by comparing their organic isotope spectra. However, probably the main future application of this is for assigning liability for hydrocarbon and solvent spills by differentiating unique isotopic signatures. For example, oil spills in coastal areas can be traced back to specific ship leakages if the ships carried oils from different production zones.

There has been some research on using the $\delta^{15}\text{N}$ signatures of individual molecules. Individual amino acids have been analyzed to trace pathways for nitrogen incorporation (Macko et al., 1987) and comparative biochemistry in fossil materials (Hare et al., 1991). The $\delta^{15}\text{N}$ values of different amino acids appear to be related to kinetic isotope effects associated with their

synthesis (Macko et al., 1986). Because some of the amino acids consumed by an organism are directly incorporated into new tissue, if the amino acids contributed from different sources have characteristic isotopic signatures, analysis of the amino acids in a consumer will provide information about the dietary sources (Engel and Macko, 1984, 1986). This will probably lead to more accurate determinations of food web relations than is presently possible by the analysis of bulk tissue samples. For example, it may allow the determination of the species-specific diet and, hence, feeding areas of migratory animals. Other recent advances with the new compound-specific instruments include the separation and analysis of mixtures of N-bearing gases and analysis of N_2O for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.

Analysis of specific dissolved or solid compounds in the soil organic N pool for $\delta^{15}\text{N}$ may provide much new insight into soil processes. One study showed that about 80% of the N in soil organic matter is found in amide/peptide structures and 10% in free and alkylated amino groups (Knicker, 1993). Microbially produced DOC that has a high N content because of large amounts of proteins and amino acids, will probably have distinct $\delta^{15}\text{N}$ "spectra" compared to the low-N DOC produced from degradation of lignin. These isotope signatures of individual molecules may then evolve during degradation in a regular fashion. DON produced by degradation of different types of organic matter (e.g., different plant types or applied-waste types) will probably have different isotopic "fingerprints"; hence, the relative contributions of runoff from different land-uses can perhaps be estimated.

16.7.4 Use of isotopic techniques to assess impacts of changes in land-management practices and landuse on water quality

Mariotti et al. (1988) suggested that if it could be determined whether electron donor availability or diffusion were the main control on the extent of denitrification in an aquifer, then the effects of changes in management practices on N cycling might be predictable. For example, an increase in pumping rate in a system where denitrification is controlled by transport (i.e., nitrate diffusion) should result in a significant decrease in denitrification potential. In contrast, in a system where denitrification is controlled by the electron donor availability, changes in pumping rate might have no effect.

One powerful potential application of technological advances in the age-dating of young groundwater (see Busenberg and Plummer, 1992; Plummer et al., 1993; Dunkle et al., 1993; Ekwurtzel et al., 1994; Chapter 9) is to evaluate the impact of changes in agricultural management practices on water quality (Figure 16.5). For example, by age-dating parcels of groundwater along flowpaths contributing to streamflow, researchers may be able to show that the reason nitrate concentrations in some streams are still high despite changes in management practices designed to eliminate over-fertilization of agricultural fields is that the groundwater recharged **since** the changes in management practice has not yet reached the streams. In other words, the old high-nitrate water has not yet been flushed out of the system. By combining nitrogen isotope analyses with ground-water dating and chemistry, it is possible to trace the sources of non-point contamination, evaluate the extent of natural denitrification, predict when contaminated or remediated groundwaters will reach the streams, resolve the effects of changing agricultural practices from the effects of denitrification, and see the influence of groundwater residence times and reaction zone geometrics on surface water NO_3 loads (Böhlke and Denver, 1995; McMahon and Böhlke, 1996). Other examples of environmental changes that can be assessed by this method include: changes in the amount and types of fertilizers used, different fertilizer application times, relocation of potential pollutant sources, different remediation strategies, and the installation of drainage systems.

Additional tools such as the combined use of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate and other isotopic and chemical information will facilitate the tracing of reactions and sources (Section 16.6.1). The analysis for $\delta^{18}\text{O}$ might provide information about seasonal changes in nitrate production rates and source types. Possible controls on the seasonal changes in nitrate content include fertilizer application time and/or amount, dilution of ground water by rain, runoff amount (influenced by plowing or irrigation), uptake by plants, extent of denitrification, nitrification rates, etc.

Because the $\delta^{15}\text{N}$ of DIN can be used to determine whether the nitrate is predominantly derived from fertilizer vs. animal sources, it is obvious that the $\delta^{15}\text{N}$ values are providing landuse information. If this DIN is later incorporated into terrestrial or aquatic plants and organisms without major blurring by various nitrogen cycling reactions, the $\delta^{15}\text{N}$ of the plants and animals can also be used to trace landuse changes. A recent catchment-scale application was conducted by Harrington et al. (1998) where the $\delta^{15}\text{N}$ values of nitrate, algae, insects, and salmon from streams draining agricultural lands were found to be higher than in streams draining forests; hence, the $\delta^{15}\text{N}$ values reflect landuse. They also observed a positive correlation of $\delta^{15}\text{N}$ values of salmon and the percentage of agricultural land in the catchment, and concluded that the combined use of N and Sr isotopes provide a means of determining the origin of juvenile salmon. Other workers have noted increases in the $\delta^{15}\text{N}$ of food webs affected by animal waste (e.g., Van Dover et al., 1992) but this study was one of the first to investigate this “anthropogenic signal” in food webs at the catchment scale. Preliminary data from a continental-scale study of the C, N, and S isotopic compositions of fish and seston at sites monitored by the USGS shows strong positive correlations of $\delta^{15}\text{N}$ in fish and drainage areas, in basins ranging from 5 thousand to 10 million square miles in size, and strong regional patterns in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ (Gilbert Cabana and C. Kendall, unpublished data, 1998). Given the importance of water-quality problems and the demonstrated usefulness of these isotopic approaches, there will undoubtedly be many more large-scale studies of impacts of human activities on ecosystems in the near future.

In another landscape-scale application of isotopes, Kendall et al. (1998) analyzed periphyton and mosquitofish samples from over 100 marsh sites in the Everglades (USA) to assess whether the local and regional ranges in their C, N, and S stable isotope ratios might provide insight into the environmental conditions resulting in methyl mercury (meHg) production and bioaccumulation. These organisms were chosen because periphyton (floating algal mat) communities play an important role in the ecosystem, and the ubiquitous mosquito fish might be a useful indicator species for meHg bioaccumulation studies. Both periphyton and mosquito fish show wide ranges in isotopic composition throughout the marshes, and areas with high meHg contents commonly have high $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ values. The C, N, and S isotopic compositions appear to be controlled to a large extent by spatial variability in reducing conditions in the marshes that favor methane production, sulfate reduction, and (perhaps) denitrification.

The isotopic compositions of aquatic plants appear to integrate the more variable water-column isotopic compositions produced by redox reactions (and other factors) in the ecosystem, and these same patterns are incorporated throughout the food chain. These compositions are relatively stable over time because the biomass remains in the system and is actively recycled without significantly affecting the isotopic compositions of the residual material. Therefore, zones frequently dominated by particular redox reactions appear to be labeled by the C, S, and N isotopic compositions of local organisms. Isotopic compositions of biomass may prove to be more cost-effective and reliable indicators of prevailing environmental conditions that favor meHg production than other parameters currently being considered because biomass isotopic

compositions are much more difficult to perturb than the more transient concentrations of aqueous species. Hence, the spatial isotope patterns are likely to provide a valuable integration of long-term environmental conditions in the Everglades.

16.7.5 Use of a multi-isotope or multi-tracer approach

Reactive solute isotopes such as ^{15}N , ^{13}C , ^{34}S , and ^{87}Sr can provide valuable information about flowpaths for geochemical and hydrologic modeling because they reflect the “characteristic” reactions taking place along specific flowpaths (Bullen and Kendall, 1991; Kendall et al., 1992, 1995c; Chapter 18). Furthermore, solute isotopes usually are affected by a smaller number of processes than chemical constituents, making interpretation of changes in isotopic composition perhaps less ambiguous than the simultaneous changes in solute concentrations (Kendall, 1993). Reactive solute isotopes can serve as additional thermodynamic constraints in geochemical computer models such as NETPATH (Plummer et al., 1991) for eliminating possible geochemical reaction paths (Plummer et al., 1983). NETPATH is a mass balance model that allows the calculation of plausible geochemical reaction paths linking water compositions along a flowpath. For example, the increases in $\delta^{15}\text{N}$ during progressive denitrification may produce changes in $\delta^{13}\text{C}$ or $\delta^{34}\text{S}$ because nitrate reduction may be associated with oxidation of organic matter or sulfides, respectively. An excellent example of use of NETPATH for evaluating the mass balance of reactions accompanying denitrification is Böhlke and Denver (1995). Postma et al. (1991) modeled denitrification in a redox gradient by using PHREEQM, that simulates equilibrium geochemical reaction paths in a one-dimensional mixing-cell transport model. A multi-isotope approach can be particularly useful in tracing the reactions specific to a flowpath because the strengths of one isotope may compensate for the weaknesses of another.

Although this book is aimed at *isotope* tracers, it is important to remember that there are many other tracers that by themselves or combined with isotopes can be valuable tracers of water and solute sources. For example, fertilizer and animal feed additives (i.e., lithium, boron, phosphate) can provide distinctive tracers of waters that have contacted these materials. These species can also be analyzed for isotope ratios, as perhaps a more diagnostic tool. For a brief discussion of chemical tracers useful for age-dating young waters (i.e., caffeine, brighteners, pesticides, etc.), see Plummer et al. (1993).

16.7.6 Development of linked hydrologic/geochemical models

Shallow waters moving along a flowpath through a relatively uniform material and reacting with minerals probably do not achieve equilibrium but gradually approach some steady-state composition. One can define a *reaction progress* term that describes the gradual approach of the water composition to this steady-state composition. If the chemical composition of waters along a specific flowpath is related to topography, mineralogy, initial water composition, and antecedent moisture conditions, then within a uniform soil/rock layer, the degree of geochemical evolution is some function of residence time. Residence time of water within a hydrologic unit can be conceptualized as a function of both the topographic position of the unit (e.g., steep units have shorter residence times than flat-lying units) and antecedent moisture conditions -- thus providing a link to hydrologic models like TOPMODEL (Beven and Kirkby, 1979). Different flowpaths may produce distinctive water *signatures* related to the topographic position, mineralogy, and hydrologic history of the water (Bullen et al., 1996). A more direct linkage of geochemical evolution and residence time can be accomplished by age-dating the young groundwaters with CFCs and other methods (see Chapter 9).

16.8 Summary

The dominant use of isotopes in catchment research in the last few decades has been to trace sources of waters and solutes. Generally such data were evaluated with simple mixing models to determine how much was derived from either of two (sometimes three) constant-composition sources. The world does not seem this simple anymore. With the expansion of the field of isotope hydrology in the last decade, made possible by the development and increased availability of automated preparation and analysis systems for mass spectrometers, we have documented considerable heterogeneity in the isotopic compositions of various sources of waters and solutes, including nitrate. We are still grappling with how to deal with this heterogeneity in our hydrologic and geochemical models. A major challenge is to use the variability as signal, not noise, in our models; the isotopes and chemistry are providing very detailed information about sources and reactions in shallow systems, if only we can develop appropriate models to use the data. This integration of chemical and isotopic data with complex hydrologic models constitutes an important frontier of catchment research.

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Carbon Cycling in Terrestrial Environments

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17.1 Introduction

Carbon (C) is an important element in the biosphere. It is the basis of the food chain on earth and plays a key role in every part of biogeochemical processes. Carbon dioxide (CO₂) is an important greenhouse gas. Its concentration in the atmosphere has increased from an estimated 270 ppm at the beginning of the industrial revolution to ~ 360 ppm at present (Keeling et al., 1989; Schlesinger, 1991). This change in CO₂ concentration represents a global increase of about 30% in less than 200 years. Ocean-atmosphere general circulation models predict that global mean-annual temperatures may increase by 0.03 °C yr⁻¹ if the current rate of CO₂ increase continues (Gates et al., 1992). Because of the potential to affect global climate, processes that affect the carbon cycle have become of paramount interest in recent years.

Techniques for studying carbon cycling processes using stable and radioactive isotopes of carbon are gaining increasing importance because of advances in analytical techniques and increases in the complexity of research questions. Isotopic techniques provide tools for studying the exchange pathways among atmospheric, biological and geological pools. For example, photosynthesis actively discriminates against heavier C isotopes to a greater or lesser extent depending upon the photosynthetic pathway. Climatic conditions and atmospheric CO₂ concentration also influence isotopic discrimination during photosynthesis. In addition, cosmogenically and anthropogenically produced radiocarbon "labels" biomass and soil organic matter with distinctive isotopic signatures. Natural and anthropogenically induced variations in the carbon isotopic abundance can be exploited to investigate carbon transformations between pools on various time scales.

In this chapter we review a number of applications of isotopic techniques for the investigation of carbon cycling processes. We begin with a discussion of carbon isotope terminology and the scientific basis for variations in isotopic abundances in different carbon pools. We describe how soil forming processes affect the radiocarbon age of soil organic matter, and how C isotopes can be used to study soil carbon turnover and the problems related to soil carbon response to environmental change. An overview of isotopic studies of dissolved organic C in ground water is provided, followed by a discussion on the use of the isotopic composition of dissolved organic C for interpretation of the biogeochemistry of humic substances in lacustrine environments. In the final section, we provide a brief overview of the use of isotopic techniques to study terrestrial C cycling processes. These techniques have been applied to questions

regarding the imbalance in the current global carbon budget as well as the potential response of terrestrial ecosystems to climate change. [See Chapter 18 for a discussion of the use of C isotopes for determining sources of dissolved inorganic carbon in groundwater and streams as a function of weathering reactions. See Chapter 22 for several discussions of uses of C isotopes in plants, animals, and water for investigating environmental (climatic) change.]

17.2 Carbon Isotopes and Terminology

Carbon has three isotopes that are useful tracers in the terrestrial ecosystem: stable ^{12}C with an abundance of 98.89%; stable ^{13}C with an abundance of 1.11%; and radioactive ^{14}C which has a half-life of 5730 years. ^{12}C is also called the "light" C isotope, in comparison with ^{13}C and ^{14}C , the "heavy" C isotopes. Natural ^{14}C is produced in the atmosphere by interactions of cosmic-ray produced neutrons with stable isotopes of N (nitrogen), O (oxygen) and C, and has a natural abundance in the atmosphere of ~ 1 atom ^{14}C per 10^{12} atoms ^{12}C . ^{14}C is also produced in nuclear reactors and during nuclear weapons testing. Stable and radioactive C isotopes are partitioned into different phases or materials with different efficiencies. Although natural variations in the $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ ratio are very small, the differences in the ratios of the "heavy" to "light" C isotopes (i.e. $^{13}\text{C}/^{12}\text{C}$ or $^{14}\text{C}/^{12}\text{C}$) are sufficient to trace various chemical, physical and biological processes.

The $^{13}\text{C}/^{12}\text{C}$ ratio is generally expressed as the difference in parts per thousand (‰) from a standard:

$$\delta^{13}\text{C}(\text{‰}) = [(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{PDB}} - 1] \times 1000 \quad (17.1)$$

where the standard is PDB (PeeDee Belemnite), a Cretaceous mollusk. Stable C isotope measurements are made on CO_2 gas produced using a variety of preparation methods. For organic material, CO_2 is produced by combustion of the sample with CuO and silver foil at 875°C (Minagawa et al., 1984), and purified cryogenically. The stable C isotopic composition of purified CO_2 is then measured on a stable isotope ratio mass spectrometer. Variability of $\delta^{13}\text{C}$ values in natural materials is summarized in Figure 17.1.

Plants incorporate C into organic matter from atmospheric CO_2 through photosynthesis, and in the process they discriminate against the heavier C isotopes. Plants are divided into three categories according to their photosynthetic pathways: C_3 (using C_3 or Calvin photosynthetic pathway), C_4 (using C_4 or Hatch-Slack photosynthetic pathway), and CAM Plants (Crassulacean Acid Metabolism). C_3 plants, which include all trees, most shrubs and cool-season grasses, have $\delta^{13}\text{C}$ values ranging from -20 to -35‰, with an average of -27‰ (Deines, 1980; O'Leary, 1988). C_4 plants, which include warm season grasses and a few shrubs, have $\delta^{13}\text{C}$ values between -9 to -17‰, with an average of about -13‰ (Deines, 1980). C_4 plants demonstrate more favorable high-temperature physiological performance and water use efficiency than C_3 forms, and are adapted to low latitude and altitude environments with summer precipitation (Teeri and Stowe, 1976; Ode and Tieszen, 1980). CAM plants use both C_3 and C_4 photosynthetic pathways, having $\delta^{13}\text{C}$ values between C_3 and C_4 plants (Farquhar et al., 1989). Cacti and other succulents are examples of CAM plants.

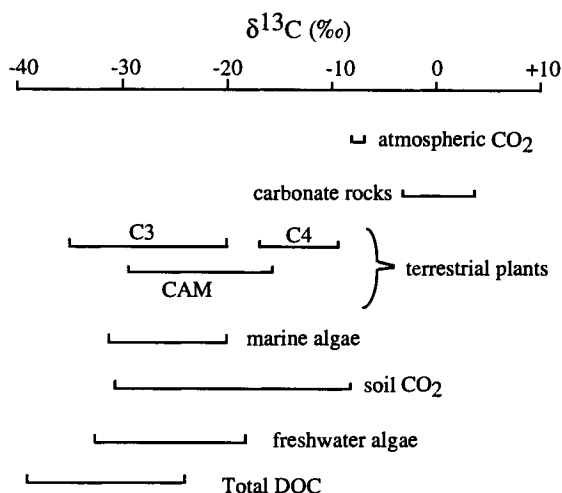


Figure 17.1. Observed range of $\delta^{13}\text{C}$ values (modified from Deines, 1980).

The reason for the wide range in the $\delta^{13}\text{C}$ values of C_3 plants is primarily twofold. There is a tendency for C_3 plants to have ^{13}C -enriched values under water-stressed conditions (Farquhar et al., 1989). On the other hand, the C isotopic composition of plants is related to that of the atmospheric CO_2 . The pre-industrial value for atmospheric CO_2 was about -6‰; it is now about -8‰. Under a forest canopy, the partial pressure of CO_2 can rise considerably due to emission of CO_2 from the soil, and the isotopic composition of the air near the forest floor can be quite negative, on the order of -9 to -14‰. Forest floor plants growing in this ^{13}C -depleted environment will have more negative $\delta^{13}\text{C}$ values (Farquhar et al., 1989).

Soil organic matter has a stable carbon isotopic composition comparable to that of the source plant material (Dzurec et al., 1985; Schwartz et al., 1986; Guillet et al., 1988), and changes in C_3 and C_4 vegetation types will result in a corresponding change in the $\delta^{13}\text{C}$ value of the soil organic matter. Therefore, recent changes in the relative proportion of C_3 and C_4 plants can be detected by measuring the carbon isotopic composition of the current plant community and soil organic matter (Dzurec et al., 1985; Wang et al., 1993). $\delta^{13}\text{C}$ values of soil organic matter can also be used to study C turnover in soils where C_3 vegetation was replaced by C_4 plants or vice versa (Balesdent et al., 1987).

^{14}C is a cosmogenic nuclide formed in the atmosphere. The atoms of ^{14}C are incorporated into carbon dioxide (CO_2) molecules by reactions with oxygen or by exchange reaction with stable carbon isotopes in molecules of CO_2 . The molecules of $^{14}\text{CO}_2$ are mixed rapidly throughout the atmosphere and the hydrosphere, and attain relatively constant levels of concentration representing a quasi-steady-state equilibrium. Living plants exchange ^{14}C with the atmosphere through photosynthesis and have the same $\Delta^{14}\text{C}$ value as that of the contemporary atmosphere. When plants die, they no longer absorb ^{14}C from the atmosphere and their ^{14}C content declines as a result of radioactive decay. ^{14}C content of organic matter can, therefore, serve as a "clock" to trace the rate of C cycling in various C reservoirs (e.g. soils). Nuclear weapons testing in the 1950's and 1960's injected significant quantities of ^{14}C into the atmosphere; this "bomb" ^{14}C

resulted in much higher than "normal" ^{14}C levels in the atmosphere. Following the test ban agreement in 1963, the ^{14}C content of the atmosphere has been declining towards the pre-bomb levels (Figure 17.2). This "bomb" ^{14}C is a useful tracer in studying the rates of C turnover in various C reservoirs (O'Brien and Stout, 1978; Trumbore et al., 1989, 1990; Trumbore, 1993).

^{14}C measurements can be made either by decay counting or by accelerator mass spectrometry (AMS). AMS ^{14}C measurement has the advantage of allowing rapid sample throughput and much smaller sample sizes over the traditional decay counting method. For AMS ^{14}C measurement, samples are first converted to CO_2 and purified cryogenically. The purified CO_2 is then reduced to graphite with H_2 over Fe (or Co) and its $^{14}\text{C}/^{13}\text{C}$ ratio is measured on an AMS. The common methods of reporting ^{14}C data are summarized in Table 17.1.

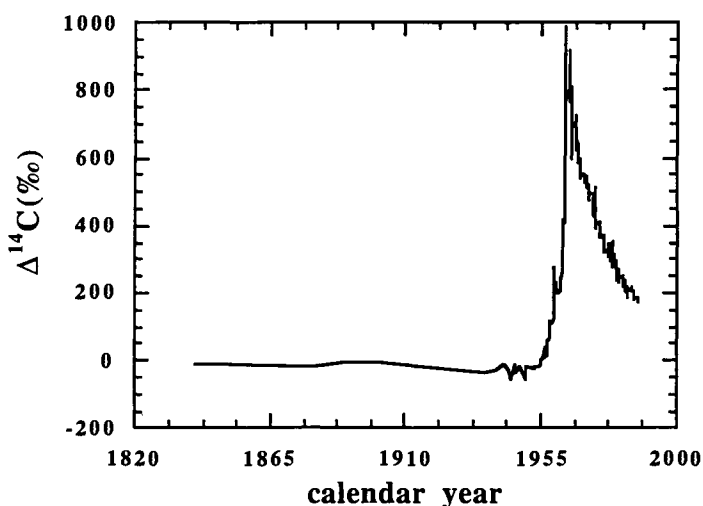


Figure 17.2. Temporal trend of atmospheric $\Delta^{14}\text{C}$ in the northern hemisphere (Suess, 1955; Stuiver, 1965; Levin et al., 1985; Manning et al., 1990).

17.3 Carbon Dynamics in Soils

Carbon is present in soils in both organic and inorganic forms. The global soil C reservoir is estimated to be in the range of 1200 to 1500 Pg (1 Pg = 10^{15} g) C (Post et al., 1982; Schlesinger, 1977; Eswaran et al., 1993). Between 20 and 40% of the C in this reservoir has turnover times of centuries or less. Recent studies have proposed that soil organic matter acts both as major net source (Houghton et al., 1991; Melillo et al., 1988; Lashof, 1989; Jenkinson et al., 1991; Raich and Schlesinger, 1992; Schimel et al., 1994; Oeschel et al., 1993) and sink (Melillo et al. 1993; Fisher et al., 1994; Harrison et al., 1993; McGuire et al., 1992) for atmospheric CO_2 . Soil organic matter is a source of atmospheric CO_2 when net decomposition exceeds C inputs to the soil. Decomposition can exceed inputs as a result of land use changes such as clearing forests for agriculture (Houghton et al., 1991; Davidson and Ackerman, 1993) or as a result of global warming and subsequent increases in soil organic matter decomposition rates (Lashof, 1989; Schimel et al., 1994; McGuire et al., 1992; Jenkinson et al., 1991). Sinks of C have been

calculated using values for ecosystem C uptake and tree growth rates (Wofsy et al., 1993) and from estimated increases in net C inputs as a result of CO₂ or N - fertilization of plants (Harrison et al., 1993). The magnitude and timing of the soil C reservoir changes as a result of climate and land-use change is difficult to quantify and is a large source of uncertainty in global C cycle models. Improving the ability of global C cycle models to predict future atmospheric CO₂ concentrations will require better understanding of soil C dynamics. C isotopes are valuable tools for the study of soil C dynamics and soil C turnover.

Table 17.1. Common methods for reporting ¹⁴C data (after Stuiver and Polach, 1977).

Method	Explanation
$\Delta^{14}\text{C}(\text{‰}) = \left(\frac{A_{\text{SN}}}{A_{\text{abs}}} - 1 \right) \times 1000$	A_{SN} is the specific activity of a sample (which is proportional to the ¹⁴ C/C ratio in the sample) normalized to $\delta^{13}\text{C} = -25\text{‰}$, and A_{abs} is the absolute ¹⁴ C activity in the international isotopic standard (NBS oxalic acid).
$\text{PMC (percent modern carbon)} = \frac{A_{\text{SN}}}{A_{\text{abs}}} \times 100$	
$\Delta^{14}\text{C}(\text{‰}) = \left(\frac{\text{PMC}}{100} - 1 \right) \times 1000$	
$\text{Radiocarbon Age (years BP)} = -8033 \ln \left(\frac{\text{PMC}}{100} \right) - \frac{(y-1950)}{1.03}$	y is the year of ¹⁴ C measurement.

17.3.1 ¹⁴C age of soil organic matter

¹⁴C-dating of soil organic matter has been used to study the chronology of soil development (Herrera and Tamers, 1971; Paul et al., 1964; Jenkinson, 1968; Martel and Paul, 1974; Goh et al., 1977a,b; Hammond et al., 1991). However, the interpretation and significance of dates and ages is a perplexing problem, because soil organic matter is the product of dynamic processes driven by climatic, biological, and soil physicochemical variables (Campbell et al., 1967a,b; Gerasimov and Chichagova, 1971; Grant-Taylor, 1972; Perrin et al., 1964; Scharpenseel, 1971a,b, 1972, 1976; Scharpenseel and Becker-Heidmann, 1991; Hammond et al., 1991).

The ages obtained from the ¹⁴C activity of the bulk soil organic carbon have been recognized as too young because of the "contamination" by recent carbon. Historically, a solution to the problem has been to obtain, through chemical or physical means, portions of the soil organic matter which are presumed to be of greater age than the remaining fractions (Gerasimov and Chichagova, 1971; Scharpenseel, 1971a,b; Tate, 1972; Grant-Taylor, 1972; Martel and Paul,

1974; Gilet-Blein et al., 1980; Goh, 1991; Hass and Dalbey, 1991; Tornqvist et al., 1991). Unfortunately no extraction technique has proved reliable and results for a given procedure can vary with different soils. Fresh carbon is continuously incorporated, but at varying rates, into any defined fraction (e.g. humin, humic acid, fulvic acid, lipids, etc.). Because there is no physical or chemical treatment to eliminate this recent fraction, or isolate the original material contemporaneous with the sediment, ages from ^{14}C dating of soil organic matter or fractions of organic matter from soils have been interpreted as minimal ages for soil genesis (Perrin et al., 1964; Scharpenseel, 1971a, 1972, 1976; Cherkinsky and Brovkin, 1991). Alternatively, the age of the bulk soil organic carbon has been interpreted as the "mean residence time" (MRT) of the steady-state soil organic matter. However, there has been no clear definition of what MRT implies and its relation to steady-state (Paul et al., 1964; Campbell et al., 1967a,b; Goh and Stout, 1972; Scharpenseel, 1972).

One of the criteria for accurate ^{14}C dating is that the system must be closed with respect to ^{14}C . Soils which form over long periods of time represent open systems with respect to carbon and are in apparent violation of this criterion. Obviously, the standard ^{14}C dating models are not applicable to soils. However, assuming organic matter decomposition is the only mechanism for carbon loss in soils, the variation in organic carbon over time for a soil or any of its horizons can be described by the following equation (Trumbore, 1993; Wang et al., 1996a,b):

$$\partial C / \partial t = \phi - kC \quad (17.2)$$

where C is the organic carbon content (moles/cm³); ϕ is the production of C in the soils (moles/cm³/yr); and k is the decay constant (1/yr). A similar equation can be written for ^{14}C isotopic species:

$$\partial {}^{14}\text{C} / \partial t = \phi {}^{14} - (k + \lambda) {}^{14}\text{C} \quad (17.3)$$

where λ is the decay constant of ^{14}C (0.0001245/yr). When a soil is at steady-state, the steady-state input rate ϕ and decay rate k can be calculated from the above equations. Then ϕ and k can be used to calculate the organic carbon, ^{14}C content and ^{14}C ages of organic matter vs. soil depth at different times of the soil's development.

As an example, we recently studied two different pre-bomb soils: a forest soil and a desert soil from California (Wang et al., 1996a). The carbon inventory, ^{14}C content of the bulk soil organic matter, and calculated steady-state input and decay rates are shown in Table 17.2.

Table 17.2. Organic carbon and ^{14}C content of pre-bomb soils with calculated steady-state input and decay rate.

soil type	location	depth (cm)	organic C (10 ⁻⁴ moles/cm ³)	C-14 content (PMC)	$\phi_{\text{steady-state}}$ (10 ⁻⁶ moles/cm ³ /yr)	$k_{\text{steady-state}}$ (10 ⁻⁴ /yr)
desert soil	Barstow, CA	3.8	1.76	8.4	0.00202	0.1148
		7.2	1.28	7.2	0.001232	0.0963
forest soil	Fresno, CA	11.5	14.67	95.3	3.6754	25.0593
		37.0	6.42	88.7	0.629	9.799
		60.0	5.08	76.1	0.2018	3.9704

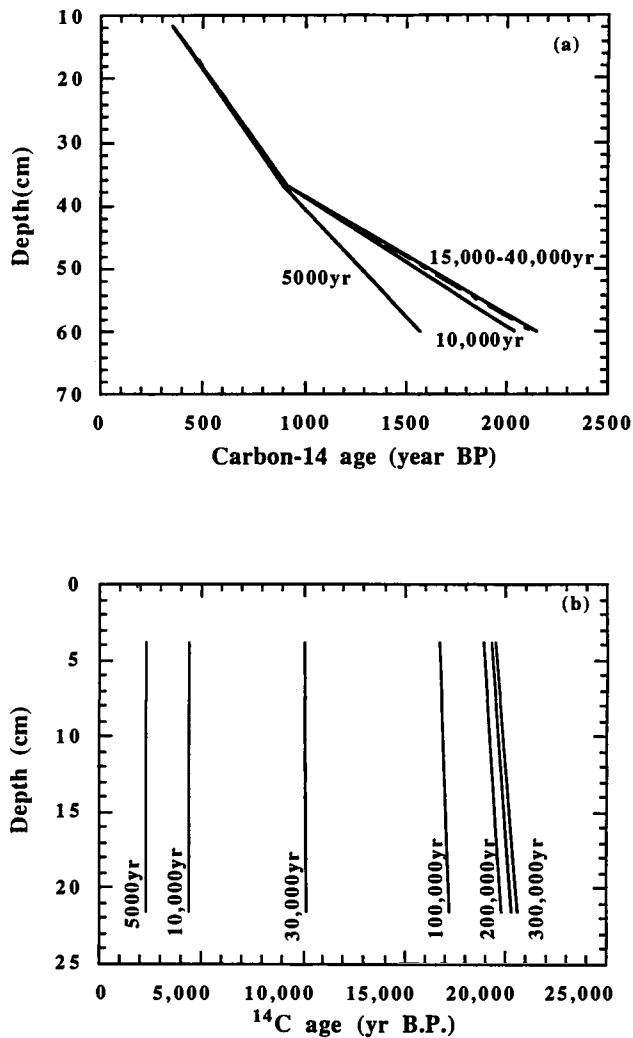


Figure 17.3. Evolution of ^{14}C age of soil organic matter in a forest soil (the upper diagram) and in a desert soil (the lower diagram). Different curves represent the calculated ^{14}C ages of soil organic matter at different times of a soil's development (after Wang et al., 1996a). Numbers along the curves indicate the true age of the soil.

Using the data in Table 17.2 we calculated the ^{14}C content and ^{14}C ages of soil organic matter vs. depth at different times of the soils' development as shown in Figure 17.3. These diagrams show that (1) ^{14}C age of soil organic matter increases with soil depth; (2) the ^{14}C age of soil organic matter is always younger than the true age of the soil due to a continuous input of fresh organic matter; (3) the ^{14}C content of soil organic matter will eventually reach a steady-state, provided that no climatic or ecological perturbations occur; and (4) "steady-state ^{14}C age", defined as the minimum time required for a soil horizon or a soil to reach steady-state, increases with depth.

Once a soil or a soil horizon is at steady-state, the ^{14}C content of organic matter becomes constant with respect to time, and the resulting ^{14}C age, therefore, can not give any indication of the age of the soil. The time for this to occur varies greatly with climate (from less than 5000 yr in temperate climates to greater than 300,000 yr in arid climates) and also with depth in a soil profile. These diagrams show that the measured ^{14}C ages at any time can be significantly different from the true ages of the soils. For example, soil samples taken from 25cm depth in a 40,000-year old forest soil before atomic weapons testing will have a measured ^{14}C age of about 500 yr before present (BP) (Figure 17.3).

The most important factor affecting the measured ^{14}C ages of soil organic matter is the rate of organic carbon cycling in soils; differences in the dynamics of soil carbon among different soils or soil horizons will result in different soil organic ^{14}C signatures. As a result, the deviation of the measured ^{14}C age from the true age could differ significantly among different soils or soil horizons. For the forest soil, higher input and decay rates result in younger "steady-state ^{14}C age". On the other hand, the desert soil has the lowest input and decay rates, and the oldest "steady-state ^{14}C age" (Table 17.3). Clearly it is not prudent to compare the ages of different soils by simply comparing the measured ^{14}C dates of soil organic matter or its fractions. For the same type of soils in the same climate, the measured ^{14}C ages of soil organic matter from the same depth interval can give some indication of the relative ages of the soils. However, for different types of soils, differences in the dynamics of soil carbon can result in different ^{14}C ages even when they have the same true age.

Table 17.3. Steady-state ages of organic matter for two soils studied.

Depth (cm)	Forest soil, CA	Desert soil, CA
10	<5000 yr	>300,000 yr
20	5000 yr	>300,000 yr
30	8000 yr	
40	10,000 yr	
50	15,000 yr	
60	15,000 yr	
70	>15,000 yr	

Our modeling exercise demonstrates that ^{14}C method of dating soil organic matter will be limited by the "steady-state ^{14}C age" of a soil or a soil horizon. However, it is possible to estimate the age of a soil provided that the input and decay rates are known and the steady-state has not yet become established. The relatively young steady-state ^{14}C ages at shallower depths in the forest soil suggest that samples taken from deeper depths (>50 cm) would be more suitable for ^{14}C dating.

In areas where a series of terraces or geomorphic surfaces of different ages can be identified based on geomorphological and soil development evidence, the soil on the oldest terrace can be assumed to be at steady-state, and steady-state input and decay rate can be determined from its ^{14}C and C content. Because of "bomb" ^{14}C contamination, archived samples (i.e. pre-bomb soils samples) best serve this purpose. However, in environments such as deserts where C

inputs are low, deep soil horizons may be effectively utilized. The calculated steady-state input and decay rate are then assumed to be representative of the soils in the nearby locations and can be used to estimate the ages of the other younger geomorphic surfaces in the area. This method has been applied to date alluvial fan surfaces in the Providence Mountain area in the Mojave Desert (Wang et al., 1996b). The modeled ^{14}C ages of soil formation based on measured ^{14}C ages of soil organic matter were consistent with the relative ages suggested by geomorphological evidence and also were compatible with ^{14}C model ages derived from soil carbonate.

For buried soils, ^{14}C dating of soil organic matter could overestimate the true age of the burial. An additional complication can occur in high rainfall/leaching environments. Studies in such environments (Hammond et al., 1991) have shown that downward translocation of water-soluble fulvic acid could significantly reduce the ^{14}C dates of buried soils, adding additional uncertainty to these measurements.

In summary, ^{14}C ages of organic matter or any organic fraction in a soil horizon can be better understood by evaluating the evolution of ^{14}C content of its organic matter. Measured ^{14}C ages of soil organic matter are always much younger than the true age of the soil. The most important factor controlling the measured ^{14}C age of soil organic matter is the rate of organic carbon cycling in soils. Differences in the dynamics of organic carbon in different soils or soil horizons will result in significantly different ^{14}C signatures of soil organic matter even when the true ages of the soils are the same. ^{14}C ages of soil organic matter increase with depth and time, but will eventually reach a steady-state. When a soil or a soil horizon is at steady-state, ^{14}C dating of soil organic matter gives no indication of the age of a soil. It is possible, however, to estimate the age of a soil if the input and decay rates of organic matter are known and the soil is not at steady-state.

17.3.2 Use of ^{14}C to study C turnover in soils

Soil organic matter is a complex mixture of substances with a range of turnover times from days to millennia. As a result, soil carbon dynamics are difficult to study. To simplify this complex system, soil organic matter can be separated into three identifiable C pools with three distinctly different mean-turnover times. The "active" pool contains root exudates and rapidly decomposed components of fresh plant litter. The "passive" pool contains stabilized organic matter that persists in soils over several thousands of years. The "intermediate" or "slow" C pool is not easily defined in physical terms. It has turnover times in the range of years to centuries. The term "fast-cycling C" pool is often used to refer to all non-passive C (the combined active and intermediate pools).

^{14}C is a powerful tracer in the study of the C turnover in soils. In general, the amount of C and ^{14}C decreases with depth in soils. Decrease in the C and ^{14}C content of soil organic matter with depth in soil profiles indicates the increasing importance of passive organic matter with depth (O'Brien and Stout, 1978; O'Brien, 1986). Passive soil organic matter persists in disturbed soils even after a century or more of cultivation. Thus, the ^{14}C content of organic matter in disturbed soils is often less than in undisturbed soils. Soils sampled after the 1960's show the influence of ^{14}C produced by atmospheric nuclear weapons testing, which has been incorporated into fast-cycling organic matter pools. Small increases in the ^{14}C of passive C pools can be used to quantify net accumulation of C over time (Harden et al., in review).

The ^{14}C 'age' of passive organic matter may give clues to the mechanisms that sequester C in soil over millennial time scales. To begin, an independent estimate of the passive fraction ^{14}C content is often essential to interpreting ^{14}C measurements in soils collected since 1960. Three approaches have been used to quantify the passive C fraction of the bulk soil.

In the first, the ^{14}C 'age' of passive soil organic matter is determined by measuring the ^{14}C content of specific (operationally defined) physically and chemically separated fractionations of the organic matter. Several investigators (Campbell et al., 1967a,b; Goh et al., 1984; Scharpenseel, 1972, 1976; Trumbore et al., 1990) have used repeated extraction with acids and bases of increasing strength to obtain a soil organic matter residue with a lower $^{14}\text{C}/^{12}\text{C}$ ratio than the starting material. Such operationally defined methods work for most soils, but do not isolate a passive fraction in soils formed from volcanic ash (Osher et al., 1994a).

In a second approach, O'Brien and Stout (1978) and O'Brien (1986) proposed the use of a ^{14}C measurement from deep in the soil as an estimate of the passive pool ^{14}C content. Using this approach, the ^{14}C value is taken either at the depth where ^{14}C values level off (O'Brien and Stout, 1978; O'Brien, 1986), or at the depth where the deepest measurement was taken (Harrison et al., 1993). Decreases in C and ^{14}C with increasing soil depth are attributed to a decrease in the abundance of fast-cycling C pools. Passive C pool size is assumed to remain constant over the same depth interval. The O'Brien and Stout (1978) model assumes that the contemporary C is transported to the deep soil via 'diffusion' from surface layers. Their model does not account for the additions by living roots present at depth (Trumbore et al., 1995).

The third approach uses chronosequences (Harden et al., 1992; Schlesinger, 1990) to estimate turnover rates in the passive fraction. A chronosequence is a series of soils of different age that have developed on the same parent material and are assumed to have had similar vegetation and climate over time. During the first several hundred years of soil formation, as vegetation inputs increase to a steady state condition, C accumulation in chronosequences is rapid. After several hundred to several thousand years of soil development, the rate of C accumulation is decreased, reflecting a slow accumulation of passive carbon with time. Accumulation of passive C over long time scales in soils should cause a steepening with time of the ^{14}C -depth profile (Goh et al., 1976; Amundson et al., 1994). This may be due to the formation of authigenic soil minerals which provide new surfaces for organic matter stabilization.

The amount of fast-cycling (active+slow) soil organic matter can be measured using the bomb ^{14}C tracer provided by atmospheric thermonuclear weapons testing (Harrison et al., 1993; Townsend et al., 1995; Anderson and Paul, 1984; O'Brien and Stout, 1978; Goh et al., 1977a,b; Hsieh, 1993; Harkness et al., 1986; Jenkinson et al., 1992; Trumbore, 1993). Investigators using this approach compare ^{14}C measurements of soil organic matter sampled prior to 1960 with that of contemporary samples from the same location (Trumbore et al., 1989, 1995, 1996; Hsieh, 1993). In such studies, a large increase in ^{14}C content over the past thirty years indicates that significant portions of the soil organic matter are exchanging carbon with atmospheric CO_2 on decadal and shorter time scales.

Using this technique, Trumbore et al. (1996) compared the ^{14}C content of archived (pre-1962) soils with soils sampled in 1992 at the same locations along an elevation transect in the Sierra Nevada Mountain Range, central California to investigate the role of temperature in soil organic matter dynamics. Mean-annual temperature decreases with increasing elevation along

the Sierra transect sites according to the atmospheric lapse rate. Low density ($<2.0 \text{ g/cm}^3$) carbon is 50 - 80% of the total soil organic matter in A horizons. Hydrolyzable carbon ($>2.0 \text{ g/cm}^3$) is 10 - 30% of total soil organic matter in those same horizons. The difference in $\Delta^{14}\text{C}$ values between archived and 1992 soil C fractions, defined here as $\Delta(\Delta^{14}\text{C})$, is a direct measure of the average turnover time of fast cycling carbon. $\Delta(\Delta^{14}\text{C})$ values for low density organic matter decrease with decreasing temperature and increasing elevation (Figure 17.4). Turnover times increase from 7 years at sites with high (17.8°C) mean-annual temperature (470m elevation) to 75 years at sites with low (4°C) mean-annual temperature (2900m elevation) (Figure 17.4). The dense organic matter ($>2 \text{ g/cm}^3$) has ^{14}C increases that are less than or equal to those of the low density soil C. In hydrolyzable C fractions, maximum turnover times (>100 years) are observed in the soils with highest clay content (22 - 40%) along the transect. Turnover times for this fraction (not shown here) do not have a simple relation with elevation.

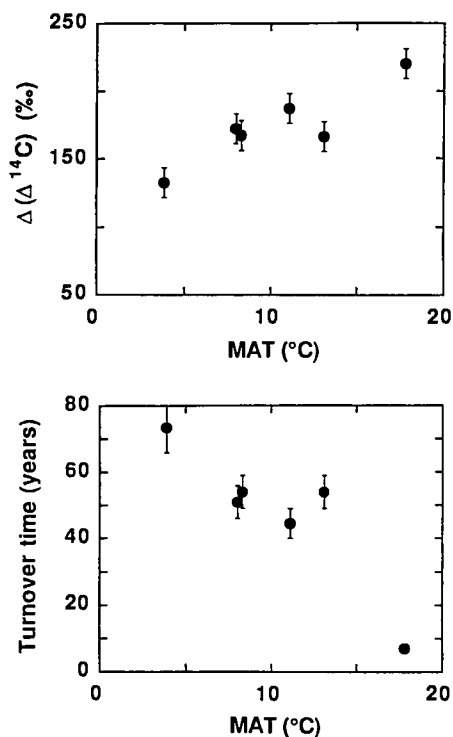


Figure 17.4. $\Delta(\Delta^{14}\text{C})$ of low density C extracted from soils (the upper diagram) and turnover times (the lower diagram) along the Sierra Nevada temperature transect (low temperature is high elevation).

In forest soils, losses of soil carbon to fire tend to confound the models for organic matter turnover, especially where averaged over several decades or centuries. The ^{14}C bomb spike can be used to estimate carbon loss to fire using a pair of burned and unburned sites. As part of the Boreal Ecosystem-Atmosphere Study (BOREAS) and Global Change and Climate History Program of the US Geological Survey, two sites were sampled on either side of a burn scar indicated on a 1964 aerial photograph. By selecting a 1964 burn scar, we could be assured that

any regrowth since the burn would be greatly enriched with “bomb” ^{14}C (Figure 17.2). One site (GR3) had burned in 1964 and regrown to a mixed Jack Pine and Black Spruce forest dominated by sphagnum moss; the other site (GR4), which was unburned, was located behind the fire scar of the 1964 burn and was overlain by sphagnum and mature Black Spruce. Both sites were underlain by clay subsoil in a remnant of Lake Agassiz sediment. Trees within the older GR4 site had been damaged by the 1964 fire, as indicated by asymmetrical growth around the trunk. These trees were ~ 65 years old, thus site GR4 burned in a previous fire around 1900.

$\Delta^{14}\text{C}$ values of the upper sphagnum layers, which are above the charred remnants of the burn layer, mimic the atmospheric curve (Figures 17.2 and 17.5), indicating very little mixing or decomposition for the upper layers. The lack of isotopic mixing in the plant (i.e. consistency with atmospheric values) is typical of non-vascular plants (Schell and Ziemann, 1983; Vitt, 1990; White et al., 1994). Isotopic mixing also would occur if decomposition were significant (Trumbore, 1994). As a result of the consistent upward growth and lack of mixing, the sphagnum layers above the char can be dated by simply matching the ^{14}C values of sphagnum (Figure 17.5) to those of the atmosphere (Figure 17.2).

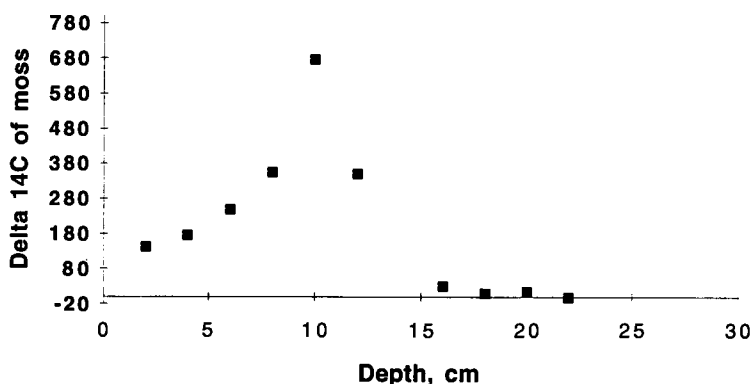


Figure 17.5. Radiocarbon content of sphagnum leaves over time and depth intervals.

The unburned site (GR4) has the past 30 years represented in the upper 12 cm, whereas the burned site (GR3) has the past 30 years recorded in the upper 22 cm because of its lower bulk density. Areal accumulation rates are very similar at the two sites, suggesting that there is a regional or species control rather than a local control on growth rates. Cumulative growth rates over the past 30 years (Figure 17.6) are extremely high compared to most ecosystems (Schimel et al., 1994) and even compared to millennial accumulation in most wetlands (Harden et al., 1992; Luken et al., 1985). Such recent and localized rates, however, are mediated by fire and decomposition, as evidenced from the slower accumulation in the older, deeper section of peat (Reader and Stewart, 1972). Although curves have been fit to such data to determine decomposition coefficients for upland peats (Clymo, 1984), it is clear that fire also plays a critical role in the carbon balance.

By comparing C inventories at both burned and unburned sites, the amount of moss burned at GR3 is estimated to be about 40% to 70% of the regrown (post-1900 fire) moss. These data

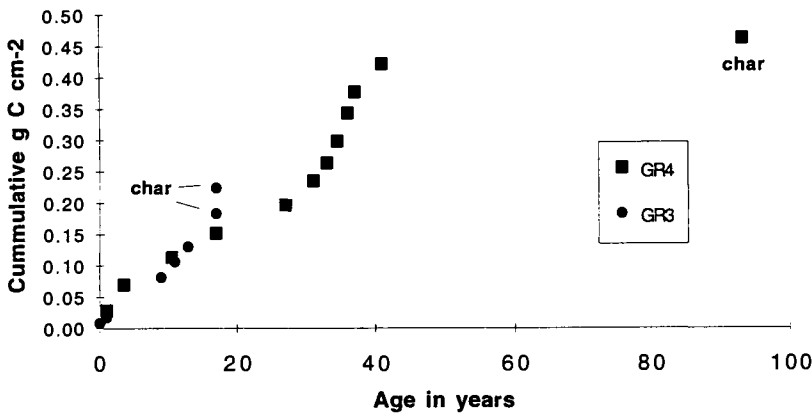


Figure 17.6. Cumulative mass of carbon as a function of basal age in sphagnum moss and peat at sites GR3 and GR4. Carbon storage of sphagnum layer are added cumulatively from the top and plotted against age of the basal layer from top down (modified after Clymo, 1984).

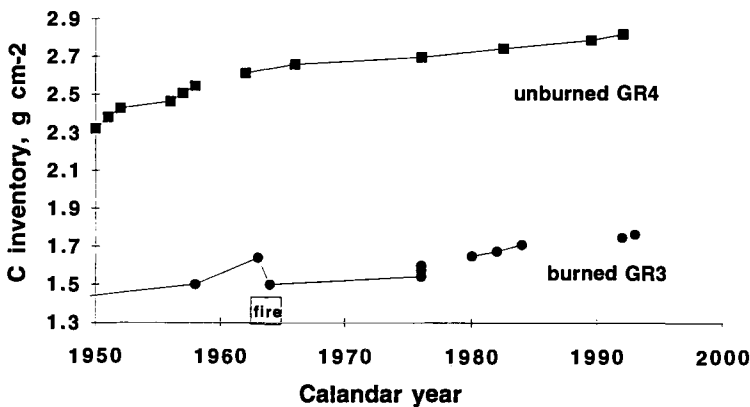


Figure 17.7. Reconstruction of carbon accumulation and loss at two sites overlain by sphagnum moss. Carbon storage of sphagnum layers are added cumulatively from the base and plotted against calendar year from old to young. Amount of carbon lost to fire at GR3 is based on growth and comparison to GR4 (see text).

compare favorably with estimates (Stocks et al., 1989) for drier sites. Since 1964, 0.24 g C cm⁻² have accumulated in moss layers at each site (also see Harden et al., 1994), an amount that exceeds the carbon lost to the fire in 1964. Despite the significant losses of carbon to fire (Figure 17.7) and uncertainties in the data, there is little doubt that these wetland sites are net sinks of CO₂ over most time periods.

In summary, ¹⁴C is an ideal tracer to study carbon cycling through soils on decadal (bomb ¹⁴C) and longer (natural ¹⁴C) time scales. ¹⁴C can be used to study the effect of climate, vegetation, parent material, land use, fire, and time on the accumulation and decomposition of organic matter in soils. ¹⁴C also can be used to identify the processes that are controlling C accumu-

lation and decomposition. However, the quantification of these processes is still in the early stages. Of the roughly 1200 - 1500 Pg of C stored in organic matter in soils, an estimated 250 - 530 Pg resides in C pools with turnover times of decades or less. Response of this fast-cycling soil C pool to global warming would play an important role in affecting future atmospheric CO₂.

17.3.3 The use of ¹³C to study C turnover in soils

Stable C isotopes may be used to study C dynamics in soils where the natural ¹³C abundance in an introduced vegetation is different from that found in the native vegetation. This approach has been used to study soil C turnover after continuous cultivation of C₄ crops on sites where the previous vegetation had been C₃ forests (Balesdent et al., 1986; Desjardins et al., 1994; Raich, 1983; Skjemstad et al., 1990, 1994; Vitorello et al., 1989), and C turnover on sites where C₃ plants were cultivated on originally C₄ dominated prairies (Balesdent et al., 1987; Martin et al., 1990). Stable C isotopes also have been used to investigate the effect of tillage on soil C dynamics (Balesdent et al., 1990) and as a tracer for the study of biodegradation of roots in soil (Mary et al., 1992).

Despite the success of conventional physical and chemical techniques for C turnover studies, until recently there were no fractionation techniques available to separate carbon pools by age in volcanic ash soils. Volcanic ash soils have no difference in age of carbon isolated from different aggregate sizes (Frey et al., 1993), particle size or density fractions (Townsend et al., 1995). A study using solid-state ¹³C NMR spectroscopy of organic materials isolated in particle size and density fractions of soils shows functional group compositions that vary across particle size in all soils except volcanic ash soils (Baldock et al., 1992). The lack of variation may be a result of the poorly crystalline mineralogy of the volcanic ash soils which confounds the ability to reliably separate fractions by size or density. For this reason, previous studies of soil organic matter turnover in volcanic ash soils after deforestation have not separated soils into fractions (Kelly et al., 1993, Veldcamp, 1994). This has hindered attempts to quantify C turnover in these soils and prevented a more precise understanding of both effects of clearing on C storage and on mechanisms of C sequestration.

A new method (Osher et al., 1994a), based on our understanding of the surface chemical properties of variable charge minerals, was developed to fractionate volcanic ash soils into different age C pools. This technique uses a sequential extraction procedure which includes a sodium pyrophosphate extraction step to remove C associated with Fe and Al oxide minerals, a hydrogen peroxide oxidation step to remove C that is most labile, leaving carbon that is associated with allophane minerals. The extraction is done sequentially; only the first step is done on whole soils.

This method was used to study C turnover in volcanic ash soils in Hawaii (Osher et al., 1994b). Soil samples were collected from two locations on Hawaii's Hamakua Coast where mean-annual rainfall exceeds 3500 mm per year. Surface and subsurface soils from beneath forest and pasture were collected at each location. Locations had soils with distinctly different age volcanic parent materials: 15,000 and 120,000 years. Pasture sites chosen had been cleared from forest approximately 80 years BP.

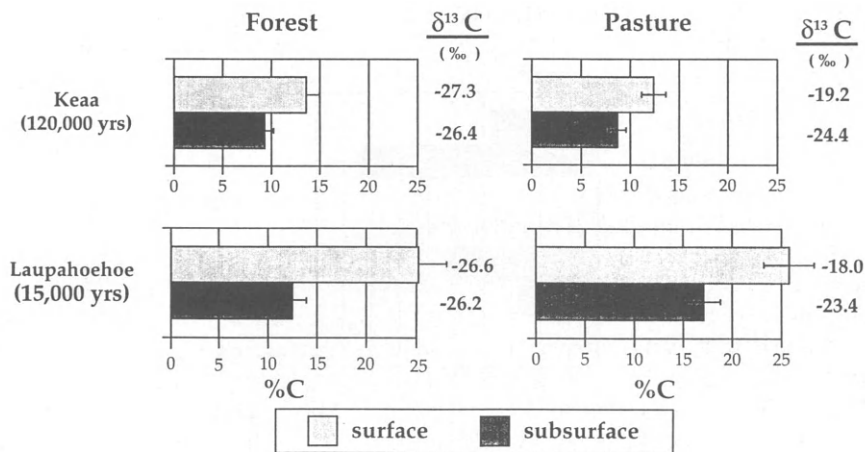


Figure 17.8. Carbon percent and δ¹³C for whole soils.

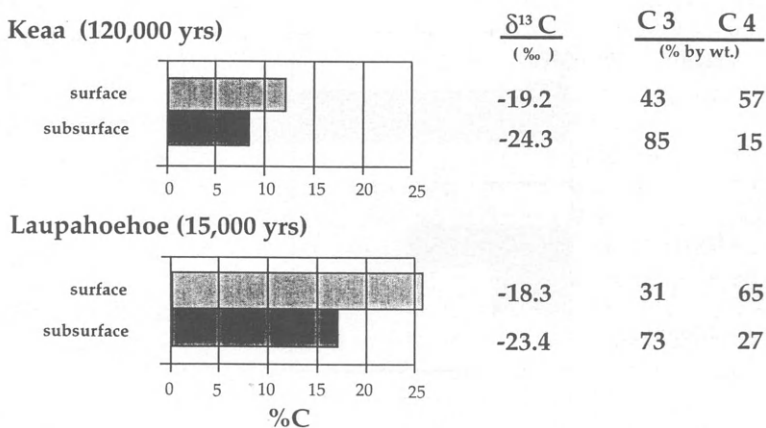


Figure 17.9. Carbon turnover in whole soils after about 80 years of pasture.

Percent carbon by weight was determined for one surface and one subsurface horizon from each profile. Soils on the younger parent material have greater carbon content in surface and subsurface horizons than soils on older land forms (Figure 17.8). Total carbon content in surface and subsurface horizons did not change significantly after 100 years of pasture in either age of parent material. These results, taken alone, may indicate that no loss of carbon has occurred as a result of deforestation. The stable carbon isotope ratios of all forest horizons (Figure 17.8) are similar to those of C₃ plants (δ¹³C = -27‰), whereas the ratios of pasture soils, specifically surface horizons, are indicative of a mixture of C₃ and C₄ (δ¹³C = -16‰) plants. The less negative ratio in the pasture soils represents a loss of older carbon (derived from forest organic matter) and addition of younger C from the C₄ plants that have been growing since deforestation (Figure 17.9).

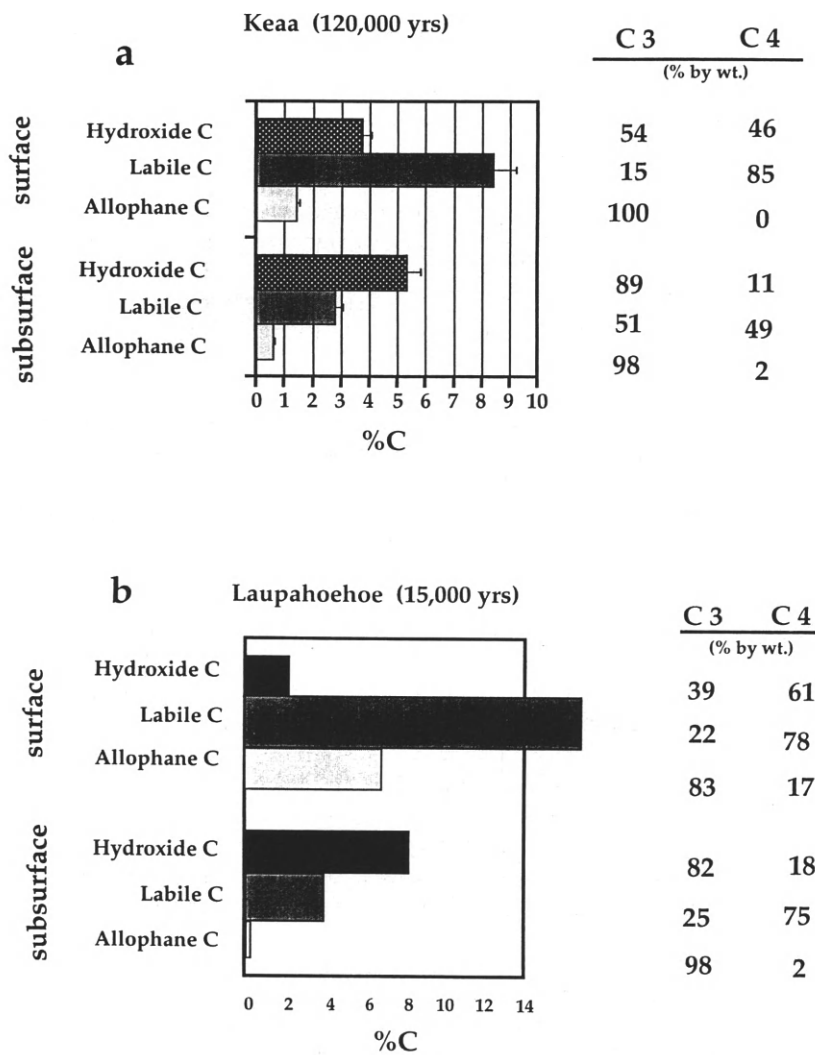


Figure 17.10. Carbon turnover on each fraction after about 80 years of pasture, a. Keaa site (120,000 yrs) and b. Laupahoehoe site (15,000 yrs).

Carbon from paired forest and pasture soils was separated into three pools (Figures 17.10a,b). The stable C isotopic signature of the soil organic matter was used to estimate C turnover in each fraction since clearing of the C₃ (forest) vegetation (as in Cambardella and Elliott, 1992).

The stable C isotope ratios of each pool reflected different rates of C turnover with time (Figures 17.10a,b). In the pasture soils, 80+ years after forest clearing, the pool with the stable C isotope ratio closest to C₄ plants has the highest turnover rate, the shortest residence time, and contains the youngest carbon. At this time, this fraction is referred to as the "Labile" C (i.e., the youngest fraction separated by this method). It is removed by peroxide oxidation. The

oldest carbon, which bears the original C_3 signature, is that carbon still occluded in mineral material after the extraction sequence. This fraction is identified as Allophane C. The intermediate age carbon pool, which has $\delta^{13}C$ values between C_3 and C_4 plants, is that liberated from mineral association by the sodium pyrophosphate extraction. This fraction is called the Oxyhydroxide C.

The size of carbon pools varies with parent material age and soil depth. The Labile C pool is larger in surface than subsurface horizons, and larger in the younger soil than in the older soil. The Allophane C pool is smaller in both horizons of the older soil than the younger soil. In all horizons, the size of Allophane C pool decreases after 100 years of pasture. At the younger site (Figure 17.10b), this decrease is large, and may indicate that mineral weathering has accelerated as a result of deforestation.

In summary, this research on volcanic ash soils demonstrated the usefulness of stable C isotopes in the study of soil C dynamics. The extraction method developed in this study seems to be able to separate C in volcanic ash soils into three pools with different turnover times. The approach can be used to evaluate the role of specific vegetation change accompanying land use change on soil carbon sequestration, turnover, and fluxes in volcanic ash soils.

17.3.4 Use of carbon isotopes in understanding carbon dynamics in peatlands

Peatlands are sites of carbon accumulation and are a significant terrestrial carbon reservoir, particularly in northern latitudes (Gorham, 1991). Carbon cycling in peatlands affects the global atmospheric concentration of greenhouse gases such as CO_2 and CH_4 . Wetlands constitute 20% of current global atmospheric CH_4 source and northern peatlands contribute up to 65% of wetland CH_4 flux (Matthews and Fung, 1987). Also, peatlands can frequently be a source of dissolved organic C (DOC) and dissolved inorganic C (DIC) within watersheds and thus affect downstream water quality and food webs. Perturbations in carbon cycling in peatlands are a likely consequence of altered water tables resulting from changes in climate or land use.

Both ^{13}C and ^{14}C isotopes are useful in examining the dynamics of carbon storage and release in peatlands. In the peat column, ^{14}C gives insight into the source of dissolved carbon and the influence of hydrology on carbon cycling (Aravena et al., 1993). For example, in a small boreal forest peatland in Canada, ^{14}C ages of dissolved CH_4 , DOC and DIC in peat porewater are much younger than the ^{14}C age of the peat at the same depth below the acrotelm or living vegetative layer (Figure 17.11). Because peat accumulates vertically, dissolved carbon produced from peat at a given depth in situ should have the same ^{14}C age as the peat substrate, assuming no mixing with C from root growth and decay. However, in this case, a significant fraction of the dissolved carbon has been produced in another (shallower) part of the peatland and transported to this area. The presence of tritium throughout the peat profile confirms the presence of an active hydrologic flow regime even in peat of low hydraulic conductivity. The ^{14}C data emphasize the importance of understanding the hydrologic flow regime in order to correctly interpret the carbon dynamics within peatlands.

In other studies on peatlands, ^{14}C also has been used to examine the origin of CH_4 in bubbles emanating from wetland ponds in the Hudson Bay Lowlands (Deck et al., 1992) and the accumulation rates of peat carbon (Malmer, 1992).

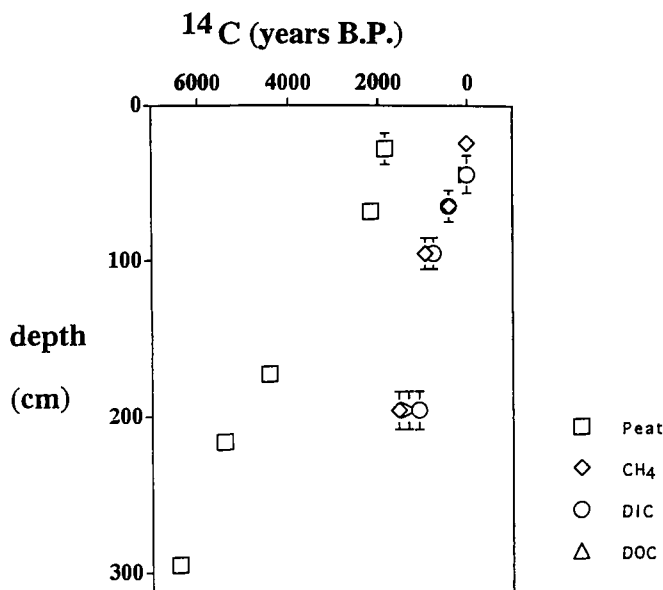


Figure 17.11. ^{14}C Of solid peat carbon and dissolved DIC, DOC and CH_4 in a small boreal forest peatland in Canada (Data from Aravena et al., 1996).

The stable carbon isotope, ^{13}C , yields insight into the pathway of methanogenesis within peatlands (Lansdown et al., 1992; Whiticar et al., 1986) and the potential for release of CH_4 from the peatland surface to the atmosphere. Isotopic fractionation occurs during microbial methanogenesis. The resultant CH_4 is isotopically light (Figure 17.12) and residual DIC within the peat porewater becomes increasingly enriched with depth. In northern temperate and boreal peatlands, the observed DIC and CH_4 $\delta^{13}\text{C}$ signatures in peat porewaters are consistent with methane production via CO_2 reduction (Figure 17.12; Lansdown et al., 1992).

Although large quantities of CH_4 are produced in peatlands, the escape of CH_4 from the peat to the atmosphere can only occur if the CH_4 is not completely oxidized within the acrotelm near or above the water table. Methane oxidation causes isotopic enrichment in ^{13}C of remaining CH_4 (Figure 17.12) but only after a significant fraction of CH_4 has been oxidized (Lansdown et al., 1992). Porewater profiles in small boreal forest peatlands show that significant methane oxidation occurs within 20 cm below the water table. C isotopic composition of methane collected from static gas-flux chambers located on the peat surface also indicates that a large fraction of CH_4 produced within the peat has been oxidized (Figure 17.13), except in areas where the water table intersects the peat surface. Wetland ponds are another significant source of CH_4 to the atmosphere (e.g. Hamilton et al., 1994), although a large quantity of methane in these wetland ponds has been oxidized (Figure 17.13). In contrast, bubbles escaping directly to the atmosphere that are produced in the pond sediments or within the peat carry methane that is not affected by oxidation (Figure 17.13). The stable ^{13}C isotope approach also has been fruitful in other studies of carbon cycling in wetlands to examine methane flux measurements (Chanton et al., 1992) and to address the role of emergent macrophytes on the atmospheric flux of CH_4 (Chanton et al., 1993).

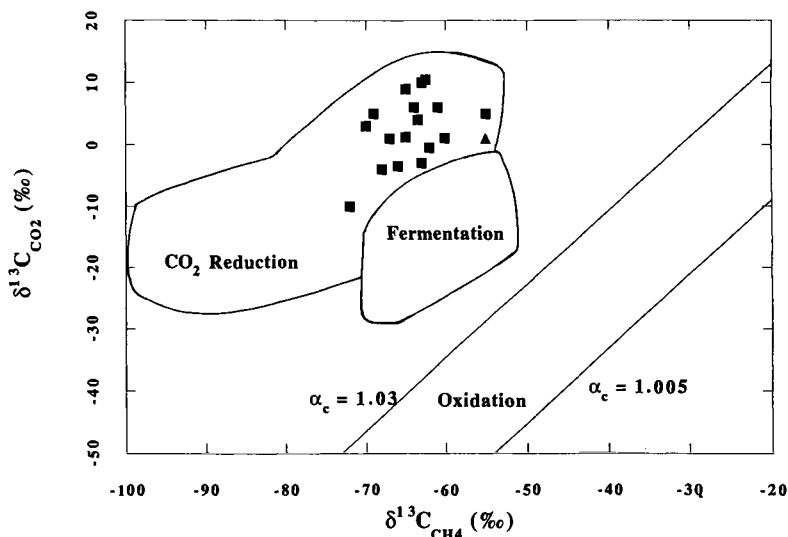


Figure 17.12. ^{13}C in CO_2 and CH_4 showing expected isotopic ranges for waters with methanogenesis via a CO_2 reduction pathway, methanogenesis via an acetate fermentation pathway and methane oxidation. Data points are peat porewaters at greater than 50 cm below the peat surface in a small boreal forest peatland in Canada. (Modified from Lansdown et al., 1992).

17.4 Isotope Studies of Dissolved Organic Matter in Groundwater

Groundwater is an important source of drinking water for many countries, municipalities, and rural communities, and is an important component of watershed hydrology. High concentrations of DOC in groundwater can lead to degradation of water quality and unacceptable aesthetic properties. In Canada and the United States the suggested drinking water maximum for DOC is between 5 and 10 mg C/L. DOC beyond 5 - 10 mg C/L often causes groundwater to appear pale yellow or brownish, and unappealing as drinking water, depending on the concentrations of humic substances in the water (Thurman, 1985a,b).

High DOC concentrations can lead to detrimental effects such as enhanced bacterial growth in water treatment and supply systems. The flux of labile DOC to groundwater may control the initiation of subsurface bacterial oxidation-reduction sequences (O_2 reduction, denitrification), and hence can profoundly influence the evolution of groundwater chemistry and quality (Appelo and Postma, 1993). Dissolved humic substances, which are a mixture of high molecular weight biopolymers (fulvic and humic acids), may comprise between 20 - 90% of the total DOC in groundwater. Humic substances are of considerable interest as they may enhance transport of trace and heavy metals, radio nuclides, and the solubility of relatively insoluble organic contaminants (Thurman, 1985a,b). Dissolved humic substances have also been linked to chloroform production during treatment of municipal water supplies. For these reasons there has been considerable interest in understanding the geochemical properties, sources, and cycling of DOC and its various fractions in groundwater systems over the past decade (Thurman, 1985a,b). The purpose of this section is to summarize relevant literature, specifically where stable and radiocarbon isotope techniques have been used in groundwater DOC research.

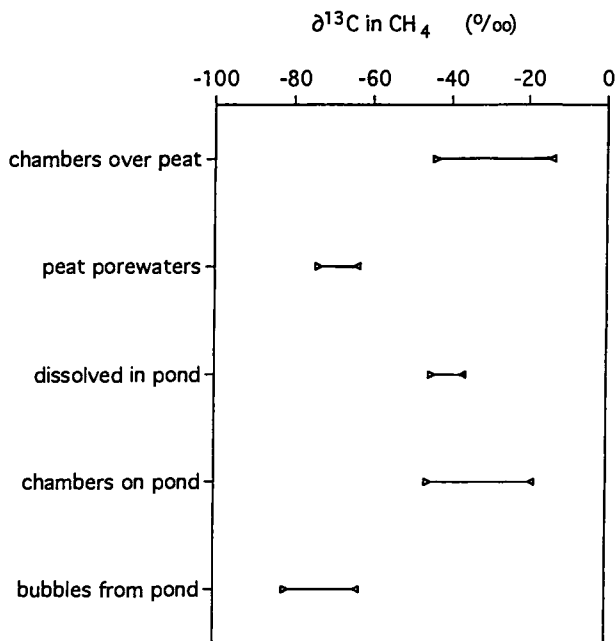


Figure 17.13. Observed $\delta^{13}\text{C}$ in CH_4 collected from static gas flux chambers on the peat surface, peat porewaters, wetland pond and bubbles from two small boreal forest wetlands in Canada.

As indicated earlier in the chapter, dissolved organic matter is comprised of a wide continuum of organic molecules that can range from simple C_1 compounds to complex macromolecules with molecular weights of 10,000 or more (e.g. aquatic humic substances). Bulk dissolved organic matter in groundwater is typically composed of between 40 - 60% carbon, 30 - 46% oxygen, 4 - 7% hydrogen, 0.5 - 3% nitrogen, 0.5 - 10% sulfur, and contains trace amounts of other elements and metals (Thurman, 1985a,b; Wassenaar et al., 1990a). Because of the complexity of the organic molecular continuum, a number of operational definitions were introduced to simplify analysis or preparative isolation (Thurman, 1985a); these operational aspects have to be kept in mind when interpreting isotopic data on DOC fractions. The total organic carbon (TOC) content of a groundwater sample is defined as all dissolved organic matter in unfiltered samples. This includes suspended colloids, suspended bacteria, and small organic particles. Dissolved organic carbon (DOC) is defined as the organic matter that passes through a 0.45 micron filter. The difference between TOC and DOC is defined as particulate organic carbon (POC), and this is negligible in most groundwater. Volatile organic compounds (VOC's) such as dissolved methane gas or semi-volatile organics ($< \text{C}_4$) are purged prior to analysis and are not considered part of the DOC measurement, although they may be intimately linked (Aravena and Wassenaar, 1993). Aquatic humic substances are defined as DOC fractions that can be isolated from groundwater using liquid chromatography, with subsequent chemical separations to further define aquatic fulvic and humic acids (Thurman and Malcolm, 1981; Aiken et al., 1985). Quantitative DOC and TOC measurements are made using a variety of chemical and analytical techniques, the most common being commercially available TIC/TOC analyzers.

The three reduced organic carbon pools in groundwater systems are TOC, VOC, and sedimentary organic matter (SOM) emplaced within the geologic materials. DOC in groundwater may originate from several sources. The first is transport of DOC from decomposing organic matter in the soil zone by groundwater recharge (Thurman, 1985a,b). The amount, type and isotopic characteristics of DOC infiltrating to the groundwater depends on a number of factors which include climate, vegetation, watershed and hydrologic flow system, unsaturated zone thickness, and the major DOC sinks: microbial oxidation, adsorption, and precipitation (Aiken et al., 1985). In temperate climates much of the DOC (> 80%) transported downward from the soil zone may be lost to soil CO₂ gas or sorbed in the unsaturated zone (Wassenaar et al., 1991a). A second possible source of DOC in groundwater may be from SOM in the form of peat, paleosols, or kerogen in the aquifer matrix (Thurman 1985a,b; Aravena and Wassenaar, 1993). SOM in most ancient sediments is highly refractory, insoluble, and present in minute amounts, and so may contribute very little to the groundwater DOC pool (Artinger et al., 1995).

The lighter isotopes (D, ¹³C, ¹⁵N, ³⁴S, ¹⁴C) are well suited to DOC studies because sources and processes affecting the organic carbon cycle of groundwater may be discerned from the interpretation of stable isotope ratios and radiocarbon ages. Nevertheless, the use of stable isotope ratios and radiocarbon age determinations of DOC from groundwater is relatively new. A number of factors contribute to the few isotope studies of DOC in groundwater. First, the amount of DOC in most groundwater systems is often very low, typically less than 1 - 2 mg C/L (Thurman, 1985a,b). Although not a serious limitation for stable carbon isotope analyses (several liters needed), large amounts of water were required to isolate sufficient material for other isotopic analyses by conventional techniques. This was a hindrance in the past when several grams of carbon were required for a single ¹⁴C analysis (hundreds of liters). Similarly, the trace amounts of nitrogen and sulfur (< 2 wt. %) present in DOC limited stable isotope research in these areas. Presently these limitations are largely overcome with accelerator mass spectrometry (AMS) for radiocarbon dating, and the advent of continuous-flow isotope ratio mass spectrometers (CF-IRMS). Radiocarbon age determinations are easily possible on milligram quantities by AMS, and simultaneous δ¹³C, δ¹⁵N and δ³⁴S isotope analyses are now attainable on microgram quantities of isolated DOC using CF-IRMS technology. δD analyses of DOC are still possible using conventional dual inlet technology, and may require further quantification of exchangeable hydrogen on DOC functional groups.

In general, isotope measurements have been made on 1) total DOC or 2) specific DOC fractions isolated from groundwater samples. For total DOC, ¹³C or ¹⁴C measurements are made on CO₂ produced by UV/photochemical oxidation of the DOC pool (Spalding et al., 1978; Wallis, 1979; Bauer et al., 1991; Purdy et al., 1992), or on DOC from freeze-dried water samples (Schiff et al., 1990). The first radiocarbon measurements of total DOC were made on groundwater samples that were acidified to remove inorganic carbon and then subjected to intense UV oxidation (Spiker and Rubin, 1975). Methodological problems, in all cases, potentially arise with large sample requirements, incomplete DOC oxidation, and incomplete removal of DIC or VOC. Interpretation of total DOC isotope data is somewhat restricted in the sense that certain fractions of DOC could vary considerably in age and reactivity. In the second instance, isolated DOC fractions have included aquatic humic substances (fulvic and humic acids) isolated using a variety of extraction techniques (Thurman and Malcolm, 1981; Petterson et al., 1989; Petterson and Allard, 1991), and low molecular weight DOC fractions sorbed into molecular sieves (Murphy et al., 1989a,b; Wassenaar et al., 1989; 1991b). Isolated DOC fractions such as fulvic acids are usually freeze dried, and a variety of isotope measurements

(e.g., D, ^{15}N , ^{34}S) can easily be made on them. Unfortunately, specific isolated DOC fractions may represent as little as 20% of the total DOC pool in groundwater, potentially leaving a large percentage of the DOC unmeasured. Further, harsh chemical extremes during DOC fraction isolation could affect or change the DOC structure. Nevertheless, useful information can be gained by studying the isotopic compositions of both total and DOC fractions. Ideally, a DOC extraction system should quantitatively isolate 100% of the DOC from groundwater without structural compromise or chemical alteration.

The most promising technique to date is the use of reverse osmosis (Sun et al., 1995; Artinger et al., 1995), which allows for rapid concentration and recovery of 98 - 100% of DOC from large groundwater samples, with no exposure to harsh chemical extremes. The DOC concentrate resulting from reverse osmosis isolation can be further processed into various size or chemical fractions using ultra-filtration, gel permeation and size exclusion chromatography, molecular sieves, or XAD liquid chromatography, depending on the information and analyses required. Current difficulties with reverse osmosis occur in groundwater with high total-dissolved solids (inorganic salts are concentrated also), or in highly reducing groundwater environments (Fe^{3+} /DOC precipitates). Development of isolation and fractionation methodologies as well as multi-elemental isotopic characterization of DOC fractions from groundwater is an area where much research and work is still needed.

17.4.1 Stable carbon isotopes

A considerable number of $\delta^{13}\text{C}$ measurements have been made on DOC and fractions from groundwater. These generally have been used to infer sources. The stable carbon isotope values of DOC reported a range between -18‰ to -46‰ (Spiker and Rubin, 1975; Spalding et al., 1978; Thurman, 1985a,b; Murphy et al., 1989a,b; Schiff et al., 1990; Wassenaar et al., 1989; 1990a,b; 1991a,b; Purdy et al., 1992; Aravena and Wassenaar, 1993; Geyer et al., 1994; Grøn et al., 1996). As expected, in terrestrial settings most $\delta^{13}\text{C}$ values of DOC and fractions vary about -26 to -30 ‰, which are typical of C_3 terrestrial plant material, and similar to values of soil organic matter and terrestrial humic and fulvic acids (Deines, 1980). DOC $\delta^{13}\text{C}$ values up to -18 ‰ occur where C_4 type plant cover is prevalent (Spalding et al., 1978). The few published $\delta^{13}\text{C}$ values on low molecular weight DOC fractions varied widely from -18 to as low as -40 ‰, but there has been no further work or satisfactory explanation regarding the large variation or depleted values (Murphy et al., 1989b; Wassenaar et al., 1991a,b). In general, the $\delta^{13}\text{C}$ values of DOC in most groundwater tend to reflect the average carbon isotopic composition of local decomposing plant materials.

Distinct carbon isotopic values are evident for DOC fractions from groundwater at different geographic locations. In other groundwater systems the $\delta^{13}\text{C}$ values of aquatic humic substances may be variable, or change along the groundwater flow path (Wassenaar et al., 1990a) due to any number of factors such as diagenetic effects, multiple organic carbon sources within the groundwater system (e.g. soil, peat, kerogen), isotopic alteration in the carbon sources as a result of climatic change or human activities (e.g. forest to corn; Spalding et al., 1978), or microbial processes. Grøn et al. (1996) were able to successfully use the $\delta^{13}\text{C}$ values of DOC to distinguish subsurface terrestrial and marine source rocks in groundwater systems in Denmark.

17.4.2 Nitrogen, sulfur and hydrogen isotopes

Few data exist on the $\delta^{15}\text{N}$, $\delta^{34}\text{S}$, and δD composition of groundwater DOC fractions (Wassenaar et al., 1990a; Geyer et al., 1994; unpublished data). In a study of fulvic DOC fractions from water table wells in limestone gravel near Munich, Germany, a trend of higher $\delta^{15}\text{N}$ values with increasing water table depth was observed (-0.28‰ to $+1.49\text{‰}$ over 2 to 13 meters depth). Fulvic DOC fractions along a 30 km flowpath in the Keuper sandstone in central Germany had higher $\delta^{15}\text{N}$ values than the shallow water table wells, between $+3$ and $+8\text{‰}$, and showed a trend of $\delta^{15}\text{N}$ enrichment with increasing age and distance along the flow path (Geyer et al., 1994). The $\delta^{15}\text{N}$ values of DOC humic/fulvic acid pairs from the Gorleben aquifer system in Northern Germany ranged between $+1.49$ to $+6.09\text{‰}$ (Geyer et al., 1994), with fulvic acid DOC fraction $\delta^{15}\text{N}$ value increasing with residence time. During organic matter degradation isotopically lighter breakdown products are produced, resulting in ^{15}N enriched residual organic material. Numerous profiles of soil humic matter show this $\delta^{15}\text{N}$ enrichment (from -3 to $+7\text{‰}$) occurs in the upper 50 cm of soil horizons (Letolle, 1980). DOC fractions in groundwater appear to emulate the soil $\delta^{15}\text{N}$ trend. These first results suggest $\delta^{15}\text{N}$ enrichment of DOC occurs as a result of fractionation during progressive degradation with increased residence time in the unsaturated zone and groundwater system, but over far larger spatial scales than soil as a result of advective transport in groundwater. Thus $\delta^{15}\text{N}$ appears to be a good indicator of progressive DOC evolution and aging.

Only a handful of $\delta^{34}\text{S}$ values for groundwater DOC fractions exist. In the Gorleben aquifer system in Germany $\delta^{34}\text{S}$ analysis of 9 fulvic and humic acid DOC pairs yielded values between -3 and $+17\text{‰}$. In all cases, paired fulvic and humic DOC fractions of different ages and sources yielded relatively similar $\delta^{34}\text{S}$ values. Evidence from marine sediments suggest that sulfur is incorporated into humic macromolecules by reactions with $\delta^{34}\text{S}$ depleted H_2S produced by sulfate reduction (Francois, 1987). Thus, $\delta^{34}\text{S}$ content of humic DOC fractions in reducing groundwater also is likely to be affected by existing redox conditions in the groundwater system. Although inconclusive, the lightest $\delta^{34}\text{S}$ values of fulvic and humic DOC fractions occurred under the most reducing conditions, suggesting incorporation of H_2S from sulfate reduction could indeed be an important control on the sulfur content of DOC in groundwater. Clearly, more research is needed on organic sulfur cycling in DOC fractions.

The deuterium content of organic matter is primarily dependent on the isotopic composition of the water available to the plant, which largely depends on climate (Yapp and Epstein, 1982). δD values of fulvic DOC fractions in several Canadian groundwater systems ranged from -169‰ to -114‰ (Wassenaar et al., 1990a). Functional group hydrogen isotope exchange occurs, but is minor in the case of humic DOC fractions. Thus, the δD of DOC will reflect the δD of local organic carbon sources. The possibility of using δD of DOC from age-constrained groundwater for paleo-climatic studies has not been attempted.

17.4.3 Radiocarbon in DOC

Radiocarbon measurements of groundwater DOC can provide additional insight into organic carbon sources and cycling in the subsurface. Because of the potential complexity of DOC, it may be expected that different molecular fractions have different turnover times. Because DOC is a polymeric mixture of young and old organic carbon components, ^{14}C ages should not be

considered true ages, but rather the mean residence time of the DOC mixture. In groundwater systems, radiocarbon ages of DOC fractions are especially useful as a tracer. For example, if DOC were derived solely from ancient soil organic matter no measurable ^{14}C would be expected (Long et al., 1994). Thus, any measurable ^{14}C activity represents the minimum mean residence time of the DOC in the soil and vadose zone, the residence time of the DOC in the groundwater flow system, plus potential dilution from old SOM.

Recent research has shown that DOC ^{14}C measurements are an invaluable tool for estimating groundwater ages (Murphy et al., 1989a,b; Wassenaar et al., 1989; 1991a,b; Petterson and Allard, 1991; Purdy et al., 1992; Geyer et al., 1994; Aravena et al., 1995; Artinger et al., 1995), and this technique is particularly applicable in aquifers where soil organic matter is low (Artinger et al., 1995). Decay of DOC ^{14}C along a groundwater flow path provides the basis for determining groundwater ages. In most of the studies the fulvic acid DOC fraction provided ^{14}C groundwater ages that were in good agreement with other groundwater dating and hydrologic methods. The initial ^{14}C content of humic DOC fractions entering groundwater systems appears to range between 75 to 110 percent modern carbon, depending on location, soil development and water table depth (Wassenaar et al., 1992).

More recently, research has focused on developing techniques to assist in determining the contribution of soil organic matter to groundwater DOC (Aravena and Wassenaar, 1993; Artinger et al., 1995; Aravena et al., 1995; Grøn et al., 1996). Whereas the majority of conventional chemical and structural analyses of DOC do not give much information in this regard (Grøn et al., 1996), progress is being made in understanding soil organic matter contributions by a combination of chemical, isotopic, and spectrographic measurements (Artinger et al., 1995; Aravena et al., 1995). Basic questions still exist regarding various aspects of DOC cycling in groundwater. Groundwater DOC is different chemically from both soil and surface water DOC, which appear to occur as a result of unsaturated zone processes (Wassenaar et al., 1990a,b). Yet, information concerning the isotopic composition, geochemistry and transport of DOC in the unsaturated zone is virtually non-existent. Basic research on DOC cycling in the unsaturated zone is needed.

17.5 Isotope Study of DOC in Lacustrine Environments

Dissolved organic matter (DOC) can influence the chemical and physical characteristics of an aquatic ecosystem through a variety of processes, e.g. buffering of pH, complexation of trace metals, and attenuation of light. As discussed in the previous section, humic substances can be isolated from natural waters using column chromatography (Thurman and Malcolm, 1981). Characterization of the isotopic composition of the carbon in DOC can be a useful tool in interpreting the biogeochemistry of humic substances in lacustrine environments.

We present results below that illustrate the utility of ^{14}C data of fulvic acid for identifying modern and old sources of fulvic acid in Lake Fryxell, an antarctic closed basin lake. The permanent ice cover and saline bottom waters result in a highly stable water column, with essentially no vertical mixing. In the lake, fulvic acid accounts for about 25% of the DOC at all depths (McKnight et al., 1993). The depth profile of DOC resembles that of conductivity (Figure 17.14), indicating diffusion of DOC, including fulvic acid, from the lake sediments, produced by the long term decomposition of algal biomass (Aiken et al., 1991). The other

sources of DOC and fulvic acid to the lake are the glacial meltwater streams (McKnight et al., 1993; Aiken et al., 1995). In the streams, fulvic acid is only 5 - 10% of the DOC, reflecting the relatively recent production from the microbial mats in the streambed. The depth profile of the ^{14}C age of the fulvic acid (Figure 17.14) confirms that fulvic acid derived from both old and new sources of organic carbon are present in the lake. The vertical separation of the modern fulvic acid in the upper water column and the old (3000 yrs) fulvic acid in the bottomwaters provides further evidence for the long-term stability of the water column, and illustrates that ^{14}C measurements of persistent organic material such as fulvic acid can be complementary to other isotopic measurements. The slight decrease in age of fulvic acid for the deepest sample (18 m) may be caused by decomposition of newly fixed algal material, or some injection into deeper water of surface water fulvic acid, and certainly suggests an area for further research. Application of ^{14}C measurements of fulvic acid may be similarly useful in biogeochemical studies of meromictic lakes in temperate regions.

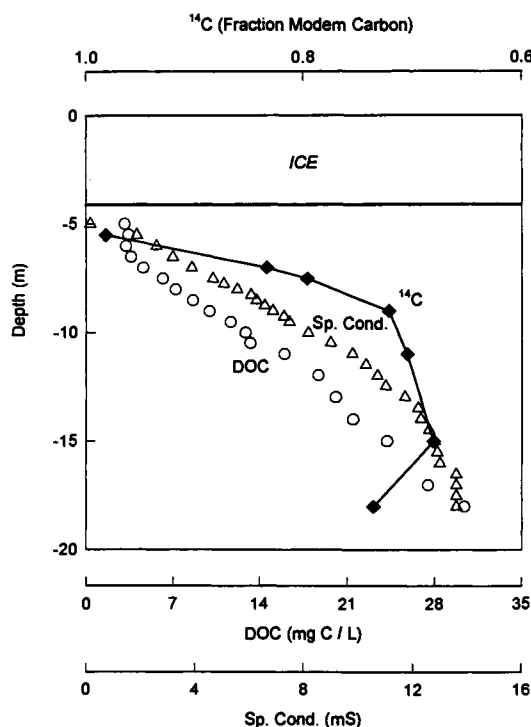


Figure 17.14. Comparison of ^{14}C (Fraction Modern Carbon), DOC (mg C/L) and specific conductivity depth profiles in Lake Fryxell.

Another isotopic attribute of aquatic fulvic acid is the $\delta^{13}\text{C}$ of the precursor organic material. We studied fulvic acids in alpine and subalpine lakes in Loch Vale watershed, Rocky Mountain National Park (Baron et al., 1991; Baron, 1992). The alpine lake, Sky Pond, is surrounded by talus slopes containing minimal vegetation and has abundant algal populations during the summer, and the phytoplankton in the lake in August has a $\delta^{13}\text{C}$ of about -22‰ (McKnight et

al., 1995). The sediments of Sky Pond are composed of rocks, boulders and organic-rich gyttja with high interstitial DOC concentrations. The subalpine lake, The Loch, is surrounded by a spruce-fir forest and has 5 - 10 fold lower abundance of algae than Sky Pond. During snowmelt, the $\delta^{13}\text{C}$ of the fulvic acid flushed into Sky Pond from the sediments reflects an algal sediment source. The values in surface water of The Loch reflect a soil/plant source although a lighter value was found in the bottomwater. After snowmelt, the values in Sky Pond became heavier, matching those in The Loch. This change could indicate a shift in the source of fulvic acid in Sky Pond to the sparse alpine soils, or a shift to more direct generation of fulvic acid from organic material produced by the planktonic algae, such as extracellular mucopolysaccharides. This study shows that C isotopes can be useful in studying seasonal dynamics controlling fluxes of fulvic acid in freshwaters.

Dissolved organic carbon and fulvic acids in particular are increasingly being studied to understand processes in aquatic ecosystems and to elucidate important controls on water quality. For example, the fulvic acid concentration of drinking water is the main determinate of the quantity of trihalomethanes generated during chlorination of drinking water supplies. For this reason, water-resource managers are concerned about watershed sources of fulvic acid to reservoirs, and are trying to quantify hydrologic controls on seasonal variations in fulvic acid concentrations. Application of isotopic characterization of fulvic acid is, therefore, a useful tool that can help answer such fundamental questions.

17.6 Isotope Studies and the Carbon Budget

Increasing atmospheric CO_2 and the potential for "greenhouse warming" and climate change has focused considerable debate on uncertainties in the global carbon budget. Estimates of global CO_2 sources exceed known CO_2 sinks by 1 to 3 Gt C/yr (1Gt = 10^{15} g) (Detwiler and Hall, 1988; Tans et al., 1990; Sundquist, 1993; Dixon et al., 1994). The evidence strongly suggests that the "missing sink" is located in northern temperate regions (Detwiler and Hall, 1988; Tans et al., 1990). Mechanisms such as carbon sequestration in vegetation and soils, accumulation in lakes and reservoirs due to autochthonous carbon production, and burial of river-transported sediments in reservoirs and other depositional environments have been suggested but the nature and magnitude of the terrestrial sinks remain uncertain.

Ciais et al. (1995) used $\delta^{13}\text{C}$ measurements of atmospheric CO_2 collected in a global network to infer partitioning of CO_2 uptake between terrestrial and oceanic systems with an atmospheric transport model. They also used global runs of the CENTURY soil model (Parton et al., 1988; Schimel et al., 1994) to calculate C distribution in the terrestrial biosphere, incorporating active (detrital and microbial) and passive (recalcitrant soil organic matter) pools. They concluded that in 1992, northern temperate and boreal terrestrial ecosystems were a net sink, as large as 3.5 Gt C. A sink of this magnitude could explain even the highest estimates of the "missing sink". In another analysis, Quay et al. (1992) compared changes in ^{13}C of atmospheric CO_2 with oceanic stable carbon isotope ratios to assess the recent terrestrial carbon budget. They concluded that from 1970 to 1990 decreased ^{13}C in the ocean reflected fossil fuel combustion and deforestation, but that there had been no net release of CO_2 from the biosphere.

Jenkinson et al. (1991) used the Rothamstead model to predict significant net releases of CO_2 from soils in response to global warming. The Rothamstead model was developed with carbon

isotope studies on the temperature dependence of the decomposition of soil organic matter. To scale their model to other biomes they used ^{14}C based decomposition studies conducted in different parts of the world. They estimated that the additional release of CO_2 from soil organic matter over the next 60 yr will be 61 Gt C if world temperatures rise by $0.03^\circ\text{C}/\text{yr}$. This is about 19% of the CO_2 that would be released by fossil fuels in the next 60 yr if present use continues unabated.

Harrison et al. (1993) estimated how much of the “missing sink” carbon (1.8 Gt C/yr) could be accounted for by sequestration in soils, litters, and biomass using an analysis of ^{14}C . They estimated soil organic matter residence times using the ^{14}C enrichment following atmospheric nuclear testing. Their model includes two soil organic matter pools: a fast or active pool and a slow or passive pool. They estimated that the surface 10 cm had a fast pool (25 yr) having 75% of the carbon and a slow pool (3700 yr) having 25% of the carbon. For the soil profile as a whole, they estimated a fast pool (25 yr) having 50% of the carbon and a slow pool (3700 yr) having 50% of the carbon. Their model assigns substantially more carbon to the fast pool than some previous estimates. Harrison and Broecker (1993) also assumed that, historically, for every 10% increase in atmospheric CO_2 vegetative growth and soil organic matter increased by 3.5%. They concluded that 60% of the current imbalance in the CO_2 budget could be accounted for by increases in carbon accumulation in biomass and soils driven by historical increases in atmospheric CO_2 .

Recent studies have provided valuable information on carbon inventories in forest vegetation and soils (Dixon et al., 1994; Birdsey et al., 1993; Sedjo, 1992; Musselman and Fox, 1991) and the effects of land-use changes on terrestrial carbon storage (Huntington, 1995; Wofsy et al., 1993; Johnson, 1992; Johnson et al., 1988). The magnitude of these terrestrial carbon stores and fluxes is so large that even relatively small changes that affect forest biomass and soil pools will affect the global carbon cycle. Isotopic techniques may provide a better understanding of the processes affecting carbon storage and the historical pattern of carbon storage and release. This information will be required to predict how terrestrial carbon storage will respond to future changes in climate and land use.

Carbon isotopic techniques also have been used to understand carbon dynamics in soil plant systems under controlled experimental conditions with ^{14}C -enriched CO_2 atmosphere in growth chambers. One such study involved wheat grown at 350 and 700 ppm CO_2 for 49 days where temperature was held constant between treatments (Lekkerkerk et al., 1990). It was determined that (1) total respiration was higher under 700 ppm, (2) most respiration under elevated CO_2 was due to root-derived, easily decomposable material rather than native soil organic matter, and (3) soil organic matter contents increased under elevated CO_2 because of greater detrital production and a preference by microbes for root-derived material over native soil organic matter. Despite the recent advances in understanding carbon cycling in terrestrial ecosystems, prediction of future atmospheric CO_2 concentration and climate must be tempered by large uncertainties in estimates of carbon storage and fluxes and in how carbon cycling processes will be affected by future environmental changes. These uncertainties are illustrated by the contrasting predictions of various atmosphere-ocean general circulation models and the variety of assumptions about plant and microbial response to environmental change (Smith et al., 1992; Gates et al., 1992; Smith and Shugart, 1993; Post et al., 1992; Schlesinger, 1993; Jenkinson et al., 1991; Prentice and Fung, 1990; Schleser, 1982). Among the challenges currently facing investigators in this field is the paucity of data on carbon turnover compared with data on

carbon inventories, the lack of information on the kinetics of the responses of soil carbon reservoirs to changes in climate and land use, and the general lack of information on the long-term response of terrestrial ecosystems to both CO₂ enrichment and changes in soil temperature. Carbon isotope studies likely will be of great help with these challenges at a variety of spatial and temporal scales.

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Tracing of Weathering Reactions and Water Flowpaths: A Multi-isotope Approach

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18.1 Introduction

18.1.1 Rationale for using water and solute isotopes as tracers in catchments

Forested catchments provide a unique hydrogeologic setting in which to study the effects of processes such as climate change, acid deposition, deforestation, and encroaching urbanization. However, major uncertainties evident from attempts to model the hydrology and chemistry of forested catchments are the quantification of water delivered from various hydrologic flowpaths to stream flow, and the determination of weathering reactions that mobilize solutes along those flowpaths. Reliable tools for the assessment of both water and solute sources are essential if we are to fully understand the impacts of both natural and anthropogenic perturbations on catchment function.

Oxygen and hydrogen isotopes (i.e., "water isotopes") are now commonly used tools for determining water sources in catchments. The main use of O and H isotopes in catchment research is for determination of contributions of "old" and "new" water to stormflow (Sklash et al., 1976; Sklash and Farvolden, 1979; Bishop, 1991), where "old" water is defined as the water that existed in the catchment prior to a particular storm or melt event, and "new" water is defined as the water that triggered the event. The water isotopes are such effective tracers of water sources ("time-sources" in the terminology of Sklash et al., 1976) because oxygen and hydrogen are the constituents of, and thus move with water molecules. Under favorable circumstances, waters flowing along a particular flowpath may have distinctive O- and/or H-isotopic compositions; hence, the water isotopes can sometimes be viewed as tracers of water flowpaths. The processes that affect water isotope composition and the application of water isotopes to catchment studies are addressed in several chapters of this book, and the reader is referred to those chapters for discussion of the theoretical bases of the oxygen and hydrogen isotope systems.

In contrast, the solute isotopes (e.g., strontium, carbon, lead) are as yet under-utilized in catchment research compared to the water isotopes. Detailed analysis of the isotopic composition of Sr in stream waters, organic and mineral soil horizons, biomass, and atmospheric input at a handful of sites has provided insight into the cycling of Sr, and by analogy Ca and related nutrients in catchments (Graustein, 1989; Aberg et al., 1989; Gosz and Moore, 1989; Miller et al., 1993; Bailey et al., 1996). The stable C isotopes provide unique

information on the origin of carbonate alkalinity and the relative importance of processes such as carbonate mineral dissolution, silicate hydrolysis, oxidation of organic matter and methanogenesis (Mills, 1988; Kendall, 1993; Katz et al., 1995). Pb isotopes can be used to distinguish shallow flowpaths, dominated by atmospheric Pb, and deep flowpaths, dominated by Pb from catchment minerals. However, Pb isotopes have been employed in only a handful of catchment studies (Sirahata et al., 1980; Erel et al., 1991; Bullen et al., 1994) and are not generally recognized as useful tracers in catchments.

Solutes do not necessarily move conservatively with the water, and thus solute isotopes can trace only solute sources, not water sources. They can, however, serve as useful tracers of flowpaths in the sense that different geologic units and their constituent minerals ("geographic-sources" in the terminology of Sklash et al., 1976) encountered along those flowpaths may have contrasting isotopic compositions. For example, flowpaths through the soil zone may be characterized by different chemical and solute-isotope compositions compared to those that typify flowpaths through the bedrock. In addition, solute isotope tracers are often used to test hypotheses developed from other criteria, such as interpretations of water chemistry or hydrology. In particular, they can be used to substantiate or eliminate possible geochemical reaction paths (Plummer et al., 1983). Because solute isotope ratios are usually affected by a smaller number of processes than chemical concentrations, interpretations of changes in isotopic composition are often less ambiguous than the simultaneous changes in water chemistry (Kendall et al., 1995).

The purpose of this chapter is to demonstrate that by synthesizing the information provided by several isotopic tracers, one can realize greater understanding at the process level than mere hypothesis confirmation. A "multi-isotope approach" can take advantage of the fact that unreactive tracers (such as H and O isotopes) and reactive tracers (such as Sr, Pb and C isotopes) provide very different information about how a catchment "works". For example, the water isotopes can be used to test the validity of a flowpath predicted from hydrologic measurements, and analysis of solute isotopes in waters collected along the flowpath can provide information about the minerals that are contributing to the water chemistry. In the absence of the solute isotope analyses, attempts to uniquely define the reactive mineral assemblage from water chemistry would likely be confounded by the mineralogic complexity of the catchment, even if both mass balance and reaction path chemical models are simultaneously applied (see Chapter 8). Likewise, in the absence of the water isotopes it would be difficult to constrain samples to a single flowpath, due both to the non-conservative nature of most solute species and to the inherent uncertainties resulting from assumptions in hydrologic models.

We view the Sr, Pb and C isotopes to be potentially the most widely applicable solute isotope tracers for catchment research, particularly when considered in light of constraints provided by the water isotopes. In this chapter, we present a discussion of the theoretical bases of the Sr, Pb and C isotope systems, establish the criteria for their successful application, and discuss the factors that influence solute isotope composition in catchment waters. We then present an overview of three catchment studies that employ a multi-isotope approach in addressing specific reaction path or flowpath issues. Finally, we discuss the theoretical bases and potential applications of several other solute isotope tracers.

18.1.2 Theoretical bases of the strontium, lead and carbon isotope systems

A general discussion of the geochemistry of isotopic tracers in catchment systems can be found in Chapter 2. In addition, an introduction to the application of Sr, Pb and other "lithogenic" isotopes to catchment studies is presented in Chapter 8. In this chapter, we present a more detailed synopsis of the fundamentals of the Sr, Pb, and C solute isotope systems, followed by a section on case studies using these isotopes. For the radiogenic Sr- and Pb-isotope systems, we stress the importance of the differential distribution of radiogenic Sr and Pb and their parent isotopes in catchment minerals and atmospheric/anthropogenic sources. For the stable C-isotope system, the discussion centers on processes affecting isotope compositions within both carbonate-bearing and carbonate-free catchments.

Rubidium (Rb) - strontium (Sr)

The alkali-earth metal Sr has four stable, naturally-occurring isotopes: ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr . Only ^{87}Sr is radiogenic (i.e., produced by radioactive decay of another isotope) and gradually increases in minerals due to beta-decay of the radioactive alkali metal ^{87}Rb , which has a half-life of 48.8×10^9 years. Thus, there are two sources of ^{87}Sr in any material: that formed during primordial nucleosynthesis along with ^{84}Sr , ^{86}Sr and ^{88}Sr , as well as that formed by radioactive decay of ^{87}Rb . The ratio $^{87}\text{Sr}/^{86}\text{Sr}$, which provides a measure of the relative proportion of radiogenic to stable Sr, is the parameter typically reported in geologic investigations. The present-day $^{87}\text{Sr}/^{86}\text{Sr}$ of a Sr-bearing mineral is a function of the initial $^{87}\text{Sr}/^{86}\text{Sr}$, the ratio of Rb to Sr ($^{87}\text{Rb}/^{86}\text{Sr}$), and the age of the mineral:

$$^{87}\text{Sr}/^{86}\text{Sr}_{\text{present-day}} = ^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}} + ^{87}\text{Rb}/^{86}\text{Sr}_{\text{present-day}} (e^{\lambda t} - 1) \quad (18.1)$$

where $\lambda = 1.42 \times 10^{-11}$ ($\ln 2/\text{half-life}$). $^{87}\text{Sr}/^{86}\text{Sr}$ in minerals and rocks ranges from about 0.7 to greater than 4.0 (Faure, 1972). As a general rule, carbonates and plagioclase feldspars contain the least radiogenic Sr, whereas K-feldspars and micas contain the most radiogenic Sr of typical reactive minerals in catchments.

Differences in the absolute proportion of radiogenic ^{87}Sr among mineral and other sources provide the diagnostic tracer of those source materials. Therefore, measured differences in $^{87}\text{Sr}/^{86}\text{Sr}$ in different materials due to stable isotope fractionation (primarily due to thermal effects in the mass spectrometer) must be corrected for. Fortunately, the stable isotope pair $^{88}\text{Sr}/^{86}\text{Sr}$ can be used as an internal monitor of both natural and analytical fractionation. In the absence of stable isotope fractionation, $^{88}\text{Sr}/^{86}\text{Sr}$ should be identical in all materials, with an accepted value of 8.37521 (IUGS: International Union of Geological Scientists). When the Sr (and other) isotopes fractionate, the amount of fractionation between pairs of isotopes is proportional to their mass ratios. Therefore, as a standard analytical procedure, $^{87}\text{Sr}/^{86}\text{Sr}$ is measured simultaneously with $^{88}\text{Sr}/^{86}\text{Sr}$, and the measured $^{87}\text{Sr}/^{86}\text{Sr}$ is adjusted by an amount proportional to that required to correct the measured $^{88}\text{Sr}/^{86}\text{Sr}$ to the accepted value. Consequently, the reported $^{87}\text{Sr}/^{86}\text{Sr}$ is "fractionation-corrected".

The utility of the Rb-Sr isotope system results from the fact that different minerals in a given geologic setting can have distinctly different $^{87}\text{Sr}/^{86}\text{Sr}$ values as a consequence of different ages, original Rb/Sr values, and initial $^{87}\text{Sr}/^{86}\text{Sr}$. For example, consider the case of a simple igneous rock such as a granite that contains the Sr-bearing minerals plagioclase feldspar, K-feldspar,

hornblende, muscovite and biotite. If these minerals crystallized from the same magma, each mineral had the same $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$ as the parent melt, but different relative proportions of Rb to Sr depending on the lattice-site preference for these two chemically contrasting elements. Typically, Rb/Sr increases in the order plagioclase, hornblende, K-feldspar, muscovite, biotite. Therefore, given sufficient time for production of radiogenic ^{87}Sr , $^{87}\text{Sr}/^{86}\text{Sr}_{\text{present-day}}$ will be different in the minerals, increasing in the same order. The evolution of variable $^{87}\text{Sr}/^{86}\text{Sr}$ in the granite minerals is shown schematically in Figure 18.1, a traditional Rb-Sr "isochron" diagram. Similar differences in $^{87}\text{Sr}/^{86}\text{Sr}$ should likewise occur among catchment minerals derived from multiple lithologic sources (e.g. in catchments nested in glacial deposits), although the order of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ in the minerals may differ from that for the simple granite system. For example, the aggregate of hornblendes derived from numerous sources may have greater $^{87}\text{Sr}/^{86}\text{Sr}$ than the K-feldspar aggregate. Rigorous mineral separate work is required to confirm the order of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ among minerals from any catchment.

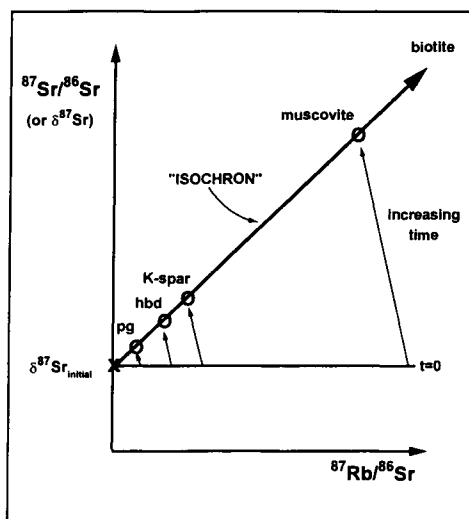


Figure 18.1. Cartoon of Rb/Sr "isochron" for a hypothetical granite mineral system, showing relative distribution of Sr isotope compositions of the minerals after sufficient time for ingrowth of radiogenic Sr. At the time of their formation, each mineral had $\delta^{87}\text{Sr}$ equivalent to the point labeled $\delta^{87}\text{Sr}_{\text{initial}}$. The isotopic composition of each mineral evolves along negatively-sloping lines that represent the gain of one ^{87}Sr atom for each decayed ^{87}Rb . Pg = plagioclase, hbd = hornblende, K-spar = K-feldspar.

The important concept for isotope tracing is that Sr derived from any mineral through weathering reactions will have the same $^{87}\text{Sr}/^{86}\text{Sr}$ as the mineral. Therefore, differences in $^{87}\text{Sr}/^{86}\text{Sr}$ among catchment waters require either differences in mineralogy along contrasting flowpaths, or differences in the relative amounts of Sr derived from the different minerals. The latter situation can arise in several ways. First, because waters approach saturation with respect to different minerals at different rates, progressive changes in water chemistry along flowpaths will cause parallel changes in the relative dissolution rates of, and the amount of Sr derived from the minerals (Plummer et al., 1983). Differences in factors such as pCO_2 and organic acid content of catchment waters may enhance the contrasts in dissolution rates. Secondly,

differences in the relative mobilities of water at scales ranging from inter-grain pores to the catchment level may also profoundly affect $^{87}\text{Sr}/^{86}\text{Sr}$ (Bullen et al., 1996). For example, the chemical and Sr-isotope compositions of immobile waters at a plagioclase-hornblende grain boundary will be different from those at a quartz-mica grain boundary. Third, differences in the relative "effective" surface areas of minerals due to selective "poisoning" of reactive surfaces by organic and/or metal-hydroxide coatings will also cause differences in water chemistry and Sr-isotope composition.

In a fundamental sense, it is unrealistic to expect that waters sampled along contrasting flowpaths through a multi-mineralogic catchment should have similar $^{87}\text{Sr}/^{86}\text{Sr}$. Rather, the waters moving along specific flowpaths react with the minerals in a characteristic manner and gradually approach a distinctive chemical equilibrium over long time-periods. In fact, the chemical composition of stream water in several catchments can be largely explained by the simple mixing of two or more chemically-distinct end members, each having constant composition (Hooper et al., 1990). For example, at Panola Mountain in the Georgia Piedmont, U.S.A. over 80% of the variability in Ca, SO_4 , Na, Mg, SiO_2 , and alkalinity in stream water can be explained by mixing of three waters, each having constant and distinct compositions: organic horizon water, hillslope water, and groundwater (Hooper et al., 1990). Given the range of water residence times typical of small catchments, waters within specific catchment units may have reached some sort of steady-state chemical composition, and thus might be expected to have steady-state and hopefully distinct Sr-isotope compositions.

For catchments nested in multi-mineralic materials, $^{87}\text{Sr}/^{86}\text{Sr}$ in any water parcel usually represents a mixture of Sr from several sources, and thus the exact contributions from individual minerals are difficult to determine with the Sr-isotope data alone. However, when considered in conjunction with water chemistry, the Sr isotopes provide a powerful tool for distinguishing among solute sources. For example, when attempting to develop a reaction model to explain the progressive increase of Mg in groundwater along a flowpath by the dissolution of either hornblende or biotite, the Sr isotopes should provide an effective discriminant because Sr derived from hornblende will be substantially less radiogenic than that from biotite.

Once in solution, Sr should behave chemically in a manner similar to that of the alkaline-earth element Ca (Elias et al., 1982). As a cautionary note, however, we point out that $^{87}\text{Sr}/^{86}\text{Sr}$ is not in itself a sure indicator of Ca sources in a catchment because Sr can be contributed by both Ca-rich and Ca-poor minerals. For example, sodic plagioclase and K-feldspar contain little Ca but substantial Sr, and because of their relatively-high Rb/Sr contain more radiogenic Sr than calcic plagioclase. The isotopic composition of Sr derived from the simultaneous weathering of all three types of feldspars would have an intermediate value that could be similar, for example, to that in hornblende. Based on the Sr isotopes alone, one might erroneously conclude that the bulk of Ca in solution was derived from hornblende, even though dissolution of hornblende may have played only a minor role in water chemical evolution. Clearly the Sr isotopes should be closely integrated with water chemistry in order to identify the important contributing minerals along reaction paths.

A brief discussion of reporting notation is warranted here. Throughout the geologic literature, the isotopic composition of Sr in natural materials has traditionally been reported in terms of a four- to six-place decimal notation for $^{87}\text{Sr}/^{86}\text{Sr}$ (eg., 0.71024). For consistency within this volume, we use a "delta" notation for reporting isotope composition whenever possible. As

with the standard notations for the oxygen and hydrogen isotope systems, the δ -value for a sample relative to a standard is given by the equation:

$$\delta^{87}\text{Sr} = 1000 * [(^{87}\text{Sr}/^{86}\text{Sr}_{\text{sample}}) / (^{87}\text{Sr}/^{86}\text{Sr}_{\text{standard}}) - 1] \quad (18.2)$$

The problem with using the δ -notation for the Sr-isotope system is that there is no consensus concerning what standard to use. Consequently, other researchers have chosen standards such as present-day sea water (Miller et al., 1993), local precipitation (Graustein, 1989), and "bulk earth" to suit their particular needs. Obviously the use of different standards makes inter-study comparisons difficult, although one could argue that the range of isotopic composition at any study site is generally the critical parameter. Regardless, in order to provide a more uniform basis on which to compare Sr-isotope composition between study sites, we propose here that the Sr-standard SRM987 be used as the standard for the delta calculation. This widely-distributed metal from the National Institute of Science and Technology (N.I.S.T.) is used by virtually every isotope laboratory in the world as the replicate standard. The decimal value obtained for the standard over the long term is typically reported in technical documents; in our lab, the value is 0.71024. Therefore, the general use of SRM987 as the basis for the delta calculation will allow direct comparison of both absolute values and ranges of Sr-isotope composition among study sites.

Uranium (U) - thorium (Th) - lead (Pb)

Pb has four stable, naturally-occurring isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb . ^{206}Pb , ^{207}Pb and ^{208}Pb are all radiogenic, and are the end products of complex decay chains that begin at ^{238}U , ^{235}U and ^{232}Th , respectively. The corresponding half-lives of these decay schemes vary markedly: 4.47×10^9 years, 7.04×10^8 years and 1.4×10^{10} years, respectively. In geologic investigations, each radiogenic isotope is typically reported relative to ^{204}Pb . Growth (decay) equations analogous to those for the Rb-Sr system can be written for the U-Pb and Th-Pb systems. The ranges of isotope ratio values for the majority of geologic materials are 14.0 to 30.0 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.0 to 17.0 for $^{207}\text{Pb}/^{204}\text{Pb}$ and 35.0 to 50.0 for $^{208}\text{Pb}/^{204}\text{Pb}$ (Doe, 1970), although numerous examples of values outside these ranges are reported in the literature. Because of the three-component nature of the Pb isotope system, there is no simple means of converting the decimal values for isotope composition into a meaningful δ -notation. Therefore, throughout this chapter Pb isotope compositions are reported in the decimal notation.

As with the Sr isotopes, corrections must be made for stable isotope fractionation both in nature and during analysis. However, there is no stable, non-radiogenic pair of Pb isotopes that can be used as the basis for a fractionation correction. To circumvent this problem, Pb isotope analyses are typically corrected for fractionation during analysis using factors determined by repeated analyses of some Pb standard, such as the N.I.S.T. SRM 981, 982 and 983 reference materials. However, there is no obvious means of correcting for possible fractionation in nature; thus, we assume that the Pb isotopes do not fractionate perceptibly in nature due to their high mass values. Although probably valid, the uncertainty associated with correcting for analytical fractionation renders Pb isotope analyses inherently less precise than those for Sr. Fortunately, the range of Pb isotope composition observed in nature is substantial.

The utility of the U-Th-Pb isotope system lies in the fact that in a single rock, individual minerals attain diagnostic Pb-isotope signatures due to long-lived differences in U/Pb, Th/Pb,

and Th/U. An example is shown in Figure 18.2, which compares the uranogenic and thorogenic Pb-isotope compositions of primary aluminosilicate minerals separated from soils developed on granitoid alluvium near Merced, California (Bullen et al., 1997). Because feldspars incorporate Pb but do not have lattice positions for U and Th, they have relatively unradiogenic Pb-isotope compositions compared to those of hornblende and micas that both have lattice positions for the transuranics and incorporate U- and Th-rich trace phases. Hornblende tends to have greater Th/U, and thus greater $^{208}\text{Pb}/^{204}\text{Pb}$ at given $^{206}\text{Pb}/^{204}\text{Pb}$ than that in micas because of the preferential incorporation of trace phases such as Th-rich monazite in hornblende and U-rich zircon in biotite. Although resistant to weathering themselves, these trace phases provide radiogenic nuclides to the lattices of their ferromagnesian hosts through the alpha-particle recoil processes that accompany spontaneous decay of ^{232}Th and ^{238}U . Because U, Th and Pb behave so different geochemically, the fact that the Pb isotope composition of any material is the composite of the three independent decay chains creates the potential for greater differences in isotope values between minerals of a single rock relative to that for the Rb-Sr system.

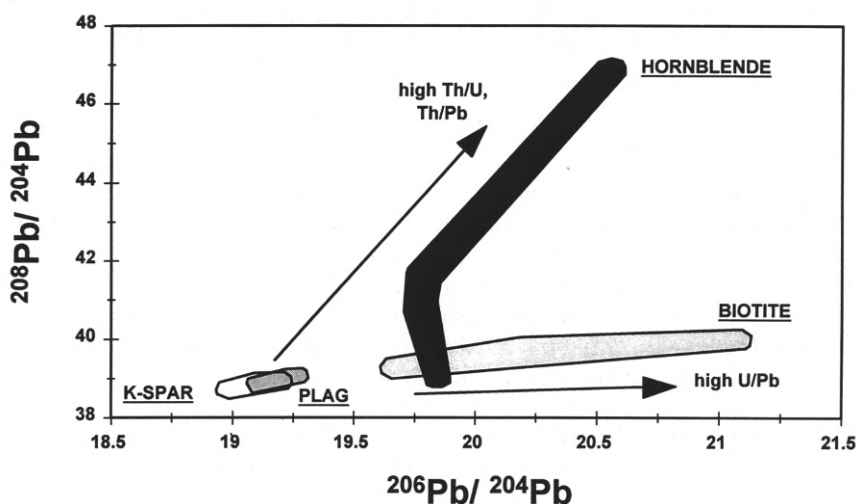


Figure 18.2. Pb isotope evolution in minerals from Merced (CA) granitoid alluvial soils, showing relative distribution of Pb isotopic compositions of the minerals after sufficient time for ingrowth of radiogenic Pb. At the time of their formation, each mineral had the isotopic composition of the K-feldspars. Minerals follow different evolutionary trajectories on this diagram depending on their Th/U and U/Pb ratios. Kspar = K-feldspar, plag = plagioclase.

Carbon

Carbon has two stable, naturally-occurring isotopes: ^{12}C and ^{13}C . Neither isotope is radiogenic, and therefore differences in $^{13}\text{C}/^{12}\text{C}$ among minerals, waters and gases are the result of isotopic fractionations in various biogeochemical environments. Carbon isotope compositions are reported in a δ -notation where:

$$\delta^{13}\text{C} = 1000 * [(\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{sample}}) / (\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{standard}}) - 1] \quad (18.3)$$

The standard for computation of $\delta^{13}\text{C}$ is the Peedee Belemnite, abbreviated PDB. In general, analytical precision for $\delta^{13}\text{C}$ is about 0.1‰.

Different carbon-bearing materials in catchments can have characteristic $\delta^{13}\text{C}$ values. Carbonate rocks typically have $\delta^{13}\text{C}$ values of $0 \pm 5\text{‰}$; hydrothermal carbonates can be outside this range. Plants convert atmospheric carbon ($\delta^{13}\text{C} = -7\text{‰}$) to organic compounds via photosynthesis. There is a bimodal distribution of the $\delta^{13}\text{C}$ values of terrestrial plants resulting from differences in the photosynthetic reaction utilized by the plant. C_3 plants (e.g. pine and apple trees) have $\delta^{13}\text{C}$ values of about -25‰ (range: -22 to -33‰), whereas C_4 plants (e.g. corn) have $\delta^{13}\text{C}$ values of about -12‰ (range: -10 to -20‰) (Bender, 1971; Deines, 1980). $\delta^{13}\text{C}$ of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) in catchment waters is generally in the range of -5 to -25‰ . More negative values usually indicate the presence of oxidized methane.

The primary reactions that produce DIC are: (1) weathering of carbonate minerals by acidic rain or other strong acids; (2) weathering of silicate minerals by carbonic acid produced from the dissolution of biogenic soil CO_2 by infiltrating water; and, (3) weathering of carbonate minerals by carbonic acid. The first and second reactions produce DIC having identical $\delta^{13}\text{C}$ to that in the reacting carbonate or carbonic acid, respectively, whereas the third reaction produces DIC with a $\delta^{13}\text{C}$ value exactly intermediate between the compositions of the carbonate and the carbonic acid. Consequently, without further information, DIC produced solely by the third reaction is identical to, and cannot be distinguished from DIC produced in equal amounts from the first and second reactions.

If the $\delta^{13}\text{C}$ values of the reacting carbon-bearing species are known and the $\delta^{13}\text{C}_{\text{DIC}}$ of the stream determined, in theory we can calculate the relative contributions of carbonate minerals and carbonic acid to the production of stream DIC and carbonate alkalinity, assuming that: (1) carbonate mineral dissolution occurs under closed-system conditions (i.e. isolated from potential reservoirs of CO_2 in the soil zone or atmosphere); and (2) there are no other sources or sinks for carbon (Kendall et al., 1992). With additional chemical or isotopic information, $\delta^{13}\text{C}$ values can be used to estimate proportions of DIC derived from the three reactions listed above. However, other processes that may complicate the interpretation of stream $\delta^{13}\text{C}$ values include CO_2 degassing, carbonate precipitation, exchange with atmospheric or soil CO_2 , carbon uptake by aquatic organisms, methanogenesis, and methane oxidation (Kendall, 1993). Correlation of variations in $\delta^{13}\text{C}$ with changes in chemistry and other isotopes such as Sr, factors that will not be affected by these processes, may provide evidence that such processes are insignificant.

18.1.3 Geological/environmental factors leading to successful tracing with solute isotopes

Isotope hydrogeologists are often asked whether isotopic techniques can help answer specific research questions. Here we present some basic criteria that researchers can apply to their own catchments to determine whether solute isotopes will provide important information. First and foremost, for solute isotopes to be effective tracers of weathering reactions and water flowpaths, there must be significant contrasts in isotopic composition among catchment minerals and weathering solutions. The C isotopes are inherently excellent tracers of weathering reactions involving carbon-bearing rocks and/or acids. For Sr and Pb isotopes, age of the minerals and distinctiveness compared to atmospheric/anthropogenic inputs are the important considerations. For example, Sr isotopes would be a poor tracer of differential mineral weathering in a catchment set in a volcanic terrain so young that insufficient time has passed

to allow development of significant differences in $\delta^{87}\text{Sr}$ among catchment minerals. At the same catchment, however, $\delta^{87}\text{Sr}$ could be a useful tracer for distinguishing contributions from weathering and precipitation. Secondly, the weathering solutions must be capable of carrying the tracer nuclides away from the weathering site. For example, even for a catchment set in an old granitic terrain, Pb isotopes would be an ineffective tracer if the weathering solutions were unable to mobilize the Pb liberated from the lattices of the weathered phases.

For Sr, C and Pb isotopes to be useful as tracers of water flowpaths, the rock-water reactions along these flowpaths must impart distinctive isotopic compositions to the waters. Isotopic compositions of waters developed along shallow and deep flowpaths are likely to be distinct because of the consequent differences in water chemistry and residence times. For example, in variably-weathered soil profiles, chemical evolution along shallow pathways is dominated by cation exchange and dissolution of remnant resistant phases such as K-feldspars and perhaps clays. In contrast, chemical evolution along deep pathways, perhaps at the saprolite-bedrock interface, is dominated by dissolution of more abundant reactive phases such as ferromagnesian minerals, plagioclase feldspar and calcite. A similar isotopic contrast between shallow and deep pathways could be established if the atmospheric/anthropogenic input to the catchment is isotopically distinct from that due to weathering, and shallow flowpaths transport solutes derived primarily from atmospheric sources. Differences in mineral soil thickness could also promote variability in radiogenic isotope signatures developed along different flowpaths.

Differential access of water to reactive minerals along flowpaths is an additional consideration. For example, waters having different chemical composition can develop in response to variability of their residence times in a given portion of the catchment. Infiltration waters traveling slowly by tortuous matrix flow may inherit solutes from a different mineral assemblage than water that is flushed through the system more quickly via macropores, even though the paths of both waters are relatively shallow or traverse the same distance (Kendall, 1993). Likewise, different water compositions can develop in fractured rock, where the fractures might act as preferential conduits and may be lined by distinctive minerals such as calcite. The combined use of Sr and C isotopes may provide an especially powerful tracer of flow through this type of fracture system.

In order to assess the applicability of any solute isotope system as a tracer, each researcher must consider the issues being addressed in their particular catchment study in light of hydrologic and geochemical factors such as those above. Factors such as age of minerals and heterogeneity of lithologic sources, extent of development of the weathering profile, mobility of fluids and solutes through various portions of the catchment, and sources of atmospheric/anthropogenic inputs to the catchment are all important. Moreover, the researcher must recognize that conclusions based on application of a single isotope system are likely to be ambiguous, and thus use of the multi-isotope approach in concert with available chemical and hydrologic data is necessary to reduce the ambiguity.

18.2 Influences on Isotopic Composition of Sr, Pb and C in Catchment Waters

18.2.1 Lithologic controls on the isotopic composition of strontium and lead

From a solute perspective, catchments can be viewed as "reaction vessels" through which meteoric waters are processed. In the absence of gross lithologic variability, it is tempting to

think that the weathering contribution of a catchment might have a unique, characteristic "signal", determined primarily by the particular mineralogy. However, even in catchments characterized by uniform mineralogic distribution, numerous lithologically-controlled factors such as mineral dissolution rate, cation exchange capacity, fluid mobility, and reaction kinetics at mineral surfaces together determine the net solute inventory added to an evolving water parcel along a flowpath (Bullen et al., 1996). In this section, we discuss how these factors affect the isotopic composition of Sr and Pb in catchment waters. The most fundamental observation is that a range of both Sr and Pb isotope compositions can be attained from a multi-mineralic source material because of isotopic variability among the constituent minerals. Therefore, one should not expect a single, characteristic isotope signal from weathering processes in a catchment. This point is particularly critical when attempting to estimate atmospheric/anthropogenic inputs to the catchment.

Differential weathering rates of minerals

It is now widely recognized that minerals dissolve or react at different rates, depending on a variety of factors such as mineral composition and structure, and temperature and chemistry of weathering solutions. In a multi-mineralic system, these differential weathering rates should result in progressive changes in mineral proportions and net solute load with time and flowpath length. In theory, one could predict the isotopic composition of Sr and Pb provided by weathering based on the knowledge of the constituent minerals and their rates of dissolution. Unfortunately, estimation of weathering rates at individual catchments is problematic at best due to the assumptions inherent to the reaction models traditionally used to make those estimates (e.g., the estimates are no better than the assumptions made about parameters not easily measured). Moreover, there continues to be a nagging discrepancy between rate estimates calculated for weathering in the field compared to those determined in laboratory experiments (Paces, 1983; Velbel, 1985; White and Peterson, 1990). Although the reaction models are clearly becoming more powerful, they are still too simplistic. Likewise, although the laboratory experiments are becoming more complex, they still fail to accurately simulate the effects of long-term weathering under field conditions. A key unknown in all discussions of weathering is how dissolution rates of minerals change with progressive weathering and evolution of weathering solutions in a multi-mineralic catchment.

In an attempt to assess weathering in a simple granitoid system, White et al. (1996) and Bullen et al. (1997) reported on mineralogic, chemical and isotopic studies of a soil chronosequence from the Merced River drainage in central California (Harden, 1987). The soils range in age from 10 Ka to 3 Ma, and are developed on successive deposits of glacial alluvium derived from a geographically-restricted group of Sierra Nevada granitoid plutons. These alluvial deposits probably had similar mineralogies and bulk compositions, and their constituent minerals clearly had similar Sr- and Pb-isotope compositions prior to soil development. Hydrologically the system has probably been dominated by vertical infiltration of precipitation over the 3 Ma span of soil development.

Based on progressive changes in observed mineral proportions in six members of the chronosequence, mineral weathering rates apparently decrease in the order biotite, hornblende, plagioclase and K-feldspar. This order of mineral weathering is consistent with that determined in other studies of weathering in granitoid terrains (Lasaga, 1984). The calculated average dissolution rate for plagioclase ($10^{19.9}$ mol/cm²/s) is actually greater than that calculated for hornblende ($10^{20.1}$ mol/cm²/s), but the far greater reactive surface area on hornblende grains

results in its greater effective weathering rate. K-feldspar is clearly the most resistant phase to weathering, and is the only primary aluminosilicate mineral remaining in the 3 Ma soils (White et al., 1996). The inferred order of mineral weathering is likewise supported by trends in the isotopic composition of Sr that is exchangeable from the soils using pH-buffered ammonium acetate. Exchangeable Sr is most radiogenic in the youngest soils, consistent with a preferential contribution of relatively radiogenic Sr from biotite, and becomes less radiogenic with soil age, reflecting a progressively greater contribution of relatively unradiogenic Sr from plagioclase and hornblende (Bullen et al., 1997).

On the other hand, the mineralogic and isotopic data suggest a more complex interpretation for the origin of Sr in the weathering solutions. For example, although biotite abundance decreases in the first 40 Ka of weathering, its abundance remains essentially constant through the remainder of the 3 Ma history. Furthermore, although biotite separated from the soils is the most radiogenic of the original granitoid phases, its $\delta^{87}\text{Sr}$ is substantially less than, and its Sr content is greater than that in biotites separated from the granitoids themselves (compared to analyses reported by Kistler et al. (1986)). These observations suggest that biotite "weathering" actually involves uptake of relatively unradiogenic Sr from the weathering solutions. Further confounding the issue is the fact that although exchangeable Sr is most radiogenic in the youngest soils, its $\delta^{87}\text{Sr}$ is consistently nearly identical to but slightly less than that in K-feldspars separated from the soils. One could argue that K-feldspar, the granitoid mineral most resistant to weathering based on observed mineral proportions, actually supplies the greatest proportion of Sr to weathering solutions in the youngest soils, perhaps due to leaching of defect sites on K-feldspar grain surfaces in the presence of dilute solutions (Bullen et al., 1997).

Another weathering scenario in which a presumably resistant mineral phase provides a greater solute contribution than supposedly more reactive phases occurs during the evolution of dilute groundwaters in a sandy silicate aquifer in northern Wisconsin (Bullen et al., 1993; Bullen et al., 1996). In this case, the early chemical evolution of groundwaters emanating from a dilute seepage lake is dominated by contributions from plagioclase, as evidenced by strong progressive increases in dissolved Na, Si and particularly Sr. However, after approximately 15 years of evolution along the flowpath, the rate of Na and Sr increase slows dramatically whereas Ca and Mg concentrations continue to rise, presumably as dissolution of relatively Sr-deficient calcic ferromagnesian phases begins to dominate. The parallel behavior of Na and Sr in this situation argues against a simple cation exchange mechanism to control their concentrations in the evolving waters. Furthermore, the progressive decrease in plagioclase contribution in favor of the ferromagnesian phases along the flowpath is consistent with both mass balance and reaction path models. Clearly the simple rules for the behavior of reactive phases in granitoid weathering systems must be applied with caution, particularly when attempting to interpret isotopic variations along a flowpath.

Reaction kinetics at mineral surfaces

Traditionally, the susceptibility of a given mineral to weathering has been estimated by its presumed or calculated extent of disequilibrium with specific weathering solutions. With respect to conditions at the earth's surface, the ferromagnesian silicate minerals are more out of equilibrium than the feldspars, and the plagioclase feldspars are more out of equilibrium than the K-feldspars. However, an increasing number of studies of reaction kinetics at mineral surfaces have documented that factors other than mineral composition are critical to the determination of mineral dissolution rates (Schott and Petit, 1987; see also reviews by White,

1990 and Blum, 1994). Of key importance is the concept that weathering solutions must be able to access the soluble ions within the mineral lattice or structure, and factors that either limit or enhance such access will have a pronounced effect on measured dissolution rates.

Based on calibrations using simple mineral-fluid systems, the degree of undersaturation of a mineral phase with respect to a complex fluid chemistry can be estimated using any of a number of geochemical computer codes (e.g., WATEQ (Truesdell and Jones, 1974), SOLMINEQ.88 (Kharaka et al., 1988), NETPATH (Plummer et al., 1991)). The mineral dissolution rate is presumably correlated with the degree of undersaturation, and is generally assumed to slow in an exponential manner as saturation is approached. However, recent experimental work in the system albite-H₂O has demonstrated that feldspar dissolution is more closely approximated by a step function, such that dissolution slows abruptly at some critical degree of undersaturation. The step decrease in dissolution rate is presumably related to a decreased ability of the fluid to form etch pits on the surfaces of feldspar grains (Burch et al., 1994). This sort of step function in part explains the fact that laboratory dissolution experiments using fresh mineral grains and distilled water progress at rates two to three orders of magnitude greater than those observed in field studies of weathering (White and Peterson, 1990). The obvious implication is that for a given catchment mineralogy, the relative contributions of solutes from the various minerals, and thus the isotopic composition of those solutes can change considerably as a result of subtle changes in the chemical composition of the weathering solutions, particularly in dilute systems.

Another factor that probably limits access of weathering solutions to a particular mineral phase is the formation of secondary minerals that use the surfaces of the primary minerals as growth platforms. In most silicate weathering systems, solutions quickly become saturated with respect to clay minerals and, under oxidizing and neutral to alkaline conditions, iron oxyhydroxides. Intuitively, if "poisoning" or "armoring" of mineral surfaces by these secondary minerals is to occur, the likely substrate for the initiation of secondary mineral formation will be the surfaces of the relatively unreactive primary minerals. In contrast, secondary mineral growth nuclei that attempt to attach to more reactive phases should be quickly disrupted as vigorous etch pitting of the surfaces of those reactive phases progresses (Velbel, 1993). Clearly, detailed optical and chemical examination of mineral surfaces along specific flowpaths in catchments is required in order to document the importance of preferential mineral surface "poisoning" or "armoring" as means of restricting access of weathering solutions to certain mineral phases.

Cation exchange

The cation exchange pool at any location along a flowpath reflects contributions from both mineral weathering reactions and atmospheric and anthropogenic inputs to the watershed. Presumably, mobile elements such as Sr are efficiently exchanged at mineral surfaces, and the ratio of a cation such as Sr to other exchangeable cations (e.g., Sr/Ca, Sr/Mg, Sr/Na) in the exchange pool remains relatively constant for given clay mineralogy, water pH and water chemistry; see Davis and Kent (1990) for a thorough review of the theoretical bases of cation exchange and mineral surface complexation processes. Once established, the exchange pool effectively buffers the water chemistry against minor fluctuations. Strong perturbations to the system, such as changes in pH caused by acid rain input, produce changes in both the concentration of Sr and other exchangeable cations, as well as the ratio of Sr to those cations in the exchange pool. Regardless, given sufficient time for a steady-state situation to develop, the fluid and the exchange pool should have identical $\delta^{87}\text{Sr}$. Unfortunately, there is currently little data on the time required to attain a steady state.

Departures from steady-state, such as the rapid movement of chemically-diverse infiltration waters into the unsaturated zone via macropores, can provide a situation in which the fluid and exchange pool will be out of exchange equilibrium. The system will then respond to restore a new equilibrium by mineral dissolution and ion exchange, although the time factor for Sr isotopes has not been determined experimentally. Regardless, catchment waters transported to a certain depth along macropores may have substantially different $\delta^{87}\text{Sr}$ than waters that have migrated to the same depth via matrix flow, and may not be in Sr-isotopic equilibrium with the exchange pool at that depth. For example, our unpublished data for two clay-dominated catchments in Georgia and Puerto Rico show that the soil waters are not in Sr-isotopic equilibrium with the soil cation exchange pool at the sampling depths, as measured by ammonium acetate exchange. Moreover, a model for the temporal evolution of $\delta^{87}\text{Sr}$ of the cation exchange pool in the Merced (CA) chronosequence soils discussed previously requires that exchange efficiency for Sr must decrease significantly as soil age increases (Bullen et al., 1997). Clearly, laboratory experiments to determine the time required for isotopic equilibration of Sr between fluids and the exchange pool in various soil types are necessary.

In contrast to Sr, Pb is strongly sorbed onto mineral surfaces and bound by transition metal-oxyhydroxides. Pb is transported as a solute only in low-pH solutions; in higher pH environments, it may be transported as organo-Pb complexes (Erel et al., 1991). Therefore, even though a relatively Pb-rich phase such as a feldspar may be reacting along a flowpath, the Pb from that feldspar has little tendency to enter solution unless pH is low or total organic carbon (TOC) is high; the Pb otherwise becomes immediately bound at surface sites or is incorporated in precipitating secondary phases. These characteristics make Pb difficult to use as a tracer of weathering reactions and water flowpaths in young systems in which solution pH tends to be near neutral and the cation exchange pool is developing rapidly in response to clay formation, unless TOC is particularly high. On the other hand, the Pb isotopes can be an especially powerful tracer for older, clay-dominated weathering systems in which the pH of soil solutions is relatively low, or for systems in which transport of Pb as organo-Pb complexes is an important process.

Fluid mobility in multi-mineralic matrices

As a dilute fluid migrates through a multi-mineralic matrix, solute concentrations increase in response to dissolution reactions. The thermodynamic stability of any mineral with respect to the chemistry of the fluid in large part determines the rate at which that mineral reacts. Any parcel of the fluid in contact with a given mineral will continue to scavenge solutes from that mineral as long as undersaturation persists. Stagnant pore fluids in contact with only a single reactive mineral such as a feldspar grain in a quartz-rich matrix can evolve chemically only to a limited extent determined by the saturation indices. On the other hand, more mobile fluids have a high probability of coming into contact with all reactive phases of the assemblage, and thus water chemistry will reflect contributions of solutes from several minerals. With progressive chemical evolution, the water soon reaches saturation with respect to minerals such as clays and iron oxyhydroxides, forcing their precipitation and removing solutes inherited from the reactant minerals. The formation of secondary minerals thus stimulates continued dissolution of the reactant minerals. Chemical evolution can thus continue to form relatively concentrated solutions.

In general, model calculations suggest that catchment waters are substantially more undersaturated with respect to ferromagnesian silicates than they are with respect to feldspars

(Garrels and Mackenzie, 1967; Schott et al., 1981; Siegel and Pfannkuch, 1984), which supports the observation that feldspars are the most resistant reactive phases in silicate weathering systems over time. Thus, under stagnant conditions and neglecting potentially important factors such as mineral surface poisoning by secondary precipitates, fluid in contact with ferromagnesian minerals should evolve to a greater extent than fluid in contact with feldspars. Furthermore, the chemistry and solute isotope composition of the bulk stagnant fluid should reflect a greater contribution from the ferromagnesian phases than would a fluid formed under more mobile conditions. An additional complexity might arise if the catchment consisted lithologically not only of individual mineral grains but multi-mineralic rock fragments as well. Even under stagnant conditions, the multi-mineralic fragments would act as minute reactive centers around which protracted chemical evolution could occur (Bullen et al., 1996). When this stagnant fluid is later mobilized, the bulk fluid would have chemistry and solute isotope composition reflecting a greater relative contribution from the multi-mineralic fragments than would a fluid formed under mobile conditions. A case study that describes this phenomenon is presented in a later section.

18.2.2 Atmospheric/anthropogenic inputs of Sr, Pb, and C

Several investigators have reported Sr concentrations and isotopic compositions in precipitation at catchments (e.g. Gosz and Moore, 1989; Graustein, 1989; Miller et al., 1993; Bullen et al., 1996, 1997). Precipitation has measurable Sr, with concentrations on the order of several ppb and $\delta^{87}\text{Sr}$ close to that of present-day seawater ($\delta^{87}\text{Sr} = -1.4\text{‰}$). Our current database of approximately 50 samples of precipitation from numerous watersheds throughout the United States and Puerto Rico show a range of $\delta^{87}\text{Sr}$ from -3.50‰ to $+1.50\text{‰}$. Dry deposition also has measurable Sr, with $\delta^{87}\text{Sr}$ reflecting that of particulates possibly derived from great distances from the catchment. The relative importance of external and internal contributions of Sr will obviously vary between catchments, and may be difficult to determine if the isotopic composition of atmospheric Sr overlaps that of internal catchment minerals.

Throughfall provides the main Sr input to the catchment surface, and is typically dominated by recycled Sr that has been taken up by plant roots and exuded at leaf surfaces (Bailey et al., 1996). In most catchments, Sr mobilized from the soil zone should be well-averaged, with $\delta^{87}\text{Sr}$ reflecting the local extent of mineral weathering. For catchments in which weathering extent is spatially variable, $\delta^{87}\text{Sr}$ of root uptake and thus of throughfall will likewise be variable. External sources of Sr are generally of minor importance for catchment waters, although significant contributions from aerosols have been documented; the extent of those contributions is dependent primarily on canopy type (Graustein and Armstrong, 1983; Gosz and Moore, 1989; Miller et al., 1993; Clow et al., 1997).

In contrast to Sr, Pb is both highly particle reactive and easily complexed by organic species (Davis and Kent, 1990). Dissolved Pb concentrations in catchment waters are thus extremely low, typically less than 1 ppb, and highly susceptible to contamination. Although necessitating extreme care during sample collection and laboratory preparation, these characteristics make Pb isotopes an especially sensitive tracer of atmospheric/anthropogenic inputs to a catchment. Pb derived from external sources enters the catchment either as dry deposition or in precipitation, and is effectively bound in the organic-rich, upper few centimeters of soil (Erel et al., 1991). Waters mobilized from this shallow zone will carry a small proportion of this Pb

as organo-Pb complexes. If sufficiently distinct isotopically from catchment minerals and thus from waters developed in the mineral weathering zone, the atmospheric/anthropogenic Pb becomes a unique tracer of both infiltration waters and waters mobilized along shallow flowpaths through the O-horizon, as demonstrated for a headwater catchment in Vermont by Bullen et al. (1994). This application is analogous to the use of DOC as a tracer of shallow flowpaths (Hornberger et al., 1994).

Erel et al. (1991) took advantage of the different Pb isotope compositions of atmospherically-derived and rock weathering-derived Pb sampled at a Sierran stream to demonstrate that Pb in stream water during snow melt is supplied primarily from the organic soil accumulation reservoir. They further pointed out that whereas rock weathering-derived Pb should be relatively constant in isotopic composition over time, the isotopic composition and amount of atmospherically-derived Pb has changed markedly over time. This change is due primarily to the effective elimination of Pb additives to automobile gasoline since the 1960's. The success of efforts to reduce this source of Pb pollution is clearly recorded as progressively-lessened Pb concentrations in growth rings of corals from the western Atlantic Ocean (Patterson and Settle, 1984). Therefore, in addition to thorough analysis of potential lithologic sources of Pb, understanding the atmospheric-Pb deposition history at any catchment is essential to successful interpretation of the Pb isotope variations in catchment waters. Detailed isotopic analysis of Pb in throughfall and open-air precipitation at any catchment should help to differentiate Pb derived from local sources (i.e., dust from agricultural operations or nearby industrial emissions) from generally well-averaged regional/global "atmospheric" Pb.

The contribution of C as DIC from precipitation is negligible for most catchment systems. For rain with a pH of 4 and temperatures in the range of 10-25°C, the equilibrium carbonic acid content is ~ 10-20 μ molar (Stumm and Morgan, 1980). If one makes the reasonable assumption that the carbonic acid is in isotopic equilibrium with atmospheric CO₂ (-7‰), it would have a $\delta^{13}\text{C}$ value of -8‰ (Deines et al., 1974). Because very little rain falls directly on the stream channel, as the rain flows over and through the soil the DIC has ample opportunity to exchange isotopically with soil CO₂. Therefore, the contribution of DIC from precipitation to streamflow is probably much less than the total atmospheric input. The effect of the atmospheric source of DIC is likely to be more significant in the winter rainy season than during the summer because of lower average DIC values of the stream, lower rates of CO₂ production in the soil, and higher ratios of runoff to infiltration in the winter and spring (Kendall, 1993).

On the other hand, relative contributions of DIC from carbonate minerals in dry deposition may be considerable, as has been postulated for several alpine catchments such as Loch Vale, Colorado (Clow et al., 1993). Unfortunately, it is unlikely that carbonates in dry deposition will have sufficiently different $\delta^{13}\text{C}$ than that of carbonates in catchment lithologies for $\delta^{13}\text{C}$ to be useful as a tracer of atmospheric input to the catchment. However, because carbonates typically contain considerable Sr, the combined use of C and Sr isotopes may provide a powerful means of distinguishing internal and external sources of carbonate contributions to catchment waters (Clow et al., 1997).

18.2.3 Effects of organic and inorganic cycling on isotopic composition of carbon

The biosphere, and particularly a number of soil processes have a tremendous influence on the $\delta^{13}\text{C}$ of DIC in catchment waters. Soil CO₂ is comprised mainly of a mixture of atmospherically

derived ($\delta^{13}\text{C} = -7\text{‰}$) and microbially-respired CO_2 . Respiration is a type of biologic oxidation of organic matter, and as such produces CO_2 with approximately the same $\delta^{13}\text{C}$ value as the organic matter (Park and Epstein, 1961); hence, areas dominated by C_3 plants should have soil CO_2 with $\delta^{13}\text{C}$ values around -25‰ . The $\delta^{13}\text{C}$ of soil CO_2 can also be affected by fermentation which produces methane ranging in composition from -52 to -80‰ (Stevens and Rust, 1982). As fermentation progresses, the compositions of the CO_2 or DIC byproducts become increasingly enriched in $\delta^{13}\text{C}$ (Carothers and Kharaka, 1980). The carbon produced would be more enriched in ^{13}C than calcite, with values greater than $+10\text{‰}$ not uncommon. Oxidation of methane produces CO_2 with approximately the same composition as the original methane. Reduction of sulfate during degradation of organic matter having $\delta^{13}\text{C}$ of about -25‰ produces DIC of about -20‰ (Presley and Kaplan, 1968).

If DIC in soil water or groundwater exchanges isotopically with other carbon-bearing species, then the isotopic signatures may be blurred and conservative mixing of two distinctive end-member compositions cannot be assumed. The evolution of the isotopic compositions of carbon-bearing substances in uncontaminated systems where carbon is derived from carbonate minerals and soil CO_2 is controlled by two limiting cases: open systems where carbonate reacts with water in contact with a gas phase with a constant $p\text{CO}_2$, and closed systems where the water is isolated from the CO_2 reservoir before carbonate dissolution (Deines et al., 1974). The conditions under which carbonate is dissolved fall between these two extremes, both of which assume water residence times long enough for significant isotope exchange between the gas and the aqueous phase to take place.

The predominant carbon species at typical soil pH values of about 5 to 6 is carbonic acid. The equilibrium isotope fractionation between CO_2 and carbonic acid is 1‰ (Deines et al., 1974). DIC produced by the dissolution of calcite ($\delta^{13}\text{C} = 0\text{‰}$) by carbonic acid ($\delta^{13}\text{C} = -22\text{‰}$) has a $\delta^{13}\text{C} = -11\text{‰}$. If this dissolution occurs under open-system conditions, the DIC would exchange with the soil CO_2 reservoir (-21‰) and reach a $\delta^{13}\text{C}$ value of about -22‰ , thus eliminating any carbon isotopic evidence that half the DIC was derived from dissolution of calcite. Of course, if the $\delta^{87}\text{Sr}$ of calcite were distinctive relative to the $\delta^{87}\text{Sr}$ of other catchment minerals, dissolution of the calcite may have left its "signature" in the $\delta^{87}\text{Sr}$ of the water.

The carbon in subsurface waters that flow into streams is not in chemical and isotopic equilibrium with the atmosphere. For example, CO_2 concentrations in the soil zone are often as high as 5%. Therefore, because the atmospheric concentration is about 0.03%, CO_2 is rapidly lost as soil water seeps into a stream bed. Laboratory experiments performed by Mook (1968) indicate that the $\delta^{13}\text{C}$ of DIC rapidly increases by about 0.5‰ during degassing. Furthermore, isotopic exchange between DIC and atmospheric CO_2 is inevitable. In streams with pH values of from 5 to 6 and temperatures of 20°C , the equilibrium $\delta^{13}\text{C}$ of stream DIC should be around -8‰ . Hence, if the residence time of water in the stream is long enough, the $\delta^{13}\text{C}$ of DIC will gradually approach -8‰ . However, because there is usually no evidence of any increase in $\delta^{13}\text{C}$ downstream besides the 0.5‰ caused by degassing (Kendall, 1993) isotopic exchange between stream DIC and atmospheric CO_2 does not appear to be a problem in the first and second-order streams of forested catchments.

Additional in-stream processes can affect the $\delta^{13}\text{C}$ of DIC. Assimilation of DIC by aquatic organisms produces organic material with a composition about 30‰ depleted in ^{13}C relative to the composition of carbon utilized (Rau, 1979), resulting in an increase in the $\delta^{13}\text{C}$ of the

remaining DIC. In contrast, precipitation of calcite will cause a decrease in the $\delta^{13}\text{C}$ of the remaining DIC, due to the equilibrium fractionation between calcite and DIC of about 2‰.

If any of these soil-zone or in-stream processes are significant sources or sinks of carbon, they may complicate the interpretation of stream $\delta^{13}\text{C}$ values (Kendall, 1993). However, correlation of variations in $\delta^{13}\text{C}$ with changes in hydrology, chemistry, or other isotopes such as Sr may provide evidence that such processes are insignificant. For example, lack of any systematic increase in $\delta^{13}\text{C}$ downstream, particularly in the summer when flow is slow, would argue against significant exchange of stream DIC with atmospheric CO_2 . Similarly, low pH of stream water would rule out precipitation of calcite as a means to decrease $\delta^{13}\text{C}$ of stream DIC. Finally, a strong positive correlation between $\delta^{13}\text{C}$ and DIC of stream water, and a typically negative correlation between these parameters and $\delta^{87}\text{Sr}$ together argue convincingly for calcite dissolution.

18.3 Multi-isotope Studies at Selected Watersheds

18.3.1 The combined use of O, H and Sr isotopes to understand differences in chemical evolution along different flowpaths in a sandy aquifer in northern Wisconsin

In aquifers dominated by silicate minerals, groundwater quality is controlled in large part by dissolution of reactive phases such as feldspars and ferromagnesian minerals. Considerable differences in the isotopic composition of Sr can exist among these phases, and thus $\delta^{87}\text{Sr}$ can be a useful discriminant of both the relative contribution of each phase to aquifer chemistry and the relative reactivity of each phase along different flowpaths. We have recognized large variations in $\delta^{87}\text{Sr}$ of groundwater from a sandy silicate aquifer in northern Wisconsin, even though the mineralogic distribution is relatively uniform (Bullen et al., 1996). The aquifer developed approximately 10,000 years ago in glacial outwash derived from a Precambrian terrain. Considering the minerals present in the aquifer sand, the variations in $\delta^{87}\text{Sr}$ imply preferential contributions of Sr from relatively unradiogenic phases such as plagioclase, hornblende, and diopside along some flowpaths, and from more radiogenic phases such as K-feldspar and biotite along others. This hydrologic setting, characterized by numerous seepage lakes nestled in a relatively homogeneous aquifer, is ideal for applying the multi-isotope approach because O and H isotopes can be used to identify distinct flowpaths through the aquifer, and Sr isotopes can then be used to constrain the differing mineral dissolution reactions that must occur along those flowpaths.

In terms of Sr, O and H isotopes, there are two conceptual end-member water components in the system: (1) relatively unradiogenic, evaporated precipitation; and (2) substantially more radiogenic, unevaporated groundwater derived from infiltration of precipitation in the uplands surrounding the lakes. The composition of lakes in the region can generally be described as mixtures of these end-member water types (Figure 18.3). Aquifer recharge plumes that emanate from the compositionally-diverse lakes constitute a third water component, being distinctive relative to the surrounding groundwater in terms of both water isotopes and chemistry. Each of these water components can contribute, for example, to wetland areas, and consideration of the isotopes and chemistry together should provide a means of estimating their relative solute and water contributions.

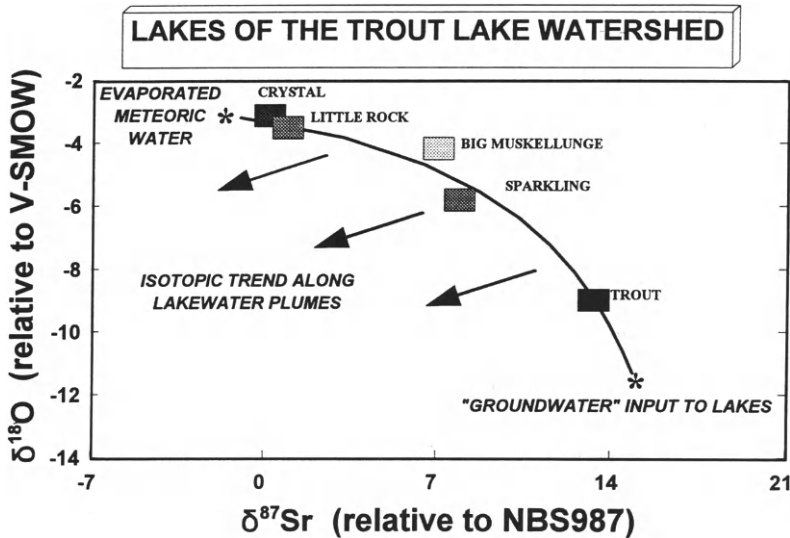


Figure 18.3. Covariation of $\delta^{87}\text{Sr}$ and $\delta^{18}\text{O}$ for five lakes in the Trout Lake watershed of northern Wisconsin. The curve drawn through the points is a best-fit mixing hyperbola between two assumed end-member water types: evaporated meteoric water and unevaporated shallow groundwater that discharges to the lakes. The arrows show the evolutionary trend along plumes of lake water that recharge the aquifer.

Crystal Lake is situated near the top of the watershed and, consequently, has the most chemically-dilute and isotopically-enriched water composition of lakes in the region. $\delta^{87}\text{Sr}$ of the lake is about 0‰, essentially identical to that in precipitation. The strongly evaporated O- and H-isotope signature of Crystal Lake can be used to trace the predominant flowpath (i.e. center of mass) of a plume of water that emanates from the littoral zone of the lake and moves downgradient beneath the narrow isthmus separating Crystal Lake and Big Muskellunge Lake (Figure 18.4). Along this well-constrained flowpath, $\delta^{87}\text{Sr}$ initially decreases with progressive chemical evolution and approaches the value analyzed in plagioclase from the aquifer sand. Na, Si, Sr and to a lesser extent Ca concentrations increase rapidly as $\delta^{87}\text{Sr}$ decreases, as expected of plagioclase dissolution. After approximately 15 years, the flowpath intersects a thin but extensive silt lens, immediately beyond which Sr and Na concentrations and $\delta^{87}\text{Sr}$ stabilize. However, Ca, Mg and Si concentrations continue to increase, suggesting a greater role for dissolution of relatively unradiogenic hornblende and/or diopside at the expense of plagioclase.

Big Muskellunge Lake lies just down-gradient from Crystal Lake and contains a greater component of solute-rich groundwater, yet has far more radiogenic Sr ($\delta^{87}\text{Sr} = +7\text{‰}$). This suggests that groundwater flowpaths other than lakewater plumes are the source of the more radiogenic Sr. In fact, waters sampled from three piezometers driven into the bed of Big Muskellunge Lake at a zone of aquifer discharge have restricted O- and H-isotope compositions that lie on the local meteoric water line, and $\delta^{87}\text{Sr}$ that ranges from +8‰ to +23‰. The most radiogenic sample is from the piezometer nearest to shore, which samples the shallowest groundwater discharge from this portion of the aquifer. The restricted range of water isotope compositions exhibited by the piezometer samples suggests that precipitation input is efficiently averaged within the shallow groundwater system. Elevated $\delta^{87}\text{Sr}$ implies that highly-

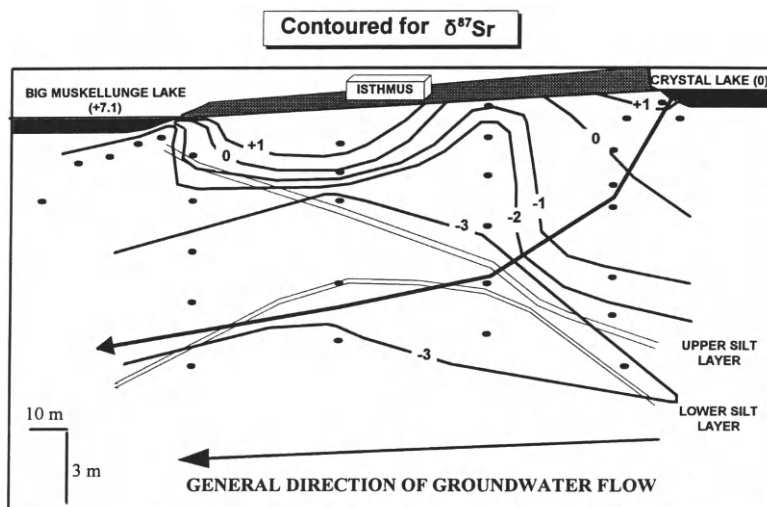


Figure 18.4. Contour diagram of $\delta^{87}\text{Sr}$ in groundwater beneath the isthmus separating Crystal Lake from Big Muskellunge Lake. The dots represent piezometer sampling points. The curved vector emanating from Crystal Lake defines the locus of "heaviest" (most evaporated) groundwater samples, and thus the predominant pathway taken by Crystal Lake water that recharges the aquifer. The locations of two extensive silt layers are shown.

radiogenic minerals such as K-feldspar and biotite have been preferentially sampled along these flowpaths. In one sample of aquifer sand used for experimental studies, K-feldspar and biotite occur together primarily as the major constituents of multi-mineralic rock fragments. A bulk sample of K-feldspar- and biotite-rich fragments separated from the sand has $\delta^{87}\text{Sr} = +19\text{‰}$. $\delta^{87}\text{Sr}$ of the K-feldspar is probably less than this value, whereas that of biotite is probably greater.

One important distinction between the upland and lake water plume flowpaths is that waters may spend considerable time immobilized in the unsaturated zone during infiltration of precipitation through upland areas, whereas the waters along the lake water plumes evolve under saturated and continuously mobile conditions. The results of a laboratory experiment (Bullen et al., 1996) using the aquifer sand indicate that differential mobility along these flowpaths is an important control on $\delta^{87}\text{Sr}$. In this experiment, de-ionized water continuously passed through a column of sand inherits relatively unradiogenic Sr from the minerals, whereas water that is allowed to stagnate in the sand matrix for a period of several hours inherits relatively radiogenic Sr. The entire range of Sr-isotope composition observed in waters from the natural system was observed in the resultant experimental waters.

The implication is that meteoric waters traveling along upland flowpaths obtain their relatively radiogenic Sr during successive periods of stagnation in the unsaturated zone. In contrast, more mobile groundwater, such as the waters along lake water plumes, inherit relatively unradiogenic Sr. We attribute this contrast in Sr flux to differences in the likely distribution of clay-mineral weathering products under stagnant and mobile conditions. For example, dissolution of plagioclase and hornblende provides not only relatively unradiogenic Sr to the weathering solutions, but aluminum destined for clay mineralization as well (Garrels and McKenzie,

1968). In contrast, in young weathering systems more radiogenic Sr is lost from K-feldspar mainly by leaching of near-surface lattice sites (Bullen et al., 1997) and from biotite by inter-layer cation stripping in order to maintain charge balance in the lattice (White and Yee, 1985), with no corresponding loss of Al to form clays. Under stagnant conditions, clay-mineral nuclei should form quickly and effectively "poison" the reactive surfaces of their sources, the phases that contain relatively unradiogenic Sr. Under mobile conditions, clay minerals may form but should be distributed uniformly throughout the aquifer matrix and thus will not limit dissolution of any particular phase.

In many ways this study showcases the power of the multi-isotope approach. For example, in the absence of O and H isotope analyses, flowpaths must be determined by applying hydraulic measurements to hydrologic models. Such models are subject to numerous assumptions such as boundary conditions and degree of physical heterogeneity within the aquifer, and can provide ambiguous results (Krabbenhoft et al., 1994). In contrast, the evaporated isotopic signature of the Crystal Lake plume is clearly traceable through the aquifer, and uniquely defines a flowpath along which chemical compositions record the progressive geochemical evolution of lake water by reaction with aquifer minerals. Even having identified this flowpath, however, it would be difficult to uniquely constrain the mineral dissolution reactions in the absence of Sr isotopes. For example, the increase in Mg along the flowpath could be explained by the dissolution of either hornblende or biotite. However, because these minerals have vastly different $\delta^{87}\text{Sr}$ values, Sr isotopes provide a dependable indicator of which mineral is being dissolved.

This study further demonstrates that the "weathering component" in a multi-mineralic system cannot be assumed to have a single Sr isotope composition, unless the minerals themselves have identical $\delta^{87}\text{Sr}$. Careful experimentation with the natural materials is required to determine the range of $\delta^{87}\text{Sr}$ attributable to weathering, as well as to identify the different processes that can lead to divergent Sr isotope compositions in weathering solutions. Obviously, reaction models that attempt to simulate chemical evolution along watershed flowpaths must be able to incorporate a changing reaction assemblage in the calculations.

18.3.2 Sr, Pb and C isotopes as surrogate tracers of water movement at a catchment nested in calc-silicate rocks, Sleepers River, Vermont

At the Sleepers River Research Watershed in northern Vermont (Shanley et al., submitted), stream chemistry is largely determined by the relative contributions of two predominant flowpaths through glacial till dominated by the underlying Devonian calc-silicate Waits River Formation: shallow flowpaths through the carbonate-free unsaturated zone and deeper flowpaths through carbonate-bearing (less-weathered) materials. Although dissolution of the carbonate fraction of the till along the deeper flowpaths provides the major chemical flux to the streams, variations in ratios such as Ca/Si and Ca/SO₄ both along individual streams and between basins of different scale suggest that pathways through the unsaturated zone likewise contribute to stream chemistry. As a result of storage within and transit through the unsaturated zone, event waters are likely to scavenge Sr, Pb and C that are isotopically distinct from those solutes in shallow groundwater. Furthermore, the isotopic composition of Sr, Pb and DIC in shallow groundwater should vary over the watershed depending on factors such as depth to groundwater and extent of groundwater recharge through the soil zone. In order to better delineate the complex water pathways that provide solutes to the streams, the isotopic

compositions of Sr, Pb and DIC have been analyzed in streamflow, groundwater and soil water collected at several times over a one year period from three catchments within the watershed ranging in size from 20 hectares to 111 km² (Bullen et al., 1994; Kendall et al., 1994). The catchments are characterized by mixed deciduous and coniferous cover and have varying topography and proportions of open space.

Waters in the unsaturated and saturated zones of catchments should have different solute isotope compositions. For example, preferential weathering of minerals that contain relatively unradiogenic Sr (e.g. plagioclase, hornblende, calcite) as well as oxidizing conditions often result in the persistence in the unsaturated zone of minerals that contain relatively radiogenic Sr (e.g., K-feldspar, biotite alteration products). As a result, $\delta^{87}\text{Sr}$ of water from a highly-weathered unsaturated zone should be greater than that in shallow groundwater, although the isotopic composition and flux of atmospherically-derived Sr must be taken into account. Atmospherically-derived Pb, itself well-averaged and often distinct isotopically from Pb supplied by catchment minerals, is initially immobilized as organo-Pb complexes in the O-horizon, and thus is a potential tracer of water that passes through the shallow soil zone (Erel, 1991). The isotopic composition of DIC will vary depending on the particular weathering micro-environment. For example, the main factors that determine the isotopic composition of DIC are the relative proportions of carbonate and silicate minerals, and of carbonic and strong acids in the weathering solutions. Given a particular carbonate:silicate mineral ratio, DIC will become lighter as soils thicken and carbonic-acid weathering dominates. Given a particular mix of carbonic and strong acids, DIC will become lighter as the silicate:carbonate mineral ratio increases.

At Sleepers River, we have recognized a persistent stratigraphy of chemical and Sr isotope compositions of waters. In a relative sense at any site, unsaturated-zone water has low Ca/Si and radiogenic Sr, shallow groundwater has high Ca/Si and unradiogenic Sr, and deeper groundwater has low Ca/Si and radiogenic Sr. Furthermore, Ca/Si of shallow groundwater increases and $\delta^{87}\text{Sr}$ decreases with increasing soil thickness and/or depth to groundwater. This compositional and Sr isotope stratigraphy can be interpreted in terms of decreasing influence of carbonate weathering with depth. For example, calcite has largely been stripped from the shallow soil zone, and thus relatively-radiogenic silicate minerals determine the solute flux to shallow soil waters. On the other hand, calcite is present in the deeper mineral soils, and thus the compositions of deeper soil solutions that contribute significantly to shallow groundwater are probably influenced by calcite weathering. Calcite is likewise present in the deeper groundwater system (i.e. in bedrock), but is apparently more resistant to weathering than are the coexisting silicates. The relative proportions and compositions of waters that move through the shallow soil, deep soil and bedrock portions of the catchment probably determine the relative susceptibility of carbonate to weathering.

Sr isotopes also show correlations with catchment scale. The $\delta^{87}\text{Sr}$ of base flow decreases as basin scale increases (Figure 18.5), and is inversely correlated with both Ca/Si and Ca/SO₄, both of which are greater in shallow groundwaters than in unsaturated-zone waters. This implies a lesser contribution of infiltration waters through the unsaturated zone to baseflow in the larger basins. Moreover, as shown in Figure 18.5, individual stream sampling sites have remarkably uniform $\delta^{87}\text{Sr}$ throughout the year, even during snow melt and other events that result in substantial increases in discharge. However, as more data accumulates for the well-studied headwater catchment W9, a subtle trend is emerging in which $\delta^{87}\text{Sr}$ decreases slightly

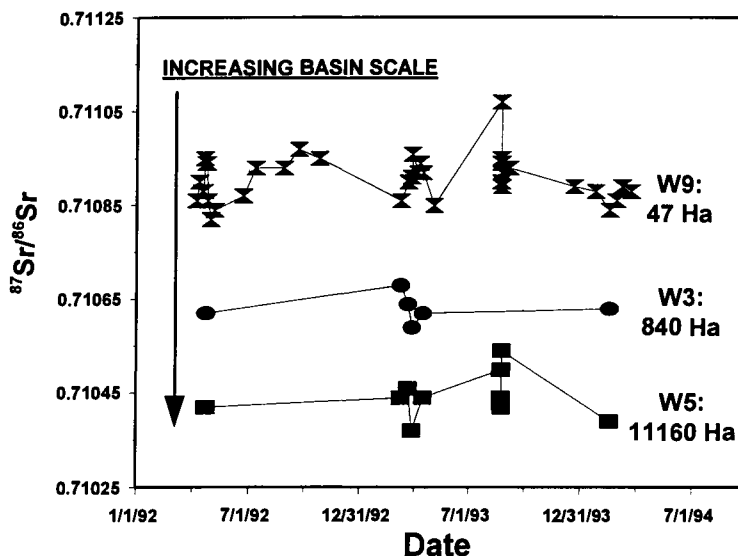


Figure 18.5. Variation of $\delta^{87}\text{Sr}$ over a one-year period for streams measured at the outlets of three catchments of different scale within the Sleepers River research watershed in northern Vermont. Basin scale increases in the order W9-W3-W5, and is inversely correlated with $\delta^{87}\text{Sr}$. The clusters of points during March and April of each year represent the snow melt events.

immediately following snow melt, then steadily increases over the summer months to values observed during the onset of snow melt. This pattern is consistent with the progressive addition of relatively radiogenic Sr in recharge to groundwater through the soil zone over the summer months.

The Pb isotopic composition of deeper groundwaters from throughout the catchment, strongly enriched in uraniumogenic Pb scavenged from the till and bedrock minerals, can be distinguished from that in waters that follow flowpaths through the organic soil horizon where atmospheric Pb is sequestered. All deeper groundwaters analyzed thus far have $^{206}\text{Pb}/^{204}\text{Pb} > 20.0$, whereas throughfall and O-horizon leachates using pH-buffered ammonium acetate both have $^{206}\text{Pb}/^{204}\text{Pb} \sim 19.0$. Shallow groundwater has intermediate values that increase with depth, implying contributions of Pb from the overlying unsaturated zone during groundwater recharge (Bullen et al., 1994). On a plot of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$, streamflow is intermediate between leaf wash and deeper groundwater compositions, suggesting that the Pb isotopes can be explained in terms of a simple two-component mixing system (Figure 18.6). In other words, increasing $^{206}\text{Pb}/^{204}\text{Pb}$ in streamflow requires an increasing contribution from groundwater.

To demonstrate the utility of the Pb isotopes for determination of water sources, the variation of $^{206}\text{Pb}/^{204}\text{Pb}$ in streamflow at the headwater basin during two significant events (snowmelt and a summer storm) is shown in Figures 18.7a and 18.7b. Over the course of the 1993 snowmelt (Figure 18.7a), $^{206}\text{Pb}/^{204}\text{Pb}$ generally decreased from a value approaching that of groundwater to values requiring a greater contribution of water that had passed through the shallow soil zone (i.e. meltwater). Over this period, snowmelt actually occurred in two main pulses (Shanley et al., submitted). During the first minor pulse, $^{206}\text{Pb}/^{204}\text{Pb}$ of streamflow decreased slightly at the

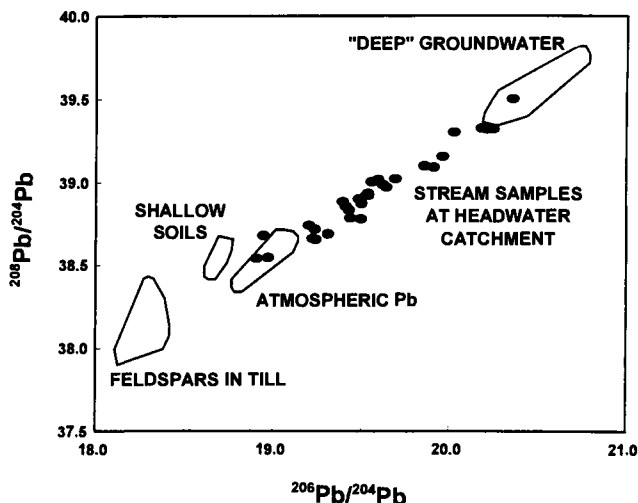


Figure 18.6. Variation of Pb isotopes in streamwater, groundwater, precipitation, throughfall and a leaf wash at Sleepers River, Vt. Pb in streamwater is intermediate in isotopic composition between Pb in groundwater (derived from rock weathering) and Pb in leaf wash (derived from atmospheric sources), suggesting a simple two-component mixing system.

onset of melting but later increased as melt intensity diminished. With the later major pulse that followed a major precipitation event, $^{206}\text{Pb}/^{204}\text{Pb}$ of streamflow decreased to a greater extent and remained at a relatively low value well beyond the time when the stream hydrograph had returned to normal. The persistence of the intermediate $^{206}\text{Pb}/^{204}\text{Pb}$ implies continued drainage of shallow soil waters well after snow had disappeared from the catchment.

The variations in $^{206}\text{Pb}/^{204}\text{Pb}$ during an August rain storm (Figure 18.7b) are similar to those during the initial snowmelt pulse. $^{206}\text{Pb}/^{204}\text{Pb}$ was relatively high in baseflow prior to the storm, but decreased significantly with the initial rise of the hydrograph. However, by the time of peak flow $^{206}\text{Pb}/^{204}\text{Pb}$ had returned to and remained at high values approaching those of deeper groundwater. The dominance of the more radiogenic Pb values implies that groundwater, rather than shallow soil waters is the major contributor to the storm hydrograph. This conclusion is consistent with the variations observed for $\delta^{18}\text{O}$ during this storm (J. Shanley, pers. comm.).

The $\delta^{13}\text{C}$ of streamwater shows complicated relationships with basin scale, soil thickness, and residence time. Under baseflow conditions, $\delta^{13}\text{C}$ and Ca/Si of streamflow increase with increasing basin scale. This suggests that carbonate weathering has a stronger effect on the chemical composition of baseflow in larger basins than in the headwaters. On the other hand, $\delta^{13}\text{C}$ in the headwater catchment (W-9) decreases with ground surface slope, soil drainage efficiency and, presumably, increasing importance of carbonic acid relative to strong acid as weathering agents (Figure 18.8). In addition, $\delta^{13}\text{C}$ of streamwater at baseflow displays a strong seasonal variability, generally with highest values in the winter and lowest values during the biologically-productive summer months. During snow melt, $\delta^{13}\text{C}$ of streamwater correlates positively with $\delta^{18}\text{O}$, which itself is negatively correlated with the proportion of melt water in the stream. The addition of more negative $\delta^{13}\text{C}$ during the melt event probably reflects scavenging of DIC from the calcite-barren unsaturated zone by the melt waters.

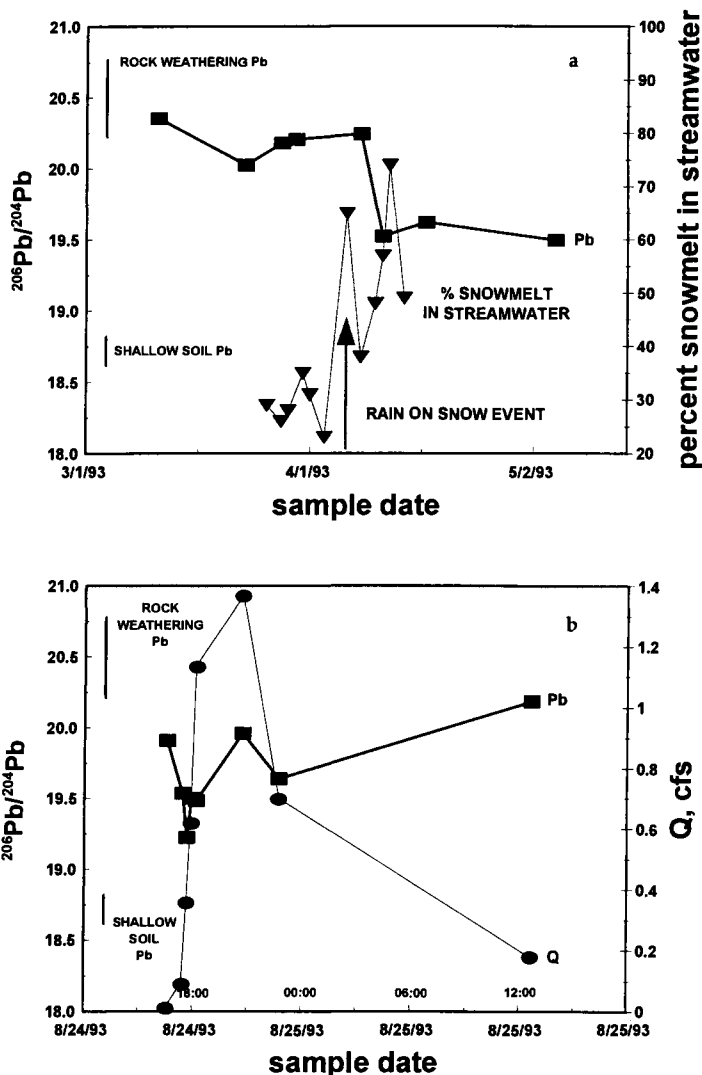


Figure 18.7. Variation of $^{206}\text{Pb}/^{204}\text{Pb}$ during snowmelt (a) and a summer storm (b) in stream discharge from the 47 ha. catchment W9 at Sleepers River. The range of values identified as "shallow soil Pb" is defined by several throughfall samples and a leaf-litter wash. The range of values identified as "rock weathering Pb" is defined by deep groundwater samples collected throughout the watershed. In Figure 18.7a, % snowmelt in streamwater is calculated using water isotopes.

Considered together, the Sr, C and Pb isotope data can be used to construct a rather complex picture of catchment hydrology during events. The Sr isotope data suggest that flowpaths providing base cations to streamflow are nearly constant over time for any sampling site, reflecting the local balance between older shallow groundwater and younger recharge to groundwater through the unsaturated zone. Although limited intra-stream variability in $\delta^{87}\text{Sr}$ has been observed during snow melt, the Sr isotope data further suggest that event waters con-

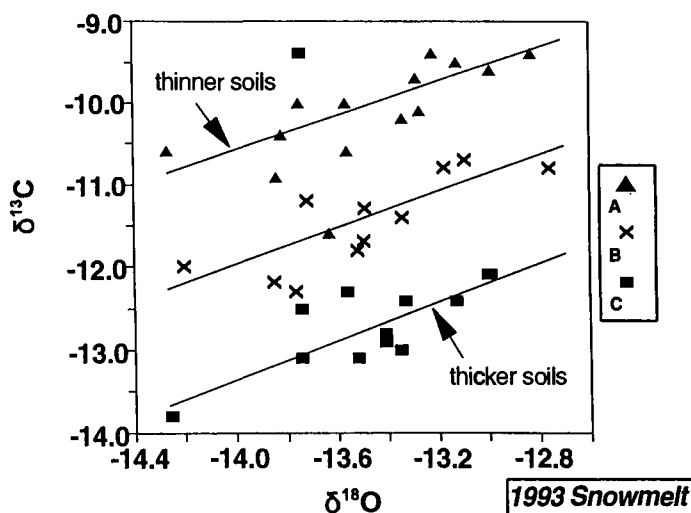


Figure 18.8. Covariation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for three tributaries in the headwaters catchment (W-9) at Sleepers River; the tributary draining areas with thin soil has higher $\delta^{13}\text{C}$ values than the tributary draining areas with thicker soils.

tribute relatively few cations from the catchment soils to the streams; and thus must travel along solute-poor pathways. The C isotope data clearly show that flowpaths through the unsaturated zone have a significant effect on $\delta^{13}\text{C}$, and that the proportion of streamflow derived from shallow flowpaths during events increases with increasing basin scale. The Pb isotope data support the notion that event waters add and remobilize atmospherically-derived Pb as complexes with organic carbon, but contribute significantly to increases in the hydrograph only during major events such as snowmelt. Over the remainder of the year, event waters mainly provide recharge to the water table. Downward transport of atmospheric Pb during water table recharge provides a mechanism for the observed Pb isotope stratification of groundwater.

18.3.3 C and Sr isotopes as tracers of sources of carbonate alkalinity at Catoctin Mountain, Maryland

At Catoctin Mountain, Maryland, Hauver Branch and Hunting Creek drain two forested catchments developed on Precambrian calcite vein-bearing greenstone. Although the two streams are only 1 km apart, they differ significantly in chemistry and hydrologic response to storm events. Hauver Branch has less calcium, alkalinity, calcium/alkalinity and, on average, more negative $\delta^{13}\text{C}$ than Hunting Creek. Moreover, Hauver Branch drains an area (550 ha) half the size of Hunting Creek (1040 ha), has deeper soils, and has a slower hydrologic response.

Although variations in stream $\delta^{18}\text{O}$ during storm events can easily be interpreted in terms of relative contributions of "new" and "old" waters in the two catchments, the $\delta^{18}\text{O}$ data do not reveal how the water is delivered to the stream or how these flowpaths change during the event. Because $\delta^{13}\text{C}$ of DIC has been shown to be sensitive to differences in reactions occurring along shallow versus deep flowpaths (Kendall et al., 1992), samples were analyzed for both $\delta^{13}\text{C}$ and

$\delta^{18}\text{O}$. During storm events, the $\delta^{18}\text{O}$ shows small gradual changes in water sources in response to changes in rain intensity in contrast to rapid oscillations in $\delta^{13}\text{C}$. For example, during a single three-day storm event in March 1987, $\delta^{13}\text{C}$ in both streams oscillated rapidly over a 3‰ range, whereas $\delta^{18}\text{O}$ varied only gradually and less than 1‰. The oscillations in $\delta^{13}\text{C}$ apparently reflect more complex changes in flowpaths, as well as mixing among waters derived from various flowpaths, than is apparent based on $\delta^{18}\text{O}$ alone (Kendall et al., 1992).

Processes that would contribute carbon to DIC include strong acid dissolution of calcite, carbonic acid dissolution of calcite, and silicate hydrolysis in the presence of carbonic acid. As noted above, $\delta^{13}\text{C}$ of DIC derived from each process would have a distinct value; thus, each process could be viewed as supplying carbon from a distinct source. For example, based on analyses of both calcite and soil gas from the catchment, strong acid dissolution of calcite should produce DIC having $\delta^{13}\text{C}$ equal to that of the calcite, because all the carbon produced by the process is derived from the calcite. Similarly, silicate hydrolysis in the presence of carbonic acid should produce DIC having $\delta^{13}\text{C}$ equal to that of the soil gas because no C is supplied by the silicate minerals. Carbonic acid dissolution of calcite results in an intermediate value of $\delta^{13}\text{C}$, because equal amounts of carbon are derived from the soil gas and calcite, according to the stoichiometry of the chemical reaction.

Presumably $\delta^{13}\text{C}$ in streamwater could be used as a tracer to distinguish waters that have traveled along different flowpaths. A spectrum of shallow and deep flowpaths can be envisioned, such as pathways through the shallow soil zone from which most of the calcite has been dissolved, or flow through bedrock fractures with exposed calcite crystals. The chemical evolution along each flowpath should produce DIC having $\delta^{13}\text{C}$ that, in concert with the chemistry, would tie the water to that specific flowpath. However, non-conservative processes that fractionate the carbon isotopes, such as exchange with atmospheric CO_2 and open-system reactions at mineral surfaces could play a significant role. Because variations in the isotopic composition of Sr in the waters would reflect differences in contributions from the various sources, consideration of the degree of correlation of $\delta^{13}\text{C}$ with $\delta^{87}\text{Sr}$ provides a means to determine whether the oscillations in $\delta^{13}\text{C}$ are controlled by flowpath-dependent source contributions or non-conservative processes. To address this issue, we have analyzed $\delta^{87}\text{Sr}$ in base flow and storm-event stream waters, as well as in groundwater samples from wells and springs, calcites, greenstone, and soils from each catchment (Bullen and Kendall, 1991).

At baseflow just prior to the storm event mentioned above, $\delta^{87}\text{Sr}$ and $\delta^{13}\text{C}$ are -2.45‰ and -10.8‰ at Hauver Branch, and 0‰ and -9.0‰ at Hunting Creek. As with $\delta^{13}\text{C}$, $\delta^{87}\text{Sr}$ oscillates rapidly during the storm. On a plot of $\delta^{13}\text{C}$ vs. $\delta^{87}\text{Sr}$ (Figure 18.9), the data for the two streams form distinct clusters that together define a strong positive correlation. The majority of intrastorm C- and Sr-isotopic fluctuations likewise correlate positively (Figure 18.10), although during high flow significant negatively-correlated shifts cause each stream to have lesser $\delta^{87}\text{Sr}$ and greater $\delta^{13}\text{C}$ than at baseflow. Regardless, the overall positive inter-isotopic correlation implies that the oscillations of $\delta^{13}\text{C}$ are mainly source-controlled.

The simplest interpretation of stream chemistry based on the water isotopes is that stream water is a combination of old shallow groundwater and event waters that have traveled over and through the unsaturated zone. The groundwaters from the Catoctin Mountain area analyzed thus far (mostly springs and Park Service wells) have $\delta^{87}\text{Sr}$ of -2.3‰ to +5.9‰ and $\delta^{13}\text{C}$ of DIC of -18.8‰ to -24.8‰. Of the potential Sr and C lithologic sources we have measured, the green-

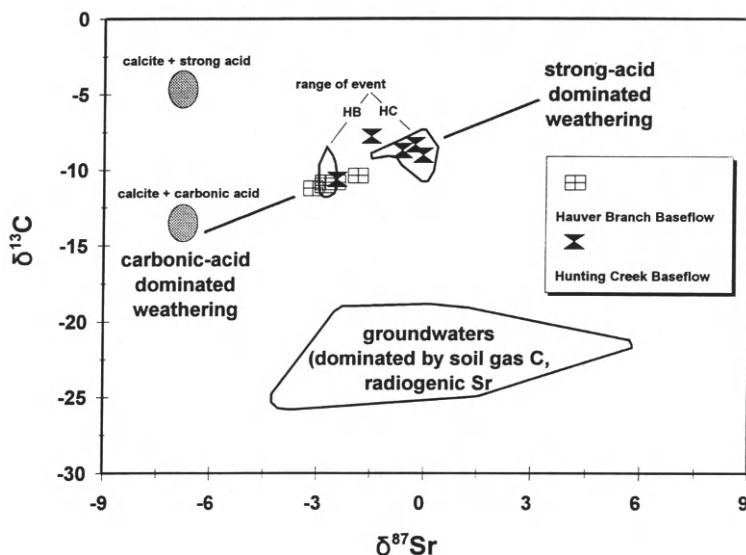


Figure 18.9. Covariation of $\delta^{87}\text{Sr}$ and $\delta^{13}\text{C}$ for two streams at Catoctin Mt., MD. The fields labeled "HB" and "HC" outline the range of event samples discussed in the text for Hauver Branch and Hunting Creek, respectively. The symbols mark the compositions of baseflow at several sampling times throughout the year. Groundwater samples are from national and state park wells, as well as from springs from throughout the area.

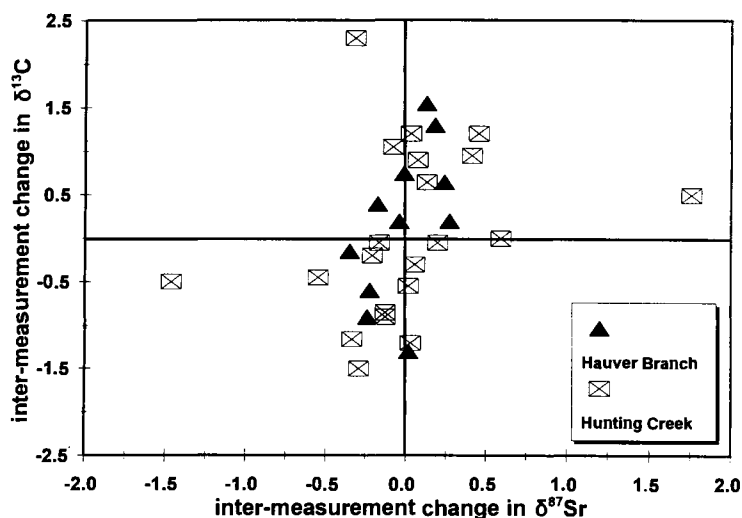


Figure 18.10. Covariation of the inter-measurement change in $\delta^{87}\text{Sr}$ and $\delta^{13}\text{C}$ in stream waters at Catoctin Mt. for the event samples discussed in the text. The sampling interval was variable, but on average was about 10 minutes. A positive value for the change indicates that the delta value increases from one measurement to the next. The overall positive slope to the data array indicates that the variations are correlated with each other, and thus represent changing source contributions.

stone has whole-rock $\delta^{87}\text{Sr}$ of -6.8‰ , and the calcites have $\delta^{87}\text{Sr}$ of -6.8‰ and $\delta^{13}\text{C}$ of -5‰ . Weak-acid leachates of soils from the catchment have more positive $\delta^{87}\text{Sr}$ than the greenstone and calcite, indicating that the groundwaters derive their Sr from relatively radio-genic residual mineral phases in the soils. The range of $\delta^{13}\text{C}$ of DIC in the groundwaters is similar to that for biologically-generated soil gas sampled from the two catchments, and reflects only a relatively small contribution of calcite dissolution by either carbonic or strong acid.

The range of $\delta^{87}\text{Sr}$ in stream water overlaps that in the groundwaters, whereas stream water DIC is much heavier than that in the groundwaters and is derived in large part by calcite dissolution. Thus, stream water could be viewed as a mixture of groundwater that is chemically and isotopically similar to the sampled groundwaters, and another water type, perhaps delivered along bedrock fractures, that has interacted with and is isotopically dominated by a source of heavy carbon such as the calcites. However, $\delta^{87}\text{Sr}$ and $\delta^{13}\text{C}$ would be negatively correlated in waters derived by this particular mixing process, a fact at odds with the persistent positive correlation of $\delta^{87}\text{Sr}$ and $\delta^{13}\text{C}$ in waters from these catchments. The alternative interpretation is that the sampled groundwaters represent a distinct water type within the catchment that has little influence on streamflow generation. Unfortunately, we currently have no chemical and isotopic data on groundwater from piezometers in the riparian zone

Regardless, the stream waters could be viewed as mixtures of two conceptual end-member water types that may develop close to the stream. In order to account for the positive correlation of $\delta^{87}\text{Sr}$ and $\delta^{13}\text{C}$, one water type would have lesser, and the other would have greater $\delta^{87}\text{Sr}$ and $\delta^{13}\text{C}$ than the stream waters (Figure 18.9). These different compositions could be easily generated if the weathering environments in which each end-member water developed contained inherently different ratios of carbonic acid to strong acid. For example, carbonic acid-dominated weathering might produce solutions that have Sr- and C- isotope compositions determined by carbonic acid dissolution of calcite ($\delta^{87}\text{Sr} \sim -6\text{‰}$ and $\delta^{13}\text{C} \sim -11\text{‰}$), and water chemistry determined by interaction with the cation exchange pool rather than by vigorous attack on the silicate minerals. In contrast, strong acid-dominated weathering might produce solutions that have C-isotope compositions determined by strong-acid dissolution of calcite ($\delta^{13}\text{C} \sim -5\text{‰}$), but Sr-isotope compositions and water chemistry reflecting a more vigorous attack on the radiogenic silicate minerals ($\delta^{87}\text{Sr} > 1\text{‰}$, the value of the most radiogenic stream water yet analyzed from the catchment).

The isotopic compositions of base flow in each catchment represent the transient influence of these two water types, with solutions dominated by carbonic acid weathering having greater influence during the biologically-active summer months. We propose that at Hauver Branch, the deeper soils and slower storm response allow infiltration waters to have a longer residence time in the carbonic acid-rich soil weathering zone than at Hunting Creek. The interstream chemical and isotopic differences may result in large part from the greater contribution of deep soil-zone modified infiltration water to groundwater recharge at Hauver Branch. Although largely speculative, the various aspects of our model are eminently testable by a variety of field and laboratory experiments.

18.3.4 Synthesis: an isotopic view of a catchment

The above studies demonstrate the kinds of isotopic variability to be expected in waters contributing to streamflow at catchments. The water isotopes have the potential to be as

variable as the "new" waters delivered to the catchment during events, although some degree of groundwater averaging is likely to occur. In addition, evaporative enrichment of the water isotopes will contribute to the isotopic diversity of groundwater in catchments where lakes are a significant component. The important controls on solute isotope composition appear to be residence time of water in and thickness of the soil zone, length of flowpath to the stream and, in the case of Sr and C isotopes, the extent of silicate and carbonate mineral weathering. Figure 18.11 summarizes the expected variations in water and solute isotope composition for various generalized flowpaths through a hypothetical catchment.

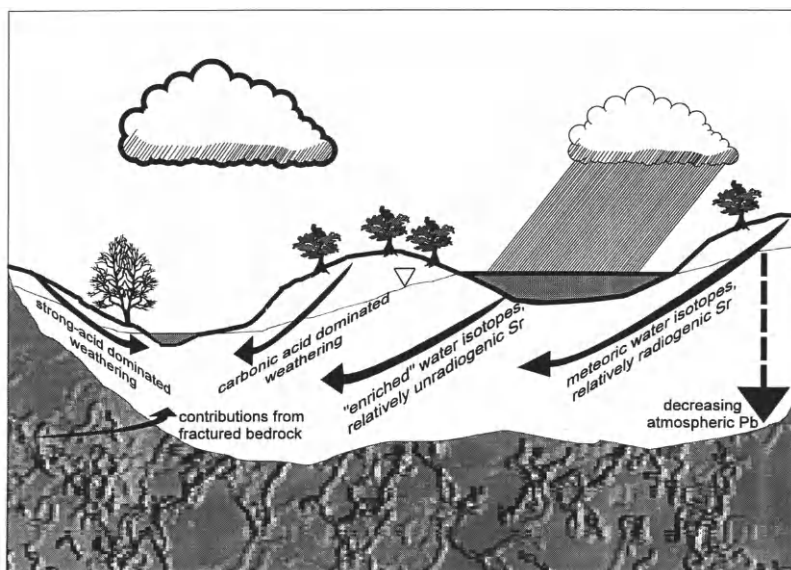


Figure 18.11. Generalized cartoon of a watershed showing relative isotopic differences that might be expected along various flowpaths (solid arrows) that ultimately contribute to streamflow. The isotopic characteristics along the path labeled "contributions from fractured bedrock" can be highly variable depending on factors such as the efficiency of fracture flow, minerals present and age of water in the bedrock.

In our view of the catchment, assumed here to contain a carbonate component, strong-acid weathering is expected to dominate where soils are thinnest, resulting in relatively heavy DIC and radiogenic dissolved Sr at the water table. As soils thicken, strong-acid weathering continues to dominate in the shallow soil horizons from which carbonate has largely been stripped, resulting in relatively light DIC and radiogenic dissolved Sr in infiltration waters. However, carbonic-acid weathering becomes important in the deeper carbonate-bearing mineral soils, resulting in intermediate DIC and less radiogenic dissolved Sr at the water table. In terms of Pb isotopes, shallow soil waters should be dominated by atmospheric-derived Pb, whereas deeper groundwater should be dominated by rock weathering-derived Pb. As soils thicken, downward transport of atmospherically-derived Pb should provide a mechanism to stratify groundwater with respect to Pb isotopes. Finally, contributions from bedrock are probably highly variable isotopically, depending primarily on the kinetics of water transport through the fracture system. In general, however, we suggest that groundwaters derived along bedrock pathways should contain relatively radiogenic Sr and Pb, and heavy C.

If we make the assumption that catchment waters develop and maintain characteristic isotopic "signatures" along the various flowpaths, then the water and solute isotope compositions observed in streamflow can be viewed as a function of contributing volume. For example, under baseflow conditions the characteristic isotopic signature of the riparian environment should dominate. However, in response to an event such as a rain storm or snowmelt, additional water will be delivered to the stream along flowpaths determined by the hydrogeologic characteristics of the catchment. Water and solute isotope compositions of the resulting streamflow will differ from those of baseflow depending on the relative mass fluxes from the various catchment "volumes" such as the organic soil horizon, shallow groundwater, and the bedrock fracture system. Although admittedly simplistic, this view of isotopic behavior in catchments is clearly testable by a variety of hydrologic, chemical and isotopic techniques. We view hypothesis testing as a critical component of any study of catchment hydrology.

18.4 Additional Solute Isotope Tracers: Li, B, Fe

From the material presented above, it is clear that Sr, Pb, and C isotopes can provide meaningful constraints for catchment studies, due to both their versatility as hydrologic tracers as well as the relatively straightforward nature of their analysis. It is worth pointing out that the vast majority of solid-source mass spectrometers currently in operation are or could be routinely used to analyze the isotopic compositions of Sr and Pb in rocks, and the transition from analyses of rocks to analyses of dissolved components in water requires only the development of laboratory procedures for separation and purification of the Sr and Pb for loading on filaments. Numerous academic and research facilities currently have the capability to analyze the isotopic composition of C in dissolved species, solids, liquids, and gases. Other solute isotope systems have been advantageously applied in catchment studies, notably the uranium- and thorium-series radionuclides (see review, Chapter 20), the sulfur isotopes (see review, Chapter 15), and the nitrogen isotopes (see review, Chapter 16). The considerable geologic and biologic literature on the behavior of these isotope systems in nature provides a strong foundation for interpretation of variations in isotopic composition observed in catchments with diverse geology and ecosystems.

In the near future, additional solute isotope systems that are currently under-utilized due to both analytical difficulties and lack of information concerning the causes and extent of isotopic variations in nature may potentially find wide applicability in catchment studies. As examples, in this section we present the theoretical bases for the Li, B, and Fe stable isotope systems. These systems have not yet been employed in catchment studies, but should provide important information particularly when applied through the multi-isotope approach. We propose that the Li and B isotopes should behave as relatively conservative tracers of water flowpaths, and should prove valuable for distinguishing contributions from weathering in the soil zone from those due to weathering at the saprolite-bedrock interface. The Fe isotopes may provide a sensitive tracer of biogeochemical redox-sensitive processes occurring within the catchment.

Lithium isotopes

Lithium has two naturally-occurring stable isotopes, ${}^6\text{Li}$ and ${}^7\text{Li}$. Unlike most other stable isotope systems, the heavy isotope ${}^7\text{Li}$ is the dominant species, such that average ${}^7\text{Li}/{}^6\text{Li}$ in nature is approximately 12.0. In the limited literature that exists for the Li isotopes, data have typically been reported relative to the N.I.S.T. standard L-SVEC in common delta notation.

Considerable variability of $\delta^7\text{Li}$ has been reported for natural materials, although many of the analytical data produced prior to the 1980s are now suspect. Because Li is such a light element, analysis in solid-source mass spectrometers has been difficult due to apparently uncontrollable thermal fractionation effects. However, recently developed alternative analytical procedures (e.g. Chan and Edmond, 1988) have made the precise analysis of the Li isotope composition in both rocks and waters relatively routine. As with any stable isotope system, however, the only true means of assuring accuracy of measurements is by running duplicates of each sample through the total analytical procedure and confirming a set level of external precision.

In nature, layer silicate minerals cause the greatest Li-isotope fractionation, as ^6Li preferentially substitutes into the octahedral sites usually occupied by Mg and Fe^{2+} . This fractionation mechanism was demonstrated for high-temperature systems by Chan and Edmond (1988) who reported isotopic compositions of Li in mid-ocean ridge thermal waters and associated solid phases. In their study, hydrothermally-produced secondary minerals were calculated to have $\delta^7\text{Li}$ as much as 19‰ lighter than the fluids with which they equilibrated. Continual hydrothermal processes at the ocean ridges and preferential accumulation of ^6Li into secondary phases over geologic time have caused a progressive heavying of Li of seawater such that it has the highest $\delta^7\text{Li}$ of natural materials yet analyzed.

Bullen and McMahon (1992) used the anticipated divergence in $\delta^7\text{Li}$ between marine and layer-silicate environments to track the chemical evolution of groundwater in a clastic coastal aquifer. Along a regional flow path, dilute recharge waters ultimately evolve to NaHCO_3 -compositions, presumably first by dissolution of aragonite in the sandy portion of the aquifer and later by Ca-for-Na exchange on clays. Consistent with this scenario, Li is relatively light in the recharge zone, becomes substantially heavier as (HCO_3^-) -concentrations increase, and becomes markedly lighter in the clay-rich portion of the aquifer where Na/Ca of groundwater climbs rapidly. Based on analyses of solid-phase materials from cores taken along the flow path, Li in aragonite is ~ 35‰ heavier than that leachable from the clay-rich aquifer material.

Based on the conclusions of these studies, some simple predictions concerning the behavior of Li isotopes in catchments can be made. Obviously, clay minerals will play an important role in the establishment of Li isotopic diversity. Clays will contain the lightest Li of catchment minerals, and catchment waters will have the most Li isotope diversity when the effect of interactions with clay minerals differs among flowpaths. For example, infiltration waters passing through an established clay-rich soil should inherit substantially lighter Li than will groundwaters traveling along and reacting at the bedrock-saprolite interface. Furthermore, dissolved Li should become progressively heavier along flow paths where precipitation of Mg- Fe^{2+} -Li-bearing clay minerals is actively occurring. An additional Li source particularly relevant to coastal catchments is marine-dominated precipitation, which will have substantially heavier Li than the catchment minerals. Assuming that isotopically-distinct sources or environments can be identified within a catchment, then Li in waters derived therefrom should behave as a relatively conservative solute tracer of those waters.

Boron

Boron has two naturally-occurring stable isotopes, ^{10}B and ^{11}B . Unlike most other stable isotope systems but in common with the Li isotopes, the heavy isotope ^{11}B is the dominant species, such that average $^{11}\text{B}/^{10}\text{B}$ in nature is approximately 4.0. An extensive literature exists for the B isotopes, particularly for geothermal and marine environments. In most studies, data have

typically been reported relative to the N.I.S.T. standard NBS-951 in common δ -notation. As with the Li isotopes, considerable variability of $\delta^{11}\text{B}$ has been reported for natural materials (e.g. Bassett, 1990). However, many of the analytical attempts at precise determination prior to the 1980s are now suspect for the same reasons as for the Li isotopes. The fairly recent development of two alternative analytical procedures has made the analysis of B isotopes in water fairly routine; the analysis of B isotopes in silicate rocks is rather difficult and a highly-specialized technique. The two methods involve measurement of either positive ions (Spivack and Edmond, 1986) or negative ions (Vengosh et al., 1991). The advantage of the negative ion analytical method, particularly for dilute systems such as catchments, is that the required sample size (~ 1 ng B) is substantially less than that for positive ion generation (~ 1 μg B). On the other hand, reproducibility of measurements is presumably worse with the negative ion analytical method, but with careful sample preparation technique can be better than 1‰.

In natural waters, B exists in two states, boric acid (H_3BO_3) and borate ion (H_4BO_4^-). The coordination environment for the B atom is affected by the difference in number of hydroxyl groups in these boron species, causing isotopic fractionation between coexisting boric acid and borate ion. Under low temperature conditions such as the marine environment, B in the borate ion is on the order of 20‰ lighter than that in boric acid (Hemming and Hanson, 1992). As an uncharged species, boric acid is essentially conservative; in contrast, the charged borate ion can be sorbed onto mineral surfaces and incorporated as an impurity into minerals such as carbonates. As with the Li isotopes, the progressive development of layer silicate-rich hydrothermal mineral assemblages at mid-ocean ridges and the abundance of clay minerals in the marine environment has resulted in the progressive heavying of B in seawater over geologic time. The range of $\delta^{11}\text{B}$ in natural materials is on the order of 100‰ (Bassett, 1990).

The distribution of B-species as a function of pH may be particularly relevant to catchment studies. At pH less than 6, dissolved B exists entirely as boric acid. With increasing pH, the isotopically-lighter borate ion becomes progressively more abundant and heavier (Kakihana et al., 1977). Thus, there could be considerable variability in $\delta^{11}\text{B}$ of dissolved B along flowpaths through different mineral assemblages, or along flowpaths characterized by different pH and geochemical evolution. The main control on $\delta^{11}\text{B}$ of catchment waters is probably the effectiveness of borate ion sorption as a function of pH and chemistry. Additional sources of isotopically unique B that may be important are carbonates from within the catchment and atmospherically-deposited salts of either marine or anthropogenic origin (i.e., boron-rich soil amendments, fertilizers).

Iron

Iron has four naturally-occurring stable isotopes, ^{54}Fe , ^{56}Fe , ^{57}Fe and ^{58}Fe . The relative abundances of the Fe isotopes in nature are approximately ^{54}Fe (5.8%), ^{56}Fe (91.7%), ^{57}Fe (2.2%) and ^{58}Fe (0.3%). Much of the past work on measuring the isotopic composition of Fe has centered on determining variations due to processes accompanying nucleosynthesis (i.e., meteorite studies) and ore formation (Volkening and Papanatassiou, 1989; Maeck, 1992). However, primarily for analytical reasons, there is a paucity of information on stable isotopic variations of Fe in low-temperature systems.

Two recent studies using improved analytical techniques are pertinent to potential work with Fe isotopes in catchments. In a reconnaissance study of Fe isotope compositions, Dixon et al. (1992) demonstrated isotopic variations induced by microbial processes at the Loihi seamount.

Their results suggest that microbially-mediated Fe reduction favors the breakage of bonds involving the lighter iron species. In another study of Fe reduction and transport at a gasoline spill site, Bullen and McMahon (1997) demonstrated with both field and experimental evidence that microbially-mediated Fe reduction behaves as a Rayleigh distillation process, with Fe^{2+} consistently 5‰ lighter than the coexisting Fe^{3+} . An important conclusion of this study is that the Fe isotope composition of water leaving a system can be used to estimate the amount of Fe reduction that has occurred in the system, with increasingly heavy values reflecting greater amounts of Fe reduction.

The potential application of Fe isotopes to catchment studies lies in the assumption that Fe mobilized inorganically from minerals under either reducing or low-pH conditions will have a different isotopic composition than microbially-reduced Fe. To the extent that certain zones or flowpaths in the catchment can be characterized by microbial cycling of labile Fe, the Fe isotopes may provide an effective tracer of contributions from these pathways. For example, characterization of the biogenic processes along water pathways providing the Fe responsible for staining of stream beds may be one application of Fe isotopes to catchment studies. However, further experimental work is required on both development of analytical procedures for measurement of the Fe isotopes at low concentrations as well as determination of the relative fractionation efficiency of various microbial agents.

18.5 Summary

Water isotopes are very useful tools for determining water sources (time-sources) in catchments. Chemical tracers are very useful for understanding the reactions along flowpaths. However, neither isotopic nor chemical tracers are very useful for quantifying amounts of water from different flowpaths or rock/soil units--the former because water sources need not correspond to water flowpaths, and the latter because chemical constituents need not behave conservatively. Clearly, attempts to assess relative contributions from flowpaths must consider a variety of hydrologic, geochemical and isotopic tools in concert, and may not be successful.

Fortunately, reactive solute isotopes such as ^{13}C , ^{34}S , ^{15}N , ^{87}Sr , and Pb isotopes can provide valuable information about flowpaths for geochemical and hydrologic modeling precisely because they reflect the reactions that are characteristic of specific flowpaths (Kendall et al., 1992; Kendall et al., 1995; Bullen et al., 1996). First, reactive solute isotopes can serve as additional thermodynamic constraints for testing of possible geochemical reaction paths (Plummer et al., 1983). Second, the waters flowing along mineralogically-distinctive horizons are sometimes uniquely labeled by the isotopic compositions of their solutes. For example, waters flowing through the soil zone often have $\delta^{13}\text{C}$ values that are depleted in ^{13}C relative to deeper groundwaters because of biogenic production of carbonic acid in organic soils (Kendall, 1993). Similarly, shallow soil waters should transport Pb that is predominantly atmospheric in origin, whereas deeper groundwaters will transport rock weathering-derived Pb (Bullen et al., 1994). Third, a multi-isotope approach can be particularly useful in tracing the reactions specific to a flowpath (Krabbenhoft et al., 1994). Because solute isotope tracers are usually affected by a smaller number of processes than chemical constituents, interpretations of changes in isotopic composition are less ambiguous than the simultaneous changes in solute concentrations (Kendall et al., 1995).

In this chapter we have stressed the importance of using isotopes in a complementary manner, primarily to constrain and enrich models developed from hydrologic and chemical data. Clearly isotopes are powerful tracers of hydrologic and geochemical processes, but often conclusions based on consideration of a single isotope system are ambiguous at best. One strong benefit of the multi-isotope approach discussed herein is that the strengths of one isotope system may compensate for the weaknesses of another. This is not to say that all catchment studies will benefit from analysis of every analytically-available isotope system, and each researcher must carefully determine the kinds of information desired from isotopic data. Isotopes are probably best viewed as tools for testing rather than developing hypotheses, particularly in studies operating under tight budgetary constraints. However, our experience is that isotopes consistently expand our vision of catchment function, and commonly lead to unanticipated avenues of research.

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Erosion, Weathering, and Sedimentation

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19.1 Introduction

Estimating denudation rates of catchments is a difficult but important problem in geochemistry and hydrology. River-basin mass balances determined from suspended sediment measurements have been used to calculate spatially averaged rates of denudation; however, the seasonal and inter-annual variability in river fluxes, the impact of human activity, and variable sediment yields (Trimble, 1977), make such calculations uncertain particularly when the results are extrapolated over time scales longer than those over which the measurements were made. The use of a variety of radionuclides has the potential to yield estimates of catchment denudation rates integrated over geologically and historically significant time scales.

Cosmogenic nuclides are produced when cosmic rays, primarily neutrons, interact with target atoms in rocks and soils. In situ, nuclide production rates are low at Earth's surface (10^1 - 10^3 atoms $\text{g}^{-1} \text{y}^{-1}$) and generally decrease exponentially to negligible values within several meters depth. If the nuclide is immobile after production, its concentration in rock and soil will reflect the duration of near-surface exposure (Bierman, 1994; Cerling and Craig, 1994; Lal, 1991). Surfaces that erode slowly, therefore, will build up greater accumulations of cosmogenic isotopes than surfaces that erode rapidly. Assuming exposure characteristics do not change, erosion rates can thus be determined for different time scales depending on the half-life of the isotope. The most commonly measured in situ produced cosmogenic isotopes are ^3He (stable), ^{10}Be ($t_{1/2} = 1.5$ ma), ^{26}Al ($t_{1/2} = 0.7$ ma), and ^{36}Cl ($t_{1/2} = 0.3$ ma); in-situ-produced ^{14}C ($t_{1/2} = 5,730$ yr) and ^{21}Ne (stable) have also been measured (Bierman, 1994). Careful laboratory procedures are required to separate nuclides produced in situ from those produced in the atmosphere and delivered to the Earth's surface by precipitation and dry-fall.

Other naturally and anthropogenically produced isotopes are useful for understanding how catchments weather and erode. ^{210}Pb ($t_{1/2} = 22.3$ yr) is a natural component of atmospheric deposition. Pb is strongly adsorbed to particles; thus, its accumulation in lake sediments can be used to date cores and estimate erosion rates in the past 100 yr. This time frame fills a useful gap between the longer- and shorter-lived cosmogenic nuclides. ^{137}Cs and $^{239+240}\text{Pu}$ are produced from detonation of nuclear weapons and emissions from nuclear power plants. As result, the input function of these isotopes can be estimated as a function of time and the resulting concentrations in lacustrine sediments can be used to date cores and estimate rates of sediment deposition and thus catchment erosion. ^{87}Sr is a naturally-occurring radiogenic isotope in

essentially all rocks, and different lithologies in multi-lithologic terrains are likely to have different proportions of ^{87}Sr relative to the non-radiogenic ^{86}Sr . Thus the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a bulk sediment could in theory be used to estimate the relative proportions of each lithology in the sediment profile. More typically Sr isotopes are used to help determine the weathering rates of minerals (see Chapters 8 and 18 for discussions of the details of Sr isotope geochemistry).

During the last decade, advances in analytical capabilities have allowed increasingly precise measurement of small quantities of rare nuclides. For example, in 1955, kilograms of rock and weeks of counting time were used to make the first measurements of in situ produced ^{36}Cl (Davis and Schaefer, 1955); now, using a few tens of grams of rock and only several minutes of accelerator time, one can make the same measurement with a detection limit several orders of magnitude lower. The chapter that follows explains how a variety of nuclides have been applied to catchments throughout the world. Different authors summarize their work and the work of others using in situ produced ^{10}Be and ^{26}Al , atmospheric ^{210}Pb , anthropogenic ^{137}Cs , and naturally occurring Sr isotopes.

19.2 In Situ Produced Cosmogenic Nuclides

One of the most exciting new approaches for quantifying the rate at which catchments erode is the measurement of in situ produced cosmogenic nuclides. The most commonly applied nuclides for erosion rate measurements are ^3He , ^{10}Be , ^{26}Al and ^{36}Cl . Until recently, use of these nuclides was restricted to determining denudation rates of exposed bedrock outcrops; recently, several research groups have begun to measure nuclide abundances in sediments with the goal of estimating basin-scale rates of denudation.

19.2.1 Cosmogenic nuclides in exposed outcrops

The abundance of a cosmogenic nuclide in a sample of outcropping rock can be used to estimate a maximum limiting rate of rock denudation. Calculation of such model denudation rates is made assuming that the surface has been steadily eroding and that mass loss has been occurring at a scale much less than the penetration depth of the cosmic radiation; in practice, denudation rates from outcrops shedding mass in pieces up to 10 cm thick meet the assumptions of the analytic model. Lal (1991) models a variety of exposure and erosion scenarios and provides an analytic model for interpreting nuclide abundance as a function of denudation rate and exposure time:

$$N_i(t,x) = e^{-xL^{-1}} \left[\frac{P_i}{\varepsilon_i L^{-1} + \lambda} \left(1 - e^{-t(\varepsilon_i L^{-1} + \lambda)} \right) \right] \quad (19.1)$$

where N is the concentration (atom g^{-1}) of a cosmogenic nuclide as a function of overlying mass, x is the shielding depth (g cm^{-2} ; depth times density), and t is the surface exposure time in years (yr), P is the surface production rate (atom $\text{g}^{-1} \text{ yr}^{-1}$), L the effective cosmic ray attenuation length (170 g cm^{-2}) (Brown et al., 1995; Kurz, 1986; Sarda et al., 1993), λ the radioactive decay constant, (yr^{-1}), and ε_i is the erosion rate, ($\text{g cm}^{-2} \text{ yr}^{-1}$).

After sufficient time ($t \gg (\epsilon L^{-1} + \lambda)^{-1}$), cosmogenic-nuclide concentrations reach a steady state with production balanced by erosional loss and radioactive decay. This dynamic equilibrium restricts the geochronometric applications of in situ-produced cosmogenic nuclides (i.e., surface exposure dating) to surfaces with low rates of erosion or young exposure ages. Outside of rapidly eroding environments, steady-state concentrations of shorter-lived nuclides (e.g. ^{14}C , $t_{1/2} = 5.8 \cdot 10^3 \text{ yr}$) generally represent a simple balance between production and radioactive decay ($P = \lambda N$). They thus may be used to define latitudinal and altitudinal variability in cosmogenic nuclide production. In contrast, long-lived cosmogenic radionuclides can reach steady-state concentrations corresponding to a wide range of denudation rates (Figure 19.1). Assuming that erosion is a constant and continuous process, and that the rock surface has been continually exposed long enough that several meters of rock have been removed, such steady-state concentrations may be used to quantify average denudation rates.

The relatively few "cosmogenic" erosion rate measurements that have been made are generally equal to or lower than those estimated by other means. Cosmogenically based erosion rates for granites, limestones, basalts, tuffs, and cherts in a mix of continental and maritime climate regimes generally range from 0.5 to 30 m Myr⁻¹ (Bierman, 1994). The lowest cosmogenic erosion rates outside of Antarctica were measured on granites collected from arid south central Australia (0.5 m Myr⁻¹, Bierman and Turner, 1995). For comparison, most long-term, large-scale denudation rates for North America, estimated using sediment volumes, sediment transport and fission tracks, range from 20 to 60 m Myr⁻¹ within the range of erosion rates for similar geographic settings compiled by Saunders and Young (1983) and Summerfield (1991). It is likely that at least some of these contemporary and large-scale denudation rates reflect anthropogenic sediment contribution and sediment resulting from > 15 glacial/deglacial cycles and thus are higher than the average Cenozoic rate.

Cosmogenically determined erosion rates from Antarctica stand in contrast to those determined elsewhere in the world. Brown et al. (1992) used a series of ^{10}Be and ^{26}Al measurements in a core to estimate an erosion rate < 0.3 m Myr⁻¹ for a quartz sandstone surface in the Quartermain Mountains. Nishiizumi et al. (1991) report ^{26}Al and ^{10}Be abundances for 27 samples collected from four locations in Antarctica. They use these abundances to calculate maximum steady-state erosion rates ranging from < 0.1 to 15 m Myr⁻¹. Most erosion rates they measured were an order of magnitude lower than those reported from most other terrestrial locations, between 0.1 and 0.5 m Myr⁻¹, and likely reflect the near-absence of liquid water and its effect on chemical weathering and mechanical disintegration. Measurement of nearly 60 samples of granite from the inselbergs of south central Australia (Bierman and Turner, 1995 and unpublished data) shows that the tops of these landforms are eroding at rates only slightly higher than some Antarctic surfaces (0.4 - 0.6 m Myr⁻¹).

Erosion rate studies in smaller basins show rates similar to those calculated using cosmogenic isotopes; for instance, Marchand (1971) and Oberlander (1972) used dated (10 My) and incised basalt flows to calculate, respectively, average denudation rates between 11 and 24 m Myr⁻¹ for an arid part of the White Mountains in California and 1-10 m Myr⁻¹ for granite in the Mojave desert. These denudation rates are similar to those measured by Bierman (1993) and Bierman et al. (1995) using ^{36}Cl in the nearby granitic Alabama Hills. Erosion rates for granitic outcrops in the Georgia Piedmont determined using cosmogenic isotopes range from 6 to 10 m Myr⁻¹ (Bierman, 1993) and are similar to those determined by several independent techniques, 4 and 20 m Myr⁻¹ (Pavich et al., 1985; Pavich, 1989).

Rates of denudation ($2 - 30 \text{ m Myr}^{-1}$) determined using cosmogenic isotopes are similar to those determined by incision of dated surfaces, by tombstone measurements, and by sediment budgets in small to moderate size catchments. However, these rates are, in general, lower than rates determined by fission tracks and continental scale sediment budgets, including those based on present-day sediment loadings and long-term depositional volumes with the caveat that the assumption of equilibrium and the storage of sediment preclude rigorous interpretation of many of these data. From the limited data (cosmogenic and otherwise) that are available, it appears that rates of bedrock erosion in many climatic settings are grossly similar, with the exception of Antarctica, despite differences in climate and lithology. This interpretation is consistent with that of Ahnert (1970), who suggested that local relief, rather than precipitation, is the strongest control on sediment yield (denudation rate).

On the basis of the few data available, any explanation of the observed differences can only be speculative. Inadvertent sampling bias may account for what appear to be relatively low rates of erosion calculated from cosmogenic isotope measurements. So far, samples have been collected only from relatively resistant lithologies such as basalt, granite, and sandstone. In addition, it appears that samples have generally been collected from outcrops standing above the surrounding landscape. These protrusions of bedrock may erode more slowly because they shed water rapidly thus reducing the efficacy of chemical weathering.

19.2.2 Cosmogenic nuclides in sediments

Extrapolating denudation rates measured on outcropping bedrock surfaces to denudation rates averaged over an entire river basin is not straightforward. Over the past several years, several research groups have been measuring cosmogenic nuclide abundances in quartz sediments in order to estimate basin scale rates of denudation (Brown et al., 1995; Granger and Kirchner, 1994a,b; Stone, J. pers. comm.; Bierman and Steig, 1992, 1996; Bierman, 1995). All groups use similar interpretive equations although they are derived differently.

The derivation of Brown et al. (1995) is outlined below. The basin from which samples are collected is divided into n polygons of area, A_i , where average erosion rate, ϵ , and average cosmogenic nuclide, $(\bar{N})$, content of eroded material are given by:

$$\bar{\epsilon} = \frac{\sum_{i=1}^n \epsilon_i A_i}{\sum_{i=1}^n A_i} \quad \bar{N} = \frac{\sum_{i=1}^n \epsilon_i A_i N_i}{\sum_{i=1}^n \epsilon_i A_i} \quad (19.2)$$

Such an approach is viable if: 1) There is little variability in P_i , so a single production rate is appropriate for all locations in the basin. 2) Erosion is sufficiently rapid for the loss of cosmogenic nuclides to be primarily through erosion rather than radioactive decay (i.e. $\epsilon L^{-1} \gg \lambda$; see Figure 19.1). 3) There is minimal long-term sediment storage. 4) Quartz is uniformly distributed in the basin and 5) sediment leaving the basin is well mixed isotopically.

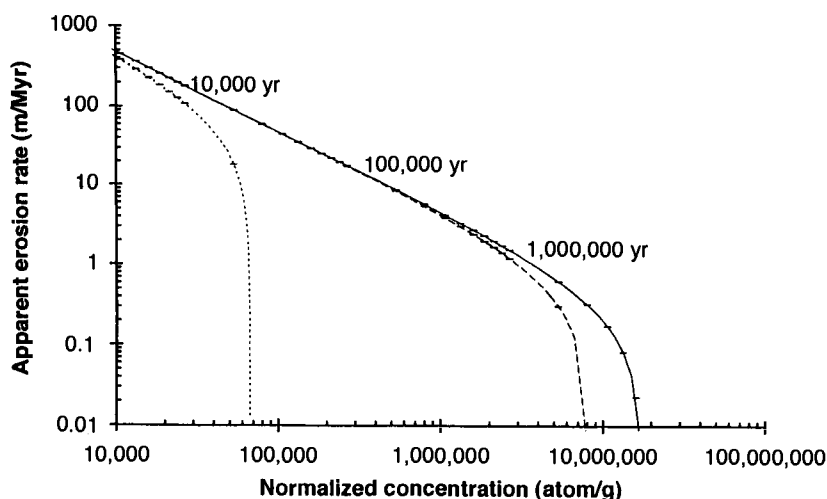


Figure 19.1. Apparent erosion rates as a function of steady-state ^{14}C (---), ^{26}Al (---), and ^{10}Be (—) concentrations. Concentrations of ^{10}Be were calculated using production rates for the Icacos watershed based on Lal [1991]; the production rates of the other nuclides are normalized to that of ^{10}Be . The horizontal ticks represent the time required to reach 95% of steady-state concentrations. Hyperbolic portions of the curves (where $\varepsilon L^{-1} \gg 1$) extend through the range where cosmogenic nuclides yield useful information on erosion rates. Analytical considerations make it impractical to work in regions with denudation rates over 1000 m Myr^{-1} . For ^{10}Be radioactive decay becomes the major loss term at erosion rates less than $\approx 0.1 \text{ m Myr}^{-1}$, and steady-state concentrations no longer yield information on erosion. This limitation is more severe for shorter-lived cosmogenic radionuclides.

The expressions in Equation 19.2 may be combined with the Equation 19.1 (with $t \gg (\varepsilon L^{-1} + \lambda)^{-1}$ and $x = 0$) to yield:

$$\bar{\varepsilon} = \bar{P} \bar{L} \bar{N}^{-1} \quad (19.3)$$

Equation 19.3 states that the concentration of a cosmogenic nuclide in material discharged by a river should represent the average concentration, weighted by the areas and erosion rates of the various erosion environments, for the basin. In principle, a single measurement of an in situ-produced cosmogenic nuclide in a representative sample of river sediment would then yield a long-term mean denudation rate for an entire basin. The long-term average denudation rates obtained through this method are insensitive to bioturbation of soils (Brown et al., 1995). Furthermore, because the average ^{10}Be concentration of material removed at a given denudation rate is insensitive to the style of erosion, long-term erosion rate estimates are not strongly affected by episodic mass wasting unless the mass wasting is on such a spatial and temporal scale that isotope concentration in outgoing sediments changes over time.

Storage in a floodplain can increase or decrease sediment cosmogenic nuclide concentrations, depending on the extent of prior exposure and the average depth of burial during transport through the fluvial system (Lal, 1985; Lal and Arnold, 1985; Nishiizumi et al., 1993; Bierman and Steig, 1996). In systems with significant sediment storage, sediment burial times can be examined using pairs of in situ-produced cosmogenic radionuclides with appropriate differing

half-lives. The ratio of ^{26}Al ($t_{1/2} = 0.7 \cdot 10^6$ yr) to ^{10}Be ($t_{1/2} = 1.5 \cdot 10^6$ yr) has been used in examination of the role of transport and deposition in formation of lateritic soils on 10^5 to 10^6 yr timescales (Brown et al., 1994). Similarly, the ratio $^{14}\text{C} : ^{10}\text{Be}$ has potential for use in examination of sediment storage over periods of 10^3 to 10^4 yr. Unfortunately, measurement of in situ produced ^{14}C is not yet routine.

19.2.3 Case studies

Luquillo Experimental Forest in eastern Puerto Rico

Brown et al. (1995) determined the abundance of in situ-produced ^{10}Be in quartz extracted from samples collected in the uppermost 3.26 km² of the Icacos River basin, a well-studied watershed in the Luquillo Experimental Forest, eastern Puerto Rico. To make these measurements, Brown et al. separated quartz from ridge crest soils, material from hillslopes affected by mass wasting, and river sediment.

The mean ^{10}Be concentration of the ridge-crest samples ($204 \pm 35 \cdot 10^3$ atom g⁻¹) corresponds to an erosion rate of 25 ± 4 m Myr⁻¹ (bedrock). In contrast, material transported by a recent hillslope mass-wasting event had lower concentrations of ^{10}Be , indicating higher average denudation rates on hillslopes. In this material, the ^{10}Be concentration in 0.25- to 0.50-mm sand ($35 \pm 9 \cdot 10^3$ atom g⁻¹) was greater than that in gravel-sized saprolitic material ($7 \pm 6 \cdot 10^3$ atom g⁻¹), typically present in soils at depths greater than 1.5 to 2 m. This distribution is consistent with a model of surface soil ^{10}Be abundance based on a background of the stable ridge-crest-like conditions (constant erosion at 25 m Myr⁻¹) punctuated by mass-wasting events with frequencies (10^4 yr) and magnitudes (2.0 m vertical depth) based on field studies (Larsen, 1991; Larsen and Torres-Sanchez, 1992).

In river sediments, chemical constituents are not uniformly distributed among all size fractions. Accordingly, Brown et al., (1995) determined ^{10}Be as a function of grain size in bed material from the Icacos main stem. The results reflect the relative contributions of material from ridge crests and from hillslopes. Fine sands (< 0.25 mm) have ^{10}Be concentrations ($\approx 220 \cdot 10^3$ atom g⁻¹) in the range of those observed in ridge-crest soils, suggesting that this material is from such low-energy erosional environments. In contrast, larger grain sizes (> 2.0 mm) have lower ^{10}Be concentrations ($\approx 38 \cdot 10^3$ atom g⁻¹), comparable to those of landslide material, consistent with mobilization of coarser material from depth by higher energy events.

An average ^{10}Be concentration for sediment exported from the basin was estimated using relative fluxes of quartz in each grain-size fraction. These relative quartz fluxes probably do not vary significantly with time; little variability in grain-size distributions has been observed in this system over a wide range of stream flows. The weighted average concentration ($120 \cdot 10^3$ atom g⁻¹) leads to two major conclusions. Considering the riverine sediment to be a mixture of two end members (stable ridge crests with $\approx 220 \cdot 10^3$ atom g⁻¹ and hillslopes affected by mass wasting with $\approx 35 \cdot 10^3$ atom g⁻¹) indicates that approximately 55% of exported sediment is mobilized by mass wasting and that the remainder is mobilized by sheetwash from more stable environments. These values compare favorably with estimates based on field observations and mapping (Larsen, 1991). In addition, the weighted average ^{10}Be concentration corresponds to a mean denudation rate of $43 (\pm 15)$ m Myr⁻¹. This may be compared to a rate of $75 (\pm 38)$ m

Myr⁻¹ calculated by mass-balance studies in the basin (McDowell and Asbury, 1994; Stallard and Edmond, 1983). Given the inherent uncertainties, these values are not significantly different. Moreover, they do not represent the same time period; mass balances represent “snapshots” of a few decades, whereas denudation rates based on cosmogenic nuclides represent a period of several thousand years of exposure and erosion. Furthermore, bioturbation buffers average cosmogenic-nuclide concentrations in surface soils against short-term changes in denudation rates.

Small arid drainage basins

Granger and Kirchner (1994 a,b) demonstrate that measurements of ¹⁰Be and ²⁶Al in sediments currently being deposited on two small, northeastern California alluvial fans can be used to calculate basin scale (0.1 to 0.4 km²) erosion rates similar to those deduced considering fan volume and age. They report denudation rates of 45 and 86 m/My for these very small basins. Furthermore, the authors find an inverse correlation between the slope of sub-drainages and the nuclide abundance in sediments sampled from these sub-drainages suggesting, as long suspected, that slope exerts a strong control over rates of denudation.

Larger drainage basins

Bierman (1995) and Bierman and Gillespie (in revision) measured in situ produced ¹⁰Be and ²⁶Al in 56 sediment samples collected from four basins in tectonically and climatically diverse environments (Figure 19.2). Their data show that the abundance of cosmogenic nuclides, measured in quartz-rich sediments, reflects basin-scale rates of erosion and that differences in ¹⁰Be/²⁶Al ratios can be used to understand qualitatively the transport history of some sediments. Using the isotopic data, Bierman and Gillespie estimated landscape denudation rates ranging from 4 m Myr⁻¹ at Wilpena Pound in the arid Flinders Ranges of South Australia to > 100 m Myr⁻¹ in the humid Oregon Coast Range. The erosion rates they calculate are consistent with those measured by other means and suggest that measurement of cosmogenic nuclides in sediments may be a new tool for determining long-term rates of landscape change at the scale of drainage basins and mountain belts.

To illustrate the results Bierman and Gillespie generated, we examine the data collected from Wilpena Pound, an 80-km² internally drained, synclinal basin which annually receives < 500 mm of precipitation (Figure 19.3). The flat basin floor (500 - 600 m asl) is rimmed by bare quartzite ridges (800 - 1200 m asl), has a single outlet, and is covered with a sparse mixed vegetation community dominated by Eucalyptus trees and grasses. Sediment appears to be generated on the rocky hillslopes by disintegration of the quartzite; sand size materials and cobbles are then transported down slope by slope wash and in ephemeral channels.

Eighteen isotopic measurements demonstrate that Wilpena Pound is slowly eroding (Figure 19.3). Nuclide abundances, measured in samples of quartzite from outcrops at Bridle Gap, can be used to calculate maximum limiting model erosion rates of 4 and 2 m Myr⁻¹, corresponding to minimum model exposure ages of 120 and 270 kyr. Sediment, sampled from a small (< 1 m width) ephemeral channel several hundred meters down slope of these outcrops, has similar isotopic abundances. The highest ¹⁰Be concentration was found in a rounded quartzite clast collected from a piedmont surface and demonstrates the exceptional durability of such material in the subaerial environment.

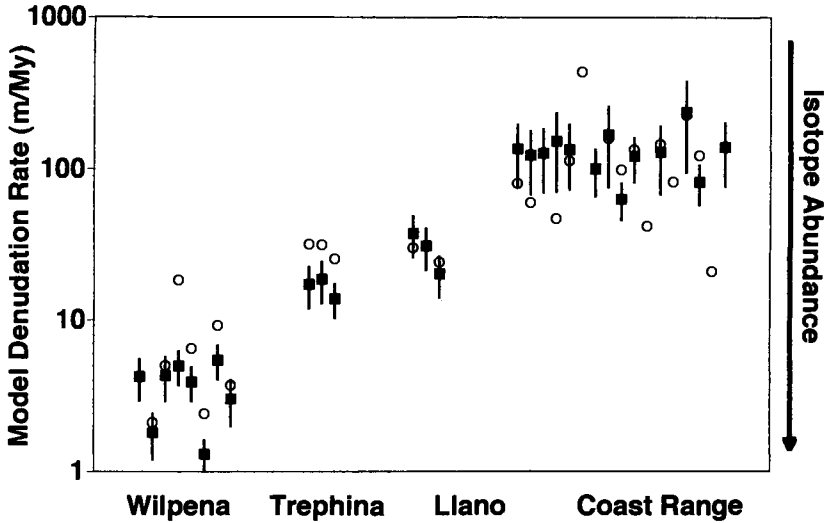


Figure 19.2. Cosmogenic isotope abundances measured in sediments and interpreted as model erosion rates. Solid squares are ^{10}Be data. Open circles are ^{26}Al . Error bars are 1σ (compounded for uncertainty in analysis production rates, half-lives, and decay constants) for comparison with erosion rates determined by other means. Wilpena Pound, south central Australia; Trepina Creek, central Australia; Llano Uplift, central Texas; Drift Creek, Oregon Coast Range.

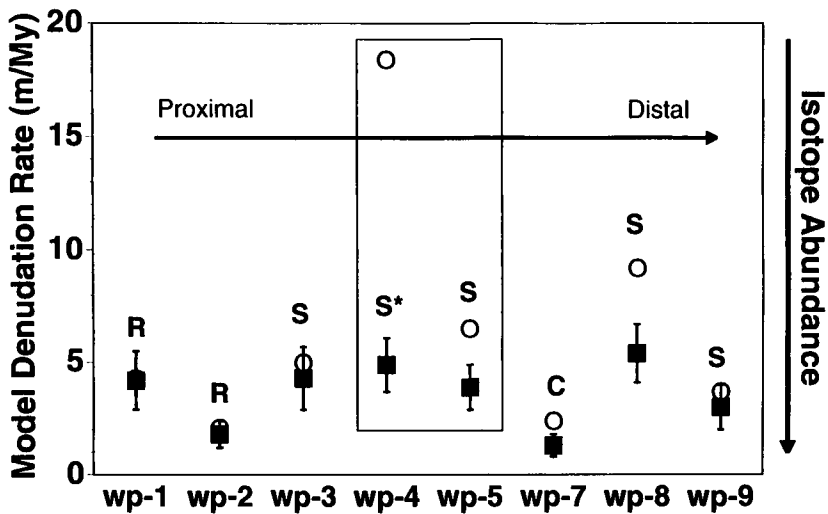


Figure 19.3. Model denudation rates for eight samples collected from Wilpena Pound, Flinders Ranges, south central Australia. Solid squares are ^{10}Be data. Open circles are ^{26}Al data. WP-1 and WP-2 collected from quartzite outcrops on ridges have coincident Be and Al model denudation rates. WP-3 collected from ephemeral wash downslope of WP-1 and -2. WP-4 and -5 collected from stream bank at depths of 120 and 20 cm below land surface, respectively; both show preferential decay of ^{26}Al during sediment transport and storage. WP-7 is a quartzite clast exposed on the surface. WP-8 is sediment from an active channel and WP-9 is sediment where the trunk stream exits the Pound. R = rock sample, S = sediment sample, C = alluvial clast, S* = sediment collected from below present land surface.

The decrease of ^{26}Al during sediment storage and transport (due to its shorter half-life than ^{10}Be) is well illustrated by several samples from Wilpena Pound which have low $^{26}\text{Al}/^{10}\text{Be}$ ratios and, as a result, discordant model ^{26}Al and ^{10}Be erosion rates. In such cases, the ^{10}Be -based erosion rate more closely meets the assumptions of the interpretive model. There is not a unique scenario by which such disequilibrium can be explained because the amount of cosmic-ray shielding probably changed over time as sediment accumulated on the basin floor and because the sediment may have been mixed by bioturbation. For example, if a sample of sediment collected 120 cm below the land surface in the side of an incised channel initially had nuclide abundances similar to material currently being shed from exposed rock surfaces, and was buried by several meters of sediment after deposition, the burial time would be about 2 Myr. Lastly, a sample collected from Wilpena Creek at the outlet of the Pound can be used to calculate a ^{10}Be denudation rate (3 m Myr^{-1}) which is consistent with rates estimated from outcrop samples and from other sediments collected within Wilpena Pound. The Al and Be model erosion rates for this sample are similar implying that the sediment had neither been stored for long periods of time during transport across the basin nor are large amounts of once deeply buried sediment being carried by the outlet stream. Erosion rates calculated using sediments from Wilpena Pound are consistent with long-term rates of denudation ($< 10 \text{ m Myr}^{-1}$) estimated for southeast Australia (east of Wilpena Pound) made using the volume of basin fills, the depth of basalt incision, and fission track analysis (Bishop, 1985).

19.3 Atmospheric Nuclides: ^{210}Pb

^{210}Pb has been used to obtain age information and determine rates of sedimentary processes in both marine and fresh-water environments (Goldberg, 1963; Appleby and Oldfield, 1992; Benninger, 1978). The half-life of ^{210}Pb is 22.3 yr, making it useful for dating stratified geological deposits formed during approximately the last 100 years. It has a range of applicability that fills part of the gap between the ranges of other useful radiochemical dating techniques, namely ^{14}C ($t_{1/2} = 5730 \text{ yr}$) and the shorter-lived radioactive isotopes, ^7Be ($t_{1/2} = 53 \text{ d}$) and ^{234}Th ($t_{1/2} = 24 \text{ d}$). ^{210}Pb is a member of the ^{238}U decay series and a progeny of ^{222}Rn , a noble gas, which accounts for its atmospheric delivery and geochemically useful departure from equilibrium with parent nuclides.

^{222}Rn is formed from the decay of ^{226}Ra , its immediate predecessor in the ^{238}U series (Figure 19.4). ^{226}Ra is present in variable amounts in rocks and soils. Some of the ^{222}Rn generated in lithogenic material at the earth's surface diffuses into the atmosphere. Separated from its parent isotope, ^{222}Rn decays ($t_{1/2} = 3.8 \text{ d}$) through four other short-lived isotopes ($t_{1/2}$ measured in minutes) to ^{210}Pb , which quickly is removed from the atmosphere by precipitation or dry fallout on land surfaces, in fresh water, and in the ocean. Runoff redistributes some ^{210}Pb from land areas to receiving waters. ^{210}Pb is particle reactive in water and tends to be rapidly incorporated into sediments of catchment basins and coastal areas. The fraction of ^{210}Pb having an atmospheric source is called "excess" or "unsupported". ^{210}Pb concentrations in areas where bottom sediments are actively accumulating are typically much higher in activity than the "supported" ^{210}Pb concentrations generated in situ by decay of parent nuclides in the sediment. The depth profile of $^{210}\text{Pb}_{\text{excess}} (= ^{210}\text{Pb}_{\text{total}} - ^{210}\text{Pb}_{\text{supported}})$ in a sediment core yields information about the rates of sedimentary processes such as sediment accumulation and bioturbation.

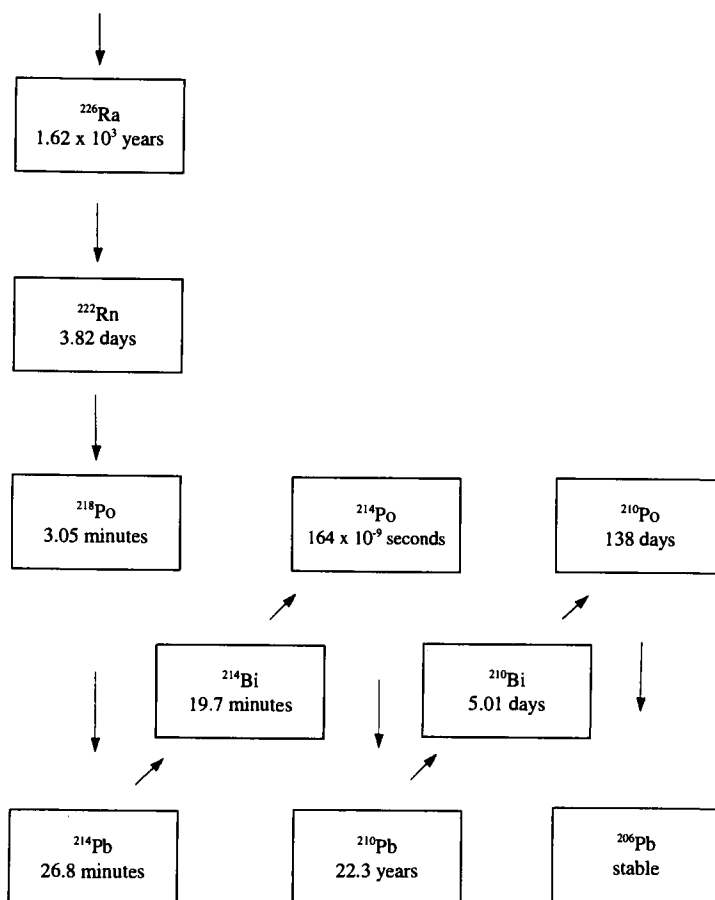


Figure 19.4. A segment of the ^{238}U decay series showing production of ^{210}Pb by radioactive decay of ^{226}Ra , ^{222}Rn and daughters. The vertical arrows indicate alpha decay, the oblique arrows beta decay.

19.3.1 Methods

Total ^{210}Pb is typically determined by measuring the alpha particle activity of one of its daughter products, ^{210}Po (Flynn, 1968), or by direct measurement of the 46.3 Kev gamma emission of ^{210}Pb (Cutshall et al., 1983). Supported concentrations of ^{210}Pb in a sample can be determined by measuring the activity of parent isotopes ^{226}Ra , ^{222}Rn , or ^{214}Pb by a variety of methods. Ideally, supported ^{210}Pb is determined on each sample. However, in cores of sediments having uniform composition and texture, the activity of parent isotopes may be constant and an estimate of the average supported ^{210}Pb activity for the whole core is derived from measurements of total ^{210}Pb below the horizon where excess ^{210}Pb is not expected (Figure 19.5).

As with any sample for which the analytical objective is to determine age-sediment depth relationships, it is critical to have the sample collected with minimal disturbance. When

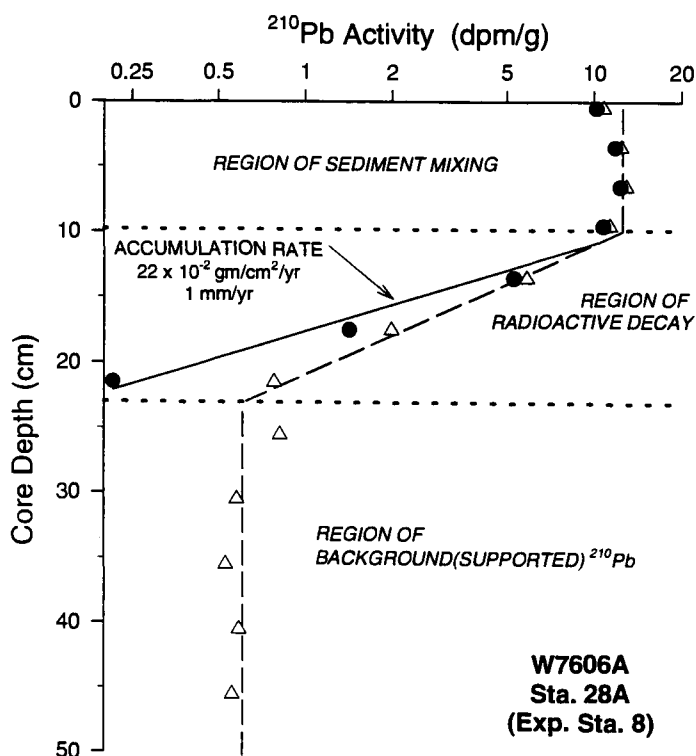


Figure 19.5. A typical profile of ^{210}Pb activity for a sediment core from the Washington shelf (after Nittrouer, 1978). Dashed line and open triangles represent total ^{210}Pb , solid line is least squares regression through excess ^{210}Pb shown as solid circles.

sampling recent lake or marine sediments with high water content, the sampling device should approach and penetrate the sediment/water interface slowly in order to minimize the bow wave and subsequent resuspension and loss of the surface material. Relatively undisturbed sediment cores can be collected by scuba divers from shallow water depths (< 30 m). Suitable coring devices which operate at any water depth have been designed to slow the entry of the collecting box or core barrel (Pamatmat, 1971, Barnett et al., 1984). Compaction of sediments during coring can be minimized by using a large diameter sampler (> 10 cm) or by using a piston in a device with slow penetration. A large diameter sampler is also advantageous because it provides enough material for analysis at smaller depth intervals, thereby increasing the depth resolution for ^{210}Pb analysis, as well as any other geochemical analyses that may be planned. The "freeze core" technique is useful for coring sediments that have a very high water content or contain methane gas. A hollow rectangular probe, insulated on three sides, is filled with dry ice and methanol and pushed into the sediments. The sediments freeze against the uninsulated side and are recovered with minimal compaction and disturbance (O'Sullivan, 1983; Crusius, 1992). Prompt measurement of ^7Be (half life 53 days) in the upper sediment section can give valuable information regarding loss of uppermost sediments during coring.

19.3.2 Interpretation

There are a number of assumptions and desirable sedimentary conditions that simplify the interpretation of ^{210}Pb profiles in recently deposited sediments. First, there is the common assumption of a closed system after deposition; that is, no gains or losses of ^{210}Pb have occurred except by radioactive decay. A second assumption is that the supply of excess ^{210}Pb to the depositional surface has been constant with time. Desirable conditions for study of ^{210}Pb include: high rates of sediment accumulation ($> \text{about } 0.1 \text{ cm/yr}$) so that subsampling can attain reasonable time/depth resolution, low rates of sediment mixing by organisms or physical processes relative to the accumulation rate, and uniform sediment texture and composition over the depth interval sampled. Deviations from these conditions can often be accommodated with ancillary data and/or mathematical models in order to assign model ages. For example, decoupling the effects of bioturbation from the accumulation rate calculated from the ^{210}Pb profile is often addressed by comparing the depth distribution of other radioisotopes, such as $^{239+240}\text{Pu}$ and ^{137}Cs , that were introduced at a well documented rate from the atmosphere. Atmospheric bomb testing in the early 1960's caused widespread deposition of these isotopes in accumulating sediments. The peak fallout in 1963 often corresponds to a distinct marker horizon in sediment. This horizon can be used both to test the ^{210}Pb -derived ages for the same sediment horizon and to estimate the amount of bioturbation, because mixing causes a broadening of the 1963 peak in the sediment-depth profile of bomb-derived isotopes. Pu isotopes may be the preferred complement to ^{210}Pb in fresh water because of lower post-depositional mobility than ^{137}Cs in some fresh water environments (Crusius and Anderson, 1995).

A semi-log plot of both total and excess ^{210}Pb vs. sediment depth (Figure 19.5) illustrates how sedimentation rates are calculated and ages assigned for a typical sediment profile. The profile of total ^{210}Pb below 23 cm shows the characteristic low and uniform activity that occurs below the point where unsupported ^{210}Pb has decayed to an insignificant level. The average ^{210}Pb concentration for this region is often taken as a measure of the supported ^{210}Pb , in this case 0.5 dpm/g. Subtracting 0.5 dpm/g from the total at each sampling depth yields the excess ^{210}Pb curve (solid line) which is uniformly high over the top 9 cm and decreases with constant slope between 10 and 23 cm. The uniform values in the surface layer are interpreted to be a result of sediment mixing by organisms or physical processes. The sedimentation rate can be calculated from the slope of the line between 10 and 23 cm using the relation:

$$A(z) = A(o) e^{-bz} \quad (19.4)$$

where $A(z)$ is the excess ^{210}Pb activity at depth z , $A(o)$ is the activity at the surface (or bottom of the uniformly mixed layer), and b is the slope defined by a regression through the data. Changing the units of slope from depth to time, the rate of sediment accumulation, S , is equal to λ/b in cm/yr, where λ is the decay constant for ^{210}Pb . The sedimentation rate can be converted to units of mass $\text{cm}^{-2} \text{ year}^{-1}$ when the grain density and water content are known. In addition, the total inventory of ^{210}Pb in the core can be estimated from bulk density measurements and compared to the calculated standing stock expected from the atmospheric flux of ^{210}Pb reported in the literature (Turekian et al., 1983). Inventories higher than the expected standing stock can be an indicator of sediment focusing, while values lower than expected can suggest sediment by-passing or erosion.

19.3.3 Applications

Baskaran and Iliffe (1993) published a study in which they used the ^{210}Pb technique to date layers in speleothems, cave deposits which are known to record climate change by means of such indicators as stable isotope ratios. Excess ^{210}Pb contents of carbonate layers in an icicle shaped stalactite and a "soda straw" stalactite showed uniform exponential decreases from younger to older layers, indicating uniform growth of 0.028 mm/yr laterally, and 1.1 mm/yr longitudinally for the icicle and "soda straw" stalactites, respectively. Supported ^{210}Pb was found to be insignificant relative to the amounts of unsupported ^{210}Pb in the nearly pure carbonate precipitate. The authors concluded that ^{210}Pb is an appropriate method for determining growth rates of speleothems deposited within the last 100 years. These growth rates may also prove useful for extrapolation in order to estimate ages of layers which are too young for other dating techniques, but too old to contain excess ^{210}Pb such as cave deposits in the range of 100 - 1000 years old.

Stihler et al. (1992) used a combination of ^{210}Pb and ^{137}Cs techniques to date lacustrine sediments in an Alaskan lake, previously dated only by counting rythmites interpreted as varves. They found the sedimentation rate to be on the order of tenths of a millimeter per year, an order of magnitude lower than the rythmite-based, previous estimate. They also applied tephrochronologic techniques to glass shards contained in the cores and estimated sedimentation rates that were in agreement with the radioisotope data. The ^{210}Pb and ^{137}Cs data helped to confirm that the rythmite layers in the lake sediment were not annual varves and that other climatological interpretations based on the varve-derived sedimentation rates should be reevaluated. These studies represent just part of the wide range of applications of applications for these isotopes in the study of modern geological processes (Appleby and Oldfield, 1992).

19.4 Combined Approaches to Catchment Landscape Analysis: ^{137}Cs and ^{210}Pb

Geomorphologists have used sediment deposits or suspended particle loads in rivers to evaluate erosive processes in catchments (e.g. Reneau et al. 1989). Linking this approach to fluxes of anthropogenic radionuclides, such as ^{137}Cs or natural ^{210}Pb opens up a new avenue for understanding processes such as particle formation via weathering, soil formation, denudation, transport, and sedimentation. In this section, we summarize the most recent applicable work.

As discussed above, ^{210}Pb ($T_{1/2} = 22.3$ yr) is a decay product of naturally occurring ^{238}U . It is formed in situ, in bedrock, soils and sediments ($^{210}\text{Pb}_{\text{supported}}$) as well as in the atmosphere due to the escape of its parent ^{222}Rn from the geosphere. After a residence time of about 10 days in the atmosphere, ^{210}Pb generated by ^{222}Rn in the atmosphere is transferred to the geosphere, where it is deposited by precipitation and dry deposition onto soils, snow or glaciers, outcropping rock and surface waters. ^{137}Cs ($T_{1/2} = 30$ yr) is of anthropogenic origin with the most significant sources being atmospheric atomic bomb tests (maximum in 1962/1963, of mostly stratospheric origin with world-wide deposition) and the accident at the Chernobyl nuclear reactor (April, 28, 1986, with deposition mostly constrained to Europe). The low levels of Chernobyl ^{137}Cs in groundwater (Waber et al., 1986) and the rapid activity decrease in rivers (Santschi et al., 1986) suggest that ^{137}Cs deposited on soil surfaces is removed from the landscape primarily by particle transport. Activities of ^{137}Cs and $^{210}\text{Pb}_{\text{excess}} (= ^{210}\text{Pb}_{\text{total}} - ^{210}\text{Pb}_{\text{supported}})$ can thus be used to understand better the geomorphic history of catchments by

analyzing lake sediments, soil and regolith, and subsurface and surface water including the suspended particle load. Information regarding fall-out fluxes (Table 19.1) represents an important prerequisite for any such study.

Table 19.1. Summary of atmospheric flux data for ²¹⁰Pb and ¹³⁷Cs.

Fallout Flux (Bq m ⁻² yr ⁻¹)	Location	Reference
²¹⁰ Pb _{excess} 140 96 130 152 74-204 130	Lake Zürich, CH Connecticut, USA Fribourg, CH Lake Geneva, CH Lake Constance, CH Black Forest, D	Schuler et al., 1991 Turekian et al., 1983 von Gunten and Moser, 1993 using a transfer velocity of 0.9 cm/s (Turekian et al., 1977). Dominik et al., 1987 Dominik et al., 1981 Hemmerich (unpubl. data)
¹³⁷ Cs deposition after Chernobyl 3.8 20.0	Lake ZH, CH Lake Lugano, CH	Santschi et al., 1988 Kuer, 1989
¹³⁷ Cs bomb fall-out 2.5 1.1 3.4	Swiss Alps California, USA Swiss Alps	Albrecht, 1995 Monaghan et al., 1992 Dominik et al., 1987

19.4.1 Lake sediments

Measured activities of ²¹⁰Pb and ¹³⁷Cs in lake sediments have been used to estimate sedimentation rates (Krishnaswami et al., 1971). The ²¹⁰Pb method is most applicable when the ²¹⁰Pb flux and the sedimentation rate have remained constant. Protocols have been formulated to obtain model sedimentation rates in less ideal settings (Robbins, 1978). The use of ¹³⁷Cs relies on the dominance of atmospheric deposition during 1963 and 1986 and the quick removal of ¹³⁷Cs from the water column in lakes via sinking suspended particles. For example, 75% of Chernobyl radiocesium deposited during May, 1986 had been eliminated from the water column by November, 1986 (Santschi et al., 1988). A sediment core from Lake Brienz (alpine front, Switzerland; M. Sturm, EAWAG, unpublished results, Figure 19.6) illustrates the depth variation of the anthropogenic radionuclide ¹³⁷Cs and the natural ²¹⁰Pb. The variation of ¹³⁷Cs with depth shows the two major peaks which are correlated with atmospheric atomic bomb testing (maximum deposition (1962/63) and the Chernobyl accident (1986). In spite of variable transport of ¹³⁷Cs from the catchment area to the lake and the possibility of mobility within the sediment these maxima can be used to date unambiguously two sections of the sediment core

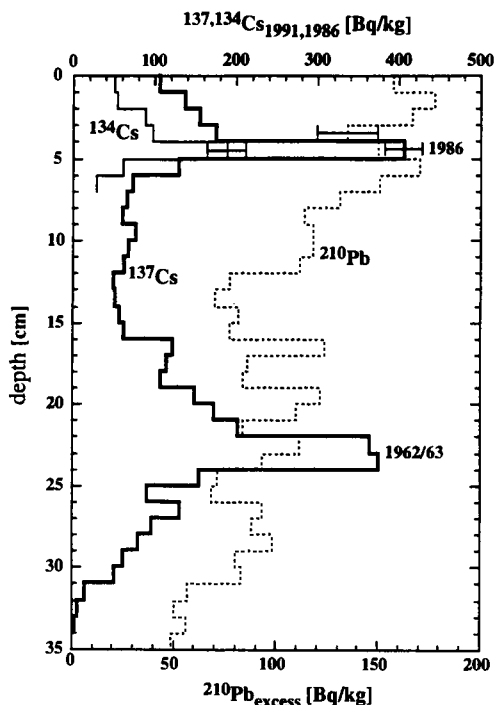


Figure 19.6. Depth distribution of the anthropogenic radionuclides ^{134}Cs (thin continuous line, decay-corrected to the Chernobyl event), ^{137}Cs (thick continuous line) and the natural radionuclide ^{210}Pb (dashed line, the former two decay corrected to 1991, the date of sediment coring). A single error-bar indicates for each radionuclide a representative 2 sigma error. Significant ^{134}Cs , due to its short half-life of 2 years, is found only in samples that deposited shortly after the Chernobyl accident. ^{137}Cs indicates both the Chernobyl accident as well as the maximum in atomic bomb related deposition. The strong variability of ^{210}Pb as a function of depth illustrates the difficulty of applying the ^{210}Pb dating method in lakes with nuclide influx from a complex catchment.

and to obtain averaged sedimentation rates for the periods 1963–1986 and 1986 to the sampling date. The variability of ^{210}Pb with depth is considerably more complex. The overall decrease in ^{210}Pb activity might give an indication of in-situ decay and therefore age, but the variability from sample to sample is considerable. One possible cause could be the changing influx of ^{210}Pb from the catchment to the lake, which varies mostly as a function of extent, stability and erosion regime of the catchment soil cover (see below).

19.4.2 Soils

The specific activity of ^{137}Cs in soils varies according to land use. If the average activity measured in pastures is defined as 1, idle land has a specific activity of 0.95, forest, 0.73 and cultivated soil, 0.24 (Ritchie et al., 1974). Unrotted soil profiles can be used to evaluate inventories for ^{137}Cs fall-out (Table 19.1). In an ideal soil profile, where ^{210}Pb enters a closed system via direct atmospheric precipitation with a known flux q , the concentration (C) of $^{210}\text{Pb}_{\text{excess}}$ follows model Equation 19.5:

$$C = \frac{\left(\frac{q}{\lambda}\right)(1 - e^{-\lambda t})}{\rho_s z_s} \quad (19.5)$$

where λ represents the decay constant (0.031/yr), ρ_s is the soil density and z_s the depth of an ideal, well mixed soil profile. The only unknown in the equation is the time t , which marks the point at which the bedrock (an inefficient adsorber, with starting condition $C(0) = 0$) is altered to a soil. The transition from bedrock to regolith to soil is exemplified by a study using ^{210}Pb and ^{137}Cs (Albrecht, 1995). An unaltered shale shows no measurable activity of ^{137}Cs ; ^{210}Pb amounts to 23 Bq kg⁻¹, which represents the in situ, radiogenically produced fraction. In a sample of altered 'muddy' clay, ^{137}Cs and ^{210}Pb increase to 75 and 67 Bq kg⁻¹, and in the top soil layer both exceed 600 Bq kg⁻¹. The higher activity observed in regolith and in soils for both ^{210}Pb and ^{137}Cs reflect the more efficient radionuclide uptake based on a larger surface area to mass ratio of soils than of bedrock.

19.4.3 Water samples

The analysis of radionuclides in water samples and transported particles links the source compartment (e.g. soils) with the final resting place of some particles, lake sediments. Nuclides are transported in both dissolved and particulate phases; recent results indicate that ^{210}Pb and ^{137}Cs can be complexed in aqueous solution by different dissolved organic substances in particular, humic substances. Continuous sampling as a function of season, run-off, altitude, and catchment pedology can give information on particle and radionuclide residence times and removal rates in the catchment. A major change in soil stability induced by climatic or anthropogenic factors will be reflected by the riverine flux of soil particles and attached radionuclides.

19.4.4 Case studies

To evaluate further the merits of paired nuclide catchment studies, several data sets will be discussed in more detail. Two study areas situated in the Swiss Alps will be discussed here, (1) the upper Rhone watershed (Canton Wallis, S central Switzerland, surface area 5220 km², minimum altitude 372 m, maximum altitude 4660 m) where the surface consists of glaciers and barren rocks (38%), forests and pastures (46%) and cultivated soils (16%) (Dominik et al., 1987), and (2) the Muttsee catchment (Canton Glarus, E central Switzerland, surface area 3.4 km², minimum altitude 2446 m, maximum altitude 2893 m) characterized by almost 100% barren shales and shaley sandstones covered only by patches of soil (Albrecht, 1995).

Rhone River

A study of riverine particle and radionuclide transport was carried out between August, 1982 and August, 1983 near the mouth of the Rhone delta in Lake Geneva. Five stations upstream were characterized by catchments with increasing portions of barren rocks and glaciers. The goal of the study was to quantify soil erosion and sediment and contaminant delivery in watersheds. The results for radionuclides in fluvial suspended matter indicated a high

variability with ^{137}Cs activities ranging from 3.7 to 59.2 Bq kg⁻¹ with an average of 26.3 ± 13.3 . $^{210}\text{Pb}_{\text{excess}}$ showed similar variability (0 - 92.5 Bq kg⁻¹; average 41.8 ± 27.0 Bq kg⁻¹). There are a few common features to data from all basins including: generally high nuclide activities during winter and summer months and low activities during the spring and fall. The spatial and temporal variation observed in the nuclide data reflect seasonal changes as well as the complex hydrologic and geomorphic setting of the 5220 km² basin. For example, in the spring, dilution of sediments containing high radionuclide levels occurs as stream beds are reworked and previously unexposed glacial till is eroded. Erosion of particles from forest or pastures (with a high specific activity) will tend to increase the activity of particles in fluvial suspension, while particles derived from cultivated soils and newly deposited till (low specific activity) have the opposite effect.

The variation of radionuclide fluxes in the Rhone as a function of distance from the source gives information regarding the source of eroded particles. The specific instantaneous fluvial outputs of $^{210}\text{Pb}_{\text{excess}}$ and ^{137}Cs (defined as the particulate fluxes divided by the watershed surface area upstream from the point of sampling) indicates the importance of the lower part of the watershed as a particle source between December and March. In May, the middle watershed becomes the dominant radionuclide source; in August it is the upper watershed which contributes greater quantities of radionuclides. Near the source of the river, the radionuclide fluxes are always relatively low. These variations can be explained by changing vegetative cover and thus changing particle sources. For example, from March through August the soil loss from cultivated fields under vegetative cover is relatively low compared to higher activity fluxes from upland forest and bare rock sites.

The calculation of a yearly nuclide budget requires a relationship between the water discharge, which is measured hourly at many Swiss hydrologic stations, and the specific radionuclide activity of suspended particles. Determining such a relationship is labor intensive. Discrete sampling at constant frequencies has been shown to result in load estimations which are systematically biased (Ongley et al., 1977; Thomas, 1983). Different relationships can be found in the literature (Dominik et al., 1987; Müller and Förstner, 1968; Ongley et al., 1977; Peters-Kümmerly, 1973), but a consensus has not yet been reached.

Muttsee Basin

The Muttsee basin was chosen as a sample site because of its simplicity. The central part of the basin is occupied by a lake with a 0.42 km² surface area. The catchment (2.95 km²) is composed of shales and shaly sandstones, minimizing groundwater movement. The water budget and sediment budgets are both well constrained. The high altitude and near lack of vegetative cover reduces chemical weathering; physical erosion thus accounts for much of the total erosion.

A comparison between radionuclides in sediments from the mid-land reservoir Lake Wohlen (situated along the Aare River NW of Bern, Switzerland) and the sediment core taken in the Muttsee (Figure 19.7) allows one to assess differences in the radionuclide deposition history. The depth profile of Lake Wohlen indicates 2 distinct peaks of ^{137}Cs related to the 1963 bomb fall-out maximum and the 1986 Chernobyl accident (characterized by the coexistence of ^{134}Cs , with a half-life of 2 years - not shown). In the Muttsee sediment core the first peak (maximum 300 Bq/kg ^{137}Cs) represents 1963 and the major peak (with a maximum of 1112 Bq/kg ^{137}Cs and 340 Bq/kg ^{134}Cs) is related to the fallout of 1986. These markers allow one to determine

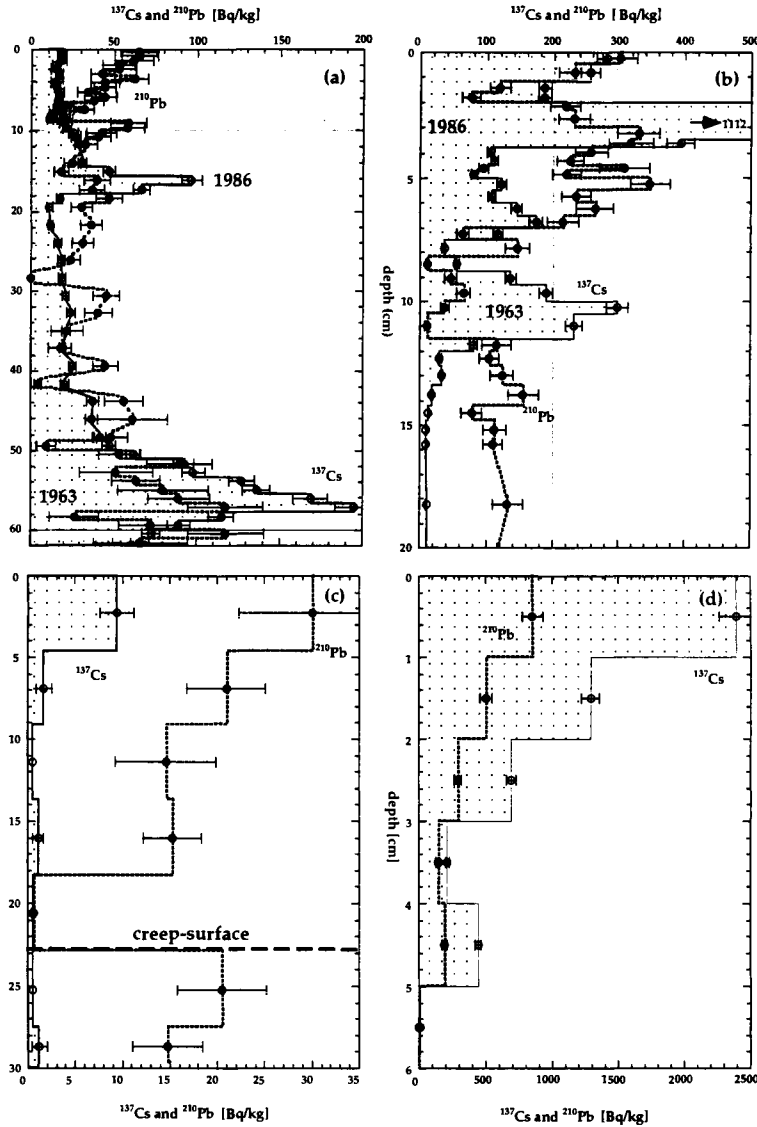


Figure 19.7. ^{137}Cs (open circles) and ^{210}Pb (filled circles) activity depth profiles of radionuclide final repositories (lake sediments, a and b) and storage compartments (soils, c and d). The lake sediment cores are taken from lake Wohlensee (a), a dam, located along the course of the Aare River NW of Bern and (b) from Muttsee, a small lake located at 2500 m elevation in east-central Switzerland. Both lakes show the increased atmospheric input of ^{137}Cs (age-corrected to the date of coring), related to the maximum atomic bomb flux in 1963 and the Chernobyl nuclear accident in 1986. ^{210}Pb (age-corrected based on the ^{137}Cs age scale), which has a roughly constant atmospheric input function, shows considerable variations correlated to ^{137}Cs outside the peak areas, bearing valuable information in regard to catchment processes. One such process is a soil erosion event that occurred in the Muttsee catchment in the 1970s. One crucial catchment variable is the presence, extent and stability of a soil cover. The two radionuclide depth profiles (c and d) are characteristic for two soil categories. The first was taken from a steep talus of the Muttsee catchment (c) and shows an irregular depth profile, with a creep horizon. The profile of category 2 taken on a plateau (d) depicts regular decrease of both radionuclides with depth.

sedimentation rates, which varied between 0.31 cm/yr during the period 1963-1986 and 0.57 cm/yr during the period 1986-1992. The third peak (maximum = 180 Bq/kg), which occurred around 1976 is not related to any significant Cs-radionuclide input and indicates a delayed, irregular radionuclide transfer from the catchment area into the lake.

Analyses of waters draining zones covered by soil and regolith compared to those draining barren rock surfaces give evidence of natural filtration via surface absorption of ^{137}Cs and ^{210}Pb ; activities were above 1 Bq m $^{-3}$ for ^{137}Cs and above 5 Bq m $^{-3}$ for ^{210}Pb only in unfiltered waters that originate in zones of barren rock (3.6 Bq m $^{-3}$ for ^{137}Cs and 16.2 Bq m $^{-3}$ for ^{210}Pb); activities in the lake water at 30 m depth are 0.3 and 2.5 Bq m $^{-3}$, respectively.

Radionuclide dating of lake sediments allows estimation of short-term sedimentation and erosion rates. Sedimentation rates of 0.31 and 0.57 cm yr $^{-1}$ for the periods 1963-1986 and 1986-1992 allow calculation of erosion rates that range between 108 and 198 m Myr $^{-1}$ ($2.9 \cdot 10^5$ and $5.3 \cdot 10^5$ Kg km $^{-2}$ yr $^{-1}$). This is rapid compared to rock surfaces in less mountainous regions (see above; Saunders and Young, 1983; Bierman, 1994). Regional rates, given in kg km $^{-2}$ yr $^{-1}$, vary between $2.7 \cdot 10^4$ for Europe (Garrels and Mackenzie, 1971), $5 \cdot 10^4$ for the Swiss lowlands, (Santschi and Schindler, 1977) and $\sim 1 \cdot 10^6$ for the Swiss alpine region, (Li and Erni, 1974). The value of $0.5 \cdot 10^6$ kg km $^{-2}$ yr $^{-1}$ for the Mutsee area is comparable to Li and Erni's determination of physical erosion rates in high alpine regions.

The increase in deposition rate between the periods of 1963-1986 and 1986-1993, the depth distributions of both ^{137}Cs and ^{210}Pb , the small amplitude of the 1963 peak, the continued input into lake sediments in spite of discontinued atmospheric ^{137}Cs input after 1963 (Figure 19.7) and the increase in ^{210}Pb activity from ~ 50 to ~ 250 Bq kg $^{-1}$, all indicate a significant change in the erosion history and soil cover of the catchment area. The pulse of ^{137}Cs , dated to ~ 1976 , suggests a sudden delivery of particle bound radionuclides from the catchment to the lake at that time. The observed increase in sedimentation rates during the last 40 years may not be a local phenomenon, as it has been observed in other Swiss lakes and reservoirs. The cause of increasing sedimentation rates is uncertain.

Because the lake basin can be considered a closed system, radionuclide budgets can be calculated using the fallout data from Chernobyl. The total deposition for the Chernobyl event amounts to $7.8 \cdot 10^9$ Bq, of which 76% is found in lake sediments. Total ^{210}Pb total deposition for 1986-1992 amounts to $3 \cdot 10^9$ Bq, of which $2.4 \cdot 10^9$ are found in lake sediments, thus 80% are retained. The similarity between the results obtained for Chernobyl ^{137}Cs and natural ^{210}Pb is most encouraging. The remaining inventory of isotopes, 20 - 25%, would likely be found in the soil and regolith cover of the catchment area.

Scandinavian Lakes

In this section, we summarize recent results of radionuclide transport and deposition in two Scandinavian catchments, one located in central southern Norway (Brittain et al., 1992) the other in central northern Sweden (Malmgren and Jansson, 1995). In both studies, the transport of Chernobyl-related ^{137}Cs from the catchment to the aquatic system was analyzed and retention by lake sediment evaluated.

In Norway, Lake Heimdalsvatn (1090 m asl; 0.78 km ^{2} surface area) and its catchment (1843 m asl highest point; 23.6 km ^{2} surface area) were chosen. After the Chernobyl accident, 150 -

200 kBq m⁻² of ¹³⁷Cs were deposited in the catchment, associated with both organic and mineral material. During March 20-24, 1990, a period during which the lake was ice-covered, the main inlet river, a major tributary and the outlet river were sampled and ¹³⁷Cs determined in the particulate and dissolved fractions. The main inflow represents only 42% of the total water input. It was used for the overall budget calculations in spite of differences in particulate organic matter concentrations between the main flow and smaller tributaries.

The following results were obtained: (1) Of the ¹³⁷Cs transported into the lake, about 80% is in dissolved, low molecular weight forms with a cut-off at 10kDalton, the rest is adsorbed to colloids or larger particles; (2) 50% of the total ¹³⁷Cs was retained in the lake system, presumably adsorbed to particles and transferred to lake sediments.

In Sweden, the catchment of the River Öre was sampled to determine rates of radionuclide and particle transfer (Malmgren and Jansson, 1995). The total catchment has a surface area of 2940 km², with altitudes ranging from 714 m to sea level. After the Chernobyl accident, between 20 and 30 kBq m⁻² ¹³⁷Cs were deposited in the catchment area. Of the total ¹³⁷Cs deposited, approximately 7 - 10% were removed during 1986. After 1987, this annual terrestrial export lowered considerably, stabilizing at 0.1 to 0.2 % of the stock. Systematic measurements along the course of the river were not performed. Lake Öträsket is the only significant trap in the course of the river. A total of 65,000 GBq of ¹³⁷Cs were deposited in the lake catchment (2173 km²). Of this stock, 4700 GBq were transferred to the river during 1986 and 900 GBq during the period 1987 to 1991. Based on sediment trap and sediment core results, the portion of ¹³⁷Cs retained in Lake Öträsket is estimated to be 500 GBq for 1986 and 100 GBq for the period 1987 - 1991, in both cases about 10%. As particles > 0.45 µm diameter are efficiently removed via sedimentation in the lake, most of the ¹³⁷Cs must have been in dissolved or colloidal form, possibly complexed by dissolved organic matter, the annual mean concentration of total organic matter is high, 9.5 mg/l.

The differences in the retention of ¹³⁷Cs by lake sediments are striking. Such differences are due in part due to different water residence times and accordingly, different reaction times between radionuclide and particles. The concentration of dissolved organic substances also likely plays a role in nuclide transport. The relatively larger amounts of dissolved organic material, which characterize waters draining from boreal forest and mires may solubilize more ¹³⁷Cs than the relatively organic-free waters draining high alpine settings lacking soil and plant cover.

19.5 Tracing of Sediment Sources and Identification of Erosion Processes Using Natural and Anthropogenic Radionuclides

In this section, we summarize the application of various radionuclides to the identification of sediment sources and the characterization and identification of catchments and depth of erosion processes. The isotopes of interest need to be distributed in a predictable fashion and should provide a high probability of providing a unique label for that sediment. Two general classes of isotopes can be distinguished: (1) Lithogenic radionuclides, which comprise ⁴⁰K, ²³⁸U and ²³²Th including the members of the U and Th decay-chains. (2) Atmospheric or fall-out radionuclides, which comprise amongst others ²³⁹⁺²⁴⁰Pu, ²¹⁰Pb, ¹²⁹I, ¹³⁷Cs, ^{7,10}Be. These isotopes are produced by different reactions but have in common the transfer to Earth's surface via precipitation and dry deposition. For the remainder of this section, we focus on radionuclides

that can be measured by γ -spectroscopy, a fast, reliable and relatively inexpensive technique (Murray et al., 1987).

19.5.1 Nuclides of importance

Of primary interest are ^{222}Rn , ^{226}Ra , members of the decay chain of ^{238}U and ^{228}Ra , and ^{228}Th , members of the ^{232}Th decay chain (lithogenic group). Due to different U/Th ratios in source rocks, different soil chemistry, and the different geochemical behavior of the radionuclides in question, variable concentrations and ratios are expected in different sediment source regions (catchments). As the work by Olley et al. (1993) has shown, sediments derived from different catchments can be distinguished on the basis of their ^{226}Ra and ^{232}Th activity ratios. In the simplest case, where sediments originate from 2 catchments, a two-component mixing model can be used to model the contributions from each catchment:

$$AX + BY = C \quad (19.6)$$

X and Y represent the relative contribution of each catchment, with $X + Y = 1$; A, B and C are the $^{226}\text{Ra}/^{232}\text{Th}$ ratios of the two input sources and the output mix, respectively.

The atmospherically derived radionuclides ^7Be , ^{210}Pb and ^{137}Cs can readily be measured by γ -spectroscopy. ^7Be (half-life = 53 days) is formed by spallation reactions on O and N in the upper atmosphere induced by cosmic rays (Brown et al., 1989). ^{210}Pb (half-life = 22.3 yr), forms through the decay of ^{222}Rn , a member of the ^{238}U decay chain. As mentioned earlier, some of the lithogenic ^{222}Rn diffuses into the atmosphere where it decays to ^{210}Pb . The world-wide distribution of ^{137}Cs is due to atmospheric atomic bomb testing during the 1950's and 60's (UNSCEAR, 1993). All 3 radionuclides are transferred to Earth's surface primarily by wet precipitation. Deposition of ^7Be and ^{210}Pb is continuous, whereas deposition of ^{137}Cs is related to human activity and has ceased in most places on Earth during the 1970's (with the exception of Europe due to the Chernobyl accident in 1986). The differential penetration depth of these radionuclides (Table 19.2) can be used to suggest the original location of sediment in the soil profile and to recognize dominant erosion processes in the catchment.

Table 19.2. Summary of half penetration depth for ^7Be , ^{210}Pb and ^{137}Cs .

Nuclide	Depth (mm)	Location and Reference
^7Be	0.7 - 10	Australia, pastured soil (Olley et al., 1993)
	0.5 - 10	Swiss Alps, patchy soil (Albrecht et al., 1996)
	40 - 50	USA, marsh soil (Olsen et al., 1985)
^{210}Pb	10 - 30	Australia, pastured soil (Olley et al., 1993)
	10 - 20	Swiss Alps, patchy soil (Albrecht et al., 1996)
	100 - 400	USA, marsh soil (Olsen et al., 1985)
^{137}Cs	30 - 50	Australia, pastured soil (Olley et al., 1993)
	10 - 20	Swiss Alps, patchy soil (Albrecht et al., 1996)

Table 19.2 shows the large range in penetration depth for the different radionuclides. The penetration depth varies as a function of soil condition and atmospheric input. In general, penetration is less in bare compacted soil than it is in soil maintaining grass cover with a well developed root system; however, it is essential to evaluate the actual penetration depth in each area under investigation. The roughly exponential radionuclide depth distribution in soil profiles can be illustrated using a soil section taken in the Swiss Alps (Figure 19.8; Albrecht, 1995; unpublished data). The half penetration depth for ^7Be for this example lies below 10 mm, for ^{137}Cs and ^{210}Pb , which have very similar depth profiles the half penetration depth lies between 10 and 20 cm.

The difference in the penetration depth between ^7Be and ^{137}Cs (and ^{210}Pb) inspired Wallbrink and Murray (1993) to develop a conceptual model that allows recognition of different erosion processes in catchments. Figure 19.8 illustrates their approach. High values of ^7Be and ^{137}Cs in suspended particles removed from the catchment should indicate an origin from the uppermost section of a soil profile, removed by sheet or minor rill erosion. High levels of ^{137}Cs and low values of ^7Be indicate a deeper origin of the eroded particles, suggesting rill erosion. When both radionuclides are very low or below the detection limit, the source of the particles is deeper, perhaps sediment was eroded from the collapsing walls of gullies. Finally, high values of ^7Be and low values of ^{137}Cs indicates that the source sediment was low in ^{137}Cs (post Chernobyl), but that the newly deposited sediment was exposed to atmospheric ^7Be from precipitation.

19.5.2 Case studies

Rainfall simulation

In a grazed paddock near the town of Goulburn in New South Wales, Australia, Wallbrink and Murray (1993) used a rainfall simulator at intensities of 100 - 150 mm hr⁻¹ to generate surface runoff. During the first experiment, sheet flow and rilling were produced on a 50 m² large area with a 5° slope. In a second experiment, the rain was directed onto a 4 m long section of an actively eroding gully wall surface and onto the contributing upslope catchment. Water and particulates draining off the catchment and the gully were sampled and measured individually. In all cases, particles suspended in run-off waters were separated using a continuous flow centrifuge. The activity of ^{137}Cs , ^{210}Pb and ^7Be in particles was determined by γ -spectroscopy. Particles collected at the beginning of the first experiment had ^7Be and ^{137}Cs activities of 320 and 35 Bq kg⁻¹, respectively. As the artificial rain-fall progressed, the ^{137}Cs remained constant, whereas ^7Be decreased steadily to 140 Bq kg⁻¹ after 280 minutes. High initial values for both nuclides indicate that sheet erosion was the predominant process acting during the beginning of the experiment. The continuous decrease of ^7Be illustrates the transition from sheet to rill erosion (see Figure 19.8). ^{210}Pb dropped from 290 Bq/kg at the beginning of the experiment to 150 Bq/kg at the end, which indicates that ^7Be and ^{210}Pb have similar, lower soil penetration depths than ^{137}Cs .

The second experiment showed that particles collected in the gully, thus the products of gully wall erosion had no detectable quantities of ^7Be , ^{210}Pb and ^{137}Cs , whereas particles derived from the upslope catchment had measurable activities ranging from 50 to 650 Bq/kg for ^7Be and 25 - 40 Bq/kg for ^{137}Cs , confirming the interpretation of the first experiment that transported particles originated from the uppermost soil mantle. However, detecting the contribution of

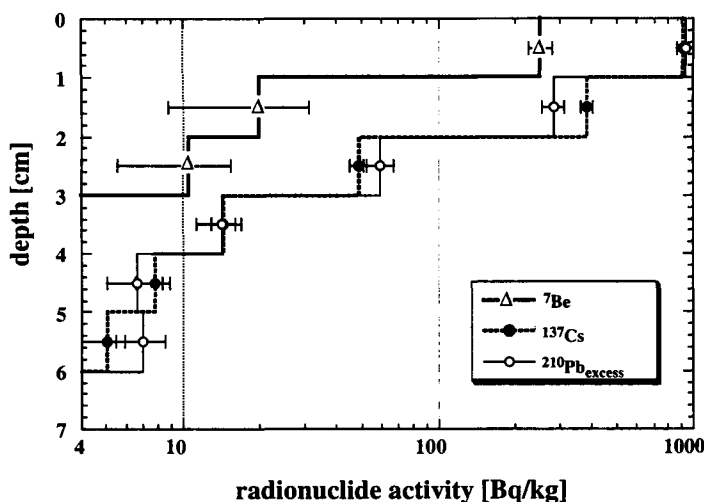


Figure 19.8. Depth distribution of the atmospherically derived radionuclides ${}^7\text{Be}$, ${}^{137}\text{Cs}$ and ${}^{210}\text{Pb}$ in a soil section sampled at 2500 m in east-central Switzerland (Albrecht, 1995). The roughly exponential activity decrease with depth and the greater penetration of ${}^{137}\text{Cs}$ and ${}^{210}\text{Pb}$ in comparison with ${}^7\text{Be}$ are general feature of soil profiles.

nuclides from overland flow may be difficult because gullying is far more efficient at entraining sediment than overland flow; overland flow had a measured particle concentration of 0.073 ± 12 g/l, whereas gully wall flow carried 26 ± 2 g/l suspended solids.

Eastern Uplands, NSW

A small area in the Eastern Uplands of Australia, between Sidney and Canberra, was selected by Olley et al. (1993) to perform a catchment identification exercise. The area, of which results are summarized here, comprises 4 catchments of which 3 are ungullied, pastured, and have not been cultivated in the last 30 years. The major catchment, which is separated from the 3 others by dams or weirs, is characterized by a major and active erosion gully. The lithogenic radionuclides ${}^{226}\text{Ra}$ and ${}^{232}\text{Th}$ and the atmospherically derived ${}^7\text{Be}$ and ${}^{137}\text{Cs}$ were measured by γ -spectroscopy in samples collected from soils, recently deposited sediments and suspended sediment. ${}^{226}\text{Ra}/{}^{232}\text{Th}$ ratios show that the bulk of the sediment sampled in the major gully is derived from erosion within the gully itself. This is in agreement with the local geology, because the gully is incised to bedrock along most of its length and its walls are composed of clay which is quite unstable. ${}^7\text{Be}$ and ${}^{137}\text{Cs}$ with activities between 0 and 130 Bq/kg support the same conclusion.

Sediments from the undisturbed, vegetated catchments in general have higher nuclide activities. This is due in part to their smaller average grain-size than gully sediments and in part due to the higher activities of their shallow source. ${}^{137}\text{Cs}$ and ${}^7\text{Be}$ activities allow one to distinguish dominant erosion processes in the different catchments. Catchment 1 has high ${}^7\text{Be}$ and high ${}^{137}\text{Cs}$ activities consistent with sheet erosion from undisturbed areas. Catchment 2 has a wide range in values from moderate to low ${}^7\text{Be}$ and ${}^{137}\text{Cs}$, indicating sediments derived by a mixture of mechanisms likely including from sheet erosion and gullying. Catchment 3 has moderate ${}^7\text{Be}$ and intermediate ${}^{137}\text{Cs}$, which is more consistent with rill erosion.

In summary, the method of sediment source tracing has shown success in qualitative estimates of the relative contributions of individual catchments to the sediment moving within a drainage network (source tracing). The method also allows one to determine whether or not sediments are derived mainly from subsoil or topsoil sources and to obtain information regarding erosion mechanisms. Such information is important to land and water managers. The technique has also been successfully extended to source finger-printing of sediments deposited in an underground karst river system (Murray et al., 1993), but has so far been restricted to small catchments with geomorphic and pedologic homogeneity.

19.6 Sr and Weathering

Unlike stable isotopes of light elements, no detectable thermodynamic fractionation of Sr isotopes occurs in nature. Changes in Sr isotope composition reflect production of the isotope ^{87}Sr through the radioactive beta decay of ^{87}Rb , which has a half-life of 48.8 Ga. The combination of time elapsed in the closed system and chemical fractionation between Rb and Sr, i.e. between alkaline and alkaline-earth elements, leads to the generation of natural reservoirs having different abundances of ^{87}Sr , expressed as the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. As these reservoirs are ultimately constituted of minerals and glass, any plutonic or sedimentary event destroying mineral or glass phases releases Sr with variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This Sr is in turn homogenized in the fluid or melt phase and taken up by newly formed minerals: after radiogenic production, mass-balanced mixing is the second natural phenomenon leading to changes in Sr isotope composition.

Sr isotope geochemistry allows estimation of the respective contribution of carbonate and silicate rocks to the dissolved load, if both are present in the drainage basin, and have distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Such an approach can also be applied to the geologic record because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the dissolved phase is preserved in biogenic carbonates. It has been proposed that differential dissolution of carbonates and silicates could be a simple function of water availability and temperature (e.g. Francois and Walker, 1992). There is also a link between weathering and atmospheric CO_2 consumption (e.g. Suchet and Probst, 1993); enhanced weathering of silicates at glacial times contributes alkalinity to the ocean, and thus generates a significant feedback with the greenhouse effect and climate (Gibbs and Kump, 1994; Munhoven and Francois, 1994; Froelich et al., 1992), although such conclusions remain uncertain (White and Blum, 1995). The limited use so far of Sr isotopes in hydrological and paleo-hydrological studies is due mainly to a lack of coordinated studies between isotope geochemists and hydrologists, limnologists, and paleo-limnologists.

19.6.1 Weathering and $^{87}\text{Sr}/^{86}\text{Sr}$

During weathering, erosion, and sedimentation, water is the medium in which isotopic mixing of Sr from different sources occurs. The discussion of $^{87}\text{Sr}/^{86}\text{Sr}$ behavior during weathering will thus reduce to the examination of mineral dissolution, a very active research field and one extensively covered in the literature. Understanding weathering reactions and the isotopic composition of the released Sr is complicated by the fact that radiogenic $^{87}\text{Sr}^{2+}$ ions created from $^{87}\text{Rb}^+$ are located in different lattice positions than the non-radiogenic Sr ions incorporated during the primary crystallization of the mineral, the so-called "initial Sr". As a consequence, the radiogenic Sr will be released at a different rate than the initial Sr, either through continuous diffusion or during geochemical events, including surface weathering.

Preferential release of radiogenic ^{87}Sr occurs in lateritic soils developed on igneous rocks from La Reunion and Nosi (Clauer, 1979); clay minerals newly formed from both low-Rb minerals such as plagioclase and high-Rb mineral biotite have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to the initial ones, which means that biotite has previously lost radiogenic Sr. This tendency to release radiogenic Sr may be enhanced by physical erosion, as suggested by Blum et al. (1993) based on data for Sierra Nevada stream waters. They determined the $^{87}\text{Sr}/^{86}\text{Sr}$ of stream waters, some draining soils glaciated during the last 10 ka and some draining non-glaciated soils, and found more radiogenic Sr in the former. They came to the conclusion that "biotite is weathering 6 times and 4 times more rapidly than plagioclase in the recently glaciated and non-glaciated drainages, respectively", and attributed this effect to the glacial milling of minerals. Alternatively, radiogenic Sr may be preferentially lost from the fresh biotites exposed in the recently glaciated areas, while biotite weathering rates as measured by K, Mg or Si fluxes may be no different than those in the unglaciated areas (cf. Bullen et al., 1997). All things being equal, the dissolution rate of a given mineral is effectively dependent upon its surface area (e.g. Lasaga et al., 1994), and mechanical strength, and may not be correlative with the release rate of a trace element such as Sr from the mineral lattice.

A limited number of mineral phases is generally recognized as controlling Sr abundance in natural waters. For instance, smectite is known to release preferentially non radiogenic Sr, probably adsorbed from pore water through ion exchange processes (Clauer, 1982). Plagioclase releases large amounts of Sr from silicate rocks and Ca-carbonates release Sr from limestone; buffering by SrSO_4 celestite, although scarce, has been reported in the literature (Stueber et al., 1975). As plagioclase and calcite are both Sr-rich and Rb-poor minerals, waters buffered by such minerals present a non-radiogenic Sr signature, which generally means substantially lower $^{87}\text{Sr}/^{86}\text{Sr}$ than the mean value of bulk enclosing rocks. For example, riverine $^{87}\text{Sr}/^{86}\text{Sr}$ is generally lower in the soluble fraction than in the particulate fraction (e.g. Anderson et al., 1994). Marine Sr coming from sea salt aerosols can also play a significant role in the Sr balance of some areas (Negrel et al., 1993). The contribution from Rb-rich silicates is modulated by climatic factors such as temperature, drainage, glacial milling and by tectonic factors controlling the exposure of fresh rock. It should be noted, however, that the relative Sr contributions from Rb-poor and Rb-rich silicates may differ among mineralogically-similar flowpaths in a given catchment, and those from Rb-rich minerals may dominate even in the presence of a considerable plagioclase component (Bullen et al., 1996).

In high alteration index environments (McLennan, 1993) where chemical erosion is essentially "weathering-controlled", the $^{87}\text{Sr}/^{86}\text{Sr}$ of the surface water will be closer to the average bulk bedrock signal than in areas where tectonic and/or physical weathering plays a significant role. In theory, it could be possible to apply the flux model initially proposed by Brass (1976) to invert the isotopic results and, assigning end-member $^{87}\text{Sr}/^{86}\text{Sr}$, to determine the respective contribution of each source rock to the Sr budget (Negrel et al., 1993). This would offer a complement to dissolved silica, bicarbonate or Ge/Si measurements (Froelich et al., 1992). The situation is more complex in areas where sedimentary rocks constitute a significant part of the drainage surface: detrital minerals have previously experienced at least one erosion cycle and are thus closer to chemical equilibrium in surface conditions than primary magmatic or metamorphic minerals, and ion-exchange processes can play a significant role. In addition, even a small contribution of limestone will overwhelm both Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ of surface water. As the global surface proportion of sedimentary rocks was estimated by different methods to be about 65%, with contributions from limestone, sandstone and shale in the proportions of 6.7 : 21.6

: 35.7, respectively (see Stewart (1993) and references therein), assignment of end-member $^{87}\text{Sr}/^{86}\text{Sr}$ is not a trivial task in most drainage basins.

19.6.2 Typical $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

Two families of silicate rocks can be distinguished on the basis of their initial, i.e. non-radiogenic, plagioclase $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Most mafic, mantle-derived rocks have initial $^{87}\text{Sr}/^{86}\text{Sr}$ in the range 0.703 - 0.706, most granitic, metamorphic and detrital sedimentary rocks have initial $^{87}\text{Sr}/^{86}\text{Sr}$ in the range 0.709 - 0.725 (e.g. Faure, 1977). Limestones "freeze" the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of sea water at the time of their deposition, which is intermediate between the continental runoff value of 0.7119 (Palmer and Edmond, 1989) and the hydrothermal basaltic component of 0.703 (Spooner, 1976). Through geologic times, sea water $^{87}\text{Sr}/^{86}\text{Sr}$ remained in the range 0.706 - 0.7092 (Veizer, 1989). As stated above, in a given area experiencing surface weathering, the $^{87}\text{Sr}/^{86}\text{Sr}$ of surface waters results from the mass balanced average of all dissolving minerals. As the prevailing contributions are in most cases those of plagioclase and Ca-carbonates, most surface waters in the world have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.706 and 0.725, as long as they drain non-monolithologic basins free of mantle-derived rocks; if mantle-derived rocks are a significant component, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of surface water is usually between 0.703 and 0.709. The higher values are logically found in rivers draining high elevation and partially glaciated areas such as the Himalayas (Krishnaswami et al., 1992), although the $^{87}\text{Sr}/^{86}\text{Sr}$ of the Rhone river is buffered at 0.7087 by limestones from the external thrust zones of the Alps (Palmer and Edmond, 1989). Also, the use of Ca-phosphate fertilizers adds a non-radiogenic component to riverine Sr.

19.6.3 Sr isotopes as tracers of solute sources

The ability to determine solute sources and mineral weathering rates is becoming increasingly important in geochemical assessments of catchments. $^{87}\text{Sr}/^{86}\text{Sr}$ has proven to be a powerful tracer of these key variables, primarily due to the geochemical similarity of Sr to Ca and the large differences in this isotopic ratio among minerals in most catchments. $^{87}\text{Sr}/^{86}\text{Sr}$ has been used successfully to address a variety of issues such as distinguishing between atmospheric and mineral weathering contributions to streamflow and catchment ecosystems (e.g. Gosz and Moore, 1989; Graustein, 1989; Miller et al., 1993; Bailey et al., 1996), recognizing changes in relative mineral weathering rates in response to climate change (e.g. Blum et al., 1993), and constraining model properties such as cation exchange efficiency as a function of soil development (e.g. Bullen et al., 1997). Other applications of Sr isotopes to catchment studies, as well as the theoretical bases of the Rb/Sr isotope system, are given elsewhere in this volume (Chapters 8 and 18). The purpose here is to discuss both the strengths and potential pitfalls of using Sr isotopes for determination of mineral weathering rates and solute sources.

Sr isotopes have generally been applied to problems at catchments dominated by granitoid minerals (i.e. feldspars, micas and hornblende), although the same rules apply for any multi-mineralic system. The common thread is that plagioclase feldspar has the lowest, and biotite mica the highest $^{87}\text{Sr}/^{86}\text{Sr}$ of these minerals. Plagioclase is generally Sr-rich (100's of ppm) and in the absence of calcite is the main mineral source of Sr. Biotite generally contains very little Sr (~ 10 ppm), but its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is so much greater than that of the other minerals that a minor contribution to soil solutions generally has a profound effect. In most catchment studies,

$^{87}\text{Sr}/^{86}\text{Sr}$ provided by weathering is generally taken to be constant and is then compared to that in precipitation to distinguish atmospheric from lithologic sources. In general, this approach is successful (e.g. Graustein, 1989; Miller et al., 1993; Bailey et al., 1996) because $^{87}\text{Sr}/^{86}\text{Sr}$ of the precipitation and weathering contributions are so different. Obviously, a rigorous hydrologic assessment of the catchment should be paired with the Sr study, to determine whether streamflow is fed by contrasting flowpaths (e.g. along shallow lateral paths; along the soil-bed-rock interface; from bedrock fractures) along which weathering processes or rates may differ.

In detail, the concept of a single $^{87}\text{Sr}/^{86}\text{Sr}$ value to characterize weathering in a catchment may be problematic. For example, biotite may lose very quickly minor inter-layer cations including its primary Sr as the mineral structure changes to that of hydrobiotite upon exposure of the granitoid body (Gilkes and Suddhiprakam, 1979). This chemical adjustment would provide a rapid pulse of radiogenic Sr (i.e. high $^{87}\text{Sr}/^{86}\text{Sr}$) to the catchment. In contrast, Sr-rich plagioclase apparently releases Sr at a very constant rate as the mineral dissolves. As a result, incipient weathering of granitoid should impart a high $^{87}\text{Sr}/^{86}\text{Sr}$, and mature weathering a low $^{87}\text{Sr}/^{86}\text{Sr}$ to catchment outflow. Blum et al. (1993) and Blum and Erel (1995) have used this differential Sr-release behavior to suggest deglaciation and the accompanying exposure of fresh mineral surfaces instigates a pulse of radiogenic Sr in alpine catchments that transfers to and can be observed in the oceanic Sr record. These workers suggest that variations in $^{87}\text{Sr}/^{86}\text{Sr}$ within catchments may in part reflect the average exposure age of the granitoid minerals to weathering solutions. This type of complexity should be considered in catchments where factors such as slope instability, soil thickness and water throughput are highly variable.

In Figure 19.9, $^{87}\text{Sr}/^{86}\text{Sr}$ of ammonium acetate-extractable Sr is plotted against soil age for two granitoid weathering systems that represent soil chronosequences (i.e. soils that develop on identical starting materials over different time spans). The Merced soils of central California are developed on glacial outwash derived from ca. 100 Ma granitoids of the Yosemite region (Harden, 1987). The Wind River soils of Wyoming are developed on morainal deposits derived from ca. 2000 Ma granitoids of the Wind River Range (references given in Blum and Erel (1995)). The ammonium acetate extraction procedure provides a measure of exchangeable Sr that should equal or at least closely approximate the $^{87}\text{Sr}/^{86}\text{Sr}$ observed in stream waters that drain the soils, although isotopic disequilibrium between soil waters and the exchange pool is more common than generally believed (see Chapter 18).

The pattern of decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ of exchangeable Sr with increasing soil age in both systems results from an early pulse of radiogenic Sr that is subsequently overprinted by less-radiogenic Sr derived primarily from weathering of plagioclase. For the Wind River soils, Blum and Erel (1995) suggest that deglaciation promotes enhanced initial weathering of (or at least Sr release from) biotite relative to that of plagioclase, but that the rate of biotite weathering slows with increasing soil age. In contrast, Bullen et al. (1997) argue that by the time the Merced outwash alluvium was deposited, biotite had largely been converted to hydrobiotite and had lost most of its original radiogenic Sr to the meltwaters. Their attempts to model the temporal evolution of $^{87}\text{Sr}/^{86}\text{Sr}$ of the cation exchange pool in these soils reveals that the early pulse of radiogenic Sr on exchange sites is derived by leaching of Sr from K-feldspar, which has nearly the same $^{87}\text{Sr}/^{86}\text{Sr}$ as extractable Sr in the youngest soils (Figure 19.9). They further suggest that the slow decrease of $^{87}\text{Sr}/^{86}\text{Sr}$ of exchangeable Sr with increasing soil age reflects a gradual decrease of exchange efficiency (i.e. % of potential Sr exchange sites that actually exchange Sr with soil solutions) with increasing soil age. The fact that plagioclase Sr still dominates the exchange

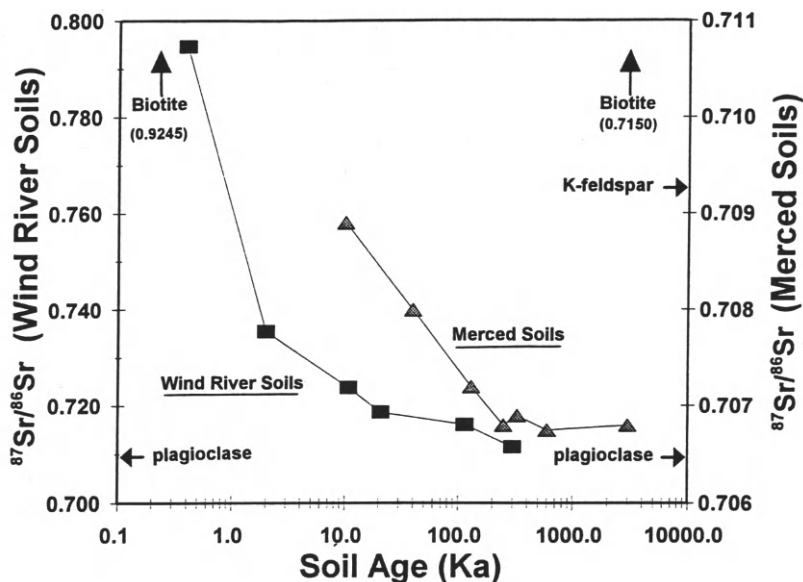


Figure 19.9. $^{87}\text{Sr}/^{86}\text{Sr}$ of ammonium acetate-extractable Sr in soils developed on morainal deposits in the Wind River Range, Wyoming and on glacial alluvium near Merced, California. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for plagioclase and biotite in the Wind River soils values for these minerals in the parent granitoid deduced from data presented (Blum and Erel, 1995). $^{87}\text{Sr}/^{86}\text{Sr}$ for plagioclase, K-feldspar and biotite in the Merced soils are for granitoid minerals separated from the soils themselves (Bullen et al., 1997).

pool of the 3000 Ka Merced soils even though plagioclase is totally consumed after approximately 1000 Ka of weathering (White et al., 1996) is strong evidence for decreasing exchange efficiency with increasing soil age.

This example points up several factors that must be considered when attempting to use Sr isotopes to identify solute sources or quantify mineral weathering rates or processes at the catchment scale. First, $^{87}\text{Sr}/^{86}\text{Sr}$ observed in streamflow probably does not reflect current weathering in the catchment, but rather a partial integration of the weathering history and the evolution of the cation exchange pool. Second, Sr release must be distinguished from mineral dissolution as a bulk mass transfer process in cases where Sr may be preferentially lost from the mineral relative to more tightly bound cations. Third, an understanding of the emplacement history of catchment soil substrates (e.g. moraine vs. alluvium; residuum vs. colluvium; fractured vs. massive bedrock) may be critical to confirming the weathering reactions inferred from the Sr isotopes. Clearly the most successful applications of Sr isotopes will result from studies where catchment history, morphology, hydrology, water chemistry and soil mineralogy are all well characterized and considered together.

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Applications of Uranium- and Thorium-Series Radionuclides in Catchment Hydrology Studies

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20.1 Introduction

Investigations of uranium- and thorium-series radionuclides in hydrologic systems have been ongoing for many years, and a wealth of information on the geochemistry of these nuclides in surface water and groundwater is available in the literature (e.g., IAEA, 1990; Ivanovich and Harmon, 1992). The objective of much of this work has been to define the environmental behavior of the various radionuclides in order to understand and predict their presence and transport in the environment as a result of mining, milling, and other technological redistributions of ores and other materials naturally high in radionuclides. Much effort has also gone toward attempting to understand the geochemistry of naturally-occurring radionuclides in order to develop techniques for locating uranium ore deposits and understanding their formation. Perhaps the greatest effort, however, has gone into investigations that would establish the usefulness of these radionuclides in solving problems and answering questions in the Earth, hydrologic, and environmental sciences. The range of applications has been impressive, including use of uranium and thorium decay products to determine the age of speleothems and archeological remains, sedimentation rates of marine and lake sediments, rates of water-rock re-equilibration in hydrothermal systems, and calculation of erosion rates on a continental scale.

The application of uranium and thorium series radionuclides to quantitatively solve problems in small catchment hydrologic studies has been largely neglected, however, until recently. Some early work using uranium isotopes to estimate the relative contributions of suspected source waters to rivers and springs in Florida was carried out in the 1960's and 1970's (Osmond et al., 1968; Briel, 1976), but development of these techniques into useful and widely accepted tools in catchment hydrology has not occurred. Recently, however, new interest has been shown in using natural radionuclides as hydrologic tracers due in part, perhaps, to the new environmental awareness of natural radioactivity and the development of new techniques which make higher-precision analysis of smaller sample sizes possible. The approaches and models used in interpreting uranium- and thorium-series radionuclide data are generally simpler and less sophisticated than those that have been developed for stable isotopes. With time and continued effort, however, more progress will likely be made in applying these radionuclides to ever-more complicated hydrologic situations.

20.2 Review of Fundamental Concepts

20.2.1 Decay chains and radioactive equilibrium

Uranium and thorium are long-lived radioactive elements found in all Earth material. Upon radioactive decay they form other radionuclides which are themselves radioactive and decay to other radionuclides, and so on until stable lead isotopes are formed. These series of radionuclides which originate with ^{238}U , ^{235}U , or ^{232}Th , are called "decay chains" or "decay series" (Figure 20.1). In a closed system where no nuclides leave or enter except through radioactive growth or decay, there is a build-up of radioactivity within the system until, at some point, the total amount of radioactivity reaches some constant level proportional to the amount of parent uranium or thorium in the system. At such time each daughter radionuclide (Figure 20.1) would have the same "activity" as the head of the chain (where "activity" refers to the number of decay events per unit time). If, for example, ^{238}U was decaying at a rate of 1000 atoms per minute, all daughters in the chain would be decaying at 1000 atoms per minute. This phenomenon, known as radioactive equilibrium or secular equilibrium, is characteristic of old igneous rocks that have remained closed systems, unaltered by weathering or fluid flow at the Earth's surface.

The time it takes for secular equilibrium to become established in each chain depends primarily on the daughter with the longest half-life in the chain, and as a practical matter is taken as seven to ten times the half-life of the longest-lived daughter. For the ^{238}U chain the daughter with the longest half-life is ^{234}U (248,000 y), so it would take the chain on the order of 2 million years to achieve equilibrium. The ^{235}U chain has ^{231}Pa as the radionuclide with the greatest half-life (32,760 y), and so this chain will achieve secular equilibrium in about 300,000 years. The ^{232}Th chain's longest lived daughter is ^{228}Ra , with a very short half-life of 5.8 y, so this chain achieves secular equilibrium very quickly, in geological terms, after only about 60 years.

The equality of radioactivity between radionuclides in a decay chain at secular equilibrium does not equate to an equality of mass (or number of atoms) of these daughter products. Some daughters have such short half-lives that they decay almost as quickly as formed, so that significant quantities can never be accumulated, even at secular equilibrium. The relationship between the amount of a radionuclide and its activity is given by the relation:

$$A = \lambda N \quad (20.1)$$

where A is the activity (disintegrations per unit time) of the radionuclide, λ is its decay constant ($\lambda = (\ln 2)/t_{1/2}$, where $t_{1/2}$ is the radionuclide's half-life) and N is the number of atoms of the radionuclide. It can be seen from Equation 20.1 that the condition for secular equilibrium (stated as $A_1 = A_2$ for two radionuclides in the decay chain) can be written:

$$\lambda_1 N_1 = \lambda_2 N_2 \quad (20.2)$$

and

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} \quad (20.3)$$

	U-238 SERIES					Th-232 SERIES					U-235-SERIES				
U	U-238 4.51x 10 ⁹ y		U-234 2.48x 10 ⁵ y								U-235 7.13x 10 ⁸ y				
Pa	↓	Pa-234 1.18m	↓								↓	Pa-231 3.2x 10 ⁴ y			
Th	Th-234 24.1d		Th-230 7.52x 10 ⁴ y			Th-232 1.39x 10 ¹⁰ y		Th-228 1.90 y			Th-231 25.6 h	↓	Th-227 18.6d		
Ac			↓			↓	Ac-228 6.13 h	↓				↓	Ac-227 22.0 y	↓	
Ra			Ra-226 1601 y			Ra-228 5.7 y		Ra-224 3.64 d					Ra-223 11.1 d		
Fr			↓					↓					↓		
Rn			Rn-222 3.825 d					Rn-220 54.5 s					Rn-219 3.92 s		
At			↓					↓					↓		
Po			Po-218 3.05 m	Po-214 1.6x 10 ⁻⁴ s	Po-210 138.4 d			Po-216 0.158 s	Po-212 3.0x 10 ⁻⁷ s				Po-215 1.83x 10 ⁻³ s		
Bi			↓	Bi-214 19.7 m	↓	Bi-210 5.0 d		↓	Bi-212 60.5 m	↓			↓	Bi-211 2.16 m	
Pb			Pb-214 26.8 m	↓	Pb-210 21.4 y	Pb-206 (Stable lead isotope)		Pb-212 10.6 h	↓	Pb-208 (stable lead isotope)			Pb-211 36.1 m	↓	Pb-207 (stable lead isotope)
Tl								Tl-208 3.1 m						Tl-207 4.79 m	

Figure 20.1. ²³⁸U, ²³²Th, and ²³⁵U decay series.

where the subscripts 1 and 2 refer to two different radionuclides. Thus, the ratio of ²³⁸U to ²¹⁴Po at secular equilibrium is equal to the ratio of the decay constant of the latter to that of the former, 1.54×10^{-10} over 1.33×10^{11} , or 1.16×10^{-21} . Thus, ²¹⁴Po is about 10^{21} times more radioactive than an equal quantity (i.e., equal number of atoms) of ²³⁸U.

20.2.2 Physical and chemical processes that redistribute U and Th series radionuclides

In a closed system all radionuclides in a decay chain will reach a state of secular equilibrium. Conditions at or near the Earth's surface, however, rarely permit the existence of perfectly closed systems. Weathering attacks rocks, dissolves minerals, transports solutes and residues from one place to another, and is in general a dispersing process with water as its main agent. During the process of establishing secular equilibrium in minerals and rocks, many different elements are formed. The ²³⁸U chain, for example contains fourteen different radionuclides representing eight different chemical elements. The change in chemical affinity from one element to the next is enormous. As a result, water will distribute these elements in different ways when a closed system is "opened" by weathering.

In addition to chemical differences causing separation of decay-chain radionuclides during weathering, a physical process (alpha-particle emission) can also redistribute decay-chain radionuclides. In this process the ejection of an alpha particle (two protons plus two neutrons) from a radioactive nucleus causes the new nucleus to recoil up to several hundred nanometers

in the opposite direction, depending on its surroundings. If the atom is near a phase boundary the recoil can transport the atom across the boundary into a new environment. For example, if a ^{238}U atom is located within a few nanometers of the surface of a quartz grain, during alpha decay it may be ejected completely out of the grain and into whatever lies on the other side, be it another grain or a pore filled with gas or liquid.

Depending upon conditions in this new environment the atom will remain there or be free to migrate in response to the new physical and chemical conditions. The important point is that the atom is introduced into a new environment as a result of a physical, not a chemical, process. This has important effects on the redistribution of decay chain radionuclides during weathering, and in fact may remove radionuclides before chemical weathering would have done so, thereby causing the recoiled radionuclide to accumulate in the new phase without its immediate parent. In this situation the radionuclide is said to be "unsupported", since its parent is not present at an equal activity in the new phase. If the supply of the radionuclide to the new phase were suddenly stopped, the daughter product that had already accumulated there would decay away at a rate determined by its half-life. This happens quite regularly in dynamic hydrologic systems and is a useful tool, as will be described in the following sections.

Once brought into solution by whatever means (alpha-particle recoil or weathering) the new atom is subject to the chemical environment in which it exists. Whether it remains in solution, precipitates, adsorbs, or exhibits some other form of behavior will depend on what element it is and in what conditions it finds itself. The primary elements this chapter will be concerned with are radium and radon, so a little understanding of the geochemistry of these elements, as well as their decay chain parents, U and Th, will be necessary in order to fully understand how these elements can be used in catchment hydrology studies.

One of the most insoluble elements in the decay chains is thorium. It has only one oxidation state in nature (+4). Due to its high charge and ionic potential (Mason, 1966), thorium forms insoluble hydroxides under most natural conditions. For this reason natural waters contain very little Th and this element is not transported very far in solution. Very quickly after it is weathered out of a rock or other solid phase thorium becomes adsorbed onto colloidal or clay-sized particles and remains near its original location, or is transported by physical erosion as suspended sediment in streams (Osmond and Cowart, 1982; Langmuir and Herman, 1980). Thorium is strongly sorbed onto kaolinite and quartz, among other solids, at pH values > 4.

Uranium has a fairly complex chemistry, with correspondingly complex behavior in near-surface and surface hydrologic systems. Uranium can be present in the oxidation states +6, +5, and +4. In oxidizing environments the +6 state is predominant and forms soluble complexes such as UO_2^{2+} , UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{HPO}_4)_2^{2-}$, depending upon the type and amount of anions present in solution and the solution pH (Figures 20.2 and 20.3; Langmuir, 1978; Wanyt and Schoen, 1991). Even though only 10^{-6} M of phosphate in water causes $\text{UO}_2(\text{HPO}_4)_2^{2-}$ to predominate over U-carbonate species at normal PCO_2 ($10^{-2.5}$ atmospheres), most fresh waters have so little soluble phosphate (Hem, 1985; Meybeck, 1982) that the bicarbonate species are generally the most abundant. Bicarbonate charged waters therefore are very effective leaching and complexing agents for uranium.

Under progressively reducing conditions uranium is reduced to +5 and +4. This generally occurs as free oxygen is removed from the system, followed by the appearance of hydrogen

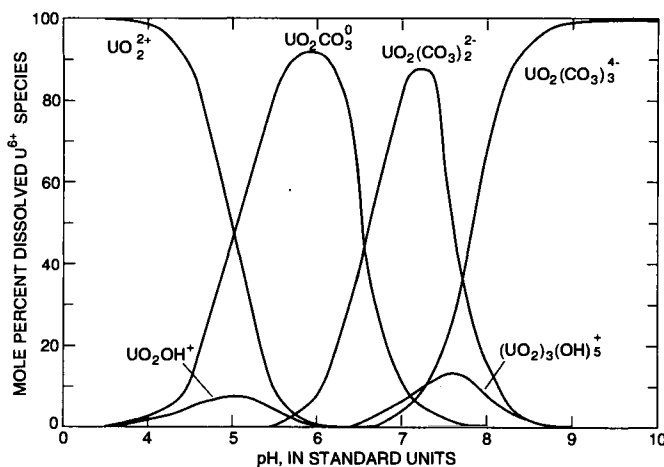


Figure 20.2. Distribution of uranyl hydroxy and carbonate complexes plotted against pH for $P_{\text{CO}_2} = 10^{-2}$ atm, and a total uranium concentration of 10^{-8} M (2.38 ppb) at 25 degrees C (from Langmuir, 1978).

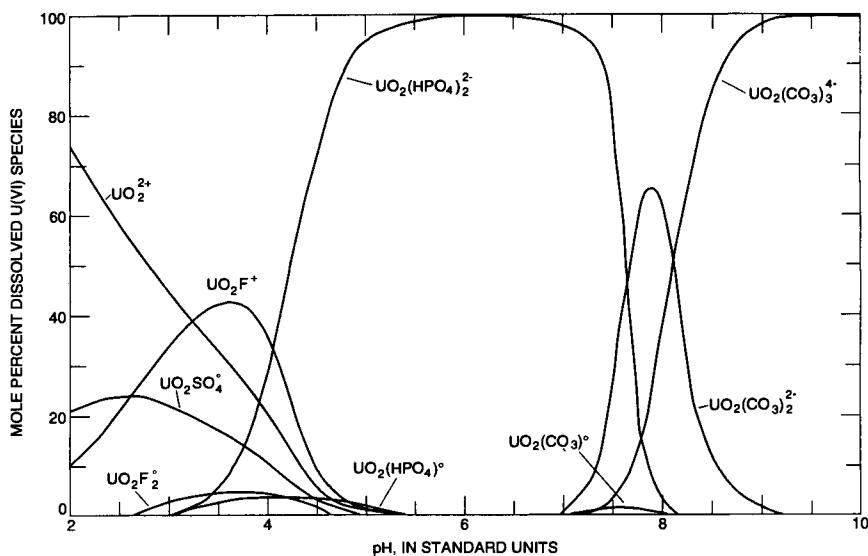


Figure 20.3. The distribution of inorganic species of uranium as a function of pH. The following aqueous concentrations were used in calculation of the curves: $P_{\text{CO}_2} = 10^{-2.5}$ atm, $\Sigma F = 1.6 \times 10^{-5}$ M, $\Sigma \text{Cl} = 2.8 \times 10^{-4}$ M, $\Sigma \text{SO}_4 = 10^{-3}$ M, $\Sigma \text{PO}_4 = 1.1 \times 10^{-6}$ M, $\Sigma \text{SiO}_2 = 5 \times 10^{-4}$ M (from Wanty and Schoen, 1991, modified from Langmuir, 1978).

sulfide. The result is the removal of uranium from solution due to the precipitation of insoluble uranium minerals. Uraninite (UO_2) or amorphous material of similar composition results (Figure 20.4), or, if sufficient silica is present, coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$) may precipitate. In groundwater systems, the movement of uranium-rich water encountering a reducing zone may cause the uranium to precipitate, producing a "roll-front" uranium deposit with several percent

U. Uranium can also be concentrated in sediment by association with organic matter. Black shales are often enriched in uranium, as are coal and asphaltic material derived from degradation of petroleum (Erickson et al., 1954; Mason, 1966; Krauskopf, 1967; Bauman et al., 1982; Holland, 1984). Uranium can also be removed from solution, even oxidizing ones, by adsorption onto solid substrates due to changing pH. Adsorption of uranium onto ferric oxyhydroxides, clay minerals and even micaceous minerals at pH values common in natural waters is well known (Hsi and Langmuir, 1985; Ames et al., 1983a, b, c, d; Warte et al., 1994; Morrison et al., 1995).

The chemical characteristics described above allow uranium to be weathered from rocks, transported long distances in solution, and then deposited by various means far from the site of weathering, or remain in solution for long periods of time. This behavior is effective in separating uranium from thorium present in weathered material, and often results in separation of uranium from its daughter nuclide ^{230}Th during a subsequent deposition process. The latter "resets the clock" for a very important geochronometer, the $^{230}\text{Th}/^{234}\text{U}$ ratio. For example, corals growing in the ocean extract uranium from sea water, but because of the insolubility of thorium, little ^{230}Th is present in sea water and therefore is not included in the coral. The initial $^{230}\text{Th}/^{234}\text{U}$ of calcite incorporated into coral is close to zero, and the ratio increases with time, reaching a value of unity (secular equilibrium) by about 750,000 yrs. By measuring the $^{230}\text{Th}/^{234}\text{U}$ activity ratio of corals it is therefore possible to establish the time of their growth.

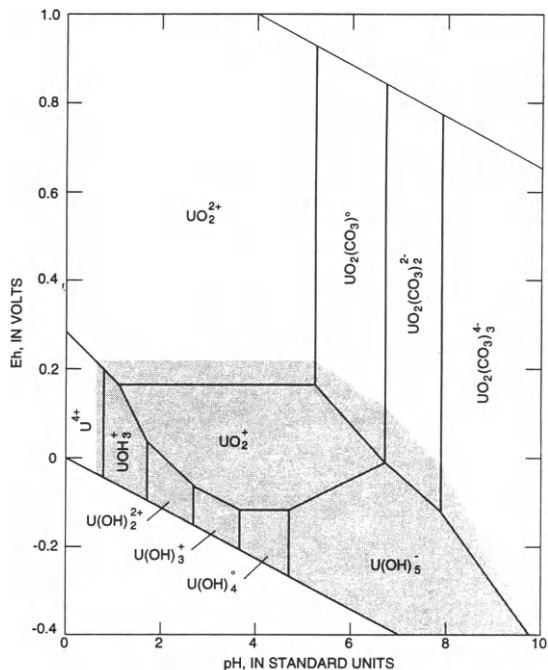


Figure 20.4. Distribution of inorganic uranium species in Eh-pH space for the system U-O-C-H at 25 degrees C and $10^{-2.5}$ atm CO_2 . The stippled area represents the stability field of uraninite at a total uranium concentration of 10^{-6} M (from Wanty and Schoen, 1991, modified from Langmuir, 1978).

Similarly, chemical precipitates such as calcite or aragonite (in cave deposits, tufa formations, etc.) can be dated by this means. This geochronometer has great utility in climate-change studies and paleoanthropology, where human remains are often associated with cave deposits.

Radium could be considered intermediate in reactivity between thorium and uranium in surface and near-surface environments. It has only one oxidation state (+2) and forms only weak complexes in solution (Figure 20.5). It is, however, very insoluble as a sulfate and will precipitate with Ba or Ca, although it never reaches concentrations high enough to precipitate as pure RaSO_4 (Langmuir and Riese, 1985). In most aqueous situations radium is subject to adsorption onto silicates, clays, and oxyhydroxides (Ames et al., 1983b,c,d; Nirdosh et al., 1987), but not as strongly as thorium. It is therefore detectable in most waters.

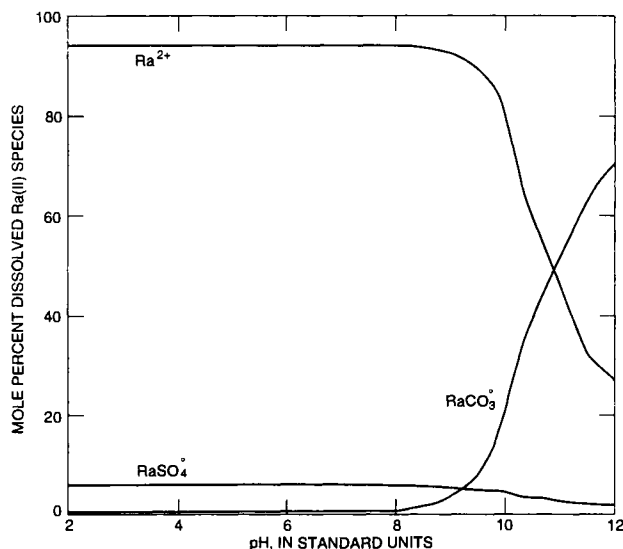


Figure 20.5. Distribution of inorganic aqueous radium species as a function of pH for the following conditions: $\Sigma\text{CO}_3 = 10^{-2}$ M, $\Sigma\text{SO}_4 = 10^{-4}$ M, and $\Sigma\text{Cl} = 10^{-4}$ M. No chloride complexes are sufficiently significant to plot on the diagram (from Wanty and Schoen, 1991).

Radium enters the aqueous phase, like the other uranium-series nuclides, during the weathering of geological materials. Dissolution of silicates and carbonates is one mechanism that releases radium into solution. Alpha-particle recoil is a second means by which radium can enter solution, since the parents of all the naturally occurring radium isotopes are alpha emitters and would operate to supply radium even if dissolution were not taking place. A third mechanism that is thought to supply radium to groundwater is the continuous reequilibration of silica between solution and a mineral grain surface such as quartz, although this probably only happens at high temperatures and salinities such as the geopressured aquifers of the U.S. Gulf Coast (Kraemer and Reid, 1984). In this environment the surface of a silicate grain seems to be continually exchanging silica with the solution. This process "uncovers" radium atoms which are then able to escape into solution where they remain because the high ionic strength of the brine prevents adsorption.

It appears that for carbonate aquifers, dissolution of the matrix is the primary route of entry of radium into water. The rock is relatively soluble in water and, because limestone aquifers generally conduct water by large fracture or conduit flow, there is relatively little surface area for alpha-recoil effects to become important. Because limestones tend to be rich in uranium and lack thorium, the radium in limestones will tend to be enriched in the ^{226}Ra isotope relative to ^{228}Ra . This signature will also be detectable in the aqueous phase in contact with limestone (Sarin et al., 1990).

For clastic aquifers the dynamics of radium entry into solution are a little more complex. As water enters an aquifer there is probably an initial dissolution phase where the water can pick up radium although, due to the low solubility of silicates, this amount is rather limited. An additional factor may be ion-exchange mechanisms which may supply Ra to solution in exchange for other cations, but again this is probably limited in most cases. The main mechanism for getting radium into solution from clastic rocks of ordinary U and Th content appears to be alpha-particle recoil. As the water moves down the flow path it receives radium which has been ejected through the surfaces of the matrix grains. Each Ra isotope will accumulate at a rate controlled by its half-life. In such a system ^{224}Ra would accumulate fastest, followed by ^{223}Ra , ^{228}Ra and finally ^{226}Ra . The growth of each nuclide to its equilibrium value would follow the equation:

$$Ra_t = Ra_{eq}(1 - e^{-\lambda t}) \quad (20.4)$$

where Ra_t is the radium activity at time t , Ra_{eq} is the radium activity that will be present at equilibrium, and λ is the decay constant of the Ra isotope. ^{224}Ra , whose half-life is only 3.64 days, would build up to its equilibrium value very rapidly, after about 30 days, while ^{226}Ra would not build up to its equilibrium value in groundwater for thousands of years. The above equation simply represents the growth of a radioactive daughter supplied to a system at a constant rate when the only loss from the system is radioactive decay. The actual or absolute equilibrium values the nuclides would achieve would depend on the rate of supply to the water, which in turn would depend on the concentration of the parent nuclides in the matrix, and the surface area to volume relationship of the aquifers.

One result of this behavior will be that "young" water (water that has been in an aquifer on a time scale of several years) would have a high $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio, since the ^{228}Ra would accumulate in the water faster than ^{226}Ra because of the great difference in their half-lives. This leads to the possibility that radium isotopes could be used to "date" groundwater flow in shallow, confined aquifers, but to date no case studies have been reported. In reality this would probably not be straight-forward to successfully accomplish because the requirement of aquifer homogeneity in terms of grain size, U/Th ratio, and absence of other sources for radium except alpha-recoil effects would rarely be met.

Other factors in addition to those discussed above control the actual amount of radium found in groundwater. For example, ^{226}Ra or ^{228}Ra may be high in groundwater if the rock contains elevated levels of U or Th in an easily attacked mineral phase, especially if the water is or becomes acidic. Also, other important mechanisms control radium in solution, such as the presence of manganese and ferric oxyhydroxides and clay minerals which could adsorb (or release) radium, and the presence of sulfate ions, which could complex with radium or, if present in great enough quantity, remove radium from solution through coprecipitation with

BaSO₄. Add to this the variability of hydrologic and geochemical conditions present in most aquifers, and the behavior of radium in solution as the water travels through the aquifer becomes complex.

When groundwater reaches the surface environment many changes can occur in response to the new environment which have an effect on the radium content of the water. Some of these changes include precipitation of iron and manganese oxyhydroxides, carbonates, sulfates, or other minerals which would cause radium to precipitate or become adsorbed onto a solid phase; mixing with water that has a different type of suspended or bottom sediment, which would cause a new equilibrium to be established between radium in solution and adsorbed onto sediment; and biological activity that could incorporate radium into tests, etc., thus isolating radium from the soluble-adsorbed environment for a time. For some of the short-lived isotopes, however, the biggest change comes simply as a result of radioactive decay. Upon entering the surface water environment the supply of the nuclide is eliminated, or severely restricted, because the matrix is left behind. As a result, each Ra isotope will decay away at a rate proportional to its half-life (²²³Ra and ²²⁴Ra disappearing in a few weeks, ²²⁶Ra and ²²⁸Ra taking longer due to their longer half-lives). In fact this process can be used to estimate residence times of water in small reservoirs. Since water coming from different subsurface zones may have different radium isotopic signatures (e.g., ²²⁸Ra/²²⁶Ra), it also becomes possible to use their signatures to estimate mixing ratios and identify source areas to streams and rivers.

Because the daughter products of uranium and thorium are so diverse in their chemical behavior, separation of one from another often takes place in geological environments, especially during weathering. For example, radon is a noble gas and begins to diffuse through the crystalline lattice of the enclosing mineral immediately after being formed from the decay of radium. Radon can therefore easily reach small cracks and imperfections in the crystal and migrate into larger pore spaces filled with water and gas. The process by which radon escapes from solid material is called emanation. The emanating power of a solid is that fraction of the radon atoms formed within it that escapes to the outside (Tanner, 1980). Small grain-size sediments usually have a greater emanating power than coarse-grain sediments, as the surface-area to volume ratio is greater. Similarly, highly-fractured granites and metamorphic rocks have higher emanating power than "solid" or sparsely fractured granite (Gundersen et al., 1988). The fact that granites are often fractured (high emanating power) coupled with the high uranium content of granite (high generating power) means water from granitic terrain often has very high radon concentrations (e.g., Schumann et al., 1994).

Radon that has migrated completely out of a solid material is mostly unsupported (the radon concentration of groundwater is usually far greater than the radium concentration). This means that unless more radon is continuously supplied, the radon will disappear due to radioactive decay. In cases where the solid and pore fractions of a rock allow radon generated from the solid phase to accumulate in the pore space, but where no radon is lost from the pore space except by radioactive decay, a closed but fractionating system exists. Radon will accumulate in the pore space until an equilibrium is reached that depends upon the fraction of the pore space to matrix volume, radium content of the solid phase, emanating capacity of the matrix, and radioactive decay of the radon. This amount of radon in the pore space will thereafter (after about 30 days for ²²²Rn) remain constant unless one or more of the factors change.

Because radon is a gas it will tend to seek a gaseous phase, although it is soluble in water and is particularly soluble in organic liquids (Clever, 1979). In a water-air system the radon will

partition itself into the air phase such that a major portion of the radon will be located there. Natural ambient radon concentrations in the atmosphere are so low that natural waters in contact with the atmosphere will continuously lose radon by volatilization. As discussed later in this chapter, this phenomenon has been used to an advantage in studies of groundwater interaction with streams and rivers (because a relatively short residence time in a stream or river channel will suffice for loss of most of the radon in a parcel of water, any significant concentration of radon in a stream or river is a sensitive indicator of local inputs of groundwater).

20.3 Radon Techniques in Catchment Hydrology

20.3.1 General considerations, mixing models

For many years, radon has been known to be present at elevated levels in the pore-space of soils and waters issuing from springs (Rogers, 1958 and references there-in). Perhaps the first to use ^{222}Rn (the longest-lived radon isotope) to find areas of groundwater discharge to a stream was Rogers (1958), who measured ^{222}Rn concentrations in streams and springs in the Wasatch Mountains near Salt Lake City. He found that points of groundwater discharge are marked by abrupt increases in the radon content of the water in the stream, and that concentrations decrease downstream from discharge points, the rate of decrease depending on "the volume and gradient of the stream, and the nature of the stream channel" (Rogers, 1958). He was able to use the increase in radon content of the water to estimate groundwater inflow into the stream by making assumptions about the physical behavior of radon under existing stream conditions (in the remainder of this chapter the word "radon" will be used to denote the longest-lived and most-studied isotope, ^{222}Rn , unless noted otherwise in a particular case).

Later studies, to be described in this section, are based upon the same assumptions used by Rogers or techniques for compensating for the non-validity of these assumptions, which are:

- 1) Stream water is well-mixed downstream of groundwater discharge areas, so water samples from these areas can be thought of as mixtures of local groundwater discharged to the channel and low-radon streamwater from further upstream.
- 2) There is no other source of radon or water except that already in the stream above the groundwater discharge area and that discharged from the groundwater source.
- 3) There is no degassing of radon between the stream sampling points upstream and downstream of the groundwater discharge area (or the rate of degassing is constant and can be measured).
- 4) The radon activity of the stream water and the groundwater entering the stream are known and constant.
- 5) Water fluxes in and to the stream are constant.

These conditions allow use of a simple steady-state mixing equation to determine the fraction of total streamflow at a downstream sampling site due to groundwater discharge between that site and a sampling site further upstream:

$$f_g = \frac{C_d - C_u}{C_g - C_u} \quad (20.5)$$

where C refers to radon concentration, the subscripts d , u , and g refer to the downstream and upstream sites and groundwater, respectively, and f_g is the fraction of total flow at the downstream site due to groundwater discharge between the upstream and downstream sites. f_g plus the fraction of flow to due streamwater from further upstream (f_u) would add to one in this simple two-component model, where $Q_d = Q_u + Q_g$ (Q designates volumetric flow rate, e.g., m^3/s). Knowing any one of the three Q values, and either of the mixing fractions (f_g or f_u) would allow calculation of the other two Q values. In practice, the Q values amenable to direct physical measurement are Q_u and Q_d , the total streamflow rates at the upstream and downstream sites. The studies summarized below all make use of Equation 20.5 in some way, with a general trend toward increasing levels of data collection in later studies, to remove some of the constraints and assumptions listed earlier.

20.3.2 Mixing model without correction for volatilization

Lee and Hollyday (1987, 1991) examined the radon content of water in Carter's Creek, a small stream in Maury County in central Tennessee with a base flow of about 1 cubic foot per second (cfs) and an average annual flow of about 17 cfs, running over thin-bedded, clay-rich Ordovician limestone. At low base flow conditions the creek is characterized by long, quiet, shallow pools and short riffles of turbulent, rapid flow. At higher flow the stream takes on a more continuous, uniformly-flowing appearance.

Two studies were carried out on Carter's Creek, one at "low base flow" conditions of about 1 cfs, and another at "high-base flow" conditions of about 10 cfs. During the low-base flow conditions two surface water flow measurements were made in June, 1986 and eleven radon measurements were made in September, 1986 (Figure 20.6). The high base flow survey and radon measurements were made in February, 1987 (Figure 20.7). The base flow surveys indicated no inputs of water by tributaries to Carter's Creek, but the stream gained flow between the upstream and downstream flow measurement points. A spring near Carter's Creek was sampled for radon, and the same radon activity (489 dpm/L, disintegrations per minute per liter of water) was assumed for the groundwater entering the stream through the bed.

In the low base flow survey (Sept., 1986) the stream shows a steady decrease in radon content downstream, which is to be expected in the absence of local groundwater inputs. At about 0.5 mile downstream, however, the radon content of the stream jumped suddenly from about 34 dpm/L to a high of 196 dpm/L, and the temperature of the water dropped considerably (Figure 20.8), indicating groundwater discharge to the stream. Application of Equation 20.5 (where $C_u = 34$ dpm/L, $C_d = 196$ dpm/L, and $C_g = 489$ dpm/L) led to $f_g = 0.36$. Using a Q_u measurement (1.04 cfs) from the previous June as a rough estimate for Q_u at the time of radon data collection in September led to an estimate of $Q_g = 0.59$ cfs (the groundwater discharge to the stream between the two stream measurement sites). Adding these Q_u and Q_g values gives 1.63 cfs, in close agreement with the measured value of Q_d , 1.62 cfs (value measured in June, like Q_u).

The second study, in February, 1987, produced a narrower range of radon values (72 to 90 dpm/L) along the same reach (Figure 20.7), probably as a result of the greater stream depth and velocity decreasing the amount of volatilization taking place as streamwater flowed through the study reach. Radon activities from this sampling suggested two reaches with gains from groundwater discharge, one of which was at the same location as in the previous study.

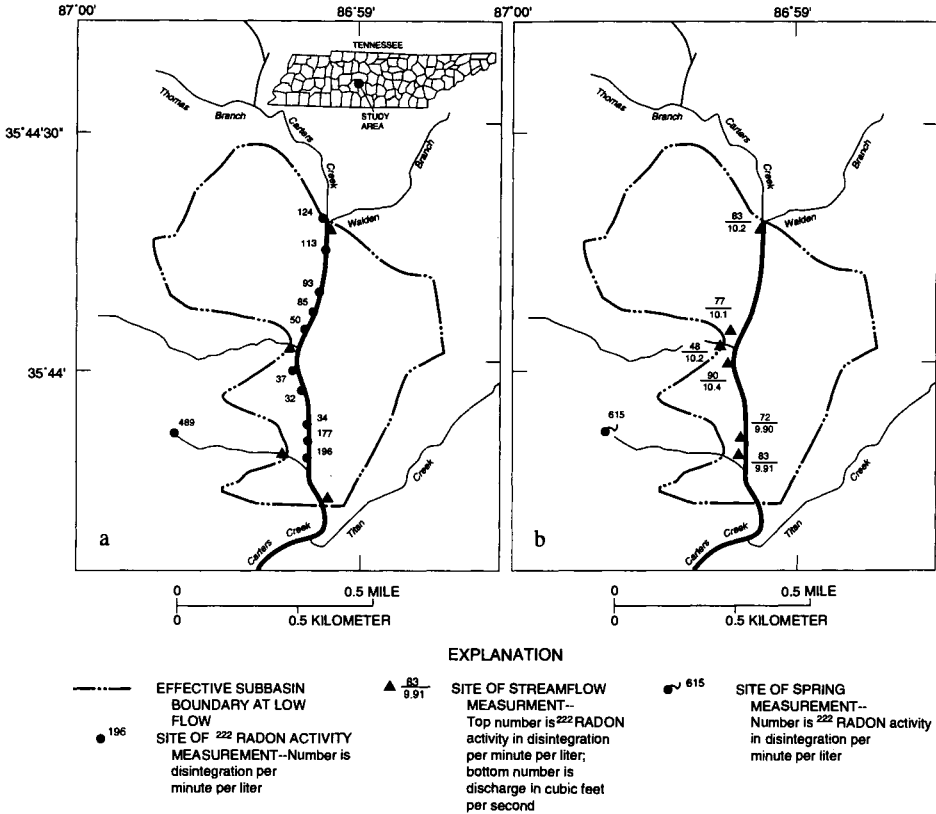


Figure 20.6. a) Location of measurements of flow and radon concentration for September 16-17, 1986, in Carter's Creek, and b) location of measurements of flow and radon concentration for February 12, 1987, in Carter's Creek (from Lee and Hollyday, 1991).

Streamflow measurements, this time made at each radon sampling point, showed only one gaining section though (with groundwater inflow of 0.3 cfs). The spring was also sampled at the time of this study, and was found to have a radon activity of 615 dpm/L. Solving Equation 20.5 (where $C_u = 77$ dpm/L, $C_d = 90$ dpm/L, and $C_g = 615$ dpm/L) led to $f_g = 0.024$, and using the measured Q_d value of 10.4 cfs led to an estimate of 0.25 cfs for Q_g . This value is close to the difference between the upstream and downstream flow measurements (0.3 cfs).

One feature of this exercise should raise a note of caution. When first sampled, the spring had a radon concentration of 489 dpm/L, but concentration had changed to 615 dpm/L at the second sampling. Implicit in the mixing method is that the groundwater radon concentration is well-known and, ideally, constant. The values from the spring change with time and this may indicate that this water is actually a mixture of two other types of water (for example, longer-residence-time groundwater and recently-infiltrated water), the proportions of which vary over time. Also, the excellent agreement between direct streamflow measurements and results from the radon mixing model are partially fortuitous, because no correction for radon transfer from the water to the air was made. Later studies have employed means of correcting for this radon loss from streamwater.

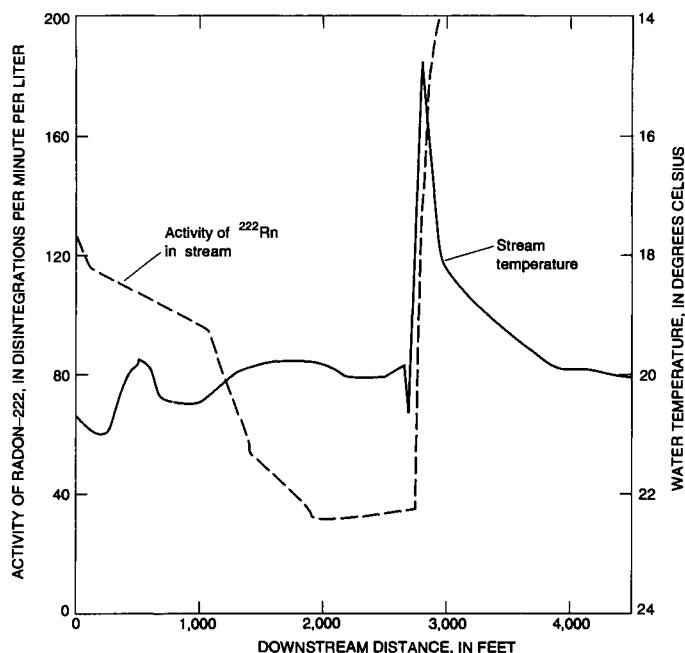


Figure 20.7. Stream temperatures and radon activities in a 0.75 mile reach of Carter's Creek for September 16-17, 1986 (from Lee and Hollyday, 1991).

20.3.3 *Mixing model with degassing correction through stagnant film model*

Attempts to use radon to quantitatively estimate lateral inflow to streams and rivers must account for radon loss from the channel by degassing. One method for doing this is to estimate the loss of radon occurring in a reach that is not receiving any groundwater inflow and use this information to correct for degassing in the stream reach where groundwater discharge is occurring. In this way a quantitative estimate of groundwater inflow can be obtained. A correction for radioactive decay can then be applied, if necessary.

In a study of the Rio Grande de Manati in Puerto Rico (Figure 20.8), Ellins et al. (1990) were able to identify areas of stream gain and loss, and estimate flow changes using streamflow measurements and radon data corrected for degassing. A stagnant film model was used to determine the rate of transfer of radon across the water/atmosphere interface. The model assumes two well mixed reservoirs of uniform concentration (water and air) separated by a zone, or film, of water representing the region where a gradient of radon exists between well mixed water and well mixed air. Transfer of radon across this boundary is by molecular diffusion. The rate at which transfer across the boundary takes place is determined by the concentrations of radon in both reservoirs and the thickness of the stagnant film (i.e., by the concentration gradient across the film). The greater the turbulence the thinner the stagnant film and hence the faster the rate of radon transfer. Using mathematical relationships developed by Elsinger and Moore (1983), Ellins et al. (1990) estimated the thickness of the film for control reaches of the Manati thought not to be receiving groundwater input, as described below.

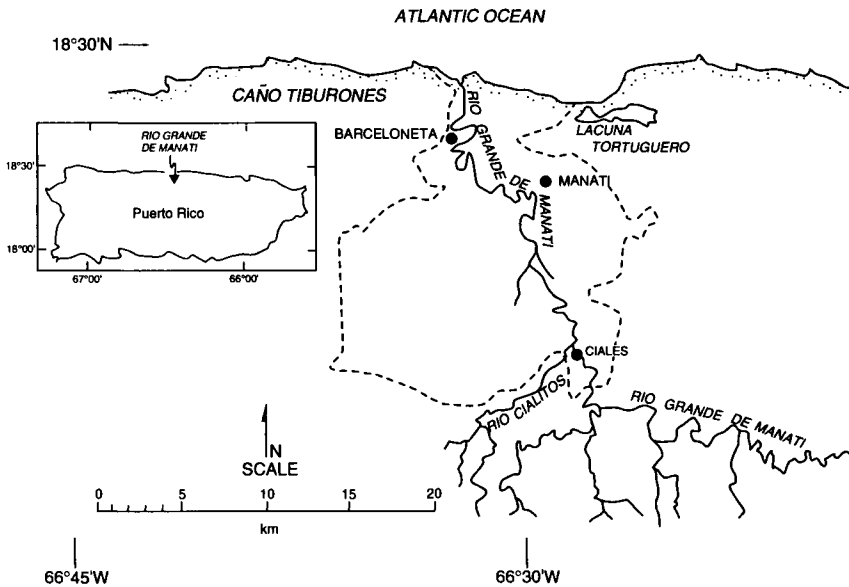


Figure 20.8. Map showing the karst basin of the Rio Grande de Manati, Puerto Rico (from Ellins et al., 1990).

For a stream receiving no groundwater discharge, the relationship among the stagnant film thickness, radon concentrations at two sampling locations on the stream, and stream channel geometry is given by:

$$C_d = C_u \exp(-Dx/zhv) \quad (20.6)$$

where D is the molecular diffusivity of radon (m^2/s), z is the thickness of the stagnant film (m), h is the average depth of the stream (m), v is the stream velocity (m/s), x is the distance between stream sampling sites (m), and C , d , and u are as defined previously. Since C_d , C_u , h , v , and x can be directly measured for the stream in question, the thickness of the boundary layer can be estimated:

$$z = \frac{xD}{\ln \frac{C_u hv}{C_d}} \quad (20.7)$$

The average film thickness obtained for each "control" reach (i.e., reach not receiving groundwater discharge) was then used to calculate the radon loss by degassing to the atmosphere between sampling points on the gaining reaches (with groundwater discharge) of similar conditions. Thus, after estimating z from nearby control reaches, C_d was calculated for each site using Equation 20.6; this value was referred to as the "predicted" concentration. The difference between the predicted concentration and the observed concentration was attributed to groundwater discharge between the upstream and downstream sampling locations.

Loss of radon by radioactive decay between sampling points can also be corrected for by the simple exponential decay equation:

$$C_d = C_u e^{-\lambda t} \quad (20.8)$$

where λ = decay constant of ^{222}Rn ($1.259 \times 10^{-4} \text{ min}^{-1}$). This correction should rarely be necessary, however, because radioactive decay will usually result in loss of a negligible amount of radon (usually the rate constant for degassing is much greater than λ). In the study of Ellins et al. (1990) radon loss due to decay was small compared to the overall uncertainties associated with the radon measurements themselves.

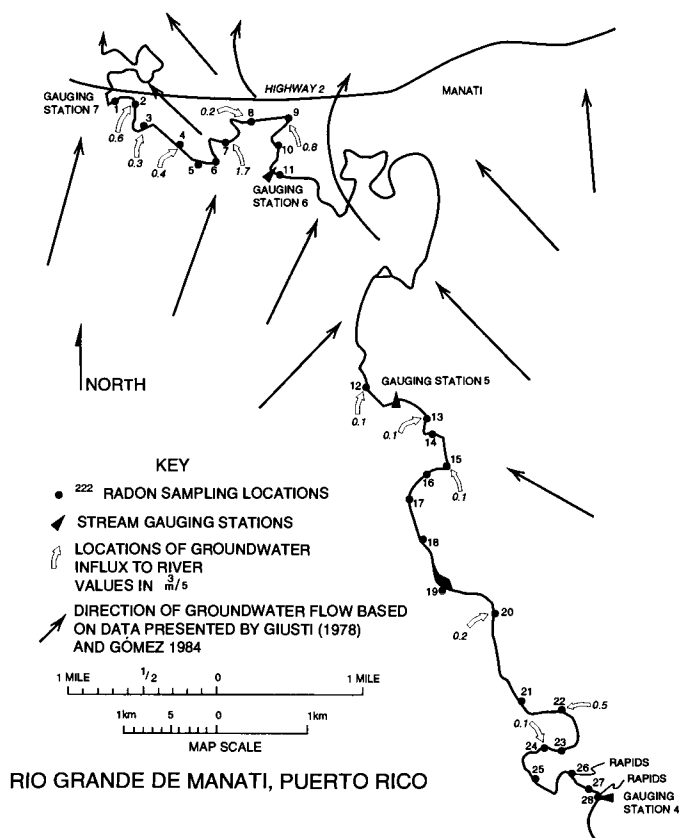


Figure 20.9. Map showing radon sampling locations and areas of groundwater inflow to the Rio Grande de Manati (from Ellins et al., 1990).

The region of the Rio Grande de Manati around U.S. Geological Survey gauging stations 4 through 7 (Figure 20.9) was used to establish stream characteristics necessary for calculating the stagnant film thickness (z). Stream characteristics change drastically between gauges 5 and 6, so the two sections were evaluated separately as Upper and Lower Manati (Table 20.1). The upper reach is characterized by a narrow alluvial valley with rapids while the lower reach is

Table 20.1. Stagnant film thickness calculation using Equation 20.7, from Ellins et al. (1990). Variables are as defined in the text, between Equations 20.6 and 20.7. Values of z are exactly as reported by Ellins et al. (1990), though our calculations using the data and Equation 20.7 give slightly different results for z in all cases (and a very different result, $7 \mu\text{m}$, for the reach defined by stream sites 18 and 17).

Stream Sites	C_u (dpm/L)	C_d (dpm/L)	x (m)	h (m)	v (m/s)	z (μm)
Upper Rio Grande de Manati, Subsection 1, length- weighted average $z = 11 \mu\text{m}$						
27-26	22	18	300	0.60	0.2	16.2
22-21	88	45	600	0.60	0.2	9.7
Upper Rio Grande de Manati, Subsection 2, length- weighted average $z = 26 \mu\text{m}$						
20-19	56	47	760	0.51	0.3	33.7
19-18	47	35	600	0.51	0.3	15.5
18-17	35	20	500	0.51	0.3	41.0
Upper Rio Grande de Manati, Subsection 3						
15-14	30	23	400	0.42	0.4	9.9
Lower Rio Grande de Manati, length- weighted average $z = 4 \mu\text{m}$						
11-10	117	77	200	0.30	0.7	2.5
7-5	200	101	500	0.30	0.7	4.6

characterized by a wide alluvial valley with a gently sloping surface and less turbulent flow. Because of significant changes in stream characteristics within this region, the upper section was further subdivided into three distinct subsections for the purpose of more accurately estimating stagnant film thickness. This was done to take into consideration the changes in average stream depth and velocity as well as changes in stream morphology and discharge that occurred at various places in the upper section.

Based on the data in Table 20.1 and radon measurements taken in control reaches of the river around the gauging stations, Equation 20.7 was used to calculate a z value to be used for each section and subsection. A distance-weighted average value of z was then calculated for each section or subsection, to be used in calculating the "predicted" concentration of radon at each sampling site in the river (as noted above, the radon concentration expected if there were no groundwater discharge between the sampling site and the next site upstream). The difference between the measured and "predicted" radon values at each site was then used to estimate the amount of groundwater discharge to the stream between the site and the next site upstream. This calculation was carried out using the basic equation introduced earlier (Equation 20.5):

$$f_g = \frac{C_s - C_p}{C_g - C_p} \quad (20.9)$$

where C refers to radon concentration and the subscripts g , s , and p refer to groundwater, measured streamwater concentration, and predicted streamwater concentration, respectively.

C_g (400 dpm/L) was determined from six samples taken from springs and wells in the area. f_g calculated in this manner represents the fraction of total streamflow at a given site due to groundwater discharge to the channel between that site and the nearest site upstream.

Figures 20.10 and 20.11 show the predicted and observed radon concentrations in the Rio Grande de Manati. The flow of the river at USGS gauging stations was also determined. This allowed determination of the magnitude of the groundwater inputs on the basis of the radon survey (Table 20.2). The flow measured at the upstream gauging station (Q_u) was multiplied by the relative groundwater contribution (from Equation 20.9) at the next site downstream to obtain Q_g at that site. This value was then added to Q_u for the upstream site, to compute Q_d for the first reach, which was also used as Q_u for the next reach, and so on down the stream. If the running radon-based Q was greater than the directly measured Q , it was assumed that the stream lost water through the channel bed by the amount of the difference. Thus, loss as well as gain can be estimated by this technique. For the lower Manati river, radon data indicated significant groundwater addition, yet the flow was nearly identical at gauging stations 5 and 6. This led Ellins et al. (1990) to believe that the river in this section lost water at the same rate at which it was gained, in agreement with potentiometric data for that section of the river.

20.3.4 *Mixing model with degassing correction through an injected tracer*

In the previous discussion it was assumed that the radon loss characteristics of similar stretches of river would be similar (e.g., the control section would mimic the experimental, or groundwater-gaining, section in radon loss to the atmosphere). One way to avoid this assumption is to inject a volatile tracer into the same river reach where the groundwater discharge occurs and measure the loss of the injected tracer over this reach. This should allow more accurate estimation of groundwater discharge to the study reach, if the radon content of inflowing groundwater is known accurately and all other conditions mentioned earlier are met. This also requires greater effort however, in that more equipment, samples, and measurements are required.

Several volatile tracers have been suggested for use in calculating gas exchange coefficients, including ^{85}Kr , ethylene, propane, methyl chloride, and SF_6 . Wanninkhof et al. (1990) used SF_6 to estimate radon degassing rates in studying a small stream on Walker Branch Watershed in Oak Ridge, Tennessee. The watershed is composed of fractured dolomite bedrock that dips steeply to the southeast and is overlain by about 2 m of soil, with 0-30 m of dense, clayey saprolite between the soil and bedrock; streamflow is monitored by a V-notch weir at the basin outlet (Genereux et al., 1993). There were two components to the experiment by Wanninkhof et al. (1990):

1. An injected tracer experiment was carried out, involving injection of tritiated water and SF_6 into the stream at a steady rate at a point near the upper limit of perennial flow (Figure 20.12), and measurement of the concentrations of both tracers at several places, up to 292 m downstream of the injection point. The purpose of the tritium (a conservative tracer on the short time scale of this stream experiment) was essentially chemical-dilution stream gauging, that is, to determine the streamflow rate at several sites along the stream and, by difference, the net rate of groundwater discharge to the stream between adjacent gauging sites. The purpose of the SF_6 was determination of gas exchange rates in the reaches between stream sampling sites, for use with radon data in the second part of the experiment.

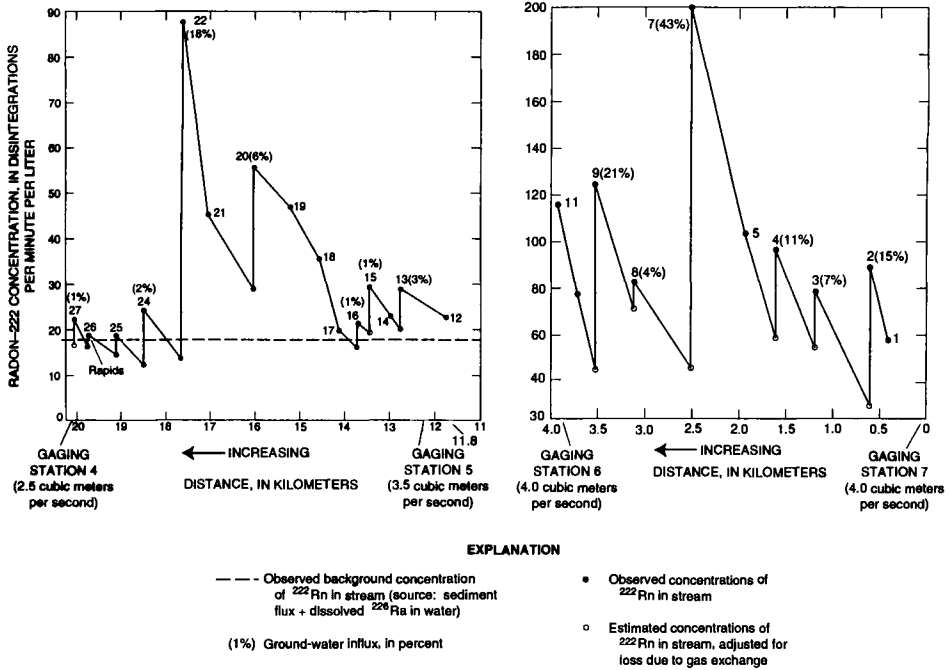


Figure 20.10. Radon profile of the Upper Manati showing the relative contributions to streamflow from groundwater discharge between adjacent sampling sites. Radon concentrations downstream of each groundwater input have been corrected for loss due to gas exchange (from Ellins et al., 1990).

2. Radon measurements were made at the same stream sites as tritium and SF_6 , in an attempt to use radon (with a degassing correction) instead of injected tritium to determine groundwater discharge to the stream reaches.

SF_6 was introduced into the stream by bubbling a standard of 0.08% SF_6 in nitrogen into a carboy of water, and injecting the water into the stream while the bubbling was occurring, but after a sufficient length of time so that the water in the carboy reached equilibrium with the gas. The injection of the SF_6 saturated water into the stream continued at a constant rate for three hours to establish a steady state throughout all the reaches of the stream before samples were taken. The samples were analyzed by gas chromatography using an electron capture detector after returning to the laboratory. Radon samples were analyzed in the field by the Lucas cell (gas-phase alpha counting) technique. The radon concentration of groundwater was evaluated by sampling four different springs along the reach of the stream (the average was 495 pCi/L, or 1100 dpm/L).

The first part of the experiment (tritium plus SF_6) was successful in documenting both the rate of groundwater discharge and the rate of degassing in several stream reaches. Though the experiment was designed for steady flow, and the rate of streamflow at the weir increased about 6% over the course of the experiment (due to a rain storm the night before the experiment), this small unsteadiness probably introduced relatively minor errors in the results.

Table 20.2. Radon-based estimates of groundwater discharge at sampling sites along the Rio Grande de Manati, from Ellins et al. (1990). "Predicted" concentrations, f_g , and Q_g are as defined in the text (Section 20.3.3). The last column is modified slightly from the original tables in Ellins et al. (1990).

Stream Site	Rn Concentration (dpm/L)		$100f_g$	Q_g (m^3/s)	Rn-based Q (m^3/s)
	"predicted"	observed			
28	start	18	0 ^a	0 ^a	2.8 ^b
27	18 ^c	22	1	0.03	2.83
26	18 ^c	18	0	0	2.83
25	18 ^c	19	0	0	2.83
24	18 ^c	24	2	0.05	2.88
22	18 ^c	88	18	0.53	3.41
21	49	45	0	0	3.41
20	34	56	6	0.21	3.62
19	44	47	0	0	3.62
18	39	35	0	0	3.62
17	30	20	0	0	3.62
16	18 ^c	22	1	0.03	3.65
15	19	30	3	0.12	3.75
14	23	23	0	0	3.75
13	19	30	3	0.11	3.86
12	13	23	3	0.10	3.96
11	start	117	0 ^a	0 ^a	4 ^b
10	88	77	0	0	4
9	51	124	21	0.8	4.8
8	71	83	4	0.2	5.0
7	47	200	43	2.2	7.2
5	99	101	0	0	7.2
4	58	95	11	0.8	8.0
3	54	77	7	0.6	8.6
2	33	87	15	1.3	9.9
1	66	57	0	0	9.9

^a by definition.

^b from direct physical measurement, not radon data.

^c assumed concentration, for those stations where measured values were slightly below 18 dpm/L.

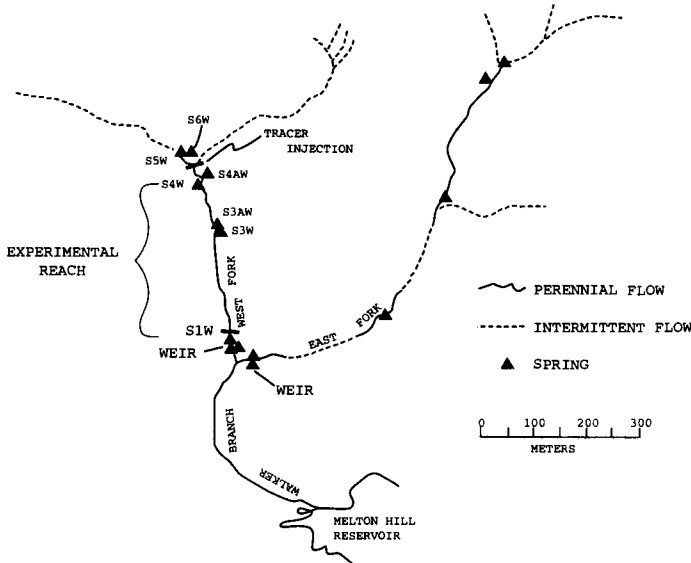


Figure 20.11. Walker Branch Watershed, with spring locations symbolized by S_W. The tracer injection point was located 342 m upstream of the weir on the West Fork (from Wanninkhof et al., 1990).

The second part of the experiment was less successful, mainly because the radon measurements were made two days earlier than the SF_6 measurements, when the streamflow rate at the weir was about half what it was during the SF_6 measurements (radon measurements occurred before the storm mentioned above). The large change in streamflow during the two days between the radon and SF_6 sampling was due to large changes in water flux into the study reaches, and was also associated with changes in the radon concentration of the water discharging to the stream, as has since been learned (Genereux et al., 1993). In principle, the proposed method should yield accurate results with simultaneous radon and SF_6 sampling (or at least steady hydrologic conditions during any period between the radon and SF_6 sampling).

The radon/ SF_6 method proposed by Wanninkhof et al. (1990) for determination of groundwater inflow to a stream involved three steady-state mass-balance equations: one each for radon, SF_6 , and water, as written below:

$$[Rn]_u Q_u = [Rn]_d Q_d + kA[Rn]_{avg} - [Rn]_g Q_g \quad (20.10)$$

$$[SF_6]_u Q_u = [SF_6]_d Q_d + kA[SF_6]_{avg} \quad (20.11)$$

$$Q_d = Q_u + Q_g \quad (20.12)$$

where quantities in brackets represent streamwater concentrations, subscripts u , d , and g have the same meanings given earlier, subscript "avg" designates the average concentration for a reach (average of the upstream and downstream concentrations), Q is volumetric flow rate, A

is the surface area of the stream reach, and k is the gas transfer velocity (length/time). The term $kA[Rn]_{avg}$ gives the total amount of radon escaping by gas exchange over the stream reach. It is assumed no radon enters the stream by diffusion from bed material or originates in the water due to production by decay of radium in the water. A radioactive decay term for radon could be added if necessary, though in this case radon loss by radioactive decay is trivial compared to that lost by gas exchange. If one measures radon and SF_6 concentrations, and the stream surface area, then four unknowns remain in Equations 20.10 - 20.12: k , and the three Q values. Wanninkhof et al. (1990) made one streamflow measurement with SF_6 , assuming no loss by degassing between the injection point and the first stream sampling site, and using the rate of SF_6 injection and the measured concentration at that first site to determine Q_u for the first reach. This leaves 3 unknowns which could be solved for the first reach, using Equations 20.10 - 20.12. Then, using the computed Q_d for the first reach as Q_u for the second, calculations progressed downstream, solving Equations 20.10 - 20.12 for the second and all subsequent reaches. In this way, Wanninkhof et al. (1990) obtained an estimate of Q_g for each reach along the stream, without use of an injected conservative tracer (such as tritium).

Table 20.3 shows the values of k , Q_g and Q_d calculated using the radon/ SF_6 technique compared with the tritium/ SF_6 method. As noted above and stated by Wanninkhof et al. (1990), the results of the radon/ SF_6 technique and the tritium/ SF_6 technique do not agree, for reasons stated above. An advantage of the radon/ SF_6 technique over using just radon is that groundwater inflow can be quantified even for reaches of stream where groundwater discharge does not cause a significant increase in radon concentration in the stream. Without knowledge of the gas exchange rate, radon measurements alone can only be used to conclusively indicate groundwater inputs when and where the radon concentration increases.

20.3.5 *Mixing model, with partitioning of water inflow into different sources*

In the previous examples it has been assumed that water entering a stream bed had only one source ("groundwater") with a uniform radon content. In these studies, radon was used to determine the rate of discharge of groundwater to the stream. A fundamentally different problem is to directly measure the rate of water inflow to the stream (as by the tritium chemical dilution stream gauging used by Wanninkhof et al. (1990)), and use radon (perhaps in concert with other naturally-occurring solutes) to partition the total water inflow into contributions from different subsurface zones. Genereux and Hemond (1990) used radon to quantify water inputs to a stream reach from two different subsurface sources: the vadose (unsaturated) zone and the saturated zone. The study site was Bickford Watershed, a forested watershed in central Massachusetts. Measurements were focused on a 34 m reach of a small stream draining a 32 ha catchment. There were no visible inputs of water such as springs or small tributaries in the study reach.

Genereux and Hemond (1990) defined water which resides in the saturated zone for less than a few days as "vadose-zone water", whereas water that resides in the saturated zone for a longer time (several ^{222}Rn half-lives, where one half life is 3.8 days) was termed "saturated-zone water". Vadose-zone water contains less radon than saturated-zone water because of the presence of a coexisting gas phase into which the radon will partition/migrate in the vadose zone. Upon entering the saturated zone, vadose zone water begins to accumulate more radon at a rate controlled by the decay constant of ^{222}Rn (0.18 day^{-1}) because there is no longer a gas

Table 20.3. Comparison of $^3\text{H}/\text{SF}_6$ and $^{222}\text{Rn}/\text{SF}_6$ methods of calculating gas transfer velocities and groundwater discharge, Walker Branch Watershed, from Wanninkhof et al. (1990). "Distance" is distance downstream from the tracer injection point. Q^a is the streamflow rate determined from ^3H data. k^a is the gas transfer velocity for each reach, determined from the ^3H and SF_6 data. Q_g^a is the groundwater discharge to each reach, determined from the Q^a data. k^b is the gas transfer for each reach, determined from the ^{222}Rn and SF_6 data. Q^b is the streamflow rate determined from the ^{222}Rn and SF_6 data. Q_g^b is the groundwater discharge to each reach, determined from the ^{222}Rn and SF_6 data.

Distance (m)	Q^a (L/s)	k^a (cm/hour)	Q_g^a (L/s)	k^b (cm/hour)	Q^b (L/s)	Q_g^b (L/s)
2	0.5				0.5	
		42.2	3.25	26.2		3.09
22	3.75				3.59	
		33.6	5.23	24.9		1.42
89	8.48				5.01	
		24.7	2.27	11.4		1.75
123	10.75				6.76	
		24.7	2.90	24.4		0.66
142	13.65				7.42	
		30.2	2.05	20.9		0.15
209	15.7				7.57	
		42.6	3.65	19.7		-0.12
292	19.4				7.45	

phase into which the radon can escape; hence, vadose zone water acquires the radon signature of saturated-zone water after it has been in the saturated zone for a few ^{222}Rn half-lives.

The methodology involved two distinct parts: 1) solving a mass-balance equation for radon around a given stream reach in order to determine the average content of water feeding the reach from the adjacent hillslopes, $[\text{Rn}]_q$, and 2) using $[\text{Rn}]_q$, along with the measured radon concentrations of vadose zone water, $[\text{Rn}]_{vzw}$, and saturated zone water, $[\text{Rn}]_{szw}$, to determine fractions of total water inflow to the reach due to vadose-zone water and saturated-zone water.

The first part of the method involves injecting two tracers, one volatile and one conservative, into the stream at constant rates, upstream of the first stream sampling site. The conservative tracer allows determination of the amount of water inflow to the study reach. The volatile tracer allows determination of the amount of radon lost by degassing over the study reach. This information, along with the radon content of the streamwater, allows calculation of $[\text{Rn}]_q$ (Genereux and Hemond, 1990):

$$[\text{Rn}]_q = \frac{[\text{Rn}]_d}{1 - S_d/S_u} - \frac{[\text{Rn}]_u}{S_u/S_d - 1} + \frac{([\text{Rn}]_u + [\text{Rn}]_d)(S_d/S_u + 1) \ln \left(\frac{G_u S_d}{G_d S_u} \right)}{4(1 - S_d/S_u)} \quad (20.13)$$

where G and S are the steady state stream water concentrations of the injected volatile and conservative tracers, respectively, and other symbols have the same meanings as previously defined. Notice that in this formulation the gas transfer coefficient or related quantities do not

appear in the equation. The volatilization term is not separated into volatilization coefficient and travel time factors, so measurement of travel time is unnecessary, simplifying field sampling procedures (only steady state concentrations need be measured). It is also unnecessary to know the injection rate of either the conservative or volatile tracer, or the absolute concentrations of these tracers in the stream water; one need only determine the ratio of their upstream to downstream concentrations.

Once the average radon content of lateral inflow to the stream reach, $[Rn]_q$, has been calculated, the fraction of this water contributed by either the vadose zone or the saturated zone can be calculated using the familiar mixing equation, a form of Equation 20.5:

$$f_{vzw} = \frac{[Rn]_{szw} - [Rn]_q}{[Rn]_{szw} - [Rn]_{vzw}} \quad (20.14)$$

where f_{vzw} is the fraction of stream inflow in the given reach due to water from the vadose zone water, and $f_{vzw} + f_{szw} = 1$.

To obtain data on the radon content of vadose zone water Genereux and Hemond (1990) placed sampling tubes of 1/4 inch copper tubing with stainless steel well screen at the end into soil on the hillslope adjacent to the stream, about 10 m from stream channel near the middle of the study reach. These tubes were used to withdraw soil gas from the vadose zone for radon analysis (gas was sampled instead of water since removal of water from the unsaturated zone would result in loss of the volatile radon by degassing). It was assumed that the radon activity of the vadose zone water and gas were in equilibrium with each other, so that the radon content of vadose zone water, $[Rn]_{vzw}$, could be calculated from that of soil gas by Henry's Law. Henry's Law constants for radon at various temperatures and water salinities are reported in the literature, for example Clever (1979). The radon analyses of all samples (gas and water) were performed by liquid scintillation counting. The radon content of the saturated zone water was obtained by digging a pit in the stream bank soil to a depth just below the water table, collecting a soil sample and sealing it in a copper pipe to allow ingrowth of radon into the radon-free water that had been flushed through it before sealing. After about one month, water samples were drained from the container and analyzed for radon concentration.

For the field application of the technique at Bickford watershed, sodium chloride was used as the conservative tracer, and propane as the volatile tracer; both tracers were selected based largely on low cost and ease of analysis. A 2.85M NaCl solution was injected into the stream at a known rate at the same time as propane was bubbled into the stream. Total injection time was about 50 minutes. Electrical conductivity of the stream water at each of two measurement sites was measured as a proxy for the conservative tracer concentration. Conductivity measurements were made every minute during the injection, until steady-state, plateau conditions were achieved. Stream water samples were also collected for propane and radon analysis. Two radon samples were collected at each site: one before the start of NaCl and propane injection, the other just after the last samples were taken for conductivity. A total of five propane samples was taken at each site to determine average injected volatile tracer concentration.

Table 20.4 lists the parameters measured before and during the volatile and conservative tracer injections. These results were substituted into Equation 20.13 to determine $[Rn]_q = 700$ dpm/L.

Table 20.4. Tracer data used to calculate the amount and radon content of water inflow to a 32 m stream reach on Bickford Watershed (Genereux and Hemond, 1990). S and G are the steady state concentrations of the injected conservative (NaCl) and volatile (propane) tracers, respectively. [Rn] is the radon content of the streamwater, while [Rn]_q is the radon content of the 50 L/min of water discharging to the stream reach. Q is the streamflow rate at the ends of the study reach.

Stream Site	S (μS/cm)	G (μM)	[Rn] (dpm/L)	Q (L/min)	[Rn] _q (dpm/L)	ΔQ (L/min)
upstream	343	6.19	167	273	-	-
downstream	290	2.99	165	323	-	-
reach	-	-	-	-	700	50

This value was then substituted into Equation 20.14 to determine the fraction of vadose-zone water and saturated-zone water making up the total input ($f_{vzw} = 0.71$). Thus, much of the water (>70%) entering the stream over the study reach seemed to be traveling to the stream via shallow, low radon pathways in the vadose zone. This is in accord with other studies of forested catchments indicating baseflow maintenance by slow, predominantly unsaturated drainage of soil on the hillslopes (Hewlett and Hibbert, 1963; Weyman, 1973; Mosely, 1979).

The method described above was also applied to Walker Branch watershed in Tennessee (in the same stream used by Wanninkhof et al. (1990) for their study), though in this case the saturated zone contribution was further separated into soil and bedrock components, giving a three-component separation into vadose zone water, soil groundwater, and bedrock groundwater (Genereux et al., 1993). Adding a third component to a mixing model required use of an additional tracer. Genereux et al. (1993) used naturally-occurring calcium (Ca) as a means of distinguishing bedrock groundwater from the soil components; bedrock groundwater was high in Ca, because bedrock in the area was composed of dolomite, while the soil (mostly highly-leached, base-poor Ultisols) was low in Ca. Magnesium would have served equally well as a second tracer.

Other than the addition of a second tracer and third component, the methods were identical to those used at Bickford. The radon content of vadose-zone water was determined by measuring the radon content of associated soil gas and assuming equilibrium partitioning of radon between gas and water according to Henry's Law. Soil gas was collected from 12 narrow diameter sampling tubes installed on both sides of the perennial stream valley. Seven of the tubes were installed so that their screened opening was located in the B soil horizon, three were installed very near the interface of the A and B horizons, and two were installed in dense clay saprolite below the B soil horizon. The Ca content of vadose-zone water was known from monthly measurements on water samples from 20 B-horizon lysimeters, between 1983 and 1986 (Johnson and Todd, 1990). Saturated-zone water for radon and Ca analysis was collected from two shallow wells made of steel pipe driven 140 and 53 cm into the soil. The wells and vadose zone sampling tubes were constructed of an outer 2.5 cm diameter pipe with well-screen at the bottom and an inner 4 mm diameter steel pipe connected to the well screen; only the inner pipe was open to the soil via the well screen, thus minimizing the inner volume of the sampling tubes, an important consideration when sampling for volatiles such as radon. Several springs both within and near Walker Branch were sampled, and their low flow radon and Ca

signatures were taken to be representative of bedrock groundwater. Figure 20.12 shows the topography of the West Fork of Walker Branch, along with the locations of the springs, wells, and weirs used in this study.

As in the earlier work at Bickford, Cl and propane were used as the injected tracers at Walker Branch (at Walker Branch, laboratory measurements of Cl concentration were used in addition to field measurements of specific conductance; Genereux et al., 1993). The primary stream sampling points (designated by their distance in meters upstream of the V-notch weir) were WB242, WB170, and WB60 (Figure 20.12). Equation 20.13 was used to determine $[Rn]_q$ for two reaches, WB242-WB170 and WB170-WB60. A similar equation was used to determine the analogous concentration for Ca, $[Ca]_q$:

$$[Ca]_q = \frac{[Ca]_d}{1 - (C_d/C_u)} - \frac{[Ca]_u}{(C_u/C_d) - 1} \quad (20.15)$$

Having calculated $[Rn]_q$ and $[Ca]_q$, and knowing the radon and Ca concentrations of the three components, one can then solve the three simultaneous mass balance equations for the three unknown mixing fractions:

$$f_{vzw} + f_{sgw} + f_{bgw} = 1 \quad (20.16)$$

$$f_{vzw}[Rn]_{vzw} + f_{sgw}[Rn]_{sgw} + f_{bgw}[Rn]_{bgw} = [Rn]_q \quad (20.17)$$

$$f_{vzw}[Ca]_{vzw} + f_{sgw}[Ca]_{sgw} + f_{bgw}[Ca]_{bgw} = [Ca]_q \quad (20.18)$$

The Ca concentrations of the vadose zone water, soil groundwater, and bedrock groundwater were 0.04, 0.065, and 0.87 mM, respectively; the radon concentrations (in the same order) were 100, 4300, and 1070 dpm/L.

Data from the upstream 72-meter study reach (WB242-WB170) provide an example of the technique. On 18 March 1990, $[Rn]_q$ and $[Ca]_q$ for this reach were 1100 dpm/L and 0.45 mM, respectively. Solving Equations 20.16-20.18 with the component solute concentrations listed above gives $f_{vzw} = 0.38$, $f_{sgw} = 0.13$, and $f_{bgw} = 0.49$.

As documented by Genereux et al. (1993), end-member radon and calcium concentrations may vary with time, space, and flow rates. Genereux et al. (1993) provide a graphic illustration of the variability that exists in the Walker Branch study area, reproduced here as Figure 20.13. The apexes of the triangle are the component tracer concentrations given above. The data points show the variability in radon and calcium that are found in the various wells, springs, and the vadose-zone in the area, as well as observed variation in the inflow into the two reaches used in the study. The triangle in Figure 20.13 was drawn so as to surround the extremes in concentration of the three components (vadose zone water in the lower left, soil groundwater in the upper left, and bedrock groundwater on the right). Some of the variation in this figure is due to variations in component waters, in space and time (well 4B and vadose zone water,

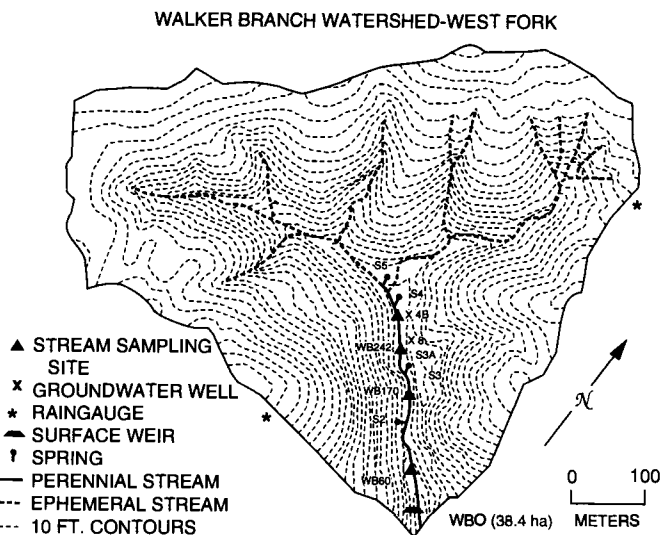


Figure 20.12. West Fork of Walker Branch Watershed (from Genereux et al., 1993).

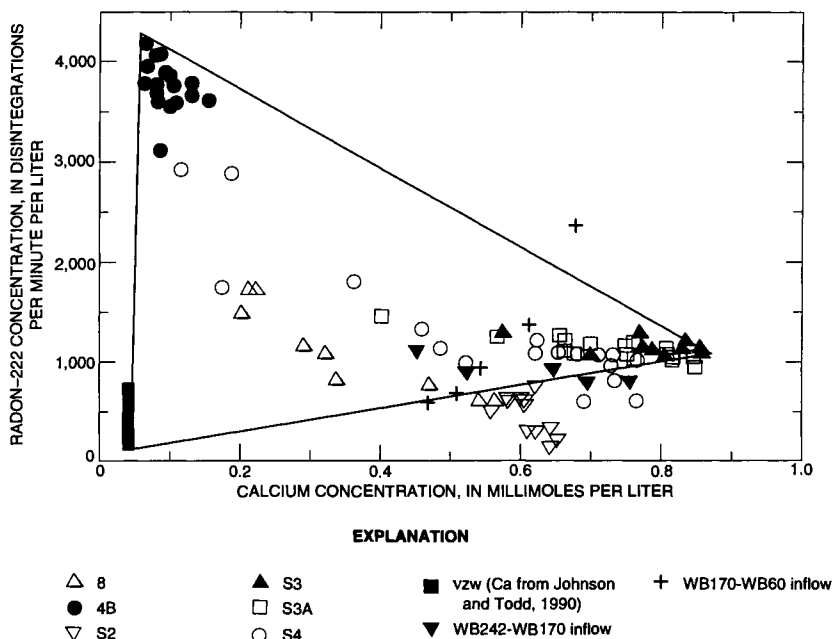


Figure 20.13. Plot of radon vs. calcium for a variety of water samples (vadose zone water, soil groundwater, springwater, and lateral inflow to two stream reaches) from the West Fork of Walker Branch. The "mixing triangle" bounds the space which could be occupied by samples that are mixtures of the solutions represented by the corners of the triangle (from Genereux et al., 1993).

for example). Samples falling outside the boundary of the triangle could indicate non-conservative behavior of one (or both) of the tracers, or the presence of an unsampled fourth component. For reasons discussed in the original paper (Genereux et al., 1993), the seven samples falling significantly below the mixing triangle (five from spring S2, two from spring S4) seem to represent low-flow spring waters that have lost radon by degassing between the spring discharge point and the sample collection point (no degassing correction was made for spring waters, which were generally sampled very close to where they discharged from the ground; degassing corrections were only applied to stream water).

The greatest source of variation in Figure 20.13 is temporal change in the mixing fractions, and these provide the basic information on the dynamics of watershed hydrology. For example, Figure 20.14 shows only the data from spring S4. As described by Genereux et al. (1993), S4 is located near the upstream limit of perennial flow of the West Fork of Walker Branch (see Figure 20.12). The small area of low slope surrounding spring S4 is hydrologically very responsive, with large increases in flow at spring S4, and increases in water table elevation, in response to storms. Hydrologic observations suggest, therefore, a shift in flowpath and water sources supplying spring S4 (toward a greater role for soil waters) as flow increases; radon and Ca data indicate exactly this, as water composition evolves from mostly bedrock groundwater at low flow (the lower right apex of the triangle in Figure 20.14) to a greater predominance of soil groundwater (in the upper left) as flow increases. In this and other examples given by Genereux et al. (1993), the tracer data fit together well with hydrologic observations in a consistent, coherent description of runoff processes on Walker Branch.

20.4 Radium Isotopic Techniques in Catchment Hydrology

20.4.1 General considerations

Like radon, radium can be used as a chemical tracer (relying on its concentration only) in environments where a large difference in concentration exists between mixing water masses, as long as the radium remains conservative. Situations where these requirements are met, however, are much less numerous than in the case with radon, a noble gas. However, since radium has several naturally occurring isotopes, the possibility exists for using radium isotopes as hydrologic tracers (relying on differences in isotopic ratios) even where no difference in absolute amount of radium exists between water masses, or non-conservative behavior occurs. An additional advantage of radium over radon is its nonvolatile behavior, although it does have a greater tendency to sorb onto particulate material than does radon.

Studies using radium to solve hydrologic problems in catchment-size basins have been few and are at a less sophisticated stage than those in which radon is used to determine water from various groundwater sources, but show great potential for further development. The following examples will show how radium has been used in catchment hydrology studies. The first involves ^{226}Ra as a tracer, while the latter ones entail use of multiple radium isotopes.

20.4.2 Radium as a tracer for groundwater input to an estuary system

Miller et al. (1990) used ^{226}Ra as a tracer to estimate the quantity of radium-rich groundwater inflow into the lower reaches of the Peace and Myakka Rivers and Charlotte Harbor estuarine

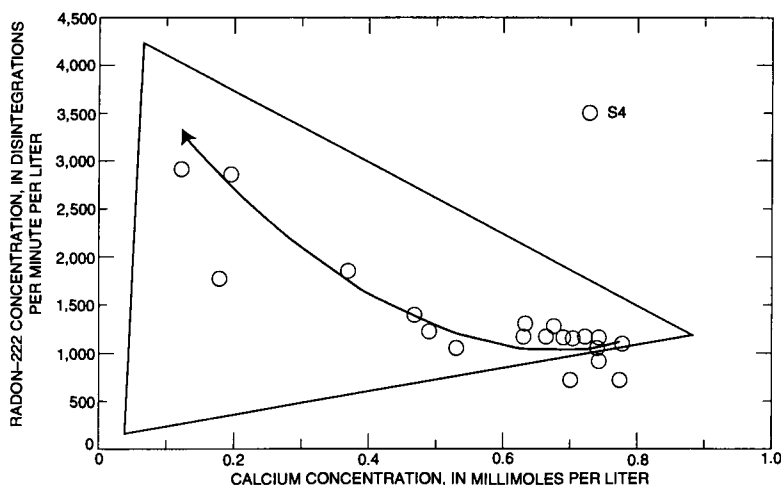


Figure 20.14. Mixing diagram showing samples from spring S4. The arrow indicates the direction of increasing flow (from Genereux et al., 1993).

area, Florida, at various times of the year. The study area included Charlotte Harbor, Pine Island Sound, and the tidal Caloosahatchee, Myakka, and Peace Rivers (Figure 20.15). The estuary is shallow and averages about 2 m in depth; the northern half (Charlotte Harbor proper) is about 1 m deeper, on average, than the southern half. The estuary is separated from the Gulf of Mexico by barrier islands, with two major and several minor passes establishing connection. The Peace River is the major source of freshwater to northern Charlotte Harbor. Both the intermediate and deep carbonate Floridan aquifers are artesian, and springs (and flowing wells) conduct water of varying salinity into the overlying surficial aquifer system and subsequently into the lower reaches of the rivers draining into Charlotte Harbor (Miller et al., 1990).

After considering and rejecting other sources as contributing major amounts of radium to Charlotte Harbor (desorption and alpha-particle recoil ejection from sediment particles, either suspended or at the sediment water), Miller et al. (1990) concluded groundwater was the source of the radium. The ratios of Gulf of Mexico water, river water, and groundwater were calculated at two locations within the estuary where the salinity gradient changes most rapidly due to the influence of the Myakka and Peace rivers (Figure 20.15), using the salinities and radium concentrations of the three assumed end-members. With this information and the flow rate of the rivers they calculated the inflow of groundwater to the estuary necessary to account for the observed salinity and radium data.

As it is usually the case, groundwater was the least well-defined end-member in terms of salinity and radium content, so Miller et al. (1990) produced three estimates of groundwater inflow using the three most likely groundwater candidates based on the stratigraphy and hydrology of the area (Figure 20.16). Table 20.5 shows the values of the end-member concentrations used in their calculations.

One groundwater end-member selected was based on water from the upper Hawthorn Formation, sampled by means of wells in the area. The upper Hawthorn is only 50 feet below the

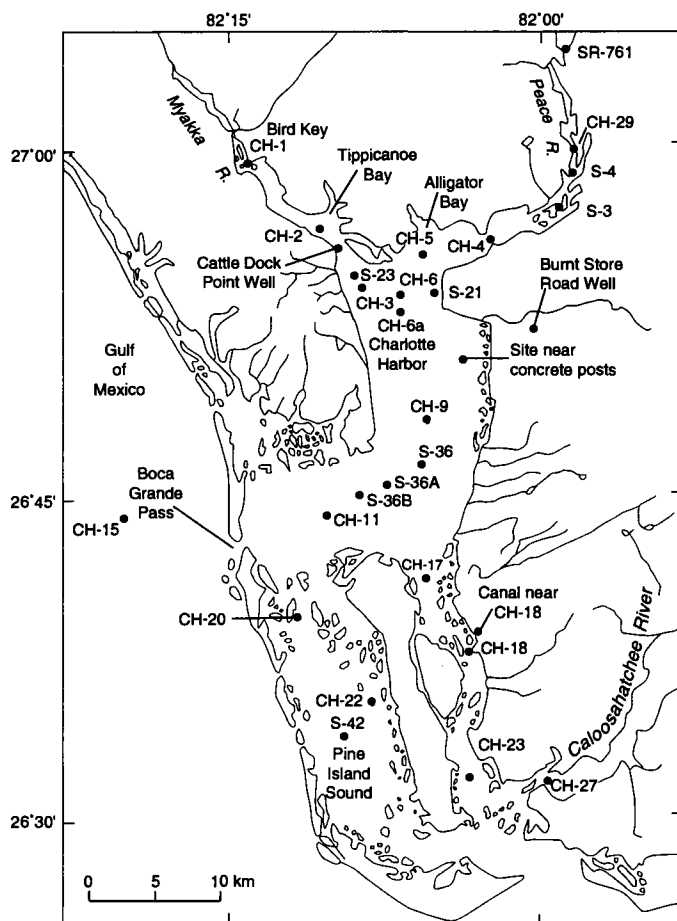


Figure 20.15. Charlotte Harbor and surrounding area, with sampling sites shown (from Miller et al., 1990).

surface in this area. A second groundwater end member selected was water issuing from a large spring in the area (Warm Mineral Springs). This water had a significantly different salinity and radium content than water from the upper Hawthorn Formation, but the spring was in the Myakka River drainage basin and was definitely supplying water to the estuary by draining into the lower Myakka just before it entered the estuary. A third groundwater end member selected was water produced from an old abandoned flowing well on land at the east side of the estuary (Burnt Store Road well), whose depth and completion interval were unknown.

The following assumptions were made by Miller et al. (1990) in calculating the results: 1) the 10 day antecedent flows of the Peace and Myakka Rivers and their tributaries, corrected for estimates of ungauged flow, are responsible for the proportion of freshwater at the sampling sites, and 2) the radium behaved conservatively during and after end member mixing, with no contribution from desorption of particulate matter, diffusion from bottom sediments, adsorption to particulate matter, or biological uptake or release.

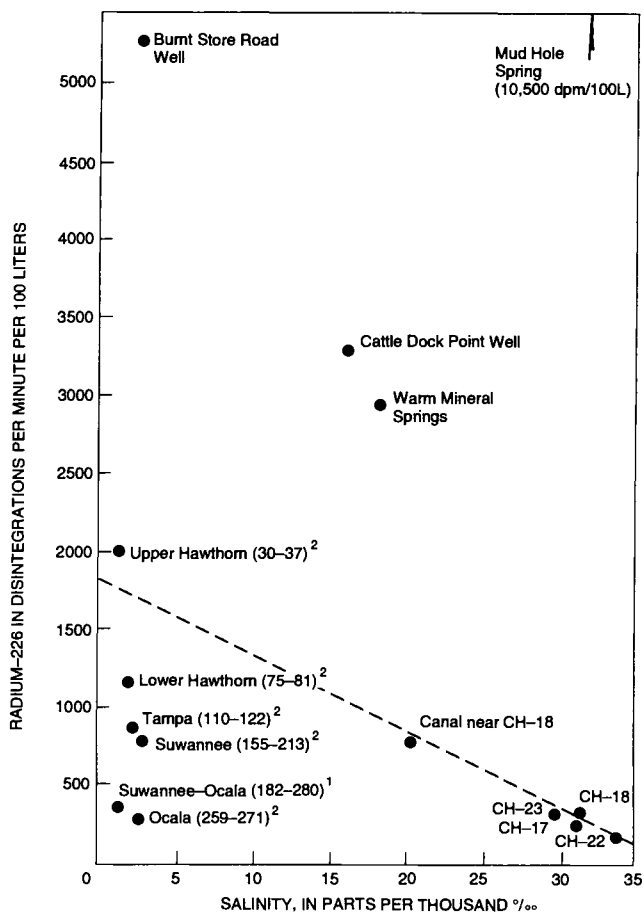


Figure 20.16. ^{226}Ra -salinity plot for water samples from Charlotte Harbor estuary (April 1986) and nearby groundwater. Superscripts 1 and 2 indicate samples from the ROMP 10 well and ROMP TR5-2 well, respectively (from Miller et al., 1990).

Table 20.5. End member water compositions used in computation of groundwater inflow to Charlotte Harbor (Miller et al., 1990).

Water	Salinity (‰)	^{226}Ra (dpm/L)
Peace and Myakka Rivers	0.2	0.40
Gulf of Mexico	35.0	0.40
Upper Hawthorn Formation Water	2.5	20.0
Warm Mineral Springs Water	18	29.0
Burnt Store Road Well Water	2.6	55.0

Three mass balance equations analogous to Equations 20.16 - 20.18 were solved to estimate the fractions of groundwater (f_g), river water (f_r), and Gulf of Mexico sea water (f_s) making up Charlotte Harbor water. Once the proportion of groundwater to river water was calculated (f_g/f_r), the amount of groundwater inflow could be derived by multiplying f_g/f_r by the flow of the river. Table 20.6 shows the results of their calculations at various times of the year using three different choices for a groundwater end-member. The significant result is that, despite the wide uncertainty in groundwater end-member composition, the estimates of groundwater influx were relatively close, ranging between about 1 and 4.5 m³/s throughout the year. These values were close to the flows of the rivers at low-flow conditions. Groundwater could be expected to have its greatest impact on the estuary at times of low river flow, provided the groundwater discharge is constant throughout the year. Not considered in this treatment is the low-salinity, low-radium content groundwater that flows into the lower river and upper estuary region resulting from recent local recharge of the surficial sand aquifer that blankets the region.

20.4.3 Use of ²²⁸Ra and ²²⁶Ra in quantifying groundwater input to a stream: conservative mixing

Radium isotopes have been used to determine groundwater inflow into a stream near Rapid City, South Dakota (Kraemer et al., in prep.). The area is located in western South Dakota, along the eastern flank of the Black Hills adjacent to and including the City of Rapid City (Figure 20.17). Rapid Creek is a major tributary to the Cheyenne River, draining about 700 square miles, with yearly flow averaging 61 cfs. The upper region of Rapid Creek basin drains Precambrian silicate rocks, whereas further downstream the creek drains the predominantly Paleozoic Madison, Englewood, and Deadwood formations. Numerous springs originate from the Madison and Deadwood formations and provide a steady source of base flow into Deerfield and Pactola Reservoirs, as well as into Rapid Creek further downstream, near Rapid City, where the spring waters rise through the Minnelusa Formation in the study area.

About 500 m upstream from Canyon Lake two springs produce water that is now used for the City of Rapid City Municipal Water Supply and a state fish hatchery (Figure 20.18). Cleghorn Springs produces water that flows through the fish hatchery and is then routed to Rapid Creek. The flow from the hatchery to Rapid Creek is measured by three weirs on its main, north, and south channels. Rapid Creek is gauged just downstream from the fish hatchery discharge and several kilometers upstream from the hatchery. All of the water produced from Jackson Springs goes into the municipal water system and does not affect Rapid Creek within the study area.

Measurements of radium concentration in Rapid Creek, Jackson Springs, and Cleghorn Springs revealed a large difference in isotopic signature of the stream water as compared to the spring water, probably as a result of the differing flow paths of the surface and ground waters. Much of the water in Rapid Creek probably drained through upland regions of crystalline silicate rock, whereas water emerging from Cleghorn and Jackson Springs had flowed through carbonate rock, picking up a relatively high ²²⁶Ra/²²⁸Ra characteristic of carbonate rock (due to the abundant U and low Th in carbonate rock), as opposed to more nearly equal ²²⁶Ra and ²²⁸Ra activities picked up by water weathering crystalline rocks, where the activities of U and Th are more nearly equal.

Table 20.7 shows the radium concentrations and flow rates of water in Rapid Creek and Cleghorn Springs on the day sampled. As in previous water mixing examples these data can

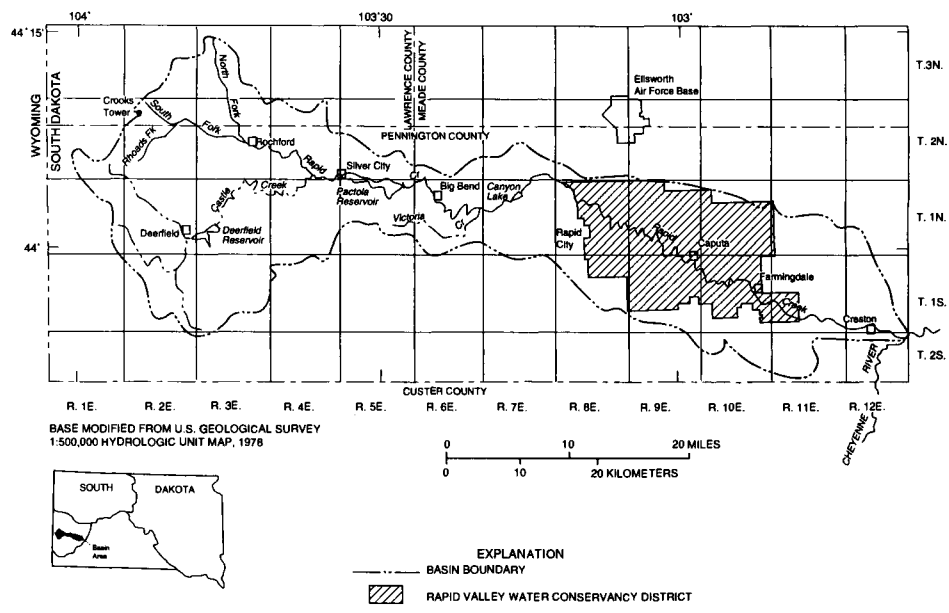


Figure 20.17. Rapid Creek basin, South Dakota.

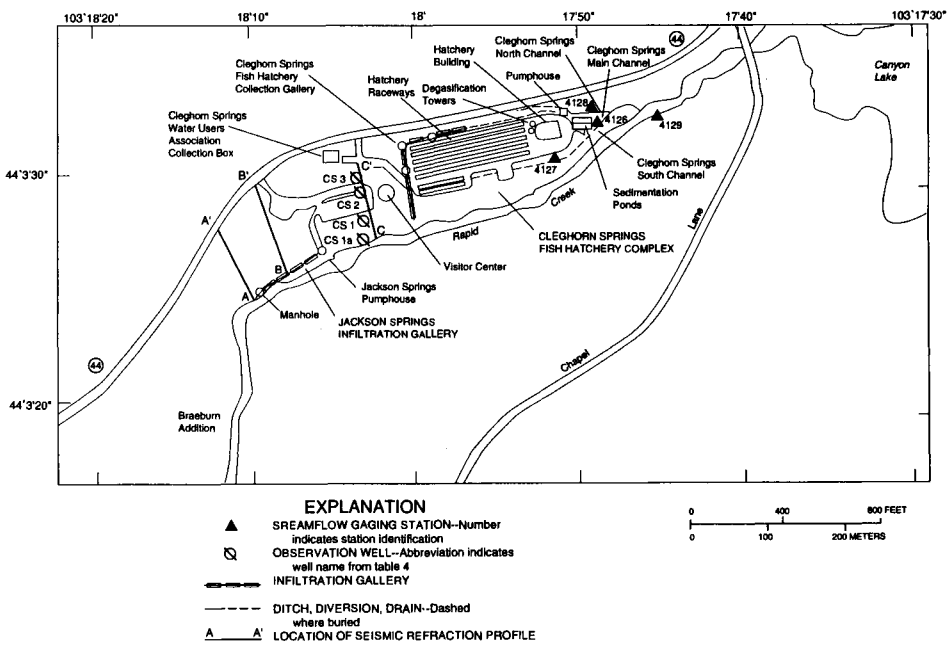


Figure 20.18. Jackson Springs infiltration gallery site.

Table 20.6. Estimate of mixing fractions (for river water, Gulf of Mexico water, and groundwater), and groundwater contribution to the Peace River at CH-4 and to the Myakka River at CH-2, Charlotte Harbor (Miller et al., 1990). S is salinity, Q_R is river flow rate, Q_g is groundwater discharge rate. A, B, and C represent different assumptions about the salinity and ^{226}Ra content of the groundwater end member: A assumes the end member is Warm Springs mineral water, B assumes it is Upper Hawthorn Formation water, and C assumes it is Burnt Store Road well water. The salinity and ^{226}Ra content of each of these waters is given in Table 20.5. *This value was reported as 13 in the original table (Miller et al., 1990).

Site	MM /YY	S (‰)	^{226}Ra (dpm/L)	River water (%)			Gulf water (%)			Groundwater (%)			Q_R (m ³ /s)	Q_g (m ³ /s)		
				A	B	C	A	B	C	A	B	C		A	B	C
CH-4	12/82	14.3	1.95	57	52	57	38	40	40	5	8	3	12.6	1.2	1.9	0.6
CH-4	8/83	5.0	1.11	85	82	85	13	14	14	2	4	1*	103.8	3.0	4.5	1.6
CH-4	1/84	11.6	1.00	66	64	66	32	33	33	2	3	1	45.8	1.5	2.2	0.8
CH-4	11/84	2.63	2.22	22	16	22	72	74	75	6	9	3	7.7	2.2	4.4	1.2
CH-4	5/86	24.7	2.84	25	18	25	66	70	70	9	12	4	2.6	0.9	1.8	0.5
CH-2	12/82	20.7	3.04	37	29	37	54	58	59	9	13	5	3.6	0.9	1.7	0.5
CH-2	1/84	16.6	1.62	51	47	51	45	47	47	4	6	2	14.2	1.2	1.7	0.6
CH-2	11/84	26.0	2.62	22	15	22	70	73	74	8	11	4	2.7	0.9	2.0	0.5
CH-2	4/86	25.2	3.22	23	15	23	67	71	71	10	14	5	3.0	1.3	2.9	0.7

Table 20.7. Flow and Ra data from Rapid Creek and Cleghorn Springs.

Location	^{226}Ra (dpm/L)	^{228}Ra (dpm/L)	$^{228}\text{Ra}/^{226}\text{Ra}$	Q (cfs)
Rapid Creek, upstream of Cleghorn Springs	0.070	0.055	0.79	25
Cleghorn Springs	0.335	0.135	0.40	11.2
Rapid Creek, downstream of Cleghorn Springs	0.160	0.080	0.50	33

be used to calculate groundwater flow into Rapid Creek. In this case, however, the water enters as a tributary to Rapid Creek, indicating that radium isotopes can be useful in surface water mixing problems as well (for example, where ungauged streams enter the main channel of a river, but where problems may prevent the accurate measurement of the tributary flow).

Because there are two relatively long-lived radium isotopes it may be possible to use radium as a tracer even if both water sources have nearly identical concentrations of radium. All that is required is that the relative amounts of the isotopes be different in each source. Where both the amount and isotopic signature are different, as at the Rapid Creek Cleghorn Springs study site, the usefulness of radium isotopes as tracers is even greater.

An equation for mixing of groundwater and upstream streamwater with differing radium concentrations and radium isotopic compositions to form downstream streamwater can be written:

$$Q_u R_u C_u + Q_g R_g C_g = Q_d R_d C_d \quad (20.19)$$

where R is the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio of the dissolved radium, C is the chemical concentration of radium in the water, Q is volumetric flow rate, and the subscripts have the same meanings as defined earlier. In practice, instead of measuring the chemical concentration (mass/volume) of radium in solution, one measures the activity of ^{226}Ra . This is representative of the mass of radium in solution, since nearly all radium in solution (by mass) is ^{226}Ra . Then by measuring the $^{228}\text{Ra}/^{226}\text{Ra}$ isotopic activity ratio on the samples, Equation 20.19 can be used to calculate mixing fractions, for example:

$$f_g = \frac{Q_g}{Q_d} = \frac{R_d C_d - R_u C_u}{R_g C_g - R_u C_u} \quad (20.20)$$

For Rapid Creek below the confluence with Cleghorn Springs, Equation 20.20 yields:

$$f_g = \frac{(0.50)(0.160) - (0.79)(0.07)}{(0.40)(0.335) - (0.79)(0.07)} = 0.314 \quad (20.21)$$

or the total flow (Q_d) was about 31% Cleghorn Springs water, and 69% upstream Rapid Creek water.

From Table 20.7 it can be seen that the gauge values of the flow measuring stations are not internally consistent in that the sum of the two inputs is 3.2 cubic feet per second larger than the output. If it is assumed that the imbalance is lost through the stream bed after complete mixing with the Cleghorn Springs water, the downstream end-member represents 69% upstream water and 31% Cleghorn Springs water. If, on the other hand, the water was lost in the more considerable distance between the upstream gage and Cleghorn Springs, the downstream water represents 66% upstream water and 34% Cleghorn Springs water. Thus, depending on the value of Q used as Cleghorn Springs water inflow into Rapid Creek, the result is either 7.9 cfs or 10.4 cfs.

Regardless of which case is closer to the truth, the mixing proportions are in good agreement with those calculated from gauge measurements under either condition discussed above. Of course, physical measurements to which tracer results are compared to test the success of an isotopic method are themselves subject to a certain amount of inaccuracy, and should be evaluated for accuracy similar to the tracer data.

In addition to an algebraic solution, radium isotopic data lend themselves to a graphical solution as well. Figure 20.19 shows the data for the Rapid Creek study plotted on a ^{226}Ra vs ^{228}Ra graph. The two end-members are at the ends of a mixing-line segment, and water resulting from mixtures of these waters will fall on this mixing line at some location between them, based on the proportions of each end member in the final mix. This graph can be used to calculate end member fractions making up a water mixture by measuring the distances between the mixture and the end-members. For example, a mixture that lies midway between the end members is made up of 50% of each end member. One that lies three-quarters of the way toward end member A is made up of 75% A and 25% B. In the case of Rapid Creek downstream of Cleghorn Springs, the mixture proportions are 66% Rapid Creek and 34% Cleghorn Springs.

20.4.4 Use of ^{228}Ra and ^{226}Ra in quantifying groundwater input to a stream: non-conservative mixing

One of the useful features of expressing radium isotopic data in graph form is that it supplies a rapid means of observing whether mixing of the water masses in question has been conservative. Because the three data points in the example in the previous section fall very nearly on a straight line, there is confidence that the mixing was conservative, with no soluble radium adsorbed onto sediment particles or adsorbed radium released from sediment to solution due to changing conditions of pH or ionic strength during the mixing of two waters. In other situations, however, the mixing may not be conservative, the most likely scenario being dissolved radium being removed from solution to suspended sediment as a relatively radium-rich groundwater or tributary water enters and mixes with a larger stream.

Figure 20.19 also shows a possible situation if the mixing of Rapid Creek and Cleghorn Springs water were not conservative. Notice that the hypothetical mixture of the two waters (point D in Figure 20.19) does not lie on a line connecting the two end members, indicating non-conservative behavior. If non-conservative behavior causes radium removal from solution it would affect each radium isotope to an equal degree (i.e., there would be no isotopic fractionation in the removal, a good assumption at the heavy atomic weights of radium isotopes). Therefore, the resulting water mixture would lie on a line connecting the origin of Figure 20.19 (zero radium, or complete removal) with the point on the mixing line where the mixture would have plotted if no removal had occurred (point C). To correct for non-conservative removal of radium during mixing one has only to extend the line connecting the origin of the graph and the non-conservatively mixed sample (point D) back to the ideal mixing line at C. Once this has been accomplished, solution for the mixing fractions can be carried out for point C, as in the previous section. The ability to detect and correct for non-conservative behavior makes radium isotopes a valuable new tool in catchment studies, and more geographic settings will likely be examined in the future.

line from each corner of the triangle through the mixture point to the opposite side, and divide it into the distance from the opposite side to the mixture point. The ratio so obtained is the mixing fraction for the component at the corner. In Figure 20.20 the lines have been scaled from 100 at the apex to 0 at the opposite side for each component, for ease of analysis. From this figure it can be calculated that the water mixture M is 20% component A, 40% component B, and 40% component C. If the flow rate of any one component is known, the flow rates of the others may then be calculated. It should be repeated that this method should be used only if it is quite certain that the radium is conservative during mixing. Adsorption would result in the movement of the mixing point along a line connecting it with the origin of the plot, as in the case of a two component mixing system. If the degree of adsorption was great, the resultant point would fall outside the mixing triangle altogether, and the effect would be obvious. However, if the degree of adsorption were slight, the resulting mixture may still plot within the mixing triangle, but not represent a true mixing point.

To ensure the most likely chances for success of this method it should be used where conditions are most favorable to radium behaving conservatively. In general, situations where suspended solids are high in any of the end-members should probably be avoided, as this increases chances for adsorption of dissolved radium. Also, slightly acidic pH values of the waters involved would be desirable, or at least no great differences in pH values among the end members. This would decrease the chances of new chemical conditions associated with mixing leading to chemical reequilibration between radium in water and bottom or suspended sediment. Finally, situations where one of the end members has significantly higher TDS (total dissolved solids) content should be avoided. The resulting increase in ionic strength of the mixture could desorb radium from suspended or bottom material, causing non-conservative behavior by increasing the radium content of the water mix.

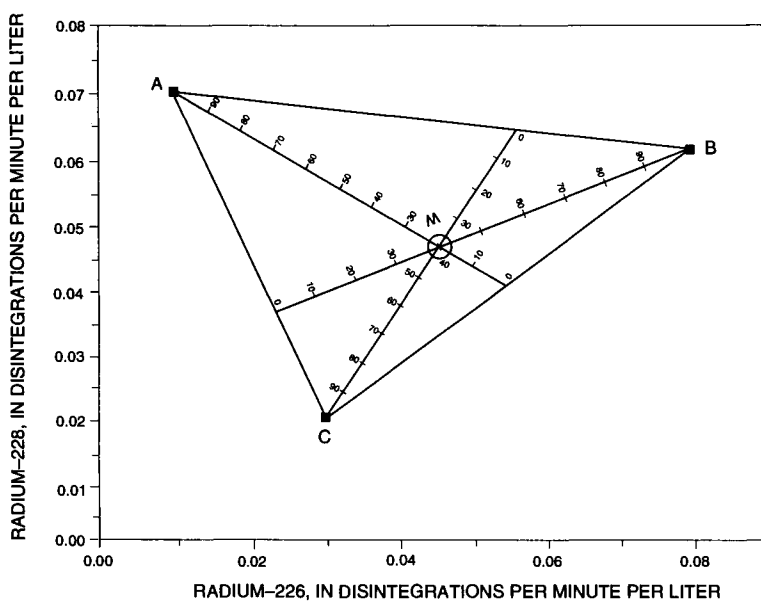


Figure 20.20. Three component mixing on a ^{228}Ra vs. ^{226}Ra plot.

20.4.6 Using ^{224}Ra and ^{228}Ra to determine residence time of water in short-residence time reservoirs

Determining the residence time of water in a reservoir is usually done by taking the ratio of reservoir volume to the rate of water inflow or outflow, or by using dye tracer studies. An alternative method involves the use of the radium isotopes ^{224}Ra and ^{228}Ra . Water in small streams generally represents water relatively recently emerged from the subsurface. While in the ground this water accumulated its load of dissolved radium through the processes of dissolution, ion-exchange, and alpha particle recoil as described earlier. Upon entry into the surface water environment the accumulation of radium isotopes in the water essentially ceases. This has little effect on the ^{228}Ra and ^{226}Ra in solution, as their half-lives are so long that they will not decay significantly during the transport of water down the stream channel; however, the short half life of ^{224}Ra (3.6 days) requires that the activity of this isotope will start to decrease measurably soon after separation from the source of the radium (the aquifer or soil grains in the subsurface). Because groundwater flow to a stream may occur continuously and at multiple points along a channel, ^{224}Ra may be found in surface water all along the length of the stream.

When stream water enters a reservoir, the ^{224}Ra activity of the water decreases due to radioactive decay. This decay in activity can most accurately be measured by comparing it to a longer-lived radium isotope, for example ^{228}Ra . In a closed reservoir, one that has been "shut-off" from new sources of radium from inflowing water, the $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratio would decrease to near zero after a few weeks. This would be true even though there is still abundant ^{228}Ra in solution which, in theory, could supply more ^{224}Ra from its own decay (Figure 20.1). The reason the activity of ^{224}Ra in solution would continue to fall below the secular equilibrium value is because of the existence of an intermediate product in the decay series. ^{228}Th has a 1.8 y half-life and is very insoluble in water. Before ^{228}Ra can produce more ^{224}Ra , it first has to produce more ^{228}Th , which, because of its long half-life compared to ^{224}Ra , would take much longer to produce compared to the time it would take the ^{224}Ra already in solution to decay. Also, because ^{228}Th , like all thorium isotopes, is very insoluble and particle reactive, it would be removed from solution soon after it is produced from the decay of ^{228}Ra .

For a well-mixed reservoir with one inflow and one outflow for both Ra and water, where Ra is lost from the reservoir only by outflow and by radioactive decay (no radium removal by sedimentation, and no addition of radium to the reservoir by diffusion from bottom sediment or direct groundwater seepage into the reservoir), the governing equation for the concentration of a Ra isotope in the reservoir is:

$$\frac{dC}{dt} = \frac{Q_i C_i}{V} - \lambda C - \frac{Q_o C}{V} \quad (20.25)$$

where C is Ra concentration in the reservoir, C_i is the Ra concentration in the inflow water, V is the volume of the reservoir, λ is the decay constant of the Ra isotope, and Q_i and Q_o are the rates of water inflow to and outflow from the reservoir. For a reservoir in steady state ($Q_i = Q_o$, V , C , and C_i constant in time), Equation 20.25 can be solved for the residence time of the reservoir:

$$t = \frac{\frac{C_i}{C} - 1}{\lambda} \quad (20.26)$$

where t is reservoir residence time. The $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratio may be used in place of concentration C , and in this case λ would be the decay constant of ^{224}Ra (0.18592 day^{-1}).

This concept was tested in a small reservoir on Rapid Creek, SD (Kraemer et al., in prep.). In November 1988, when Rapid Creek was flowing at approximately 32 cfs into Canyon Lake, a Rhodamine WT dye test was conducted (Anderson, written comm.). This test showed a dye peak passed over the lake outlet spillway 1 day after injection at the lake inlet (Figure 20.21). The residence time of the water was 1.1 days, based on the half-height half-width method.

In May, 1990, radium isotopic samples were taken at essentially the same locations as the dye injection and spillway sampling points; at this time Rapid Creek was again flowing at 32 cfs. The measured $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratios were 1.35 ± 0.09 for the inflow, and 1.00 ± 0.05 for the lake water. These radium data were used in Equation 20.26 to compute a residence time of 1.88 days for Canyon Lake. The residence times derived from the dye test and the $^{224}\text{Ra}/^{228}\text{Ra}$ data are in relatively good agreement considering the complications of the two studies. First, the dye test was carried out by an undergraduate class in hydrology not particularly skilled in measurement of Rhodamine WT dye (Anderson, 1991, personal comm.). Also, sampling technique was different between the studies. In the dye study the samples were taken at water surface near the outlet, while the radium sample was taken at depth, near the bottom of the outlet spillway. Mixing of the lake was probably not complete during either of these flow conditions, with new inflowing water possibly remaining nearer the surface. Therefore, samples taken at the surface (dye) represent younger water than samples taken at depth (radium isotopes).

A disadvantage of dye tests is the generally adverse public reaction to the test, especially if the subject reservoir is a public drinking water or recreational source. Also, there is a large team of people needed for injection, sampling, and analysis of the samples. The radium method, on the other hand, involves no injection of chemicals into the water, using instead naturally occurring constituents, and requires only a few field personnel for sampling and analysis. The radium method may therefore be more attractive for residence-time studies than the dye technique. Similarly, the radium method may be more attractive than a physical estimate relying on reservoir volume and inflow/outflow measurements, since good flow measurements and bathymetry data for many small reservoirs is not available or requires labor intensive surveys to establish.

Ideal conditions for the use of this $^{224}\text{Ra}/^{228}\text{Ra}$ method, with presently utilized analytical techniques, would be reservoirs that have a residence time on the order of ten days and also meet the conditions listed above Equation 20.25. This would cause the development of large contrast between the $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratio in the inflowing water and reservoir water, while at the same time allowing accurate measurements of both ratios. As seen in the Canyon Lake study described above, for reservoirs with shorter residence times (on the order of a few days) where incomplete mixing may be a problem, the results may not be as accurate as in longer residence time reservoirs where a greater opportunity for mixing exists.

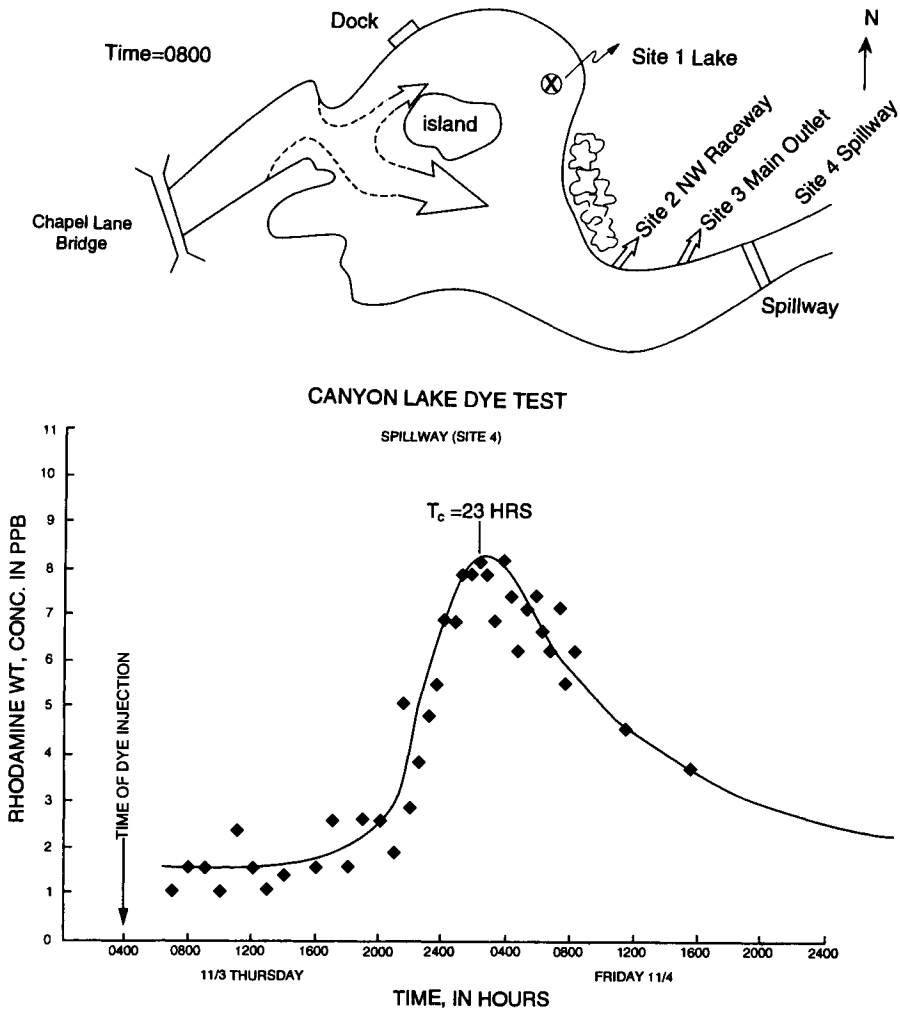


Figure 20.21. Dye study results from Canyon Lake, Rapid City, South Dakota (From Anderson, unpubl.).

20.4.7 Using radium isotopes to identify the source of water issuing from springs

Carbonate rocks generally have higher U/Th ratios than clastic rocks. Since the $^{226}\text{Ra}/^{228}\text{Ra}$ of groundwater will generally be positively correlated with U/Th, measuring the $^{226}\text{Ra}/^{228}\text{Ra}$ of water discharging at springs can provide information on the source of that water in an area with rocks having different U/Th ratios (e.g., carbonate vs. clastic). This procedure can be illustrated with Ra data from Cleghorn, City, and Jackson springs, located near Rapid City, South Dakota. These three springs originally produced water that fed into Rapid Creek, but are now used to supply water to the City of Rapid City, SD, and a state fish hatchery on the bank of Rapid Creek. Local hydrology and geology suggest that the two likely sources for the springs are the carbonate Madison Formation and the clastic Minnelusa Formation (Anderson, 1994).

Water samples from wells completed in these two formations in the area reveal two distinct fields based on radium isotopes (Figure 20.22). The Madison Formation samples form a linear trend, while those from the Minnelusa Formation plot in a broad area above the trend of the Madison samples. The isotopic data from the springs reveal they are most probably supplying water from the Madison Formation with relatively little contribution from the Minnelusa. This is in agreement with data on oxygen and hydrogen isotopes collected by Anderson (1994). In some cases a difference in stable isotopic signature may not exist between the two water types, making the radium isotopic technique of particular value in these cases.

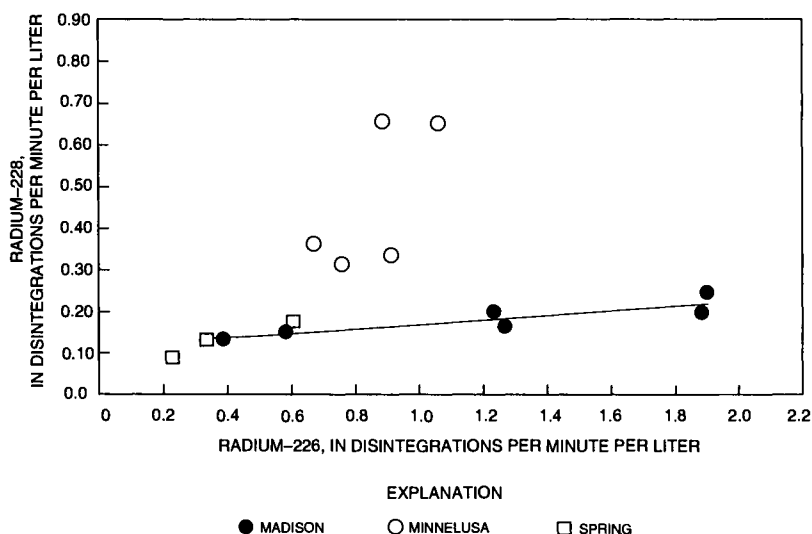


Figure 20.22. ^{228}Ra vs. ^{226}Ra for spring water, and Minnelusa and Madison groundwaters from the area near Rapid City, South Dakota.

20.5 New Research Directions

Previous studies suggest radon (specifically, ^{222}Rn) can be a highly useful tracer in studies of surface-subsurface water interaction. In areas where subsurface inputs to a flowing water body (stream, river, or canal) are dominated by water of relatively steady and homogeneous radon content, the water flux to different reaches of the channel can potentially be determined with the method of Wanninkhof et al. (1990). This approach would most likely yield good results in areas of relatively homogeneous geology, further downstream than the dynamic headwater setting in which it was originally applied. While radon's volatile nature requires a correction for degassing, it also makes radon a particularly sensitive tracer of groundwater discharge (the loss of the groundwater radon signature through degassing provides for a large contrast in radon content between groundwater discharge and streamwater at a given point). As additional experiments improve knowledge and predictability of gas exchange between water bodies and the overlying air, there may soon be accurate methods of predicting gas exchange rates based on measurable characteristics of the water body, thus obviating the need for an injected gaseous tracer to correct for radon degassing. At present however, this goal remains elusive (e.g., Genereux and Hemond, 1992).

In addition to determining total water fluxes to streams, rivers, and canals, radon offers the potential to distinguish inputs from different subsurface sources, in a way that most other solutes do not. Chemical contrasts between saturated and unsaturated zones are often minor, though the radon contrast is substantial (again, because radon is a gas). Quantitative means of integrating the hydrologic constraints generated by work with radon (saturated vs. unsaturated flow) and other tracers (e.g., event vs. pre-event water) are needed. In addition, evaluation of the importance of unsteadiness in mixing models applied during times of unsteady flow is needed (recall that all simple mixing models discussed here were steady state models).

The well-established techniques that presently exist for the determination of uranium and thorium series radionuclides are based on measuring the radioactivity of the nuclide of interest or a daughter product. However, many of these radionuclides can be measured more accurately, precisely, and in vastly lower quantities by thermal ionization mass spectrometry, "TIMS" (e.g., Volpe et al., 1991). This technique is being applied to environmental levels of uranium, thorium, radium, and lead; with TIMS the isotope is measured directly, rather than waiting for an atom to decay for a radiation measurement. Samples that contain a few nanograms of uranium can be measured accurately for isotopic composition and samples can be measured for radium if they contain quantities of only a few femtograms. These limits allow measurement of uranium and radium isotopes by TIMS to an order of magnitude better precision on sample sizes an order of magnitude smaller than is required for the best radiochemical techniques.

As a result of the new precision offered by thermal ionization mass spectrometry, investigations of uranium and thorium series radionuclides on the watershed scale should increase, as should investigations in many other environmental areas. There are two primary reasons for this. First, sample size will be greatly reduced. For example, a 20-liter sample of lake water is required to measure ^{226}Ra to an accuracy of 10% using standard radiochemical techniques. This requirement limited the total number of samples that could be collected per day when using a small boat, since frequent trips to shore were necessary to unload. Carrying such samples out of the field is also a problem when working in remote watersheds. However, using TIMS, a sample size of 1 liter is sufficient to measure ^{226}Ra to an accuracy of 1%. Second, the improved precision afforded by TIMS will allow improved resolution of the various techniques in situations where the isotopic difference between water masses is not great. For example, using radiochemical techniques in the estimation of groundwater inflow to a stream using radium isotopes, only waters of relatively large differences in isotopic ratio can be used because the average uncertainty in the individual measurements of the isotopes is about 10%. This restricts use at present, for example, to areas where surface water draining clastic or igneous terrains receives water from a carbonate aquifer. This type of situation would most likely give the largest isotopic differences between end-members. Using TIMS, however, will allow the method to be used where a much smaller isotopic contrast exists, or where several injections of groundwater from a carbonate aquifer occur at discreet points over a long reach of a river, thus changing the surface water ratio only slightly each successive time.

The increased precision of TIMS may bring back into use the first uranium series isotopic activity ratio used in hydrology to solve mixing problems, $^{234}\text{U}/^{238}\text{U}$. This technique was reported by Osmond et al. (1968), where it was used to calculate the mixing ratios of two water bodies necessary to produce the observed ^{234}U and ^{238}U activities in water issuing from a major spring in north Florida. The technique failed to gain large acceptance in the hydrologic community, however, because of the relative lack of precision of uranium isotopic analysis by alpha spectrometric techniques and the fact that most natural waters contain uranium with isotopic activity ratios between 1 and 2. This did not permit the method to take full advantage

of the potential of isotopic mixing models, because end-member mixing plots of these data would fall very nearly coincidental to non-conservative behavior lines, and the large measurement errors would preclude gaining much useful data from these plots. With TIMS, however, the increased precision allows much more precise determination of mixing ratios, as well as precise detection of (and correction for) non-conservative behavior of uranium during mixing. This would indeed be a valuable addition to the arsenal of isotopic tools hydrologists can use to solve hydrologic problems.

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Modeling of Isotope and Hydrogeochemical Responses in Catchment Hydrology

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21.1 Introduction

The recognition that natural variations of environmental isotope abundance in the flow components of a catchment's water balance could be used to complement studies of the behavior of various flow components within a catchment began in the early 1970's. At that time, environmental isotope techniques were already becoming well established in groundwater hydrology and it is only in the past fifteen years that environmental isotope tracers have become a widely used tool in catchment hydrology. Typically they are used to determine the mechanisms and processes involved in the generation and discharge of streamflow from catchments, estimate residence time distributions of water within the catchment, determine the origin of streamflow components, calibrate or validate catchment streamflow models, predict catchment response, and estimate hydrologic parameters. The transport, retardation and residence time distribution of water within the catchment are the most commonly addressed problems. More recently, the contribution of environmental isotope techniques to the study of transport, dispersion and retardation of contaminants within catchments has received increasing attention.

As in almost all branches of hydrology, the desire to extract the maximum amount of information from isotopic data in catchment processes has led to various forms of quantitative analysis. As a natural outcome of this, mathematical modeling of isotope data has evolved but there remain significant difficulties in interpretation of catchment isotope hydrological data and there is significant scope for advances in research. The approach to using isotope data in catchment modeling has been as a tool in filling in gaps in experimental or process analysis. It is increasingly recognized that there is little quantitative knowledge of basic processes at scales appropriate to system management. While processes are more or less well understood at the laboratory scale, system behavior at the field scale does not conform to what may be obtained by simply scaling up results from the laboratory. It is increasingly evident that there is little high quality experimental and field data at the relevant scale with which to constrain models of catchment processes. A number of misconceptions, oversimplifications and perhaps unrealistic expectations have limited the benefits of the use of isotope data as a tool in catchment modeling largely because of the difficulty in measuring processes in the field at the same scale as that which modeling is carried out.

The purpose of this chapter is to provide a comprehensive view of the art and science of modeling of environmental isotope and hydrogeochemical data in catchment hydrology. A

perspective is presented on the theory behind the numerous modeling formulations that have been developed for analyzing isotope responses in catchments. It is also hoped that the linkages between the different modeling approaches that are taken in analyzing isotopic and hydrogeochemical data will be clarified. Environmental tracers are those that are applied to the catchment by natural processes. In this sense, an ideal environmental tracer is one that behaves in precisely the same manner as the system response that is of interest to the hydrologist. This is a topic that presents challenges in modeling of environmental tracer behavior in catchments because the stream hydrograph reflects a complex array of hydraulic responses, whereas the tracer concentration is affected by additional processes such as mixing and dilution with whatever tracer concentration was present in the catchment prior to the rainfall.

By far the most common environmental isotopes used in catchment modeling are oxygen-18 and deuterium. Investigations generally use stable isotopic variations in rainfall, groundwater and runoff to determine some of the parameters mentioned above. Recently, radon-222 and carbon-13 and oxygen-18 in aqueous sulphate have been used as environmental tracers of catchment processes (Genereux and Hemond, 1990; Gelineau et al., 1989). The function of the mathematical model of tracer behavior in a catchment is to provide the link between the observed behavior of the tracer and how the system as a whole, or components of the system, behave. Once the model of tracer behavior is determined, it forms a useful basis for testing various hypotheses about flow mechanisms within the catchment.

The earliest use to which catchment hydrologists put isotope data was streamflow component analysis or stream hydrograph separations as discussed in Chapter 10. Since then, a wealth of knowledge and experience and an extensive literature has developed around the topic of applying environmental isotope and hydrogeochemical systematics to the studies of catchment hydrology. Probably the first study to make use of these natural signals in catchment hydrology was that of Dinçer et al. (1970) where ^{18}O in streamflow and a simple two component mass balance expression was used to predict the ^{18}O composition of meltwater. In another historically important paper Mook et al. (1974) qualitatively identified many of the characteristic isotope responses, catchment flow processes and transfer mechanisms of water that have engaged hydrologists for the following twenty years. Based on their observation of the ^{18}O response in streamflow, they identified a fast response component in streamflow caused by overland flow, the release of bank storage during the hydrograph recession and identified the significance of water table rise and groundwater contribution to baseflow. Although it was recognized that the sampling frequency was too long, a qualitative estimate of a hydrograph separation was made, concluding that pre-event groundwater contributed a minor proportion of the event streamflow.

The development of physically-based mathematical models that aid the understanding of the processes and mechanisms whereby rainfall incident to a catchment is translated into streamflow have been the subject of ongoing study in surface hydrology for many years. Parameterization, or rather over-parameterization, in rainfall-runoff modeling is a significant issue in catchment hydrology. It is important to have a clear view of how modeling isotope and hydrogeochemical data can assist with this and to ensure that the data does not contribute to the over-parameterization problem, but rather simplifies or reduces the problem.

The problem of over-parameterization results in part from too much attention being paid to the detailed study of processes at sub-catchment scale. Important processes, having been recognized, are studied in their own right, and sub-models are developed to represent them.

However, combining these sub-models leads to model representations which contain a dozen or more parameters which must be estimated. This leads to difficulties in parameter estimation, and interactions and correlations between parameters. Analysis of information contained in time series data for a catchment hydrograph typically indicates that at most 3-5 parameters are needed to represent the rainfall-runoff relationship adequately (Beven, 1989; Jakeman and Hornberger, 1993). Whether isotope data in rainfall, groundwater and runoff permits us to either eliminate or substitute for one or more of these parameters or test the validity and assumptions of model parameterization is a key element in deciding to apply isotopic methods in a catchment study. The number of parameters in a model are constrained by the data available at the relevant time and length scale. If the hydrograph contains insufficient information to identify a process explicitly, there is little benefit in representing the process explicitly in the model. Hence, determining a greater number of parameters is limited by the available data, and requires subjective judgments about which processes are important, and also of their relative contributions to the overall system. An experienced practitioner may be able to make such a judgment, but such a process is hardly objective, and inevitably depends on the prejudices of the modeler.

The subjectivity of the modeling process is sometimes a cause for concern, because one of the principal reasons for engaging in modeling is to be able to make quantitative inferences from the data. That this subjectivity is truly inherent in the process may be reinforced by a simple example of hydrograph separation. It can be shown that even for the simple mathematical formulation of a hydrograph derived from two linear stores (Wheater and Jakeman, 1993) with no rainfall losses or other non-linearities, the inverse problem of separation does not have a unique solution. Although the two time constants can be derived, the proportions of runoff attributable to the two reservoirs cannot be unambiguously determined from the hydrograph alone. The implication is that more than one model is capable of simulating the same hydrograph and that model predictions are relatively insensitive to the precise mixing proportion of the components. This may be unimportant for hydrograph prediction, but if the purpose of modeling is to investigate these proportions, then other independent data which is sensitive to these proportions is required. It is in this role that environmental isotope or hydrogeochemical tracer data and its modeling are invaluable.

One question that can be legitimately raised in the application of environmental isotope or hydrogeochemical data to catchment studies is whether or not the complementary use of the additional data simply adds to the problem of over-parameterization, in addition to imposing additional burdens to a field program and additional laboratory analysis and expense. This point needs to be very carefully reviewed before carrying out an environmental isotope study of a catchment, because the additional information provided by isotopes will only be of value if the model used to analyze the field data is correctly posed and not over-parameterized. Isotope data can only help to identify or constrain some parameters that are required if the model is not excessively over-parameterized in the first instance. Usually it is possible to develop a hydrologic model such that runoff calculated by it matches some observed runoff behavior given in a stream hydrograph. Success at matching observed and predicted runoff can be achieved by models but this does not necessarily mean that the processes and flow paths of water through the catchment are either understood or identified because a number of non-unique combinations of parameters can achieve the same success. Identifying such processes in, for example, the problems of surface water acidification is often the very purpose for which a catchment study is undertaken. Future research in catchment modeling must address problems of system and

model complexity, the length and time scales over which model components are valid and integration of model components into a balanced framework. We need to address the question of whether and where isotope and hydrogeochemical techniques have a role in addressing these. In this chapter our purpose is to review the isotope and hydrogeochemical modeling literature, provide a perspective and unifying view of modeling approaches and strategies, and present suggestions for new research areas. Discussion will be presented on the linkages between traditional hydrological models, i.e. from conceptual models through to the various physically based, distributed and time series models that are used to describe catchment behavior and the extent to which these approaches have taken advantage of isotopic and hydrogeochemical responses of catchments.

Mass balance models used for isotopic and hydrogeochemical hydrograph separation will be critically reviewed. Having identified the shortcomings associated with the neglect of response times in the mass balance approaches, consideration will be given to the concepts of transit time estimation where an attempt will be made to unify, or at least reconcile, the various model approaches to transit time estimation and determination of system response functions. Time series approaches to the modeling of isotopic and hydrogeochemical responses of catchments to determine transit times will be given. This leads to consideration of advanced time-series analysis such as the Kalman filter and its capabilities in identifying non-stationary transit time distributions.

21.1.1 Some definitions and terms

A wide range of models have been used to analyze isotopic tracer data in catchment hydrology. A model requires a theoretical knowledge of the system behavior so that a proper representation of the principal functions of the catchment can be developed. Field data and in some cases experimental laboratory data are required to calibrate and validate the model. Each model formulation used will differ in theoretical structure and the amount of field data required to estimate model parameters.

An important aspect of any discussion of system modeling is the definition of terms used to describe the catchment flow process. Several of the following definitions pertaining to catchment hydrology are taken from Diskin (1984).

System - an ordered assembly of interconnected elements that transform in a given time reference, measurable inputs into measurable outputs that are represented as functions of time.

Classification - a system may be classified under a number of criteria, but the most important classifications are whether the system is linear or non-linear, time invariant or variable, and lumped or distributed.

Calibration - following the development of a model structure, calibration involves testing of the various algorithms and routines within the model to ensure that the model reproduces physically realistic results. Parameters and state conditions within the model are adjusted until the model successfully reproduces either a set of test conditions or actual field data. Optimization routines can be invoked such that model calibration converges optimally on the test data.

Validation of a model involves ensuring that a model is a true representation of the catchment system or process that it is intended to represent. The process of model validation is carried out subsequent to

model calibration and is where the model calibration is applied to an independent or different data set to that used in calibration. The calibration is tested to examine the degree of agreement between model calculation or prediction and the observed field data.

Model identifiability refers to the ability to acquire knowledge of model states and parameters as an outcome of the process of modeling the system of interest. As Kleissen et al. (1990) state, this knowledge is of the internal description of the system's behavior or alternatively of the states and parameters of the system. This is in contrast to the external description or inputs and outputs of the system. The absence of identifiability is a condition where it is not possible to confirm or refute the constituent hypotheses of a model, given the observed behavior of the system. The identifiability of a model is determined by a combination of model structure, initial conditions, character of the input signal and, of critical importance, the availability of data on an inert isotopic tracer. Further discussion of identifiability with respect to catchment modeling based on isotopes in relation to the Birkenes catchment model is given in Section 21.4.1.

Linearity is a term that describes the response behavior of a catchment to rainfall. The linear process is that of converting rainfall excess into direct surface runoff. A linear storage or reservoir in catchment hydrology is defined as one in which the storage is directly proportional to the outflow and similarly a linear channel is one that translates water in proportion to its storage. Conversely, *non-linear* behavior of a catchment element means that the response of the element is not in direct proportion to the storage but takes on a more complex functional relation. Non-linearity in catchment response is usually identified by the fact that unit hydrographs from the same catchment are not identical. However, before concluding that a catchment displays non-linear behavior, poor data quality and variable antecedent moisture status need to be considered as possible causes of apparent non-linear behavior (Diskin, 1984).

Three excellent reviews on the calibration and validation of tracer data in groundwater systems (Maloszewski and Zuber, 1992, 1993; Zuber, 1994) present mathematical modeling approaches of tracer flow in aquifers. Some of the approaches to estimation of transit time distributions in groundwater systems described by Maloszewski and Zuber also have application in catchment hydrology and are expanded upon in following sections.

21.2 Limitations of the Mass Balance Hydrograph Separation Approach

21.2.1 Mass balance hydrograph separation models

The separation of stream hydrographs into fast and slow response components using isotope and hydrogeochemical methods has proven to be a surprisingly difficult problem to solve in catchment hydrology. The use of many different forms of mass balance hydrograph separation models of the type discussed in this section, and the identification of serious problems in interpretation of the results has led practitioners to devise ever more complicated formulations of the basic model in order to obtain interpretable results. As will be discussed in this section, a number of factors determine whether reasonable results are obtained and there are many pitfalls caused by inappropriate model selection and time varying values for input signals and rainfall intensity.

Two component models: Hydrograph separation and residence time estimation

Stream hydrograph separations using the response of the streamflow isotopic composition to individual rainfall events have been used to partition streamflow into its pre-event and rainfall components in numerous studies (see Chapter 10). The classic modeling approach to hydrograph separation involves solving mass balance equations for isotopic and water masses at each

instant during the rainfall event. The mass balance expression widely used for the two component hydrograph separation is given by Pinder and Jones (1969), Dinçer et al. (1970) and adopted by Sklash et al. (1976) and Kennedy et al. (1986). This is written for deuterium as:

$$\delta D_E V_E = \delta D_{PW} V_{PW} + \delta D_R V_R \quad (21.1)$$

where subscript *E* represents the total event runoff and *PW* represents the pre-event or "old" water in the catchment. Many isotopic studies use the δD of groundwater or pre-event streamflow (baseflow) as δD_{PW} . Subscript *R* represents rainfall or "new" water and *V* (L³) and δD (‰) are the volume and deuterium composition of the corresponding component. The $\delta^{18}O$ composition (‰) or the concentration of a hydrogeochemical parameter may be substituted for δD in Equation 21.1. The mass balance equation $V_E = V_{PW} + V_R$ is solved simultaneously with Equation 21.1 to calculate the proportion of "new" water in the event hydrograph. The combined equation is:

$$V_{PW} = \left[\frac{(\delta D_E - \delta D_R)}{(\delta D_{PW} - \delta D_R)} \right] V_E \quad (21.2)$$

This simple mass balance approach to hydrograph separation is calculated at discrete times during the event hydrograph. The calculation is most conveniently carried out based on the sampling times of streamflow over the domain of the event hydrograph. The method has been applied in numerous studies and Chapters 10, 11 and 12 list many of them. Table 21.1 summarizes their results in terms of the pre-event water contribution to the total event flow. A major finding to emerge from many analyses carried out using these equations was that stormflow was not dominated by rainwater as had been widely believed in catchment hydrology.

Probably as a consequence of the change in understanding of catchment flow processes demanded by the new isotopic results, application of the two component hydrograph separation model has met with some criticism. This is because of the simplification of the catchment flow processes and the interpretational limitations imposed by the assumption that storm generation can only be derived from two sources.

Discretization and solution of the simple mass balance expressions in Equations 21.1 and 21.2 over the domain of an event hydrograph cannot take into account the implicit time dependent nature of the catchment flow processes. In particular, the effect of either a time dependent or constant transit time for transfer of rainfall to the stream channel cannot be taken into account in estimation of the hydrograph separation. In other words non-stationary transit times cannot be accommodated by the model. In addition, it cannot take into account variation in either the isotopic composition or intensity of rainfall during an event. These simplifications lead to a breakdown in this method of hydrograph separation as shown in Turner and Macpherson (1990) and described below.

Sklash (1990) notes that the use of an average isotopic value for the "new" water poses limitations on the application of the two component hydrograph analysis because, in many

instances, the δ values in either rainfall or snowmelt input are not constant. The effect of non-constant δ values in either the rainfall or snowmelt input is that application of Equation 21.1 can lead to meaningless results. When using isotope data, this arises for $\delta D_R > \delta D_E$ when $\delta D_R < \delta D_{PW}$ or when $\delta D_R > \delta D_{PW}$ when $\delta D_R < \delta D_E$. Several recent papers (i.e., McDonnell et al. (1990) and Turner and Macpherson (1990)) have documented this situation in the field. In the latter paper, a two component hydrograph separation was attempted on a single significant rainfall event. The separation was carried out in three ways: 1) the amount-weighted mean δD of rainfall during the event was used for δD_R , i.e., δD_R was taken as being constant value for the entire event, in the manner usually used (this approach is sometimes given the term bulk total method), 2) an incremental approach was taken where the actual measured δD_R for each increment of rainfall was used with zero lag between the occurrence of the rainfall and its discharge from the catchment, and 3) the time series of δD_R in rainfall and the corresponding stream isotopic composition δD_E were used in a correlation analysis to estimate the lag between the isotopic signature in rainfall and its appearance in streamflow. The best correlation was found at a fixed lag of five hours. The two component separation was carried out as normal, but with a lag of 5 hours applied to the streamflow data. Results of the hydrograph separation carried out under the first condition showed that the amount-weighted mean δD_E of rainfall for the event was more negative than both the δD_E and the pre-event δD_{PW} during the entire event. Because of this, a reasonable estimate of hydrograph separation was obtained. Under the second condition with zero lag and taking into account actual variations in δD_R during the event, the hydrograph separation calculation broke down when δD_R became greater than δD_E . The analysis also failed under the third condition when the (lagged) δD_R was greater than both δD_E and δD_{PW} .

Three component models

Several authors have attempted to circumvent the problems with the two component hydrograph separation described above by invoking a three component hydrograph separation (DeWalle et al., 1988; Swistock et al., 1989; Ogunkoya and Jenkins, 1993). As described by Dewalle et al. (1988) and Swistock et al. (1989), the three component model includes terms to account explicitly for the contribution to streamflow from soil water storage, direct interception of rainfall by the stream surface and groundwater.

The model can be written as follows:

$$V_E = V_{CP} + V_{PW} + V_S \quad (21.3)$$

and

$$V_{SW} / V_E = \left[\frac{(\delta D_E - \delta D_{PW})}{(\delta D_S - \delta D_{PW})} \right] - V_{CP} / V_E \left[\frac{(\delta D_{CP} - \delta D_{PW})}{(\delta D_S - \delta D_{PW})} \right] \quad (21.4)$$

where $V (L^3)$ refers to the volume of the respective flow component and subscripts E , CP , PW and S refer to the total event flow, channel precipitation, pre-event groundwater and soil water, respectively. Equation 21.4 is written with δD as the tracer, but other isotopic or hydrogeochemical tracer concentrations may be substituted. The three component model applied by

Table 21.1. Compilation of studies determining the pre-event water contribution to the total event flow based on the two component hydrograph separation model.

							Pre-event water contribution (%)	
Study	Location	Area	Land use	Deposits	Tracer	Rainfall amount (mm)	To peak discharge	To total storm flow
Dincer et al., 1970	Czechoslovakia	2.65 km ²	70% Meadow 30% forest	Glacial deposits	³ H & ¹⁸ O	Snowmelt	---	Major
Crouzet et al., 1970	France	5.7-91 km ²	---	---	³ H	6-31+	---	54-99
Martinec et al., 1974	Switzerland	43.3 km ²	94% Meadow 6% forest	Glacial deposits	³ H	Snowmelt	---	Major
Mook et al., 1974	Netherlands	650 ha	---	Shallow aquifer over clay	¹⁸ O	8.2-15.7	10	Minor
Fritz et al., 1974	Manitoba, Ontario	---	Forest	Glacial deposits	¹⁸ O	---	---	50-70
Cherry et al., 1975	Ontario,	1.8-22 km ²	---	Glacial deposits	---	50	50-60	50-90
Sklash et al., 1976	Ontario, Canada	73-108 km ²	Improved farmland	Silty to coarse sand	¹⁸ O	21-28	70-75	70
Sklash and Farvolden, 1979	Ontario, Canada	1 km	Intensive agriculture	Coarse sand over silty clay	¹⁸ O	17-38	60-80	---
Sklash and Farvolden, 1979	Quebec, Canada	1.2 km	Forest	Glacial till	¹⁸ O	6-35	65-80	---
Hermann and Stichler, 1990	Bavarian Alps, Germany	18.7 km	80% Forest	Clayey glacial deposits	D	Snowmelt	---	70-85
Rodhe, 1984	Sweden	0.03-6.6 km ²	Forest	Till soils	¹⁸ O	Snowmelt	---	41-86
Christopherson et al., 1984	Birkenes, Norway	41 ha	Forest	---	¹⁸ O	Snowmelt	---	70-80
Bottomley et al., 1986	Ontario, Canada	10.5 km ²	Forest	Mafic-meta volcanics	¹⁸ O	Snowmelt 41	50-60	70

Hooper and Shoemaker, 1986	New Hampshire	42.4 ha	Forest	Glacial till	^{18}O	Snowmelt	75	60-75
Kennedy et al., 1986	Mattole R., California	620 km ²	---	Gravelly to clayey loam	D & ^3H	137-250	---	50-80
Pearce et al., 1986	Maimai, New Zealand	<4 ha	Forest	Shallow soil	^{18}O	2.7-16.2	---	97
Turner et al., 1987	Collie, W. Australia	82 ha	Forest & clay	Eathered granite	D & ^{18}O	Snowmelt	---	60-95
Dewalle et al., 1988	Pennsylvania USA	208 ha	Forest	Silt loams	^{18}O	53-239	---	75
Tanaka et al., 1988	Tokyo, Japan	0.022 km ²	Forest & silty clay	Clay loam cond.	Elect.	57-195	---	<90
Moore, 1989	Quebec, Canada	5.3 ha	Forest	Glacial	D & ^{18}O	Snowmelt	---	85
Loye-Pilot and Jusserand, 1990	Corsica, France	0.33 km ²	Forest	---	^{18}O	56.8	---	60-90
Neal and Rosier, 1990	Plynlimon, Wales	340 ha	50-70% Conifer plantation	Shallow peaty soils	^{18}O	---	---	Major
McDonnell et al., 1990b	Maimai, New Zealand	3.8 ha	Forest	Thick humic soil	D	47	---	80
Sklash, 1990	Maimai, New Zealand	3.8 ha	Forest	Shallow humic soil	D & ^{18}O	33.2-43.7	70	75-85
Turner and Macpherson, 1990	Perth, Australia	27 km ²	35% Forest 40% grazing land	Deeply weathered granite	D	120	---	58
Turner et al., 1991	NSW, Australia	600 ha	Pasture	Shallow soils	D	30	---	25
Turner et al., 1991	NSW, Australia	1000 ha	Pasture	Shallow soils	D	80	---	37

Pre-1983 data taken from Bernier, (1985). Various pre-1986 tracer data taken from Hooper and Shoemaker, (1986) and from Sklash, (1990).

Dewalle et al. (1988) overcame problems of unrealistic results in the form of impossible "new" and "old" water components determined from the two component model. For identical reasons of unrealistic component estimates using a two component hydrograph separation, Swistock et al. (1989) also adopted the three component analysis. More reasonable results were obtained with the three component analysis which showed that groundwater and soil water were major contributors to most events. In order to solve the three component hydrograph separation based on silica alone, Hendershot et al. (1992) used the empirically derived expression $V_{sw} = 0.53(V_E - 0.15)^{1.2}$ as the relationship describing the quantity of soil water contributing to the total streamflow. Despite the operational improvement obtained by the introduction of a third component into the two component hydrograph separation equation, i.e., the reduction of the problem of unrealistic component contributions, it does not overcome the primary drawbacks with either method. These are that neither constant or non-stationary transit times can be accommodated by the model's construction, that variations in either the isotopic composition or intensity of rainfall during an event cannot be accommodated, and that the introduction of a third component is not necessarily justified on the basis of the flow mechanisms.

These shortcomings point out the need for a modeling approach that accommodates non-stationary transit times. Consequently, discrete, time-based data are required on the input compositions in addition to a model that can account for different travel times for transfer to the catchment outlet. Estimation of short transit times for water in a catchment using stable isotope data must consider several complex phenomena. These include time-variant system response functions, non-linear and non-steady state input and output relations, variable tracer concentration during input and variable volume of the groundwater storage within the catchment. These phenomena and the modeling approaches to describe them are given in Section 21.3.

21.3 Estimation of Transit Times - System Response Functions of Catchments

21.3.1 System response functions

Before discussing modeling of isotopic and hydrogeochemical tracers in catchments it is necessary to establish a suitable definition of residence time. In fact different definitions of residence time may be necessary depending on the type of model being used. The simplest concept of residence time t_0 , is that of turnover time or mean residence time and is written:

$$t_0 = S/V \quad (21.5)$$

where S (L^3) is the storage of water within the system domain and V is the rate of flow through the system ($L^3 T^{-1}$). The *mean transit time* of a conservative tracer (t_t) is given by:

$$t_t = \frac{\int_0^{\infty} t c_I(t) dt}{\int_0^{\infty} c_I(t) dt} \quad (21.6)$$

where $c(t)$ is the instantaneous concentration of tracer in the input at time $t=0$. For the tracer age defined by Equation 21.5 to be equivalent to the age of the flow at the outlet to the system,

the tracer must be introduced into the system in proportion to the input volume and be measured in proportion to the outflow volume. Furthermore, Equation 21.5 applies to a conservative, non-retarded tracer and there needs to be complete mixing of the tracer within the system, i.e. no stagnant zones (Malosewski and Zuber, 1982). The first two of these requirements are satisfied with the isotopic tracers oxygen-18, deuterium and tritium.

Application of environmental isotopic tracers to estimation of transit times in hydrological systems has been investigated by several workers, e.g. Neimi (1978), Yurtsever (1983), Lewis and Nir (1978), Magrita et al. (1984), Maloszewski and Zuber (1982) and Zuber (1986 a,b) and Maloszewski and Zuber (1992, 1993). The modeling approaches developed by these and other authors have usually referred to groundwater flow (as discussed in Chapter 7) and in particular the estimation of mean transit times or mean residence times of water in the system. Depending upon the particular system to be modeled, the methods range upwards in complexity from those which assume linearity and steady state conditions, to those that have non-stationary system response functions and deal with time varying input concentrations of tracer and rainfall intensities. The following sections are dedicated to a discussion of mathematical models as they are applied to the modeling of environmental isotope and hydrogeochemical data in catchment responses to rainfall or snowmelt input and the associated generation of runoff. The modeling approach depends fundamentally on the means by which the tracer is introduced into the system. Because the majority of catchment tracer studies use the natural abundance of either oxygen-18, deuterium or possibly tritium in rainfall, the cases considered are those where the tracer is introduced to the system in proportion to the volumetric input.

21.3.2 System response functions based on the IUH

The choice of an appropriate probability density function that correctly represents the transit or service time for a catchment has a great influence on the shape of the event hydrograph. The peak, time to peak and the recession characteristics are all determined by selection of the probability density function, and consequently models of isotope response based on probability density functions will also be determined by its selection. In the following sections a number of probability density functions are described that form the basis for the analysis of isotope responses in catchments. These include models based on piston flow, exponential, dispersive and instantaneous unit hydrograph (IUH) distributions of transit time. With the exception of the piston flow model, these transit time distribution functions can be considered as special cases of the Gamma function. For example, the IUH is based on an exponential distribution of travel times as follows. A linear reservoir in catchment hydrology is defined as one in which the storage is directly proportional to the outflow. For a unit rainfall input, the IUH, $U(t)$, of a linear reservoir is:

$$U(t) = \alpha \exp(-\alpha t) \quad (21.7)$$

where α is a reservoir constant sometimes referred to as a storage coefficient. $U(t)$ gives the hydraulic response time of the system. The IUH can be considered as a distribution function in which t is the exit time of a given volume of water in storage, and $U(t)$ is the probability density at time t and is equivalent to the ratio of the volume exiting the system at t to the total storage. Because Equation 21.7 is based on an exponential distribution, it follows that the

transit times of the IUH are exponentially distributed. The gamma probability density function is written:

$$g(t) = \frac{1}{\beta^\alpha \Gamma(\alpha)} x^{(\alpha-1)} e^{(-t/\beta)} \quad (21.8)$$

where $\Gamma(\alpha)$ is a value of the gamma function defined by:

$$\Gamma(\alpha) = \int_0^\infty x^{(\alpha-1)} e^{-t} dt \quad (21.9)$$

for x , α and β all > 0 . Figure 21.1 shows that the form of the gamma distributions is skewed; in the special case where $\alpha = 1$, an exponential density is given by:

$$g(t) = \frac{1}{\tau} e^{-\frac{t}{\tau}} \quad (21.10)$$

where τ is mean residence or transit time of the system. It is shown in the next section that the dispersive model distribution of transit times is similar in form to that of the gamma function.

Where environmental tracers are used, the introduction of the tracer is not an instantaneous injection but is usually quasi-continuous, for example during the course of a rainfall or snowmelt event. The introduction of isotopic tracers into a catchment naturally occurs in proportion to the volumetric input because the tracer is introduced by the event itself. For each time increment t it is therefore necessary to include the past history of the tracer input. With conservative (i.e. non-radioactive) isotopic tracers such as deuterium or oxygen-18, and linear systems at steady flow (i.e. steady input and output flow) the tracer concentration in the output is related to the input concentration by the convolution integral which may be written:

$$c(t) = \int_{-\infty}^t c_{in}(\tau) g(t-\tau) d\tau \quad (21.11)$$

where $c(t)$ is the output isotope concentration, t is the exit time from the system, τ is the entry time to the system, $t-\tau$ is the transit time, $c_{in}(\tau)$ is the input isotope concentration and $g(t-\tau)$ is the system response function that describes the transit time distribution of the conservative tracer particles through the system. The system response function operates on $c_{in}(\tau)$ and is integrated to yield the concentration $c(t)$ at the outflow to the catchment. If the tracer concentration declines by radioactive decay, an additional term $\exp^{-\lambda(t-\tau)}$ needs to be introduced into Equation 21.11. The weighting or system response function $g(t')$ can be expressed as:

$$g(t-\tau) = \frac{c_I(t-\tau)}{\int_{\tau}^{\infty} c_I(t-\tau) dt} \quad (21.12)$$

where $c_f(t - \tau)$ is the tracer output concentration (Zuber, 1986a).

Typically, the type of model used as the system response function is selected on the basis of the physical system being considered, but can be a piston flow, exponential or dispersion formulation. The piston flow formulation is generally not applicable to catchment hydrology because the flow paths all have the same velocities. Figure 21.1 shows the form of the $g(t)$ functions for the exponential and dispersion models. The figure illustrates several points. The first is the different transit time distributions for each model and emphasizes the point that the choice of transfer model will significantly affect the interpretation of catchment response and components of "new" and "old" water in hydrograph separation analysis based on these models. An additional point is the similarity in form and skewness between the gamma function distribution and dispersion models. It is evident that the modeled "age" of flow discharging in streamflow from a catchment is dependent on the choice of model used to describe the transfer of the applied isotopic tracer. Frequently, the mean transit time of the tracer, as given by Equation 21.11, is reported as the tracer age, and to avoid any confusion between tracer transit time and water transit time, both the tracer and model used to describe its transfer from rainfall to streamflow need to be defined. This point is illustrated further in Section 21.3.3 where a formulation for the instantaneous unit hydrograph is substituted for the transfer function $g(t)$. A further example on identification of the transfer function $g(t)$ by Rodhe et al. (1996) is given in Section 21.4.2 for the special condition where there was an experimentally controlled step change in the isotopic composition of the input.

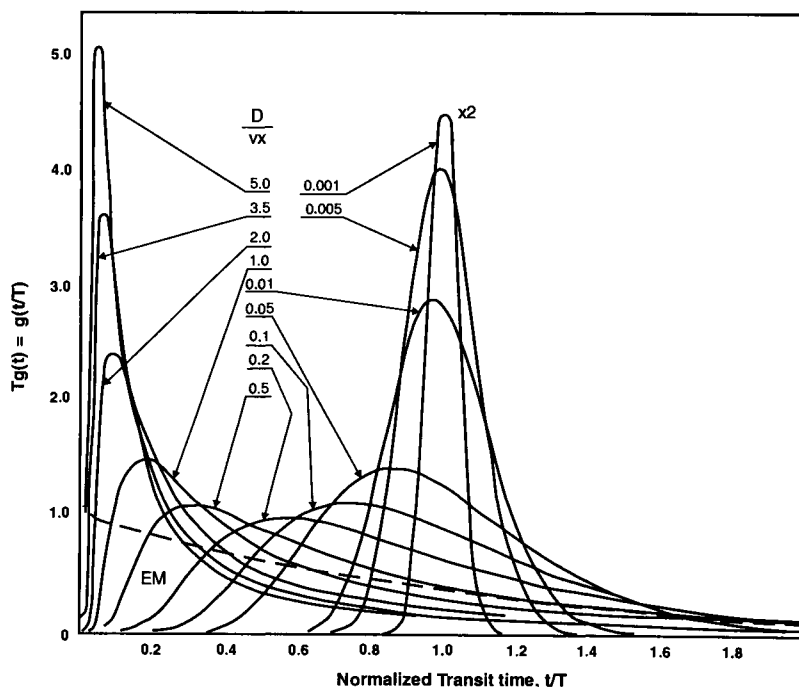


Figure 21.1. Graphs of $g(t)$ functions for a dispersive model with different values of the dispersion parameter D/vx . EM indicates the $g(t)$ function for the case of an exponential model. After Zuber (1986a).

It can be seen from Figure 21.1 that the dispersion model is a flexible transfer function and the $g(t)$ function can take a wide range of forms. As the name implies, the exponential model assumes that transit times are distributed exponentially. Where the input rainfall can be assumed to mix rapidly with pre-event ground and soil water within the catchment, and steady state, well-mixed conditions for the flow system can be assumed, an exponential distribution of residence times can be used. The exponential distribution of transit times is applicable to runoff generation processes because flow lines with very short transit times can be included. Different flow models are represented by different system response functions. The exponential system response function has the form given earlier by Equation 21.10 as a special case of the gamma function.

As shown in Figure 21.1, the form of the exponential function is restricted and limits its application in catchment studies. Because the dispersion model can accommodate a much wider range of transit time distributions and can accommodate very short transit times it has found wider use in catchment studies using environmental isotopes (Stewart and McDonnell, 1991).

Several solutions of the dispersion model have been given by Kreft and Zuber (1978). One of the solutions which is suitable for modeling catchment isotope responses is their C_{IFF} solution. In this solution, the input tracer is assumed to be introduced to the system and sampled in proportion to the volumetric flow of water and the system is also assumed to be semi-infinite. This form of the dispersion model gives a mean transit time for the tracer equal to the mean transit time of the water through the system. The distribution of residence times is given by:

$$g(t) = (4\pi D_p t / \tau)^{-1/2} t^{-1} \exp\left[-(1 - t/\tau)^2 (\tau / 4D_p t)\right] \quad (21.13)$$

where τ is the mean residence time and D_p is the dispersion parameter ($D_p = D/vx$ where D is the dispersion coefficient (L^2/T), v is the mean flow velocity and x is the length of flow line). A primary difference between the exponential and dispersive models is that in the exponential model the only flow parameter is the mean transit or turnover time τ , whereas with the dispersion model, flow is determined by both τ and D/vx . Stewart and McDonnell (1991) used this system response function to model the soil water residence times in the Maimai M8 catchment in New Zealand but in practice it was found to produce unreasonable values for parameters. Subsequently, a better fit to the soil water deuterium data was found by using a second dispersion model derived from a combination of the C_{IFF} and C_{IRR} models of Kreft and Zuber (1978). This model was:

$$g(t) = (16\pi D_p)^{-1/2} \left[(t/\tau)^{1/2} + (\tau/t)^{1/2} \right] t^{-1} \exp\left[-(1 - t/\tau)^2 (\tau / 4D_p t)\right] \quad (21.14)$$

Other models tested by Stewart and McDonnell (1991) in their simulation of δD responses in soil water to rainfall input included steady and unsteady exponential models. The non-steady mixing model approach using two components, as given in Equation 21.2, encountered problems due to the time-varying nature of the input isotopic signal as described above in Section 21.2.

In catchments with an unconfined groundwater system and homogeneous aquifer characteristics, the distribution of tracer transit times that contribute to streamflow via

groundwater recharge and discharge has an exponential distribution. A good example of the combination of the standard bulk total method of aggregating rainfall isotopic composition in the two component hydrograph separation and both exponential and dispersive models for the system response function was used by Maloszewski et al. (1983) to determine mean transit times of groundwater to streamflow in an Alpine catchment. This potentially effective approach of coupling two models that had previously only been used separately has been largely overlooked by subsequent researchers. Provided appropriate consideration of the catchment water balance and time constants is made and provided synchronization of the rapid and slow flow processes is maintained, this approach has considerable merit. A conceptual model of the catchment is shown in Figure 21.2 and included a component (γ) of rapid flow with a turnover time on the order of hours to days. The remaining proportion of input, $(1-\gamma)$ was routed to either of two subsurface stores with much longer residence times. Discharge from the deeper of these two subsurface stores was considered to represent the baseflow discharge to the stream and was considered to have an invariant isotopic composition. The simple mixing model based on the two component hydrograph separation (Equation 21.2) but using $\delta^{18}\text{O}$, and six-monthly weighted means of rainfall $\delta^{18}\text{O}$ ($\delta_{in}(t)$) was applied to make the primary separation of rainfall into its rapid and slow flow components, γ and $1-\gamma$ respectively. The slow-flow subsurface component, $1-\gamma$, was estimated to comprise 70% of the total hydrograph. The isotopic input function for the upper of the two subsurface reservoirs was approximated by a sinusoidal input function with a period of one year, reflecting the seasonally cyclic variation in the stable isotopic composition of rainfall. The dispersive model was then evaluated to give a residence time of 0.6 years for the upper subsurface reservoir.

Pearce et al. (1986) used a transfer function model approach to estimate the mean residence time of water in a catchment. As in Maloszewski et al. (1983), they took advantage of the well known seasonal variation in the isotopic composition of rainfall in temperate regions and represented the observed seasonal variation in the $\delta^{18}\text{O}$ of input rainfall ($\delta_{in}(t)$) by a sinusoidal input function. By assuming a steady state flow regime and exponential distribution of transit times the convolution integral was written as:

$$\delta_{out} = \tau^{-1} \int_0^{\infty} \delta_{in}(t-\tau) e^{(-t/\tau)} d\tau \quad (21.15)$$

where, as before, τ is the mean residence time of water in the system and the input function $\delta_{in}(t-\tau)$ is given by $A \sin(\omega t) + M$ where A is the amplitude of the seasonal variation in the isotopic composition of rainfall, M is its mean value and ω is the period of the seasonal variation. In this situation the choice of input function with a period ω on the order of months dictates that the transit time is of the same order of magnitude because the operation of the exponential system response function on a sinusoidal $c_{in}(\tau)$ and its integration will yield an output concentration $c_{out}(t)$ at the outflow to the catchment that is also sinusoidal, but with a phase shift. The mean transit time will still be dependent on ω . Thus the fast response to rainfall or snowmelt events that occur on the time scale of hours to days cannot be analyzed using an exponential system response function operating on an input function with a period of months. Obviously, selection of the transfer function model and the tracer input function must be appropriate and consistent with the time scales of the processes being analysed. This latter comment applies equally to the coupled model of Maloszewski et al. (1983) discussed above.

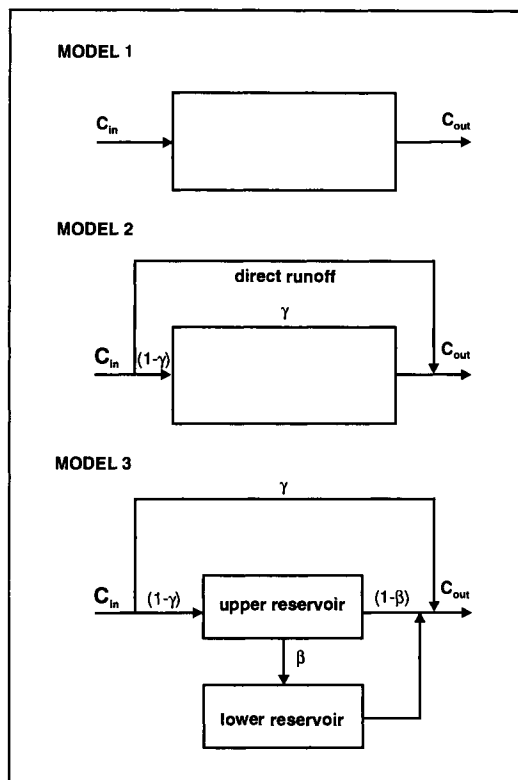


Figure 21.2. Conceptual models of catchments - Model 1: a single, well-mixed compartment, Model 2: a single compartment with a bypass component (γ) routed to surface outflow and Model 3: a two compartment model with different turnover times. After Maloszewski et al. (1983).

21.3.3 Application of system response functions based on the Instantaneous Unit Hydrograph

In this section, consideration is given to the application of instantaneous unit hydrograph theory to the modeling of isotope and hydrogeochemical data in catchment hydrology. The unit hydrograph is defined as the stream hydrograph produced by a rainfall event of given duration and uniform intensity. The stream hydrograph is due to a unit rainfall excess which may be in units of inches or millimeters. The duration of the rainfall excess is short relative to the time scale of the hydrograph and in the case of the instantaneous unit hydrograph is infinitely short, approaching zero.

The measured flux of water $q(t)$ leaving a catchment via the outlet at time t can be represented as:

$$q(t) = \int_0^\infty dt' \int_A dx dy g(x, y, t; t') P(x, y, t - t') \quad (21.16)$$

where $P(x,y;t)$ is the rate of precipitation falling on the point (x,y) in the catchment at time t , and $g(x,y,t;t')$ is the proportion of water falling on (x,y) at time $t-t'$ which is leaving the catchment at time t . As described above, the function $g(x,y,t;t')$ can be regarded as the response function or transfer function (for precipitation), or the residence time distribution.

Equation 21.16 simply expresses the observation that the flow of water leaving a catchment at any time must consist of rainwater which fell on the catchment at some previous time, with no other assumptions, apart from elementary ones regarding smoothness of the catchment. With appropriate definitions of the input quantities, a similar equation can be written for the mass flux of any component, such as solutes or tracers, or even particulate matter. However, although suggestive, it is not very useful, as the function $g(x,y,t;t')$ should implicitly contain not only all the catchment details including non-linearities and water loss by evapotranspiration, but also the history of the catchment which in general will depend on antecedent precipitation. To make progress it is necessary to invoke further simplifying assumptions, necessarily introducing errors and restricting the range of application.

For catchments which are small in relation to the size of weather systems, an obvious simplification is the assumption of spatially uniform rainfall intensity. Then Equation 21.16 can be integrated, to give a new representation of the hydrograph response in terms of the input precipitation:

$$q(t) = \int_0^{\infty} dx G(t;t') P(t-t') \quad (21.17)$$

where now:

$$G(t;t') = \int_A dx dy \gamma(x,y,t;t') \quad (21.18)$$

is the catchment residence time distribution, defined for the catchment as a whole rather than for a single point. Equation 21.17 is similar to the widely utilized Unit Hydrograph with G corresponding to the Instantaneous Unit hydrograph (IUH). Although Equations 21.17 and 21.18 have deliberately been written to suggest a linear dependence of catchment flux on precipitation input, the function G (like g) is inherently non-linear; in particular it depends on the precipitation history $P(t)$. The importance of the IUH formulation was the recognition that under certain circumstances, the non-linearities inherent in G could be avoided by concentrating on the hydraulic characteristics of the catchment, so that the output flux then depends approximately linearly on the effective precipitation P' :

$$q(t) = \int_0^{\infty} dt' H(t') P'(t-t') \quad (21.19)$$

The IUH, $U(t)$, can then be interpreted as the response time distribution of the catchment for the effective precipitation. However, it is no longer necessarily true that U can be interpreted as a residence time distribution, as explained in the example below.

As was indicated at the beginning of this section, if we now consider modeling the flow of dilute solute or tracers in the water, a simple adaptation of the above equations will suffice provided the relevant assumptions are compatible. In particular, in order to be compatible with Equation 21.19, it is necessary that the distribution of the solute or tracer in precipitation is also uniform. Other tracers such as ^{222}Rn that are generated by radioactive decay of radium in the soils and minerals of the catchment will require some modification to the model. This raises the point that it is frequently assumed that the pre-event distribution of the isotopic tracer within the catchment is uniform. The word "dilute" in the first sentence of this paragraph simply indicates that the tracer or solute concentration itself does not influence the flow directly. For example, concentrated saline solution could significantly alter the hydraulic conductivity when flowing through heavy clay soils. Under these conditions, Equations 21.16-21.19 can be modified by replacing $q(t)$ by $q(t)c(t)$ and $P(t')$ by $P(t')c_p(t')$; where c and c_p represent the output concentration (assumed well mixed) and the concentration in precipitation, respectively, on a mass basis. In particular, Equation 21.17 becomes:

$$q(t)c(t) = \int_0^{\infty} G(t;t')P(t-t')C_p(t-t') \quad (21.20)$$

It is important to note that under the above assumptions, the same response function G applies *both* to the water and the solute or tracer fluxes (Equations 21.17 and 21.20). This is an important point and the question must be asked in practical situations as to whether the same system response function applies to both water and solute or isotope fluxes. This point should be considered, particularly in regard to shortcomings of the simple mass balance hydrograph separation techniques.

As an example, consider the simplified quasi-linear storage element shown in Figure 21.3. Provided the storage level represented by h is above the threshold H , i.e. $h > 0$, the flux is proportional to H (say $q = \alpha H$, where the constant of proportionality, α , has units of T^{-1}). For a constant precipitation rate P (ignoring interception losses), the steady state value of h is just P/α . If we introduce a small disturbance $\delta P(t)$, the streamflow response $\delta q(t)$ is related to this disturbance according to the unit hydrograph formulation, Equation 21.19, with unit hydrograph as given in Equation 21.7.

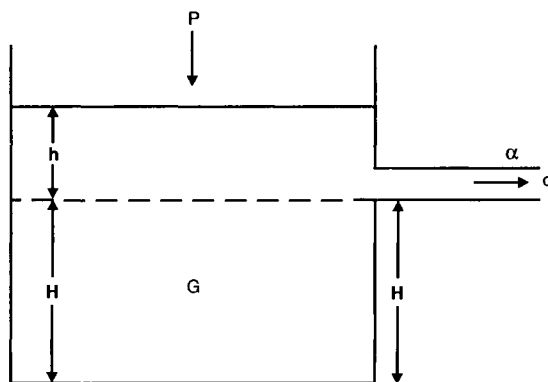


Figure 21.3. A simplified quasi-linear storage element with threshold level H and outflow flux $q = \alpha H$.

Van der Tak and Bras (1989) propose a gamma function formulation in preference to an exponential transit time distribution formulation and a gamma function could be substituted here. In fact the exponential distribution is a special case of the gamma distribution and it would be possible to unify the exponential, dispersive and IUH approaches by using a gamma function. The IUH, $U(t)$ gives the hydraulic response time distribution of the system. However assuming a well mixed reservoir, a perturbation of the input concentration, δC_p , with the flux remaining constant, results in a perturbation in output concentration given by Equation 21.17, but with the residence time distribution:

$$G(t, t') = \beta \exp(-\beta t) \quad (21.21)$$

where $\beta = \alpha P / (P + \alpha H)$ is somewhat less than α , due to the delaying effect of the dead volume represented by H . Note that although U is independent of P , G is not, and the residence time distribution, although stationary in this instance depends on the precipitation rate.

More generally, for an arbitrary precipitation input $P(t)$ and concentration input $C_p(t)$, the IUH is still given by Equation 21.21, but the exact residence time distribution is very complicated, and as well as depending on the precipitation history and antecedent moisture conditions, is non-stationary. The simplicity of the IUH is a direct result of the assumptions made for this example, chosen to reflect the requirements of the unit hydrograph formulation. The non-equivalence of the residence time distribution with the response time distribution (IUH) can then be seen to be independent of these assumptions, arising from the non-linearities of the system itself (note that for $H=0$, the distributions are identical), but which are transparent to the input-output relationship for the flux of water.

21.3.4 Identifying "old" and "new" water in terms of system response functions

By writing Equation 21.17 not as a sum over the lags t' , as at present, but as a sum over previous times $t'' = t - t'$, the catchment flux can be expressed as:

$$q(t) = \int_{-\infty}^0 dt'' G(t; t - t'') P(t'') \quad (21.22)$$

Taking the beginning of a storm as the origin $t = 0$, the integral in Equation 21.20 can be rewritten in two parts as:

$$q(t) = \int_{-\infty}^0 dt'' G(t; t - t'') P(t'') + \int_0^t dt'' G(t; t - t'') \quad (21.23)$$

and

$$= q_0(t) + q_N(t) \quad (21.24)$$

where the contribution to the total flux from the first term of Equation 21.23 is due to pre-storm water, while the second term gives the contribution from within-storm precipitation, the two terms on the right of Equation 21.24 are defined by the corresponding terms of Equation 21.23. As it is written here, it is the same function G which moderates both contributions; in the first term it is the "tail" or long-time part of the distribution G which is effective, while the second term is governed by the short time behavior of G . As there is no preferred time at which to fix G , there is no reason to model the "tail" of the distribution G any differently from the initial part. In other words, it is important that all components of flow should be modeled on equal terms at least using compatible assumptions.

We can also perform the same partitioning into "new" and "old" water, analogous to Equation 21.22:

$$q(t) c(t) = q_0(t) c_0(t) + q_N(t) c_N(t) \quad (21.25)$$

where:

$$C_N(t) = \int_0^t dt'' G(t; t-t'') P(t'') c_p(t'') / q_N(t) \quad (21.26)$$

and $c_0(t)$ is defined analogously, assuming only that the two components are well mixed. This leads to the familiar two component end member equation for hydrograph separation:

$$q_N(t) / q(t) = \frac{c(t) - c_0(t)}{c_N(t) - c_0(t)} \quad (21.27)$$

as given in Equation 21.2 with the important difference that all components (potentially) vary with time. Equation 21.27 was obtained with only very broad assumptions; namely that precipitation, intensities and concentrations are spatially uniform, and "new" and "old" waters are well mixed at the outlet. In order to use this equation, however, it is necessary to be able to measure or estimate the two concentrations, $c_0(t)$ and $c_N(t)$, and this may be as difficult as the original task of estimating the relative proportions of q_0 and q_N . To date there has been no application of the IUH approach to field data.

In many circumstances, it is common for catchment water to behave like a large well-mixed reservoir with slowly changing solute concentration. This is not true for the new water concentration $c_N(t)$. According to Equation 21.26, $c_N(t)$ is some weighted average of storm precipitation. As will be discussed later in Section 21.4.2 and incorporated in Equations 21.39 and 21.40, for the stable isotopes ^{18}O and D in precipitation, the assumption of a constant within-storm value for this quantity is rarely applicable.

21.3.5 Time series approaches to system response functions

Time series modeling approaches have been used extensively in the analysis of rainfall input signals to catchments and the subsequent streamflow and streamflow hydrogeochemical

composition (see also Chapter 7). Young (1984) presents a comprehensive introduction to time series methods in hydrology. Several time series approaches have been developed and applied to field data on hydrogeochemical characteristics of streamflow, in particular pH and aluminum, but only a limited number to isotopic tracers in catchments. Hydrogeochemical studies based upon time series models include those by Whitehead et al. (1984) and Robson and Neal (1991).

Jakeman et al. (1991) and Littlewood and Jakeman (1991) use a model based on unit hydrograph theory as given in Equation 21.19 which describes the variation in streamflow with time as the linear convolution of rainfall excess and the instantaneous unit hydrograph. The formulation for converting rainfall excess into streamflow is comprised of two components. The first is a non-linear rainfall filter that is used to produce effective rainfall. The second is a transfer function model, that in its simplest form is comprised of two linear storages acting in parallel that determine the "quick" and "slow" flow components of streamflow and provide the basis for hydrograph separation. When compared to chemical hydrograph separation results based on Equation 21.1, (the bulk incremental two component hydrograph separation) Littlewood and Jakeman (1991) make the observation that the time series model estimation of "slow" flow or deep water component of streamflow is about 16% of peak flow, while chemical hydrograph separation of peak events (Robson and Neal, 1990) estimate the same component as between 40 and 45%. This significant difference clearly raises questions concerning the validity of the simple two component hydrograph separation approach. Although data on isotopic tracers were not available in this instance, it points to a need for much better quantitative understanding of the dynamics of streamflow component mixing.

Littlewood and Jakeman (1991) recommend that hybrid models include time series models of the rainfall runoff process and either hydrogeochemical or isotopic tracer observations should be developed. To date, there are no such fully integrated models reported in the literature. This absence points to an ongoing research area that requires further effort such that the maximum amount of process information is obtained from catchment studies.

In many catchments, water residence times and transit times are of a much shorter period than that of seasonal variations in isotopic composition of inputs. Consequently, these residence and transit times cannot be observed by analysis of responses to inputs whose isotopic compositions vary over periods of time greater than the residence and response times. In many field situations, it is clear from the annual cycle of data on δD and $\delta^{18}O$ in streamflow and rainfall that short term isotopic responses to given rainfall events are superimposed on longer term seasonal trends caused by seasonal trends in the isotopic composition of rainfall. During these short term responses to such events, the assumption of a steady state in either the isotopic composition of the input or the system response function no longer holds.

Consequently, a more physically realistic approach is required where the system response function $g(t - \tau)$ is permitted to be time varying. For such cases, Equation 21.11 should be re-written:

$$c(t) = \int_{-\infty}^t c_{in}(\tau) g(t, \tau) d\tau \quad (21.28)$$

While more realistic, the reformulation of the system response function introduces additional complexity. To understand the processes and time scales of streamflow generation under these conditions, the filtering theory approach described below can be adopted. This approach consists of treating the values of $g(t, \tau)$ at different τ as stochastically varying parameters to be estimated from a time series of data of tracer input and output data. This enables the transit time for the system to be estimated directly as a time-varying quantity.

21.3.6 Kalman filtering and residence times

Recently, several papers have used an approach based on Kalman filtering techniques to establish the nature of the time varying transit time (i.e., Turner et al., 1987; Turner and Macpherson, 1990; Kleissen et al., 1990; Stewart and McDonnell, 1991). The approach is based on the assumption that the variance in the error of estimates of a parameter or state is a direct measure of its identifiability. The Kalman filter is used to calculate the error variances for the problem of making an estimate of the combined state-parameter condition. The approach has the advantage that more complex model structures can be evaluated than by deterministic methods and that the effect of observation errors can be assessed.

To estimate the time lags and hence the system response function linking rainfall to streamflow two simultaneous observation equations are required. The first observation equation describes the flow at any time t as a summation of flows arising from rainfall that occurred within a series lagged intervals prior to t as follows:

$$F_t = \sum_{i=0}^n f_{t-i} + v_{t1} \quad (21.29)$$

The second observation equation describes the product of the flow at any time t and its isotopic composition as a summation of flows arising from rainfall and its associated isotopic composition that occurred within the same series of lagged intervals prior to t as follows:

$$F_t \cdot \delta_{f,t} = \sum_{i=0}^n \delta_{r,t-i} f_{t-i} + v_{t2} \quad (21.30)$$

where F_t is the flow on day t , f_{t-i} is the amount of flow at time t arising from rain within the i th lagged period before t , $\delta_{f,t}$ is the isotopic composition of streamflow at time t , $\delta_{r,t-i}$ is the volume-weighted average δ of rain during the i th lagged period before time interval t , n is the maximum lag and v_{t1} and v_{t2} are non-serially correlated random variables with zero mean and the covariance matrix R .

For purposes of analyzing the contribution made by deep groundwater, a component f_{gw} needs to be introduced. However this component is not associated with any particular time lag. In the case of a deep groundwater component, a constant value can be used. The f_{t-i} , i.e. the components of the total flow at time t that occur as rainfall in the i th lagged period, are the non-stationary parameters of the system to be estimated. In the standard Kalman filtering manner, they can be assumed to vary through time according to the equation:

$$f_{t+1-i} = f_{t-i} + w_{ii} \quad (21.31)$$

where the w_{ii} are non-serially correlated random variables with zero mean and constant covariance matrix Q . To obtain an estimate of the time-varying lag $T(t)$, the relation:

$$T(t) = \frac{\sum \tau_{t-i} f_{t-i}}{\sum f_{t-i}} \quad (21.32)$$

is used where τ_{t-i} is the lag from time t to the middle of the i th lag period before t is estimated. The error variance of the estimate of T can be calculated from the product of the vector of the τ_{t-i} and the error covariance matrix of the f_{t-i} .

Interpretation of field data using this method has been carried out by Turner et al. (1987) and Turner and Macpherson (1990). In the first of these studies, the δD and $\delta^{18}O$ of rainfall, deep and shallow groundwater and streamflow were used to investigate the flow processes through the small 80ha (Salmon) catchment in the south-west of Western Australia. Their Kalman filtering analysis involved an investigation of rainfall-streamflow relationships. To interpret the seasonal pattern in streamflow values, attempts were made to find an integral transform of the convolution type that predicted streamflow for 190 days after first flow using the measured rainfall over the same 190 day period, together with the previous 144 days of rainfall record. The objective was to determine characteristic flow times for discharge of rainfall to streamflow.

In non-stationary models where streamflow was a linear function of lagged rainfall values, the coefficients at all lags tended to rise sharply during periods of high flow, while stationary models of this type showed low R^2 values. In other attempts to find a linear model, an extended Kalman filter was used to estimate a system in which flow was proportional to the level of a hypothetical storage variable and a shallow groundwater bore hydrograph was used as an explanatory variable in various linear combinations with rainfall. However, no reasonably stationary linear model was found. Plotting of various functions of rainfall against flow suggested a nonlinear model of the form:

$$F_t = a \exp \left[b \sum_{i=0}^{100} c^i r_{t-i} \right] \quad (21.33)$$

with c being a coefficient in the region of 0.99. Fitting this equation to the data as a non-linear, stationary model gave $R^2 = 0.658$, $\alpha = 4.52 \pm 0.26 \times 10^{-4} \text{ m}^3/\text{day}$, $b = 4.085 \pm 0.103 \times 10^{-2} (\text{mm/day})^{-1}$, $c = 0.9869$ (to improve numerical stability the value actually estimated was $c = 1/(1+\exp(-d))$, and $d = 4.3215 \pm 0.045$). Error estimates are ± 2 standard deviations.

Three models were used for streamflow dating: using δD and $\delta^{18}O$ separately and both together which all produced excellent fits to the streamflow isotope data ($R^2 > 0.999$). In the case where both isotope records were used as simultaneous observation equations, the close correlation of δD and $\delta^{18}O$ responses induced near-singular matrices in the Kalman filtering algorithm when R^2 was high and these results were discarded as unreliable. The δD and $\delta^{18}O$ records produced similar results, with the $\delta^{18}O$ signal indicating a somewhat wider range of rainfall-to-flow

delays. The results described below are those derived from the δD record since these had a higher likelihood value.

Figure 21.4 shows the variation in average estimated delay between rainfall and streamflow during the period of observations. The estimate is plotted with confidence limits of ± 2 standard deviations, derived from the estimation error covariance matrix of the flow components $f_{t,i}$. The average delay is lowest at the time of first flow. It then follows a rising trend which is reversed at the time of the major observed rainfall events and then resumes. The confidence limits become wider as the time after a rainfall event increases.

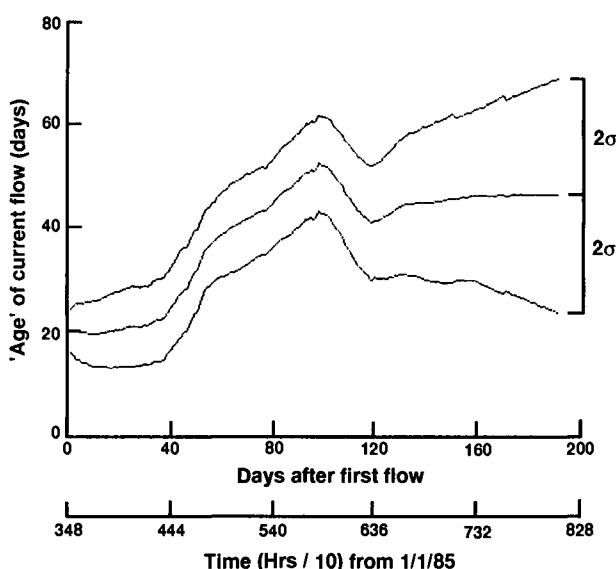


Figure 21.4. Variation in the average transit time and associated confidence intervals for transfer of rainfall into streamflow from Salmon catchment, Western Australia using an extended Kalman filter for estimation. After Turner et al. (1987).

Results of a second field study on a 19 km² catchment in Western Australia using the Kalman filter were reported by Turner and Macpherson (1990). For this study, an analytical approach was developed that could deal with non-stationary lags. The parameters described in Equations 21.29 - 21.31, correspond to a subdivision of flow into components of different ages. The associated process and observation noise covariance matrices were estimated by using a Kalman smoothing filter according to the method of Shumway and Stoffer (1982). The raw data was aggregated at the one hour level to form consistent input and output sequences. A variety of different groupings of input data into lagged sequences were tried, but it was found that there was little information below time lags of five hours, a finding consistent with a cross-correlation analysis. This was shown by insignificant flow components being assigned to such lags and by high inter-correlations between estimates of short-period components. The results reported here group inputs into the geometrically increasing lag intervals: 0 to 5, 6 to 15, 16 to 35, 36 to 75, and 76 to 155 hours.

The longest of these lags exceeded the apparent relaxation time and inputs averaged over this period are so slowly varying over most of the time period as to be highly correlated with stationary inputs such as deep groundwater. To make use of the information that flow components derived from a particular lag period must be zero when there is no rainfall in that period, a series of additional observation variables were generated corresponding to the 5 lag periods. These were set to zero when the accumulated rain in the corresponding lag period was zero.

Two series of models were estimated. In one, all parameters were associated with lagged values of rainfall. In the other, an additional parameter representing a contribution from the constant-composition deep groundwater was added. It was found that estimates for this component were highly correlated with the estimates for the slowly-varying components at longer lags, and this correlation made it impossible to produce consistent estimates for the apparent age of the rest of the flow. The results shown in Figures 21.5, 21.6 and 21.7 are for the case where no deep groundwater component was estimated. The low chloride concentration in streamflow suggested that this component was small. Flow was treated as arising exclusively from recent rainfall. The pathway by which it arrived at the stream was not specified, either in terms of the stratum traversed or the region within the catchment. Runoff would be concentrated in the first 5-hour component, and older components would increasingly have arrived via flow through the shallow groundwater system. All physically realistic models which include such pathways involved nonlinearities which would have rendered the approach more difficult or impossible. While in principle the Kalman filter can handle nonlinear models by numerical differentiation of the observation equation, in practice quite mild nonlinearities can prevent convergence on the maximum-likelihood answer, as well as making the statistical interpretation harder.

As shown in Figure 21.5, for the event considered, observations beginning 4920 hours after midnight on 1/1/87 and ending 200 hours later were processed. This analysis period began approximately 80 hours before the onset of flow in the event. Figure 21.5 shows observed and predicted values of the second input series, the product of streamflow and isotopic composition. The non-stationary model tracks the observed data well although the mean squared errors are much larger than can be attributed to analytical uncertainty in the isotope measurements. The grouping of the data makes it difficult for the stochastic model to track the high-frequency behavior of the signal without introducing an unrealistic amount of observation error. Thus there is some evidence that the non-stationary behavior of the system does not exactly follow the Kalman filtering assumptions.

Figure 21.6 shows the parameter $T(t)$ defined by Equation 21.32 as a function of time during the 200 hour period. At the beginning of the period the average "age" of the flow was slowly increasing through a period without rainfall. This increasing trend is succeeded by a plateau which is an artifact of the discretization of lag periods: at this stage the only input signal cannot be located within the longest lag period. The plateau is succeeded by an abrupt fall in the "age" of flow that corresponds to the heavy rainfall at the beginning of the event. From this time until the end of the event, a series of decreases in T are followed by slower recoveries towards the pre-event value. At its lowest value, T is approximately 30 hours: this value corresponds well with the onset of the rainfall. There is thus a suggestion of a two phase response in which immediate overland flow in an already saturated catchment is followed by a shallow groundwater response about one day later. However the 30 hour lag observable in the figure points not only to rain from the initiation of the event but also to older and younger components. It cannot therefore be interpreted directly as a residence time.

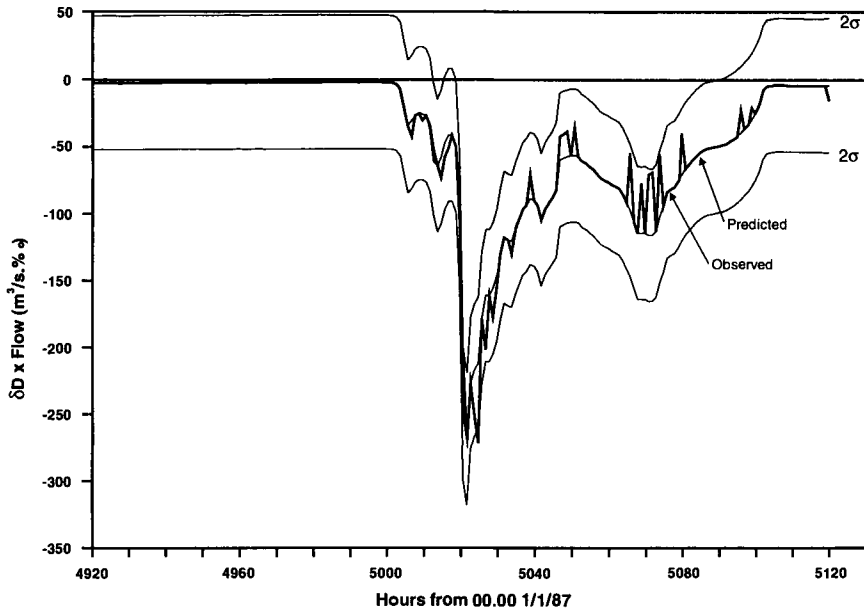


Figure 21.5. Predicted and observed product of flow and δD during a single rainfall event at Susannah Brook catchment, Western Australia, calculated using Equation 21.30 showing satisfactory tracking of observed values by the model. After Turner and Macpherson (1990).

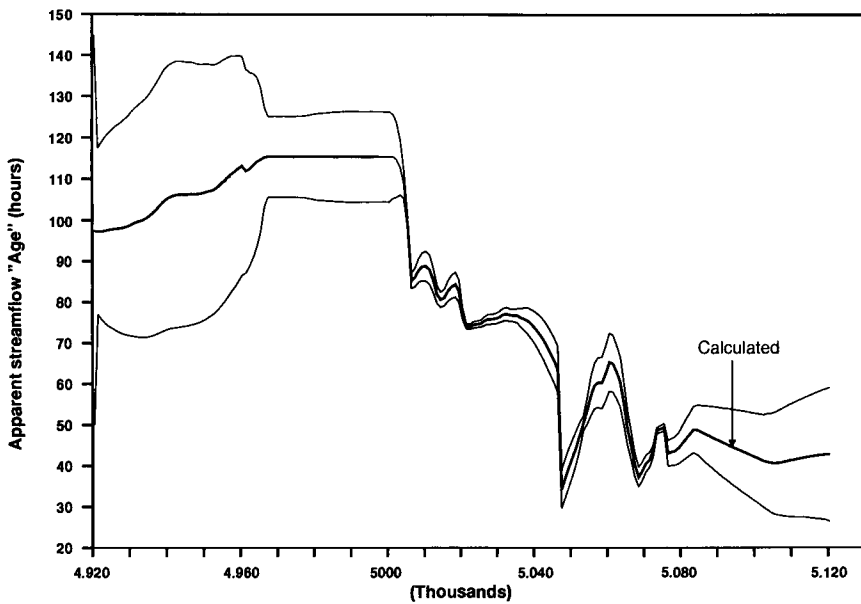


Figure 21.6. Variation in the apparent age of streamflow preceding and during the rainfall event shown in Figure 21.7 as estimated by the Kalman filter method. After Turner and Macpherson (1990).

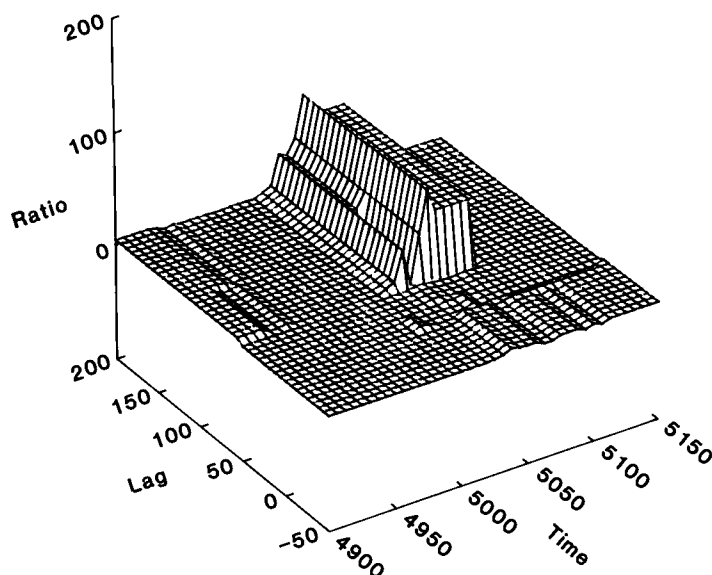


Figure 21.7. Estimated variation in the catchment system response function during the rainfall event shown in Figures 21.5 and 21.6 calculated at 40 hour intervals. The vertical axis is the ratio between output flow and input rain for a given lag ($\text{m}^3 \text{sec}^{-1} \text{mm}^{-1}$). A cross-section of the surface parallel to the lag axis is an estimate of the kernel of a linear response function for the catchment at the indicated time. After Turner and Macpherson (1990).

Figure 21.7 shows the way in which the response function of the catchment varied during the event. The vertical axis shows the estimated ratio between output flow at the indicated time, and input rain during the given lagged period indicated, in units of $\text{m}^3/\text{sec}/\text{mm}$. Thus a cross-section of the surface parallel to the lag axis is an estimate of the kernel of a linear response function for the catchment at the indicated time. The step function form of the response derived from the model is clearly a first approximation to the continuous surface that describes the time varying system response function described by Equation 21.28. Most of the variation on this surface represents great sensitivity to rainfall at the longer lag periods during the part of the event when the average age of streamflow was decreasing sharply. The maximum sensitivity estimated was $101 \text{ m}^3/\text{sec}/\text{mm}$ at 5041 hours. At this time, rainfall of the longest lag period was estimated to supply 51% of the streamflow, within narrow confidence limits, although only a small amount of this rain had fallen, and that at the very beginning of the lag window.

A physical interpretation might correspond to a brief "piston flow" effect in which rain of the given age was forced through the system by newer rain. It seems more likely that some amount of this peak in the response function is due to the fact that the model is not sufficiently non-stationary. That is, the amount of process noise in the flow components that is plausible in the maximum likelihood sense, given the whole of the data, does not permit the response function to respond as fast as it should under the shock of the rainfall event. Whatever the strength of this effect, it seems clear that the response function of the catchment exhibits considerable variation in time, this presumably being caused by a nonlinear dependence on the amount of water in the soil profile. More work is needed to determine how better to model this non-stationarity.

As discussed above, Kleissen et al. (1990) compared deterministic approaches to identifying parameter and state conditions in a simple two compartment model with a stochastic approach based on the extended Kalman filter. The Kalman filter was used to examine the identifiability of parameters in the two compartment conceptual model similar to that shown in Figure 21.8, using a combination of observed rainfall data and synthetic tracer input data. Their analysis clearly showed the advantages of using input tracer data by markedly improving the observability of compartment storage states and reducing the standard deviations of its observation. The identifiability of rate and routing parameters was also significantly improved. Introduction of a single tracer brought about the most significant improvement. Introduction of a second tracer did improve overall identifiability but not as significantly as when one tracer was introduced, in addition to the hydrological observations. Physically, the transfer function representation corresponds to a flexible configuration of linear storages connected in series or parallel.

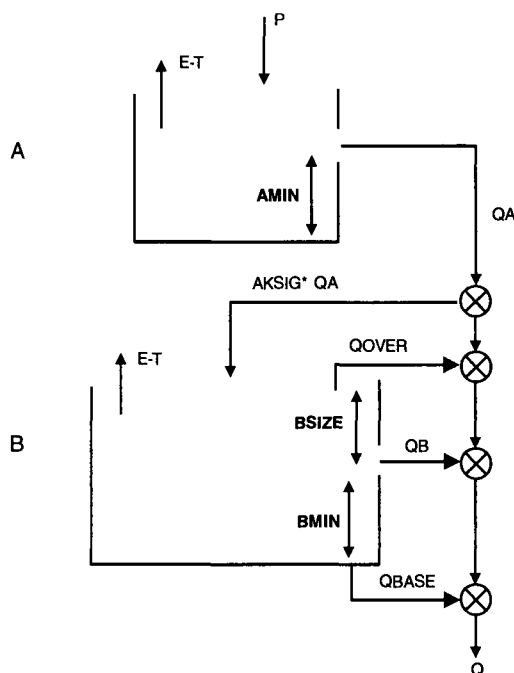


Figure 21.8. Representation of a two compartment conceptual hydrological module used in the Birkenes model (after Hooper et al., 1988), with threshold levels $AMIN$ and $BMIN$ and with the possibility that overflow from the lower store (B) can be routed directly to streamflow. Flow can also be routed from A to B by a constant of proportionality $AKSIG$. Kliessen et al. (1990) use a Kalman filter to examine the identifiability of parameters in such a two compartment conceptual model.

Some cautions were introduced into the arguments concerning the use of time series methods for parallel process modeling by Young and Beven (1991). From the first application of unit hydrograph techniques, the term baseflow had the connotation of being water that had followed a subsurface (i.e. groundwater) pathway prior to discharge to the stream. This is also the slow-flow component of the hydrograph. The remainder of the hydrograph is then either the quick-

flow component or stormflow component without any implied flow process. Young and Beven (1991) maintain that process interpretation of the fast and slow components should be avoided, particularly in hydrograph separation analysis using either hydrogeochemistry or isotopic methods. Modeling of isotopic data and calculation of the event and pre-event components of flow (i.e. the "new" and "old" components) suggests that a large proportion of the hydrograph peak, and therefore the fast component, may be made up of pre-event water. This is considered by Young and Beven (1991) to be quite consistent with rapid transmission of subsurface pressure waves within the soil being faster than the Darcian flow velocity, thereby resulting in rapid displacement of pre-event water as streamflow. There is also no process-based reason why there should be a fixed partitioning between fast and slow component responses, and indeed this is more likely to vary with time than remain constant.

21.4 Comparisons of Models of Isotopic and Chemical Hydrograph Separation

Pinder and Jones (1969) were among the first to use chemical constituents to perform a hydrograph separation using the simple two component mass balance equations (Equations 21.1 and 21.2 in Section 21.2 but written for the appropriate hydrogeochemical species). The most commonly used hydrogeochemical tracers are Mg^{2+} , Ca^{2+} and SiO_2 which are weathering products from within the soil profile or aquifer matrix and Cl^- which is often derived from cyclic salt. With the exception of Cl^- , these species are the most useful because they are indicative of contact of soil water or groundwater with the subsurface mineralogy. Silica is a useful chemical tracer for a number of reasons: (1) its concentration in rainfall is negligible and therefore contrasts with the pre-existing water in the catchment, and (2) its dissolution to form silica in the soil solution is typically rapid, reaching several mg/L in minutes to hours depending on the soil:solution ratio. Because of the rapid reaction rate, it is possible that silica can overestimate the proportion of "new" water using the two component hydrograph separation model. Using the two component hydrograph separation Equations 21.1 and 21.2 with silica, Hooper and Shoemaker (1986) in fact found that when a silica hydrograph separation was compared with $\delta^{18}\text{O}$, the silica slightly overestimated the "new" water component which they considered to be due to an erratic isotope input composition rather than a problem with the silica model. Pionke et al. (1993) also tested a two component $\delta^{18}\text{O}$ hydrograph separation against silica and found generally close agreement in estimates of the subsurface flow contribution of the total storm. Comparison of separation analysis by the peak incremental method (described in Section 21.2) gave poorer agreement between $\delta^{18}\text{O}$ and silica. Despite the differences between $\delta^{18}\text{O}$ and silica, and with silica consistently giving higher estimates of subsurface stormflow, the two tracers appear to be responding to the same flow processes. Sodium was also used in a two component separation model and generally agreed well with the $\delta^{18}\text{O}$ and silica separations; whereas Mg^{2+} and Cl^- tended to estimate higher subsurface stormflow proportions than $\delta^{18}\text{O}$ or silica. Wels et al. (1991) comment that hydrogeochemical tracers identify flow paths rather than "new" or "old" flow components and that hydrograph separations that use hydrogeochemical tracers generally show larger groundwater fractions than those that use isotopes for hydrograph separation.

A number of hydrograph separation studies have been carried out in Australia, where, because of the concern over stream salinization, chloride has been widely used as the preferred conservative hydrogeochemical tracer in conjunction with the stable isotopes (Turner et al., 1991). Studies by numerous researchers have shown that pre-event groundwater is frequently

a major component of streamflow during an event and can exceed 50% of the total water discharged (see Chapter 10). In contrast, investigations in two catchments in New South Wales, Australia have shown two cases where, for selected events, between 65 and 75% of the event runoff was derived from rainfall (Turner et al., 1991).

In the first catchment, Wattle Retreat, groundwater δD values ranged between -39 and -34‰ and the rainfall δD values were as depleted as -75‰. This event caused a rapid shift in streamflow δD to a minimum of -70‰ indicating qualitatively that the initial streamflow hydrograph response had a high proportion of rainfall. The two component hydrograph separation based on deuterium estimated that approximately 75% of the runoff was rainfall. The same separation based on chloride estimated the rainfall component as 50%, significantly less than that calculated from δD measurements. The difference between the separation based on deuterium and chloride is due to the accumulation of salt efflorescences at the ground surface in areas of the catchment close to the stream where slow groundwater seepage occurs and evaporation results in salt accumulation at the ground surface. Flushing of this accumulated chloride into the stream during an event has the effect of apparently overestimating the groundwater component in streamflow.

Hydrograph separation analysis from the second catchment, Williams Creek, in New South Wales, (Turner et al., 1991) also indicated a high proportion of rainwater in event streamflow. The stream isotope hydrograph was characterized by marked responses in streamflow δD . The two component mass balance equation was used to calculate the streamflow partitioning. The δD data showed that approximately 63% of the runoff was event rainfall. By comparison, using chloride the rainfall component was estimated as 66%, in good agreement with that calculated from the δD analysis. Following this event, about one month elapsed before the streamflow δD returned to its pre-event composition. Comparison of subsequent streamflow δD with rainfall δD for the remainder of the year showed that the streamflow δD closely followed the rainfall δD . These two observations lead to the tentative conclusion that neither deep nor shallow groundwater is a substantial component of streamflow at Williams Creek during the flow period, and that rainfall, if not discharged during the event itself, has a relatively short residence time in the shallow groundwater system prior to discharge.

Stable isotope compositions and chloride concentrations in rainfall, deep and shallow groundwater and streamflow have been used to investigate the flow processes through a small catchment (Salmon) in south west Western Australia (Turner et al., 1987). In addition to the stable isotope and chloride data, daily rainfall, streamflow rate, streamflow chloride concentrations and shallow and deep groundwater hydrographs were used in an integrated approach to determine the mechanisms of streamflow generation. Calculations for three events based on δD and $\delta^{18}O$, showed that between 69 and 95% of the event runoff was pre-event water. An analogous expression to Equation 21.2 (bulk incremental two component hydrograph separation) based on chloride concentrations was used to analyze the streamflow hydrographs for the three events discussed above and one additional event. The proportion of pre-event water in each of the selected events was estimated using chloride as between 0.60 and 0.84. Results based on chloride were in good agreement with those from the isotopic calculations for the majority of events examined.

Ogunkoya and Jenkins (1993) extended the three component hydrograph separation model by combining mass balance expressions for chloride and deuterium of the three source

components in incident precipitation, soil water and groundwater. The mass balance expressions for chloride (Equation 21.34) and deuterium (Equation 21.35) are:

$$Cl_E = \alpha Cl_R + \beta Cl_S + \gamma Cl_{PW} \quad (21.34)$$

$$\delta D_E = \alpha \delta D_R + \beta \delta D_S + \gamma \delta D_{PW} \quad (21.35)$$

where α is the proportion of incident rainfall (subscript R) in the stream, β is the proportion of soil water (subscript S) and γ is the proportion of pre-event water (subscript PW). Cl_E is the chloride concentration in the stream and δD_E is the deuterium composition of streamflow during the event as before. α is given in Equation 21.36 and β is given in Equation 21.37:

$$\alpha = \frac{-(Cl_E - Cl_{PW})(\delta D_S - \delta D_{PW}) + (\delta D_E - \delta D_S)(Cl_S - Cl_{PW})}{(Cl_S - Cl_{PW})(\delta D_R - \delta D_{PW}) - (\delta D_S - \delta D_{PW})(Cl_R - Cl_{PW})} \quad (21.36)$$

and

$$\beta = \frac{(Cl_E - Cl_{PW})(\delta D_R - \delta D_{PW}) - (\delta D_E - \delta D_{PW})(Cl_R - Cl_{PW})}{(Cl_S - Cl_{PW})(\delta D_R - \delta D_{PW}) - (\delta D_S - \delta D_{PW})(Cl_R - Cl_{PW})} \quad (21.37)$$

$$\gamma = 1 - \alpha - \beta \quad (21.38)$$

These mass balance expressions were considered under two assumptions. The first is identical to Dewalle et al. (1988), where it is assumed that the Cl and δD of the three end member components are identical to their pre-event values and that they remain constant during the event. The second allows for a continuous change in the composition of the input tracer concentration. For this case the Cl_R and δD_R input tracer compositions are determined from the weighted mean concentrations according to Equation 21.39 and are adjusted incrementally in accordance with the timing of sampling. Equation 21.39 gives the incremental weighted mean isotopic composition of rainfall:

$$\delta D_R = \frac{\sum_{i=1}^n P_i \delta D_i}{\sum_{i=1}^n P_i} \quad (21.39)$$

where δD_R is the incremental weighted mean deuterium composition in rainfall, the P_i are the increments of precipitation and the δD_i are their corresponding deuterium compositions. An equivalent expression can be written for a chemical species such as chloride. This approach

now takes into account the important fact that the input tracer concentration can vary with time and that the input tracer will mix with prior precipitation. While Ogunkoya and Jenkins (1993) have improved the validity of the component hydrograph method by incorporating one time-varying component, their method remains insensitive to either stationary or non-stationary transit times.

The mechanisms by which rainfall or snowmelt travels to the stream and contributes to event runoff were outlined in Section 21.1. The response time for each of the different mechanisms will be different, with the shorter response times associated with partial-area overland flow and saturation overland flow. Equation 21.39 gives the incremental mean and assumes that each increment of the rainfall or snowmelt contributes equally to the event hydrograph, but with a different weighted isotopic composition or concentration. However, higher intensity rainfall or snowmelt periods during an event cause changes in the streamflow generation mechanism due to the increased likelihood of saturation overland flow and partial area overland flow. McDonnell et al. (1990a) incorporated a rainfall intensity factor into the expression for the weighted mean value for the event rainfall. Because higher intensity rainfall produces more runoff, the weighting function used is an incremental intensity mean where the weighting is made in relation to rainfall intensity. The expression is a modification of the incremental mean given in Equation 21.39 and is written:

$$\delta D_R = \frac{\sum_{i=1}^n I_i \delta D_i}{\sum_{i=1}^n I_i} \quad (21.40)$$

where I_i is the average rainfall intensity (L/T) during the sample period. Using this approach, more intense rainfall events have a greater weighting in the calculation of the isotopic input signal to the catchment. This approach is suited to hydrograph separations of single, short duration events. For extended events it is not realistic because it assigns the same weight to a mass of tracer input independent of when it was incident to the catchment. Thus the same weight would be assigned to tracer input that occurred immediately before an event to that which took place weeks or months beforehand.

Taking this approach a step further, Rodhe et al. (1995) calculated the isotopic composition of discharging new water, δ_{new} from the response function of the tracer in the catchment (see also Section 21.3.3). The weighting function used to calculate δ_{new} from the rainfall input in times preceding the sampling time of the streamwater is given by the transit time distribution for the catchment. This is written:

$$\delta_{new} = \frac{\int_0^{t-t_0} \delta_{irr}(t-\tau) g(\tau) d\tau}{\int_0^{t-t_0} g(\tau) d\tau} \quad (21.41)$$

Rhode et al. (1995) use this expression to model the transient isotopic response in a small catchment where a step shift in the isotopic composition of the input was obtained by replacing the natural throughfall with isotopically enriched irrigation water (δ_{new}). The tracer concentration at the catchment outlet was calculated as the sum of daily inputs using Equation 21.41 assuming a time invariant transit time distribution. In order to use the convolution integral in Equation 21.41, the variable flow system was treated as a constant flow system by introducing a flow corrected time (t'), where time is replaced by the accumulated discharge. With such a transformation, the transit time is time invariant and the convolution integral can be used. The fraction of new water in the runoff was calculated using an equation similar in form to Equation 21.1, with δ_{new} obtained from Equation 21.41. Figure 21.9 shows the fraction of new water in the runoff calculated from Equation 21.41 as a function of flow corrected time. This figure is in effect a breakthrough curve for the new irrigation water, and the cumulative frequency distribution of transit times was obtained iteratively by least squares fitting to the smooth, monotonically increasing function:

$$C(t') = 1 - \left\{ \frac{t'^a}{b} \right\} \quad (21.42)$$

in flow corrected time where $C(t')$ is the fraction of new water in runoff and is equivalent to V_R in Equation 21.1. This function is the cumulative frequency distribution of transit times and its derivative the transit time distribution. Rodhe et al. (1996) then use an iterative approach to estimate δ_{new} using the convolution integral in Equation 21.41. The transit time distribution was found to be represented by:

$$g(t') = 0.0109t'^{0.097} \exp \left\{ -\frac{t'^{1.097}}{101} \right\} \quad (21.43)$$

and is shown in Figure 21.10. The analysis concluded that the mean transit time for the catchment was 65 days. Assuming the mean transit time was constant over several years allowed estimation of the mean transit time. This ranged between 5 and 192 days, with a long-term mean value of 85 days. The thorough analysis presented by Rodhe et al. (1996) covers a number of approaches to modeling of isotopic responses in catchments considered in this chapter and, combined with an excellent field data demonstrates the way forward for future research in this field.

In another recent study, Pionke et al. (1993) recognized that the isotopic composition of the input signal to their catchment study area was not constant. In order to deal with the time varying input function, they investigated four different methods of solving the two component hydrograph separation. In one approach they used the standard bulk total method to describe the isotopic input function as described in Section 21.2. They tested the incremental mean (Equation 21.39) method to establish the input δD . On finding that both these approaches were unsatisfactory, a novel approach was taken where the input isotopic signal during the total event was discretized into peak events. Thus, rather than discretize the input isotopic signal into fixed time increments or intensity increments as described by Equations 21.39 and 21.40 over the entire event, each peak rainfall period during the total event was treated separately. Each peak event was considered to be separate from the next if a period of a few hours of low or no

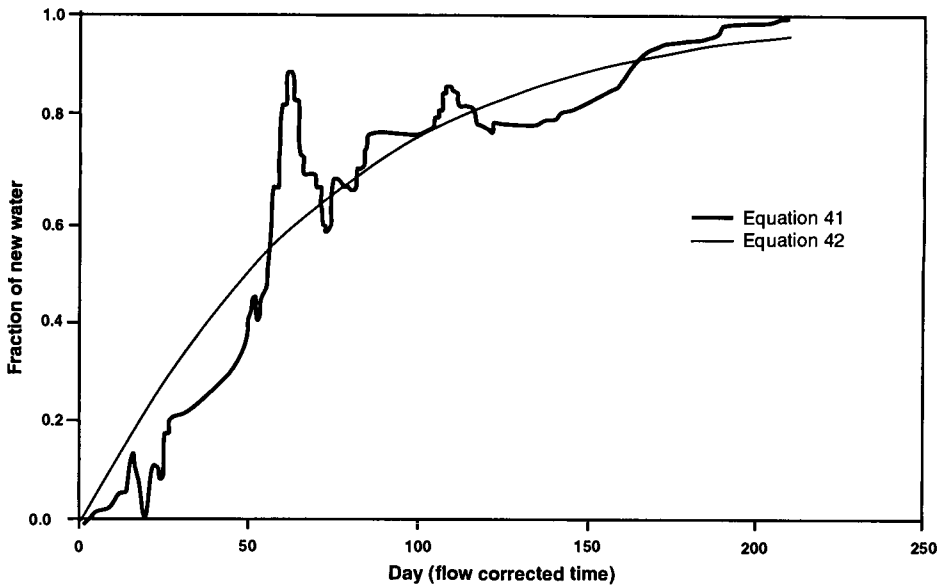


Figure 21.9. Fraction of new water in runoff from the G1 catchment (Gardsjon, Sweden) calculated using Equation 21.41, versus flow-corrected time. Also shown is the cumulative frequency distribution of transit times, obtained by least squares fitting of Equation 21.42. From Rodhe et al. (1996).

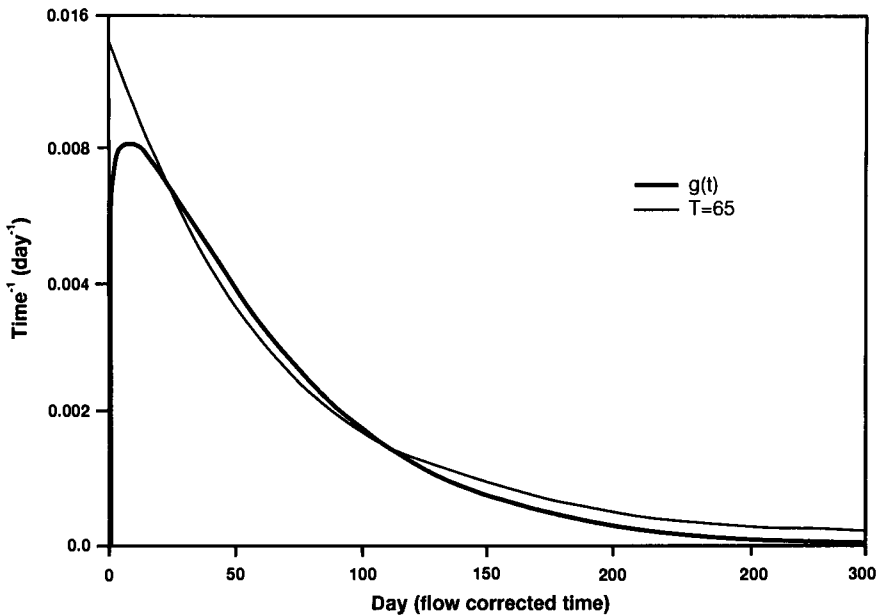


Figure 21.10. Transit time distribution obtained from the breakthrough curve for new water (flow corrected time). Also shown is an exponential transit time distribution with a mean transit time of 65 days. From Rodhe et al. (1996).

rainfall occurred between the peaks. The peak event was then analyzed using either the standard bulk total method or the incremental mean method but only over the time domain of the peak flow period. Significant differences in the estimation of surface and subsurface stormflows were found to be dependent on the method used. For one storm event the estimate of subsurface flow contributed by the storm event varied between 8 and 45%. The bulk total two component hydrograph separation consistently gave lower estimates of subsurface stormflow contribution to streamflow in comparison with the peak incremental method.

Recent papers that have modeled catchment response using either the two or three component hydrograph separation methods based on isotopes or hydrogeochemical methods have revealed a large number of inconsistencies in interpretation. It is clear that the simple two component bulk total hydrograph separation is an inadequate basis on which to interpret catchment flow processes. The most readily recognized problems that have been outlined in the previous two sections include the fact that 1) the input isotopic signal to the catchment is time dependent, 2) the mass flux of tracer into the catchment is rarely constant, i.e. the input signal is also dependent upon the rainfall intensity, 3) the mechanism of streamflow generation varies during an event, being largely due to rainfall intensity, 4) the interpretation of either water source or the hydrograph component at any time is highly dependent on the model approach, i.e. whether a two or three component model is used, and the technique used to discretize the input signal, i.e., whether a total bulk or mean incremental value is used, or whether an intensity weighted mean incremental method is used. It is clear from the above discussion that the options available to the modeler represent only a small number of possible approaches. Model selection alone has a significant influence on the identification of the dominant processes of streamflow generation and catchment flow.

21.5 New Research Directions

It is clear from this review of modeling of isotope systematics in catchment hydrology that significant advances have been made in the past ten years, and especially in the last five years. These advances include an increasing diversity in modeling approaches, with associated improvement in understanding of physical processes of flow generation in catchments. Various modeling approaches in recent years have attempted to deal with the complex issue of time-varying system response functions and this represents an important advance in thinking, although much work remains to be done. This is so particularly in terms of comprehensive field monitoring and data collection against which modeling concepts and analysis can be developed. There can be little doubt that modeling advances in catchment hydrology will continue to develop by inclusion of isotope, hydrogeochemical signals and other internal responses within a catchment reflecting its hydrological state, for example transient groundwater levels. We believe that isotope and hydrogeochemical approaches will play a key role in future developments in catchment hydrology.

There is scope for development of fully integrated models of hydrogeochemical and isotopic modeling in catchments. To date, there appears to be no reported studies where time-varying response functions based on both isotopic and hydrogeochemical observations are identified; this is one area where advances could be made. There have been numerous studies where isotopic tracers and hydrogeochemical parameters have been measured together and analyzed (for example in two component hydrograph separation), but there has not been much integration. Solute transport modeling in groundwater is another area where there has not been much

integration with isotopic data in catchment modeling studies and, as mentioned above, incorporation of groundwater level fluctuations in calibration of models is much needed. We consider that there is scope for development of isotope models based on the IUH and associated isotope relations. This approach is yet to be applied to a field study; the modeling approaches outlined in this chapter could be developed and applied to a field situation.

The novel time series approaches, such as the Kalman filter, applied to simulation of catchment hydrological and isotope data described in this chapter are very much in their infancy, and have potential for much wider development and application. Their ability to identify the time-varying response functions of catchments makes their application particularly attractive. Developing linkages between hydrogeochemical and isotopic responses based on these modeling approaches are completely new areas of research. Littlewood and Jakeman (1991) make the well-deserved recommendation that hybrid models that include time series models of the rainfall runoff process and either hydrogeochemical or isotopic tracer observations should be developed. To date there appears to be no such fully integrated models reported in the literature; this points to an area of research that requires further work.

Christophersen et al. (1993) have pointed to the use of synthetic data as a method for establishing better, scientifically based models. There are several advantages to this, namely the identification and selection of the most appropriate modeling approach. Once selected, the model parameters can be calibrated against (synthetic) observations and the problem of parameter identifiability can be examined. Finally, with synthetic data, the level at which practical implementation of a field monitoring program can be examined. Scrutiny of this can save considerable effort and cost in the field, and identify where the maximum information value can be attained from a field program. This has considerable benefit where expensive isotope analyses are required. To date the effect of transit time of water in the streamflow itself has received little attention in terms of its effect on modeling isotopic systematics in catchment hydrology. The distribution of streamflow travel times could potentially have a significant effect on determining the proportion of "new" water being discharged, i.e., the fast response isotope hydrographs in large catchments.

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Isotopes as Indicators of Environmental Change

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22.1 Introduction

In addition to providing an understanding of processes within a catchment system, isotopic techniques have been instrumental in providing reconstructions of catchment climate and other environmental indicators at various time scales. Reconstructions on longer time scales (10^2 to 10^7 yr) reveal the time frame, rate of change, and magnitude of variation in natural cycles. This framework gives us a perspective on current changes in our environment, and also provides analogs in the past (such as periods of elevated atmospheric CO_2) that gives insight about how our environment may respond to anthropogenic changes. Reconstructions on shorter time scales (10^0 to 10^3 yr) provide us with a record of how our environment has changed in historic times, and enables analysis of the role of anthropogenic activity in that change.

Global environmental change has been identified as one of the most urgent issues of earth science research as we approach the turn of the millennium (USGCRP, 1992). Global environmental change refers to the collective and cumulative environmental effects of human activity, including greenhouse gas emissions, urbanization, deforestation, changes in agricultural practices, impoundment of surface waters, and decreases in biodiversity. A fundamental challenge in evaluating global environmental change is to determine natural or background long-term conditions and the natural variations in these conditions, so that the signal (anthropogenic effects) can be clearly detected over the noise (natural variability). This task is made all the more difficult by the interrelations and feedback mechanisms among physical, chemical, and biological processes in the environment. The purpose of this chapter is to bring together isotope geochemistry, hydrology, and climatology to look at new ways of applying isotopic tracing techniques to provide information on environmental change.

Isotopic analysis has become a valuable tool in global environmental change research. For example, isotopic compositions of modern precipitation are an important part of many global climate models (GCMs). However, the most powerful application of isotopes is that they provide a record of past environmental conditions (such as temperature, humidity, vegetation, and water source) that can be compared to present-day environmental conditions. Although many climatological studies using isotopes have been conducted on marine sediments or polar

ice sheets, these provide only spatially-averaged trends in global climate. Current concern about the influence of human activity on global climate has prompted increased research aimed at reconstructing past climate in continental settings. Because global warming models predict that the warming will be distributed unevenly in space, it is of fundamental importance to establish past climatic trends and fluctuations in different land regions to evaluate how they responded to global climatic forcing.

The discussion in this chapter begins with "recent" environmental change and concludes with paleoclimate change. The section on recent change includes discussions of how isotopic techniques have been used to monitor changes in recharge water compositions, atmospheric deposition of nitrogen and sulfur, land use, and bird migration patterns. The section on paleoclimate change includes discussions of how climate change is assessed through analysis of isotopes in tree rings (to 160 yr), lacustrine carbonates (30 to 12,000 yr), ice cores in continental glaciers (to 2,000 yr), fossil wood and leaf cellulose (to 40,000 yr), secondary soil carbonates (10,000 to 50,000 yr), and clay minerals (to 10^7 yr). The role of carbon in global warming is discussed more extensively in Chapter 17.

In this chapter, we will examine how specific isotopic approaches are currently being applied in research on global environmental change. Although some of the studies presented were conducted as part of "classic" catchment research, for this chapter we broaden our consideration to include any shallow (near-surface) non-marine environment. Likewise, we include a few non-isotopic techniques (such as CFC-groundwater dating) that are commonly used in conjunction with isotopic studies.

22.1.1 *Direct and proxy records of environmental change*

Under some conditions, isotopic data furnish a "direct" record of environmental change. For example, the natural variations in the oxygen and hydrogen stable isotopic compositions of precipitation over continental areas reflect local climatic conditions such as storm track, temperature of precipitation, ambient humidity, air-mass source, and degree of rain-out (Chapter 3). Recharge waters derived from precipitation may closely reflect the isotopic compositions of the rain or may be significantly altered by evaporation, isotopic-exchange, and mixing. Hence, the variations in isotopic compositions of rain and recharge waters can be interpreted in terms of climate changes and are commonly viewed as direct indicators of environmental processes or climate. Other isotopes sometimes used as direct indicators include $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of bicarbonate, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate, and helium isotopes.

Often, isotopic data provide a "proxy" record of environmental change. For example, unaltered ancient waters, solutes, and gases are rarely preserved, but minerals may form in isotopic equilibrium with these waters, and plants and animals incorporate the isotopic compositions of various local waters and solutes into their tissues during growth. Under favorable conditions, paleoenvironmental information can be determined by analyzing ancient animal shells, lake or soil carbonates, plant cellulose, bone phosphate, clay minerals, and oxides in marine and continental sediments for isotopic composition; these compositions preserve an indirect or proxy record of the isotopic compositions of local waters and solutes at the time of formation.

The climatic records preserved in continental settings range from interannual to millennium-scale to geologic epoch-scale. Past climate patterns are deduced from the isotopic compositions of proxy indicators of climate by comparison of the proxy data with the present isotopic distributions of rain, groundwater, and surface water, taking into account known fractionation factors. Regional patterns in differences between the old and modern isotopic compositions reflect changes in climate or other environmental parameters. Advances in the use of proxy data will require a refined understanding of isotopic variations in response to changes in climate parameters, and how these variations are recorded by the proxy. In particular, both the development of modern-day atmospheric climate models and the reconstruction of ancient climatic and hydrologic models based on proxy isotopic records are hampered by limited information about current isotopic patterns in the modern hydrologic cycle.

The first fundamental lesson of geology is: "the present is the key to the past". Accordingly, isotopes cannot be used effectively to decipher paleoclimates without a broad understanding of modern hydrologic systems and the environmental factors that control the isotopic composition of proxy indicators. Ongoing research topics that promote this understanding include: processes affecting the isotopic compositions of meteoric water; the importance of evapotranspirational recycling to the hydrologic cycle; preservation of isotopic compositions of minerals and fossils over long time periods; calibration of low-temperature geothermometers; the relation of carbonate precipitates and lake fossils to meteoric waters; and the effect of inherent environmental variability on paleoclimatic estimates.

22.2 Recent Environmental Change Indicators

Many stable and short-lived radioactive isotopes, as well as non-isotopic tracers, have proved useful in assessing environmental change on historic timescales, from years to decades. In some cases, the tracers themselves are primarily anthropogenic contaminants, as in the case of tritium, ^{137}Cs , and chlorofluorocarbons (CFCs). Radioactive tracers can be used to determine groundwater age, which can then be combined with groundwater chemistry to reproduce a history of the effect of land use practices on aquifer water quality. In another application, characteristic $\delta\text{D}/\delta^{18}\text{O}$ produced by evaporation from seepage lakes (lakes with no surface water outlet) can be used to trace lakewater movement through aquifers; a record of interannual variations in lakewater δD and $\delta^{18}\text{O}$ produced by interannual climate variations is thus preserved along groundwater flow paths (see Chapter 14). Cosmogenic isotopes with short half-lives are briefly introduced here as well; cosmogenic isotopes with long half-lives are discussed in Chapters 19 and 20. Groundwater dating is discussed in detail in Chapter 8. We begin with a discussion of how isotopic techniques have been applied in shallow aquifer studies to assess recent environmental change.

22.2.1 Groundwater dating

Groundwater may hold a record of many types of environmental data. Under the right conditions (relatively homogeneous aquifer, unreactive aquifer sediments, low hydraulic gradient), water will move slowly, retain its chemical and isotopic characteristics at time of recharge, and recharge in discrete annual packets that can be dated. This ability of groundwater to serve as an archive of water quality, coupled with the possibility to determine the date of recharge by

isotopic or other means, constitutes a powerful tool to investigate time trends in water quality and relate them to changes in atmospheric deposition, land use, or land management practices.

A series of tracers can be used to estimate the age of groundwater. The range of ages obtained can vary from a few days for tracers such as ^{35}S and ^7Be (Cooper et al., 1991) to hundreds of thousands of years for ^{36}Cl . Some of these tracers (e.g., ^{35}S , ^7Be) are produced by cosmic-ray spallation, and can be considered steady-state tracers (i.e., the concentration in any given reservoir should not change with time). Others are introduced exclusively or primarily by anthropogenic processes (e.g., chlorofluorocarbons {CFCs}, ^{85}Kr). These tracers are generally restricted to studying processes occurring on decadal timescales. Another set of tracers is produced by both processes and these are among the most commonly used tracers (e.g., ^3H , ^{14}C , ^{36}Cl). When used in conjunction with data on other constituents, these tracers provide estimates on a wide range of age scales. Using the dates obtained from these tracers, information can be obtained on environmental changes occurring within the atmosphere and hydrosphere.

A partial list of the commonly used environmental tracers is given in Table 22.1. Also included is information on sources and complications from variations in input functions and chemical reactivity. The two isotopes with the shortest half-lives are ^{35}S and ^7Be . Where current concentrations are supported solely by cosmic-ray spallation, these isotopes should have a constant input not subject to geographical variations (Tanaka and Turekian, 1995). However, due to the nature of atmospheric circulation, there can be seasonal differences in deposition of ^{35}S and ^7Be , and concentrations in precipitation can vary from storm to storm. These isotopes also have a tendency to be removed by biological processes and can be adsorbed by mineral phases. However, in hydrologic systems where such effects are negligible, ^{35}S and ^7Be can be excellent tracers (Cooper et al., 1991; Michel et al., 1993).

Table 22.1. Partial list of isotopes and chemicals used for groundwater dating. Origins are cosmogenic (C), industrial (I), testing of nuclear weapons (W), or generation by nuclear power plants (N). When more than one origin is indicated, the major source is denoted first. Last 3 columns indicate whether source functions are dependent on time or geographic factors, and whether isotopes (or CFCs) are chemically reactive in groundwater. Y = yes, N = no.

Isotope	Half-Life (years)	Origin	Source Function		Reactive
			Time	Geographic	
^{35}S	0.24	C	N	N	Y
^7Be	0.15	C	N	N	Y
^3H	12.4	W, C, N	Y	Y	N
$^3\text{H}/^3\text{He}$	-	W, C, N	Y	Y	N
CFCs	-	I	Y	N	Y
^{85}Kr	10.6	N	Y	N	N
^{14}C	5,730	W, C, N	Y	N	Y
^{36}Cl	300,000	W, C, N	Y	Y	Y

Tritium is probably the most commonly used isotope for groundwater dating because of its ease of collection and analysis. It can be considered a conservative tracer for most hydrologic studies. Tritium has a natural abundance that was overwhelmed by anthropogenic production during nuclear weapons testing of the 1950's and 1960's. Nuclear power plants are an important source of tritium only in localized studies. Due to the nature of its production, tritium has a very complicated input function, and is also subject to major geographic variations. However, a large number of measurements of tritium in precipitation are available that can be used to obtain input functions (IAEA, 1981; Michel, 1989). Concurrent measurements of tritium and its daughter product, ^3He , can overcome complications of the input function.

Michel et al. (1994) used tritium to establish ages of waters sampled in an aquifer under Golden Gate Park in San Francisco, California. Ages were assigned to water samples from the aquifer to establish time trends in the quality of waters recharging the aquifer. During the past 40 years, there appeared to be an increase in sulfate, sodium, and chloride, whereas no trend was evident for nitrate. Egboka et al. (1983) used tritium to follow a contaminant plume and obtain dispersion rates at a landfill in Borden, Ontario. Section 22.2.3 has a more detailed discussion on the use of transient tracers to study changes in groundwater quality with time.

Chlorofluorocarbons (CFCs) have been released to the atmosphere through industrial processes since the 1940's (see Chapter 9). They have the advantage of having a global source function that is not subject to geographic effects, and an increase of concentration in the atmosphere that is reasonably well known (Elkins et al., 1993). Complications with the dating technique result from the need to know the temperature of the water when it last equilibrated with the atmosphere, and the possibilities of adsorption and microbial degradation of CFCs in the subsurface. Krypton-85 also has a global source function but is not chemically reactive in the subsurface. Because ^{85}Kr is measured relative to stable krypton, the temperature of equilibration is unimportant. The main drawbacks to the use of ^{85}Kr are that a large volume sample is usually needed, and analysis is difficult.

Chlorine-36 has both a bomb-produced component and a cosmogenically produced component; it can be used to study the movement of chloride and water over a large range of timescales. The recent source function is well known (Phillips et al., 1988), but variations in the production rate over hundreds of thousands of years are possible. Its use is also hampered by the ubiquitous presence of chloride in the environment. Likewise, ^{14}C is primarily used for longer-term studies. Both ^{36}Cl and ^{14}C are discussed in Section 22.3.1.

22.2.2 *Direct use of water isotopes to infer recent global change*

This section examines two case studies, one in a polar and one in a subtropical setting, in which δD and $\delta^{18}\text{O}$ of water are used directly to deduce recent environmental change. In the first study, $\delta^{18}\text{O}$ and δD measurements in inlet streams to a polar lake were used to quantify the water budget of the lake, and, specifically, to determine changes in lake ice thickness, which reflect recent climate change. Lake Fryxell, a permanently ice-covered lake in Southern Victoria Land, Antarctica, is fed by runoff from more than three glaciers in a watershed area of 230 km² (Lawrence and Hendy, 1985). The glacial ice, in general, has lighter isotopic compositions than the streamwaters. The $\delta^{18}\text{O}$ of glacial ice ranges from -28.4 to -33‰, whereas the weighted average $\delta^{18}\text{O}$ of the surface water inflows is -27.3‰ (Matsubaya et al.,

1979; Stuvier et al., 1981). This enrichment indicates that significant evaporation occurs as the glacier ice melts and flows in surface streams.

The isotopic balance of lakes using a standard mass-balance approach has been accomplished by numerous authors using the initial equation of Gonfiantini (1965). However, because of the lack of surface water outflow, groundwater inflow or outflow, and evaporative loss due to the permanent ice cover, the isotopic mass-balance equation for Lake Fryxell can be simplified greatly. At steady-state conditions, using a mean $\delta^{18}\text{O}$ of lake ice (-25.2‰) from January 1992, the ice accumulation was calculated as 34 cm/yr. However, direct ice measurements at Lake Hoare, nearby in the same valley, indicate an accumulation rate of 110 cm/yr (Wharton et al., 1992). The wide discrepancy in the calculated and measured rates of lake ice accumulation is undoubtedly due to the fact that these lakes are not in steady-state with respect to volume change. Chinn (1993) and Wharton et al. (1993), also through direct measurements, have demonstrated that over the past few decades lake ice thicknesses have decreased and lake volumes have increased. Thus, the direct use of δD and $\delta^{18}\text{O}$, combined with the determination of water fluxes, has made it possible to document thinning of the ice, and thus infer at least a short-term climatic warming.

The second study took place in the humid subtropical climate of northern Florida, where groundwater flow is vertically downward, a feature that preserves a record of the age and characteristics of recharge in chemical and isotopic signatures of groundwater with depth. The Lake Barco basin has a MAT of 21°C and a median rainfall of 128 cm (Owenby and Ezell, 1992). Close agreement among the mean annual air temperature, measured groundwater temperatures, and the calculated recharge temperature from N_2 and Ar data indicates that recharge most likely occurs throughout the year (Katz, 1993). Thus, the isotopic composition of groundwater is an indicator of mean annual temperature fluctuations. By combining the use of stable isotopes (to determine water source and recharge conditions) and CFCs (to determine groundwater age, as discussed in Section 22.2.3), valuable information was obtained on sources and rates of recharge, and changes in weather patterns over the past 40 years.

Groundwater isotopic composition upgradient from Lake Barco resembles rainfall and plots along the global meteoric water line (Craig, 1961), indicating rapid recharge of meteoric water with little or no evapotranspiration (Katz et al., 1995a,b). Groundwater that was recharged in a given year has an isotopic composition that reflects the temperature of recharge and other climate variables. For example, groundwater at shallow depth had the most depleted δD (-24.5‰) and $\delta^{18}\text{O}$ (-4.40‰). This groundwater was recharged in 1989 (CFC-dated) when the mean annual air temperature was 19.3°C . In contrast, deeper groundwater was more enriched in δD (-20.0‰) and $\delta^{18}\text{O}$ (-3.95‰), and was recharged during 1978, when the mean annual air temperature was 20.9°C . Thus, in this system it appears that annual temperature variations are preserved in the groundwater isotopic profile; this record coupled with CFC dating to pinpoint the year of recharge allows one to reconstruct recent climatic variations.

22.2.3 *Changes in land use deduced from tracer studies*

Groundwater dating can be a useful tool for understanding the effect of land-use changes on groundwater quality in surficial aquifers (Dunkle et al., 1993). In the late 1980's, concerns about nitrate pollution in the Chesapeake Bay from agricultural activity led to a study of

groundwater quality as a function of recharge date on the Delmarva Peninsula. The study used tritium- ^3H , ^{85}Kr , and CFC dating techniques (Dunkel et al., 1993; Ekwurzel et al., 1994). Groundwater ages calculated from all three methods agreed to within about ± 2 years for most samples (Ekwurzel et al., 1994). The study was conducted at Locust Grove, a small ($< 5 \text{ km}^2$) catchment. The Locust Grove surficial aquifer has 18-24 m of permeable sands underlain by very low permeability silt-clay sediments. The depth to water ranges from 0 to 6 m. Most of the catchment is in agricultural land use, including pasture, corn, soybeans, and ornamental trees and bushes. Only five percent of the watershed is covered by residential or forested lands, the latter largely restricted to a narrow strip along the stream channel. The proportion of land in agricultural use has changed little since the early 1950's.

The aquifer is well-suited to the application of CFC age dating techniques (Plummer et al., 1993). Groundwater is aerobic, suggesting that microbial degradation of CFCs should not occur. Because the water table is shallow there should be no significant lag in the transport of CFCs. Contamination of CFCs by local sources is not likely given the rural setting (Dunkle et al., 1993). CFC ages were determined from 15 wells along a 2.5 km groundwater flow-path transect from a drainage divide to Chesterville Branch, the first-order stream draining the catchment. At all but two sites, samples were collected at different depths in the surficial aquifer via nested wells. All samples were analyzed for CFCs and a wide range of other chemical constituents, including major ions, nutrients, dissolved oxygen and other dissolved gases, and the isotopes ^3H , D, and ^{18}O .

Wells from the transect at Chesterfield Branch were sampled in late 1990 and early 1991. CFC-modeled recharge dates, which have an uncertainty of $\pm 2 - 3$ yr (Reilly et al., 1994), ranged from 1985 to 1987 in samples from the shallowest wells, and from 1949 to 1967 in samples from wells finished near the base of the surficial aquifer. The oldest sample was collected from a deep well in the groundwater discharge area near the stream, where the groundwater flow paths converge. Hydraulic head measurements indicate that groundwater flow is predominantly horizontal, with upward flow important only within a few meters of the stream. A plot of nitrate concentrations as a function of CFC-modeled age indicates that nitrate concentrations in the surficial aquifer at Locust Grove have increased significantly since 1972 (Figure 22.1). Samples younger than 1972 generally have a median nitrate concentration of 13 mg/L, specific conductance $> 100 \mu\text{S}/\text{cm}$, and greater than 70% of the cations as calcium plus magnesium. In contrast, samples older than 1972 have nitrate concentrations between 3 and 5 mg/L, specific conductance less than $100 \mu\text{S}/\text{cm}$, and lower proportions of cations as calcium plus magnesium. The dominance of calcium-magnesium-nitrate in waters recharged since the mid-1970's is directly linked to increased fertilizer use at Locust Grove during this period (Denver, 1989).

Denitrification can be ruled out as the cause of the differences in nitrate concentrations between the shallow, younger waters and deep, older waters for 3 reasons: 1) In general, both the young and old groundwaters are nearly fully oxygenated, 2) none of the samples from the deep part of the flow system have excess nitrogen gas which would be present from denitrification, and 3) nitrogen isotope data gave no indication of denitrification (Böhlke and Denver, 1995).

It will take many years for improved nutrient management practices at Locust Grove to improve the water quality in the surficial aquifer. The CFC-modeled ages indicate that it can take from 20 to more than 50 years for water to travel from the shallow part of the surficial aquifer to the deep, downgradient parts of the surficial aquifer (Dunkle et al., 1993; Reilly et al., 1994). Thus,

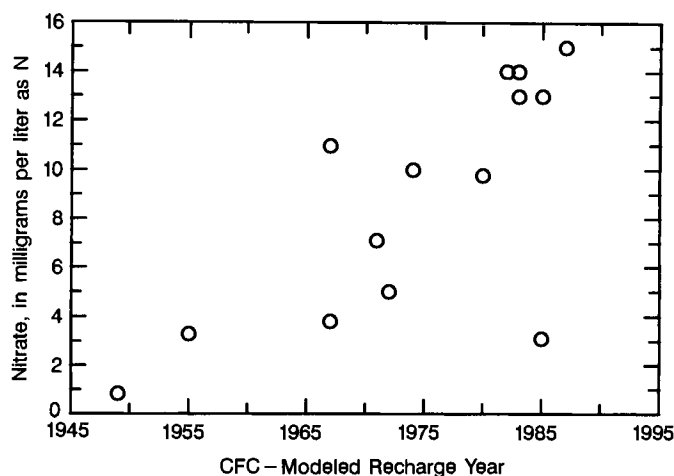


Figure 22.1. Nitrate concentration as a function of CFC-modeled recharge year for samples from a cross-section at Locust Grove, Delmarva peninsula, USA (adapted from Dunkle et al., 1993).

even if all nitrate applications ceased immediately, downgradient parts of the surficial aquifer would likely see increases in nitrate concentrations over a 10 to 20 year period, and substantial portions of the surficial aquifer would not experience declines in nitrate concentrations for decades. Studies at the Fairmount watershed in southern Delaware (Dunkle et al., 1993; Denver and Sandstrom, 1991) found traces of herbicide residues in groundwater with a CFC-modeled recharge date of 1963. These studies indicate that CFC dating combined with isotopic techniques can be very useful in understanding the persistence of water quality problems over time in shallow surficial aquifer settings.

22.2.4 Isotope tracers for tracking migratory patterns of birds

Researchers believe that environmental changes have caused a decline in many species of migratory birds, especially those that breed in the north temperate zone and migrate to the tropics in winter (Robbins et al., 1989). Recent analyses of Breeding Bird Surveys show that certain species of Neotropical migrant songbirds are declining in some parts of their breeding range but not in others (James et al., 1996). The possible causes of these declines are controversial, and may be linked to environmental changes in the breeding areas (Probst, 1986; Holmes et al., 1986; Robinson et al., 1995), in the winter grounds (Terborgh, 1989), along migration routes (Moore and Simons, 1992), or in some combination of these locations (Sherry and Holmes, 1995). Yet, despite considerable efforts (e.g., articles in Hagan and Johnston, (1992)), there is little specific information about where habitat change is affecting Neotropical migrant bird populations most (Sherry and Holmes, 1995). For example, it has been suggested that the northern forests are becoming calcium-limited from acid rain effects (Likens et al., 1996) and this may be the cause of population declines in birds (Graveland et al., 1994). Others suggest that forest fragmentation as a result of increased urbanization may be causing the declines (Robinson et al., 1995).

To investigate the effect of habitat change on migrating bird populations, it would be helpful to link birds at their wintering site to their geographic origin (breeding site). For example, do individuals from the same breeding area remain more or less together in winter, or do they disperse throughout the winter range? If it can be shown that the songbirds remain together in their wintering grounds then deforestation in one particular area within the winter locality could cause the observed population declines in discrete parts of the breeding range (James et al., 1996). On the other hand, if individuals from local breeding populations spread widely throughout the wintering area, then local areas of deforestation in the tropics could not be the cause of the patchy pattern of decline of northern breeding populations.

Unfortunately, conventional tracking methods are ineffective for Neotropical migrant birds. They are recovered too infrequently for standard tagging techniques to be useful (Holmes and Sherry, 1992) and lack morphological or molecular variation that could serve as markers for identifying geographic subpopulations (Ball et al., 1988; Wenink et al., 1994). This absence of markers with which to link breeding and wintering populations impedes understanding of their year-round population dynamics (Sherry and Holmes, 1995), and thus hinders development of appropriate conservation strategies (Myers et al., 1987). Recently, however, a number of studies have demonstrated that natural variations in stable and radiogenic isotopes provide an important marker to distinguish the geographic origin of animals, especially when used in conjunction with genetic markers.

Previous investigations have shown that natural variations in the isotopic composition of animal tissues (bone, muscle, egg shell, feathers) reflect the isotopes in the local environment (precipitation, soil, vegetation, diet) (e.g., DeNiro and Epstein, 1978; Luz et al., 1990; Mizutani and Wada, 1989; Schaffner and Swart, 1991; Hobson and Clark, 1992). These results have led to a number of studies that have used natural variations of isotopic ratios in the tissues of mammals (van der Merwe et al., 1990; Vogel et al., 1990; Koch et al., 1995), fish (Nelson et al., 1989; Meyer-Rochow et al., 1992), birds (Alisauskas and Hobson, 1993) and arthropods (Fry, 1984) to determine their geographical origin.

Most isotopic studies of birds have concentrated on determining feeding habitats and trophic relations (e.g., Mizutani et al., 1990; Hobson and Clark, 1992). Studies using isotopes to trace geographic origins are limited to Alisauskas and Hobson (1993) who showed that different subpopulations of wintering geese could be identified with carbon isotopes, Trust (1993) who demonstrated that carbon and sulfur isotopes could be used to track migratory populations of Redhead Ducks, and Chamberlain et al. (1995, 1997) who utilized stable and radiogenic isotopes to identify geographic origins and subpopulation structures of migratory birds on a large geographic scale.

Chamberlain et al. (1995, 1997) demonstrated that C, H, and Sr isotopic composition of feathers and bones of Black-throated Blue Warblers can be used to trace migratory patterns. The authors collected feathers from birds in selected locations throughout their north temperature breeding range (Figure 22.2). Feathers were used because their stable isotopic composition reflects that of the foods eaten during their period of growth (Mizutani et al., 1990, 1992; Hobson and Clark, 1992). Black-throated Blue Warblers molt completely once per year, between July and September in or near their breeding area. Thus, the isotopic composition of their feathers should reflect that of the food chain at their breeding locality.

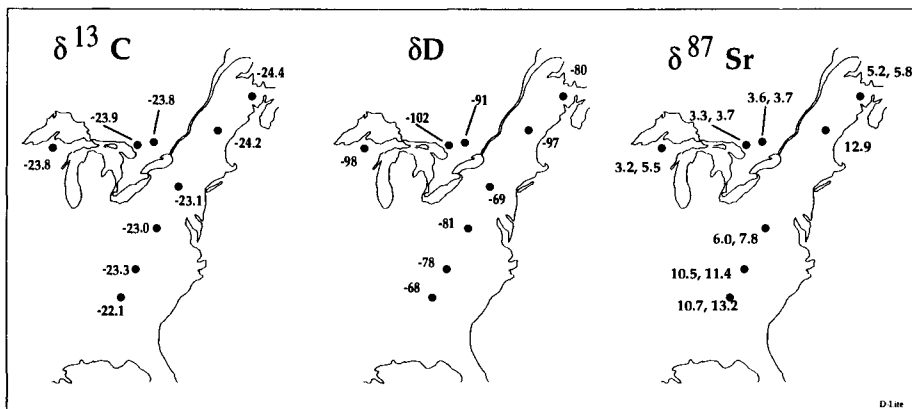


Figure 22.2. Mean δD and $\delta^{13}C$ in feathers and $\delta^{87}Sr$ in bones of Black-throated Blue Warblers collected throughout their northern breeding range.

Chamberlain et al. (1995) showed that both the δD and $\delta^{13}C$ values of feathers varied systematically with latitude: δD differed by over 30‰ from the southern end of the breeding range ($-68 \pm 10\text{‰}$) to the northern region ($-102 \pm 13\text{‰}$), while $\delta^{13}C$ varied from a high of $-22.1 \pm 0.6\text{‰}$ in the south to a low of $-24.4 \pm 0.6\text{‰}$ in the north (Figure 22.2). In addition, the δD values decreased east to west across the northern part of the breeding range, from New Brunswick to Michigan (Figure 22.2). These patterns of δD and $\delta^{13}C$ values in Black-throated Blue Warbler feathers can be explained largely by latitudinal variation in the isotopic composition of precipitation (Sheppard et al., 1969) and plants (Bird et al., 1994) occurring across eastern North America.

Local populations of northern-breeding Black-throated Blue Warblers could be further distinguished by the Sr isotopic composition of bone fragments (Chamberlain et al., 1995). The $\delta^{87}Sr$ values of bones from birds that nest along the Appalachian Mountains are high (4.2 to 9.3), reflecting the high $\delta^{87}Sr$ granitoid bedrock parent material. In contrast, $\delta^{87}Sr$ values of bones from birds that nest in the Great Lake region (Michigan and Ontario) are lower (2.2 to 3.8), reflecting the influence of easily weathered low $\delta^{87}Sr$ limestone, which dominates the $\delta^{87}Sr$ of the glacial till soil parent material and in turn the region's surface waters (Wadleigh et al., 1985). $\delta^{87}Sr$ values of birds from New Brunswick are intermediate (3.6 to 4.0), likely reflecting a strong marine atmospheric component with low $\delta^{87}Sr$. Thus, distinctive δD and $\delta^{13}C$ values of feathers or $\delta^{87}Sr$ of bones make it possible to distinguish various subpopulations of birds.

Preliminary studies of the δD and $\delta^{13}C$ values in feathers collected from Black-throated Blue Warblers wintering on the Caribbean islands of Jamaica, Hispanola, and Puerto Rico suggest that most of the birds collected in these islands were in fact from the northern parts of the breeding range. The δD and $\delta^{13}C$ values of feathers from birds on these islands were low, approximately -106‰ and -24‰ , respectively. In addition, the variation in isotopic values, as indicated by standard deviations, was generally larger in winter sites ($\pm 20\text{‰}$ for δD and $\pm 1.0\text{‰}$ for $\delta^{13}C$) than in breeding areas ($\pm 10\text{‰}$ for δD and $\pm 0.5\text{‰}$ for $\delta^{13}C$). The wider variation in winter sites most likely reflects mixing of individuals from different breeding areas.

Mixing of individuals in the southern wintering range suggests that the cause of the recent declines of Neotropical migrant songbirds is the result of habitat degradation in the northern breeding grounds. If different breeding populations of birds mix in their wintering grounds it would be highly unlikely that local areas of deforestation in the tropics would produce the observed patchy decline of northern populations (James et al., 1996). Therefore, current studies are aimed at determining whether Ca-limitation in the northern forests from acid rain effects or habitat fragmentation due to urbanization is the cause of the decline of Black-throated Blue Warblers and other Neotropical migrant birds.

22.2.5 *Changes in atmospheric deposition*

Research on acid deposition in the 1970's and 1980's greatly enhanced our knowledge about anthropogenic emissions of sulfur and nitrogen compounds to the atmosphere, and their effects on terrestrial ecosystems. Isotopic approaches have been used increasingly in these efforts to differentiate emission sources, and to understand transfers of N and S compounds between the atmosphere and terrestrial ecosystems. This section reports on some of those investigations. There are brief discussions of this topic in Chapters 15 and 16.

Nitrogen isotopes in the atmosphere and precipitation

In many catchments, atmospherically-derived nitrate and ammonium are important sources of nitrogen (Chapter 16). They are deposited from the atmosphere in rainfall and particulates, or formed from "dry deposited" gases: $\text{NO} + \text{NO}_2$ (NO_x), HNO_3 , and NH_3 . Industry and agriculture have caused marked increases in the concentrations of these gases. The resultant elevated inputs of nitrate and ammonium, which are both readily utilized by plants, can have a marked effect on plant-soil ecosystems and the catchments they occupy. Recently, $^{15}\text{N}/^{14}\text{N}$ ratios have emerged as a tool to assess both the general importance of atmospheric inputs and the nature of recent environmental changes resulting from human activity (Vitousek et al., 1989; Abbadie et al., 1992; Garten, 1992, 1993; Evans and Ehleringer, 1993, 1994; Fogel and Paerl, 1993; Durka et al., 1994; Gebauer et al., 1994; Macko and Ostrom, 1994; Nadelhoffer and Fry, 1994; Stewart et al., 1995; Poulson et al., 1995; Handley and Scrimgeour, 1997). Our understanding of the isotopic composition of atmospheric nitrogen compounds, however, is still quite limited. For this reason there has been a tendency to oversimplify the interpretation of $^{15}\text{N}/^{14}\text{N}$ data in terms of the information it may provide about the nature or amount of atmospheric inputs.

NO_x emitted by the main anthropogenic sources - vehicle engines and power stations - has $\delta^{15}\text{N}$ values in the range of -7 to +12‰ (Moore, 1977; Freyer, 1978; Heaton, 1990). In contrast, the main 'natural' source of NO_x emissions - those accompanying nitrification and denitrification in soils - is believed to have much lower $\delta^{15}\text{N}$ values (-10‰ or lower based on known isotopic fractionation effects). Recognition that anthropogenic NO_x might have higher $\delta^{15}\text{N}$ values than natural NO_x has led to the suggestion that the isotopic composition of nitrate in precipitation might be indicative of the amount of nitrate resulting from pollution. Early support for this potentially valuable isotopic indicator came from observations that the $\delta^{15}\text{N}$ values of nitrate in rainfall (typically -8 to +4‰) showed clear seasonal variations, with the lower $\delta^{15}\text{N}$ values found in summer presumed to reflect increased emission of natural NO_x during the season of greater soil microbial activity (Freyer, 1978; Heaton, 1986). However, study areas that probably have very different amounts of pollution versus natural emissions, and might therefore be anticipated to have very different mean $\delta^{15}\text{N}$ values for their atmospheric NO_x , have mean $\delta^{15}\text{N}$

values of rainfall nitrate that are almost identical (Heaton, 1987; Freyer, 1991). Later fundamental investigations by Freyer et al. (1993) have demonstrated, moreover, that variations in the isotopic composition of total NO_x are not necessarily the most important control on the isotopic composition of nitrate. They found that the $\text{NO} \leftrightarrow \text{NO}_2$ conversion reactions in the atmosphere result in a large overall isotopic fractionation ($\epsilon_{\text{NO}_2\text{-NO}} = \text{c. } +18\text{‰}$). The $\delta^{15}\text{N}$ value of NO_2 , the precursor to nitrate, therefore varied depending on the atmospheric conditions (ozone, sunlight, etc.) controlling the proportion of NO_2/NO_x . Thus, even with constant $\delta^{15}\text{N}$ values for atmospheric NO_x (c. -5‰ in their study), seasonal or diurnal changes in atmospheric chemistry could produce large isotopic changes ($>10\text{‰}$) in the $\delta^{15}\text{N}$ value of NO_2 and, by implication, the nitrate formed from it (Freyer et al., 1993).

The situation is equally complicated for atmospheric NH_3 . Enhanced emissions of ammonia, from decomposition of excrement associated with intensive animal husbandry, can have a significant effect on the chemistry of the atmosphere and terrestrial systems with which it interacts (van Breemen et al., 1982). Isotopic data for these emissions indicate $\delta^{15}\text{N}$ values in the range -15 to -9‰ , but because these negative values are the result of large, partly kinetic isotope fractionation effects, they are subject to considerable variation (Freyer, 1978; Heaton, 1986, 1987). Industrial emissions may also vary widely depending on the nature of the process. Thus coal burning may produce NH_3 emissions of -7 to -4‰ in normal boilers or, as a result of isotopic fractionation, -20‰ in a coking plant (Freyer, 1978; Heaton, 1987). Large isotope effects dependent on rainfall patterns are also associated with the solution of NH_3 to form dissolved NH_4^+ (Heaton, 1987). Probably for a combination of these reasons, ammonium in rainfall displays a very wide range in $\delta^{15}\text{N}$ values (c. -16 to $+2\text{‰}$).

The $\delta^{15}\text{N}$ value of atmospherically deposited nitrogen, based primarily on analyses of nitrate and ammonium in rainfall, is generally considered to be negative. In canopied systems, however, particularly forests where many $^{15}\text{N}/^{14}\text{N}$ studies are conducted, particulates and dry deposition washed from the canopy in throughfall may constitute a significant additional input of atmospheric nitrogen (Lovett and Lindberg, 1993). Isotopic fractionation of nitrate and ammonium in particulates and dry deposition appears to increase their $\delta^{15}\text{N}$ values to c. 0 to $+10\text{‰}$ (Moore, 1977; Heaton, 1987; Freyer, 1991). Consistently, the few available analyses of throughfall suggest that its $\delta^{15}\text{N}$ values, for nitrate at least, are higher than those in rainfall (Garten, 1992; Heaton et al., 1997). In many cases these positive $\delta^{15}\text{N}$ values for total deposition may not be distinguishable from those of inorganic nitrogen in soils.

If the use of $^{15}\text{N}/^{14}\text{N}$ data for assessing the significance of atmospheric pollution does not look promising, can such data nevertheless be used to assess the relative importance of atmospheric inputs as a whole to an ecosystem? On a regional or global scale isotopic assessment of the significance of pollutant emissions of NO_x may become possible if it can be demonstrated that natural emissions have substantially different $\delta^{15}\text{N}$ values. On a local scale $^{15}\text{N}/^{14}\text{N}$ studies might be used to assess the impact of anthropogenic emissions of NO_x or NH_3 if a specific source has a very distinct $^{15}\text{N}/^{14}\text{N}$ signature. Ecosystem studies that assess the importance of atmospheric inputs of N may also use isotopic methods if the total input can be properly characterized for the particular study area; this may require imaginative artificial collection devices that simulate a natural canopy. In general it must be accepted, however, that the ready reactivity and large isotopic fractionations between atmospheric nitrogen compounds can lead to wide variations in the isotopic composition of nitrogen deposited to the ground. Such variations will be sensitive to particular atmospheric conditions, patterns of rainfall, and

air/ground interactions. In many cases, however, $^{15}\text{N}/^{14}\text{N}$ studies may still yield useful information on the sources of atmospheric nitrogen and the implied impacts of human activity. Recent investigations of the $\delta^{18}\text{O}$ of atmospheric nitrate also show promise as a tool for distinguishing sources of nitrate (Durka et al., 1994; Kendall et al., 1995, 1996; Chapter 16).

Sulfur isotopes in atmospheric deposition

Sulfur isotope ratios can be used to determine the relative magnitude of the contributions of natural and anthropogenic sources to atmospheric sulfur deposition provided that (a) the isotope ratios of the potential sulfur sources are accurately known, (b) the isotopic compositions of the various sources differ significantly from each other, and (c) the isotope fractionation occurring during transformation processes in the atmosphere is either small or well documented (Chapter 15). Although this potential has been recognized since the late 1950's (e.g. Ostlund, 1959; Jensen and Nakai, 1961; Nakai and Jensen, 1967), there is still a lack of information on the isotopic compositions of several contributors to the atmospheric sulfur cycle.

Sulfur in the atmosphere occurs in gaseous (e.g., H_2S , SO_2), liquid (e.g., SO_4^{2-}), and solid (e.g. S^0) phases and can be of both natural and anthropogenic origin (see Chapter 15 for detailed treatment of sulfur biogeochemistry). Anthropogenic sulfur often predominates in heavily industrialized areas of the northern hemisphere, whereas natural sulfur compounds still prevail in more remote areas as they did everywhere in preindustrial times. Provided that the preindustrial sulfur deposition had a significantly different isotope composition with respect to more recent industrial sulfur additions, stable sulfur isotopes can serve as a historical tracer of anthropogenic pollution.

Our ability to quantify the extent of anthropogenic sulfur in atmospheric deposition by isotopic techniques is dependent on the knowledge of the isotopic compositions of natural sulfur sources and their seasonal and spatial variabilities. Seaspray-derived sulfate has a clearly defined $\delta^{34}\text{S}$ value near +20‰ (e.g. Nielsen, 1974; Wadleigh et al., 1994). This value is close to that of seawater and indicates no significant isotope fractionation during the sea-air transfer of marine sulfate. Biogenic reduced sulfur compounds, particularly dimethylsulfide (DMS) which is produced during assimilatory sulfate reduction by phytoplankton, constitute another oceanic sulfur source. Theoretical considerations ($\delta^{34}\text{S} \approx +20\text{‰}$; Calhoun and Bates, 1989) and "indirect" measurements ($\delta^{34}\text{S} \approx +22\text{‰}$; McArdle and Liss, 1995) suggest a $\delta^{34}\text{S}$ value for DMS-derived atmospheric S also close to that of seawater. The few sulfur isotope measurements on aerosols of DMS origin showed, however, a mean $\delta^{34}\text{S}$ value of $+15.6 \pm 3.1\text{‰}$, indicating significant isotopic fractionation during assimilatory sulfate reduction of seawater sulfate, sea-air transfer of DMS, and its atmospheric oxidation to SO_2 , methane sulphonic acid (MSA), or sulfate (Calhoun et al., 1991).

Most, but not all terrestrial natural sulfur sources are depleted in ^{34}S with respect to marine sulfur. Mean $\delta^{34}\text{S}$ values for total volcanic sulfur entering the atmosphere were estimated to be about +5‰ (Lein, 1991). The emission of reduced biogenic sulfur gases from terrestrial ecosystems is another natural source of atmospheric sulfur. Although various reduced sulfur gases such as H_2S , CH_3SCH_3 (DMS), COS, and CS_2 have been detected in forest ecosystems and wetlands (e.g., Nriagu et al., 1987; Staubes et al., 1989), there appear to be no direct measurements of their isotopic compositions reported in the literature. The main product of bacterial SO_4^{2-} reduction is H_2S . In terrestrial freshwater environments with low sulfate concentrations, the released H_2S should have nearly the same isotopic composition as the SO_4^{2-} ,

whereas at higher SO_4^{2-} concentrations significant isotope fractionation results in more depleted $\delta^{34}\text{S}$ values of the H_2S that reaches the atmosphere. If reduced sulfur gases are evolved during decay of terrestrial biomass, they are expected to be depleted by up to 5‰ in their $^{34}\text{S}/^{32}\text{S}$ ratios with respect to those of the organic source material due to isotope fractionation effects (e.g., Grey and Jensen, 1972). Because the isotopic composition of total sulfur in many soils and wetlands varies between 0 and +5‰, slightly negative $\delta^{34}\text{S}$ values would be expected for terrestrial biogenic sulfur emissions, which have indeed been observed in several case studies (e.g., Nriagu et al., 1987; Mayer et al. 1995). However, at least part of the re-emitted sulfur is likely of anthropogenic origin and thus should not be considered a truly natural sulfur source.

Anthropogenic sulfur is mainly released into the atmosphere by combustion and refining of fossil fuels and ore smelting. The $\delta^{34}\text{S}$ values of coal, oil, gas, and sulfide ores can vary between -40 and +30‰ (e.g., Nielsen, 1974), but the observed ranges of isotopic compositions of the sulfur emissions resulting from their processing are much narrower. The most common $\delta^{34}\text{S}$ values of flue gas from coal combustion were found to vary between -3 and +3‰ (Nielsen, 1974; Newman et al., 1975a; Newman and Forrest, 1991) whereas the majority of $\delta^{34}\text{S}$ values for flue gas from oil fired power plants cluster around +5‰ $\pm$ 3‰ (Nielsen 1974; Newman et al., 1975b; Newman and Forrest, 1991). $\delta^{34}\text{S}$ values for emissions from sulfide ore smelting often range between 0 and +9‰ with an average of +3‰ (e.g., Forrest and Newman, 1977; Grinenko and Grinenko, 1991). As many catchment studies initiated for acid rain research programs were and still are conducted in industrialized polluted areas of Europe and North America, it is not surprising that mean $\delta^{34}\text{S}$ values obtained for atmospheric sulfur deposition generally represent the given range for anthropogenic sulfur of -3 to +9‰ (Figure 22.3). Also, isotope measurements of ambient ground level SO_2 in the northeastern USA and Central Europe yielded mean $\delta^{34}\text{S}$ values between +1 and +3‰ (e.g., Newman and Forrest, 1991; Gebauer et al., 1994; Mayer et al., 1995), representing the average isotope composition of anthropogenic sulfur derived from fossil fuel combustion (Figure 22.3).

The isotopic composition of atmospheric sulfur compounds can only be used as a label for the identification of above characterized sources if their distinct $^{34}\text{S}/^{32}\text{S}$ ratios are preserved during chemical transformations in the atmosphere. Although sulfur isotope fractionation due to differences in rates, temperatures, and mechanisms of SO_x oxidation have been reported (e.g., Forrest and Newman, 1977; Nriagu and Coker, 1978a; Saltzman et al., 1983), these effects are often on the order of less than 2‰ and do not preclude identification of sources with their often wide variations in $\delta^{34}\text{S}$ values. However, because the isotopic range of potential sulfur sources is large and variable, the sulfur isotope technique for pollutant tracing in the atmosphere is most successful in well defined study regions: e.g. on the local scale where industrial point source contributions of sulfur differ in their isotopic composition from that of the preindustrial background. For example, at various sites in Alberta (Canada), sulfur emissions from sour gas processing plants have $\delta^{34}\text{S}$ values as high as +30‰ (Figure 22.3), thereby constituting an ideal tracer for industrial sulfur in the atmosphere and the environment (Krouse et al., 1984; Krouse, 1991).

A comprehensive summary on available methods for the delineation of anthropogenic and natural fluxes of atmospheric sulfur compounds by isotope techniques is given by Newman et al. (1991). One possibility to identify sulfur sources is to plot $\delta^{34}\text{S}$ values versus various functions of concentration (e.g. Krouse, 1980). A simple and effective way to differentiate marine from anthropogenic sulfur sources is to plot $\delta^{34}\text{S}$ values against the percentage of sulfate

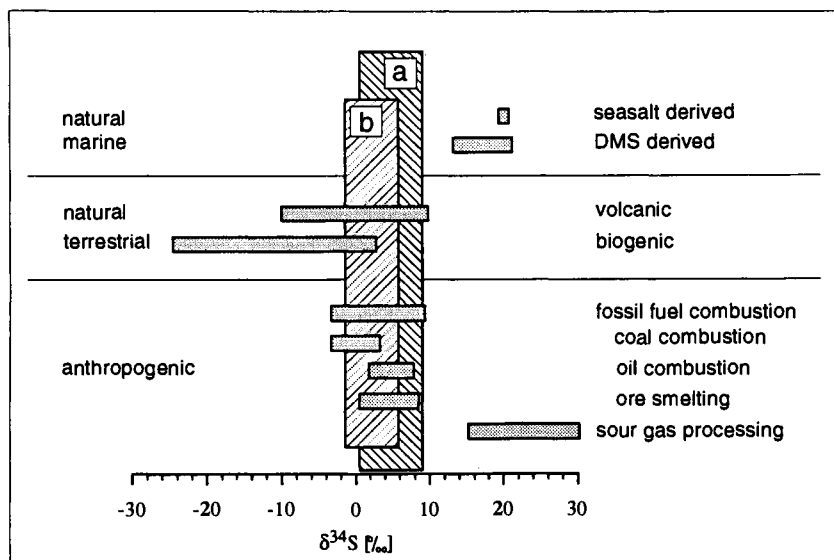


Figure 22.3. Common ranges of $\delta^{34}\text{S}$ values for different contributors to the atmospheric sulfur cycle as compared to (a) mean $\delta^{34}\text{S}$ values for aerosol, bulk precipitation, and throughfall sulfate reported from selected catchment studies and meteorological stations in Northern America, Europe, and the former USSR (Cortecci and Longinelli, 1970; Longinelli and Bartelloni, 1978; Nriagu and Coker, 1978b; Chukhrov et al., 1980; Caron et al., 1986; Fuller et al., 1986; Hesslein et al., 1988; Trembaczowski, 1991; Van Stempvoort et al., 1991; Andersson et al., 1992; Stam et al., 1992; Pichlmayer and Blochberger, 1994; Mayer et al., 1995; Mörtz and Torssander, 1995; Novák et al., 1995) and (b) the range of $\delta^{34}\text{S}$ values for anthropogenic end members from sea-salt correction calculations (Mizutani and Rafter, 1969; Cortecci and Longinelli, 1970; Wakshal and Nielsen, 1982; Wadleigh et al., 1994; Mörtz and Torssander, 1995; Herut et al., 1995).

that is sea-salt derived, calculated using chloride concentrations. Often, the data points are distributed on a two source mixing line with end members at about +20‰ for sea-salt derived sulfur and $\delta^{34}\text{S}$ values between -1 and +6‰ for anthropogenic sulfur (Figure 22.3). From two remote European sites, however, McArdle and Liss (1995) derived a triangular plot indicating that biogenic, DMS-derived sulfur is an additional sulfur source that contributed on average 15 - 20% to the atmospheric sulfur deposition. Isotopic data clearly suggest that not only in terrestrial but also in marine environments a considerable fraction of the atmospheric sulfur is derived locally from biogenic sources, particularly during the summer months (Nriagu et al., 1987; McArdle and Liss, 1995).

In many areas, industrialization has caused a change in the isotopic composition of deposited sulfur, which should be reflected in selected historical archives. In terrestrial areas, such changes are likely to be minor because terrestrial biogenic and volcanic sulfur can be isotopically rather similar to anthropogenic sources (Figure 22.3). In areas that were previously dominated by marine sulfur contributions, however, industrialization has resulted in decreased $\delta^{34}\text{S}$ values in the atmospheric sulfur deposition. A tendency of increasing $\delta^{34}\text{S}$ with age has indeed been described for a number of historical archives such as lake sediments (increase to +8‰; Fry, 1989; increase to +9 and 14‰; Kokkonen and Tolonen, 1987), glacier ice (+11‰; Pichlmayer and Blochberger, 1994), paleowaters (+9‰; Edmunds et al., 1996), and organic soil

sulfur fractions (increase to +9‰; Mayer et al., 1995). At this point, it is not clear whether these increases can be attributed solely to changes in the isotopic composition of the sulfur inputs over time. Nevertheless, stable sulfur isotopes are a promising tool for historical tracing of anthropogenic pollution and environmental change.

22.3 Paleo-Climatic Indicators

Thus far we have considered how isotopes can be used to understand primarily current and recent environmental change. We now turn to isotopic techniques that are useful in understanding climate change and environmental change on timescales from centuries to tens of millennia. Long timescale techniques are fundamental to reconstructing past climate and documenting its natural variability. The long-term perspective provides the necessary framework within which anthropogenic induced perturbations can be assessed.

22.3.1 *Groundwater as an archive of paleo-climatic information*

Long-term changes in climate can be detected using isotopic information archived in hydrogeologic environments. Patterns of variation in stable or radiogenic isotopes have been combined with one or more geochemical dating tools to determine both the age or residence time of subsurface water, and the climatic conditions at the time that groundwater was isolated from the atmosphere. Groundwater composition may be affected by the dynamic movement and mixing of water, interactions with surface water, ion exchange, dissolution and precipitation of minerals, and anthropogenic perturbations. Isotopic characterization coupled with radiometric dating is a useful way to document the chronology and interpret the effects of these mechanisms on a groundwater system.

Radioisotopic dating techniques require that decay schemes have half-lives in the same range as the age of the system or material to be dated. Ideally, initial isotopic abundances or ratios should be well known and the system or material to be dated should have been geochemically isolated from the atmosphere at the time of formation until the time of sampling. Groundwater eventually attains geochemical equilibrium with aquifer sediments, thus limiting additional dissolution or precipitation of mineral phases that could make isotopic dating techniques impractical. Variations in initial isotopic concentrations or ratios are sometimes problematic. Plots of disequilibrium with distance along a flow path may be used to extrapolate back to initial compositions (Durrance, 1986). The documentation of all inputs for a given target isotope is essential to differentiating natural variability from anthropogenic influences (Andrews and Fontes, 1992).

For groundwaters in the age range from hundreds to tens of thousands of years, isotopic dating tools include ^{36}Cl , ^{14}C , and uranium-series nuclides. Possible sources of ^{36}Cl include: (1) cosmic-ray spallation of argon and stable ^{35}Cl in the atmosphere, (2) cosmic-ray irradiation of stable ^{35}Cl in the shallow unsaturated zone, (3) solution of matrix chloride in environments where in-situ production of ^{36}Cl is significant, (4) neutron activation of stable ^{35}Cl in the oceans as a result of nuclear-weapons tests in the 1950's-60's, and (5) anthropogenic inputs from nuclear-fuel reprocessing and nuclear-power generation facilities (Cecil et al., 1992). Possible sources of ^{14}C include: (1) neutron interactions, (2) the decay of certain radium isotopes, (3)

alpha particle reactions, and (4) anthropogenic sources. For uranium-series dating methods, disequilibrium between uranium and the longer-lived members of the decay series is used for geochronology of materials with ages less than 1 million years (Ivanovich, 1982). Following precipitation of uranium-bearing materials in an aquifer, a considerable amount of time is needed to attain equilibrium among all members of the decay series. The greater the degree of disequilibrium among members of a decay series, the younger the material.

Carbon-14, with its accurately-known atmospheric source function (Suess and Linick, 1990) and 5730-yr half-life, is ideal for studying processes in aquifers where recharge occurs on long timescales (hundreds to tens of thousands of years) and thus may have implications for climatic change. Accordingly, it can be used to study changes in isotopic and chemical characteristics of recharge during the last glacial period. Despite its well-measured atmospheric source function, the ^{14}C concentration of the CO_2 that equilibrates with water that recharges aquifers is less well known. The initial bicarbonate in most groundwater originates from soil gas, whose ^{14}C can be different from that of atmospheric carbon dioxide, due to decomposition of organic matter and interaction with soil matrix material (Plummer et al., 1991). Furthermore, several reactions can occur along the flow path of the groundwater that will significantly alter the ^{14}C concentration of the bicarbonate, and these reactions must be taken into account when calculating the age of the water (Wigley et al., 1978). Plummer et al. (1990) successfully circumvented these problems to obtain accurate ages and flow rates in the large regional Madison Aquifer in the central U.S.A. With groundwater ages established, they related variations in $\delta^{18}\text{O}$ and δD of groundwater to specific past climatic events.

The $\delta^{18}\text{O}$ of calcite has provided an uninterrupted 500,000-year climate record at an open fault zone adjacent to a major groundwater discharge area at Devils Hole in south-central Nevada, USA (Winograd et al., 1992). Variations in $\delta^{18}\text{O}$ were documented for a 36-centimeter-long core of vein calcite collected about 30 m below the water table. A 500,000-year paleotemperature record was established by mass-spectrometric measurements of uranium-series isotopes and disequilibrium dating with subsequent correlation of seasonal shifts in the $\delta^{18}\text{O}$ values (Figure 22.4). It was determined that $\delta^{18}\text{O}$ variations measured on the calcite were a reflection of seasonal variations in atmospheric precipitation falling on the recharge areas for the Devils Hole groundwater system. The subsequent interpretation of seasonal variation associated with the geochronology established by uranium-series dating provided minimum ages for climatic events because these ages reflect the time that calcite precipitated from solution and not the time when recharge fell as precipitation 80 to >160 km away from the study site. This study established a radiometrically well-dated paleoclimate record spanning several glacial cycles. The record was used to determine the timing and duration of major climate shifts and is consistent with a paleotemperature record from Vostok, Antarctica for ice-core deuterium (Lorius et al., 1985) and the record of Northern Hemisphere ice volume deduced from $\delta^{18}\text{O}$ of planktonic foraminifera (Imbrie et al., 1989).

Another recent study documented the glacial chronology of the northern Yellowstone Park area using isotopic ratios of C, O, Sr, and U with uranium-series age dates (Sturchio et al., 1992). The isotopic ratios were determined in travertine to establish diagenesis including deposition temperatures and isotope ratios of paleowaters and their solutes. These data were then utilized to make inferences on the evolution of the underlying hydrothermal system and effects of glaciation. Travertine between 15,000 and 50,000 years of age had $^{234}\text{U}/^{238}\text{U}$ ratios close to the crustal abundance value of 1.00. Travertine deposits outside this age window, both younger and

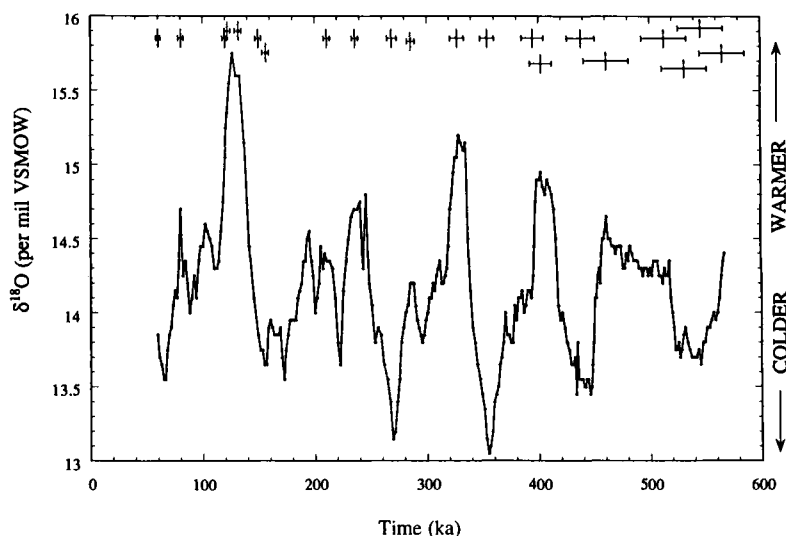


Figure 22.4. Variations in $\delta^{18}\text{O}$ in a core of vein calcite collected about 30 m below the water table at Devils Hole, south-central Nevada, USA (reprinted from Winograd et al. (1992)). Horizontal lines at top of figure are uranium-series dated intervals with associated uncertainties at 2σ shown as vertical lines.

older, had $^{234}\text{U}/^{238}\text{U}$ values generally in the range of present thermal waters, from 1.5 to greater than 3. Sturchio et al. (1992) concluded that the smaller ratios reflected increased dissolution of carbonate aquifer rock in response to increased hydrostatic pressure at depth during full glacial conditions during the Pinedale glaciation 30,000 to 40,000 years before the present.

22.3.2 Continental glaciers

Long-term records of atmospheric deposition preserved in glaciers and ice sheets are useful in recording changes in deposition chemistry and climate (Lorius et al., 1988; Thompson et al., 1988a). Continuous ice cores from the ice sheets of Greenland and Antarctica have provided important, long-term climatic information (Wagenbach, 1989). In the past, ice cores from glaciers in temperate and tropical latitudes have not been used in climate reconstruction because it was believed that meltwater would alter the isotopic composition of deposition preserved in the annual ice layers (Wagenbach, 1989). Árnason (1981) suggested that under favorable conditions, temperate glaciers may be useful in providing records of global change during the past 2,000 years. High altitude sites on glaciers and ice caps from nonpolar locations in Kenya, Peru, China, Canada, Switzerland, and the USA have been sampled for paleoclimate information. Thompson and Hastenrath (1981) and Thompson (1981) found a distinct smoothing of the $\delta^{18}\text{O}$ profiles with depth in two shallow ice cores collected from Lewis Glacier in Kenya. They concluded this smoothing was due to meltwater infiltration.

A 1,500-year climatic record was reconstructed using $\delta^{18}\text{O}$ values, specific conductance, and microparticle concentrations in ice cores from the Quelccaya Ice Cap in Peru (Thompson et al., 1984, 1986, 1988a). Thompson et al. (1988b, 1989) utilized $\delta^{18}\text{O}$ values in ice cores from the Dunde Ice Cap in China to provide long-term and high resolution climate records from the

northeastern section of the Tibetan Highlands. A 103-meter snow/ice core from Mount Logan, Canada has provided a 300-year climatic record (Holdsworth and Peak, 1985). Ice cores collected from the Colle Gnifetti site in Switzerland indicate a good correlation of the smoothed $\delta^{18}\text{O}$ values to summer air temperature at a nearby weather station.

The possible existence of historical records of climate in ice cores from glaciers in the continental USA has been evaluated only recently (Naftz, 1993; Naftz et al., 1993, 1996). In 1991, a 160-meter ice core to the bedrock underlying Upper Fremont Glacier in northwestern Wyoming was collected for paleoclimate reconstruction (Naftz and Miller, 1992). The $\delta^{18}\text{O}$ profile (Figure 22.5) was determined from 760 samples equally spaced along the length of the core. From 101.8 m to 150 m, the mean $\delta^{18}\text{O}$ value shifted abruptly to -19.85‰ , 0.95‰ lighter than the mean core value of -18.90‰ . Using an age-to-depth relation developed from ^3H and ^{14}C data (Naftz et al., 1996), this isotopically lighter section of the core corresponds to the approximate time interval of the end of the Little Ice Age (LIA), from the mid-1700's to mid-1800's A.D. (Thompson, 1992). Thus, a low resolution, stable isotope record of climate has been preserved at the Wyoming site.

Closer inspection of the isotopic profile from the core has provided additional paleoclimatic information. The 101.8 to 150-m core interval (Figure 22.5) is characterized by numerous high-amplitude oscillations in $\delta^{18}\text{O}$ values. Without seasonal dust layers to guide sample selection, the 20-cm composite samples in this section of the core could not be consistently attributed to either 100 percent winter or 100 percent summer precipitation. These large oscillations thus may reflect increased seasonality or better preservation of the annual signal as a result of the cooler summer temperatures during the LIA. For example, the isotopically enriched horizons in this interval could have resulted from decreased rates of melting of isotopically enriched summer snowfall expected from cooler summer temperatures during the LIA. In contrast, during the 1990 and 1991 field seasons, summer snowfall at the site melted within 4 days of deposition. The abrupt decrease in the large amplitude oscillations above the 101.8-m depth (Figure 22.5) indicates a sudden termination of the LIA at this site. Selected tree cores collected 2 km from the drill site consistently showed a sustained period of reduced radial growth beginning about A.D. 1790 and continuing until about A.D. 1840 (Naftz et al., 1996). This decrease in radial growth probably reflects cooler summer temperatures that reduced the growing season at these high-altitude sites.

The isotopic response to climate change at Upper Fremont Glacier appears to be linked to that at the Quelccaya Ice Cap in the Peruvian Andes (14°S , 71°W) (Figure 22.5). Although the age-dating resolution of the Upper Fremont Glacier ice-core record is lower than that from the South American site, three distinct climate-related features seem to be preserved in both sets of records. (1) $\delta^{18}\text{O}$ shifts abruptly to more negative values within core segments that were deposited during the LIA. Relative to whole-core $\delta^{18}\text{O}$ averages, the Quelccaya Ice Cap core shows about a -0.7‰ shift during A.D. 1600 to 1800 (Thompson, 1992), compared to the -0.95‰ shift in the Upper Fremont Glacier core representing snow deposited during the end of the LIA (Figure 22.5). (2) The small-scale variation in the $\delta^{18}\text{O}$ signal increases during the LIA (Figure 22.5). In the two Quelccaya ice-core records the average annual range of $\delta^{18}\text{O}$ during the LIA (A.D. 1520 to 1880) was twice the average annual range observed after the termination of the LIA (A.D. 1880 to 1980) (Thompson, 1992). Numerous high-amplitude oscillations in $\delta^{18}\text{O}$ values during the LIA were identified in the Upper Fremont Glacier ice-core record (Figure 22.5). (3) Both cores show an abrupt shift from the high-amplitude isotopic

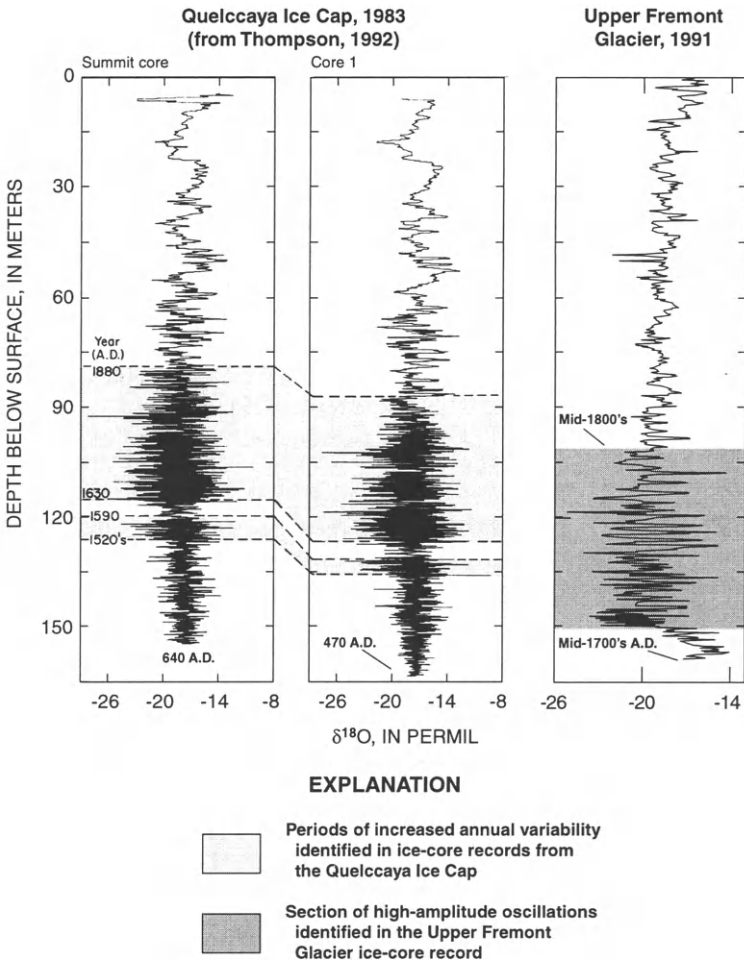


Figure 22.5. Relation of $\delta^{18}\text{O}$ profiles from the Quelccaya Ice Cap, Peru, and Upper Fremont Glacier, Wyoming, USA. Shaded areas identify areas of high-amplitude oscillations. Quelccaya Ice Cap data from Thompson (1992).

variations during the LIA to much lower amplitude isotopic variations characteristic of post-LIA ice. This transition occurs abruptly (probably in about 2 - 3 years) in all three cores. Thus, the linkages of the Upper Fremont Glacier isotopic record to the established paleoclimate record in the Quelccaya ice cores appear to support further the first documentation of the LIA in an ice-core record from a temperate glacier in south-central North America.

22.3.3 Clay minerals, oxides, and hydroxides

Minerals that form at the earth's surface acquire $\delta^{18}\text{O}$ and δD values that reflect the isotopic composition of local waters, which vary in relation to temperature, distance from source water,

elevation, and evaporation. Therefore, stable isotope ratios of surficially formed minerals can be used to constrain estimates of climatic/geographic change. In surficial environments, clay, oxide and hydroxide mineral formation is ubiquitous. The $\delta^{18}\text{O}$ and δD of these minerals reflect the soil or lake water from which they form. Savin and Epstein (1970) first documented that $\delta^{18}\text{O}$ and δD values of kaolinite, formed by weathering, compose an array roughly parallel to the meteoric water line, or the so-called "kaolinite line". Similarly, Lawrence and Taylor (1971, 1972) found a direct relationship between $\delta^{18}\text{O}$ and δD values of soil-formed kaolinite, smectite, and gibbsite with those of local meteoric waters, demonstrating that these soil-formed minerals preserve the isotopic signature of their formation water. Yapp (1987, 1993a) demonstrated similar relationships for goethite. Although it is theoretically possible to reconstruct both the $\delta^{18}\text{O}$ and δD of formation waters from single minerals, $\delta^{18}\text{O}$ can be reconstructed more reliably. Experiments on kaolinite, montmorillonite, and illite (O'Neil and Kharaka, 1976) and field studies on kaolinite (Bird and Chivas, 1988a; Longstaffe and Ayalon, 1990; Lawrence and Rashkes Meaux, 1993) show that oxygen isotope ratios of clay minerals are more resistant to post-formational exchange than hydrogen isotope ratios. Therefore studies employing $\delta^{18}\text{O}$ values to infer paleoclimate are preferred.

Despite the fact that there have been numerous field and experimental studies that demonstrate the potential utility of $\delta^{18}\text{O}$ and δD for reconstructing paleoclimates, there are few paleoclimate isotope studies using non-carbonate minerals. Instead, most studies have focused on $\delta^{18}\text{O}$ of calcite formed near the earth's surface (e.g. Winograd et al., 1992; Liu et al., 1996; Quade et al., 1989b) (see Section 22.3.4 on soil-formed calcite and Section 22.3.7 on lacustrine authigenic carbonates). There are several reasons for the lack of studies using oxygen and hydrogen isotope ratios of non-carbonate minerals, such as clay minerals or hydroxides, for paleoclimatic studies: (1) $\delta^{18}\text{O}$ measurements of silicates, oxides, and hydroxides are more expensive, more difficult, and less precise in comparison with those of calcite. (2) Fractionation factors of clay minerals and hydroxides, in part because of compositional variations, are poorly constrained relative to calcite. (3) Meaningful $\delta^{18}\text{O}$ or δD measurements of silicates or hydroxides require clean mineral separates. Acquiring pure mineral fractions of surficially formed minerals is extremely difficult due to their small particle size, and because these phases are often intergrown.

Despite these three difficulties, stable isotope ratios of clay minerals and oxide/hydroxides are useful indicators of environmental change for the following reasons:

(1) Calcite does not form in all terrestrial environments, so alternative minerals are needed to constrain the $\delta^{18}\text{O}$ estimates of paleowater. Many recent isotopic studies of surficially formed clays and oxides have focused on modern and fossil bauxites and laterites, soils containing no carbonate phase (Bird et al., 1989, 1992, 1993; Bird and Chivas, 1988b, 1989; Giral et al., 1993; Chen et al., 1988; Yapp, 1993b). For example, Bird and Chivas (1988b, 1989) found a $\sim 7\text{‰}$ increase in $\delta^{18}\text{O}$ of kaolinite in Australian "regolith" dated from Mesozoic to Late Tertiary, consistent with northward continental drift to warmer latitudes during this time.

(2) Hydroxyl-bearing minerals (in a manner analogous to cellulose, as discussed in Section 22.3.5) allow coupling of oxygen and hydrogen isotope ratios from a single phase to reconstruct both $\delta^{18}\text{O}$ and δD of the formation water (Savin and Epstein, 1970), and potentially, formation temperature (Yapp, 1993a). For example, Yapp (1993a,b) measured $\delta^{18}\text{O}$ of both goethite and phosphate from an Upper Ordovician weathered horizon to constrain both temperature and $\delta^{18}\text{O}$

of formation water. The $\delta^{18}\text{O}$ and δD of formation water calculated from values measured on goethite at this temperature fall upon the modern meteoric water line. This result suggests that the $\delta^{18}\text{O}$ and δD of Upper Ordovician ocean water (source of the precipitation) were similar to those of the modern ocean and that there has been little post-formational isotopic exchange of the goethite.

(3) $\delta^{18}\text{O}$ measurements of a suite of minerals, rather than only one, can constrain temporal variations in formation water $\delta^{18}\text{O}$ values when minerals form at different times. These data can record seasonal formation water $\delta^{18}\text{O}$ values as well as variations on the time-scales of "climatic change". For example, in a bauxite in Paragominas, Brazil, gibbsite is in isotopic equilibrium with waters much lower in $\delta^{18}\text{O}$ than today's precipitation, while the $\delta^{18}\text{O}$ values of other minerals in the soil are consistent with modern formation waters, indicating that gibbsite formed much earlier under a highly monsoonal circulation system (Bird et al., 1989, 1993). Detailed $\delta^{18}\text{O}$ studies can also indicate seasonal mineral formation. Giral et al. (1993) found that the range of $\delta^{18}\text{O}$ in lateritic kaolinites is consistent with formation from modern precipitation with its seasonal $\delta^{18}\text{O}$ variability, but that the coarser kaolinite is in isotopic equilibrium with the wet season precipitation. Analogous results have been found in more arid environments; the $\delta^{18}\text{O}$ values of neoformed palygorskite relative to smectite in Neogene lacustrine deposits (Torres-Ruiz et al., 1994) and palygorskite relative to calcite in modern calcrete soil horizons (Gauthier-Lafaye et al., 1993) show that palygorskite forms from more highly evaporated (high $\delta^{18}\text{O}$) waters than these coexisting minerals. These results suggest that isotope studies of multiple minerals in relict soils can elucidate seasonality of both mineral formation and the $\delta^{18}\text{O}$ of precipitation in the past.

These principles have been applied to the oxygen isotope values of minerals in a stratigraphic sequence of paleosols developed on fluvial deposits preserved in the Himalayan molasse (Stern et al., 1997). There is about a 3.5‰ increase in $\delta^{18}\text{O}$ of soil-formed calcite in these paleosols between 8.5 and 6.5 Ma (Quade et al., 1989b). The smectite in these paleosols shows about a 3.5‰ $\delta^{18}\text{O}$ increase at roughly the same time as the $\delta^{18}\text{O}$ increase of coexisting calcite (Figure 22.6), indicating that the smectite is pedogenic rather than detrital. However, the observed $\Delta^{18}\text{O}_{\text{calcite-smectite}}$ values average 6.1‰, about 3‰ higher than the equilibrium value. The interpretation of this apparent ^{18}O disequilibrium is that the smectite forms predominantly during the summer monsoon rains (low $\delta^{18}\text{O}$), while the calcite forms predominantly during the dry winter months when soil water evaporation drives calcite formation and causes enrichment of ^{18}O that is already high in precipitation. Thus, it appears that a monsoonal precipitation pattern was present in the Himalayan foreland by 10 Ma, and that the cause of the $\delta^{18}\text{O}$ enrichment is a change in precipitation source. These results demonstrate the utility of combining isotope data from carbonates with detailed $\delta^{18}\text{O}$ studies of co-genetic clay minerals to understand past climatic conditions.

22.3.4 *Pedogenic carbonates*

In semiarid and arid areas pedogenic (authigenic or soil-formed) carbonate commonly develops in soils formed even on noncalcareous parent material. The stable carbon and oxygen isotopic compositions of pedogenic carbonate have been increasingly used as paleoclimatic and paleoenvironmental indicators (e.g., Smith et al., 1993; Cerling et al., 1991), based on the assumption that the isotopic composition of ancient pedogenic carbonates was controlled by

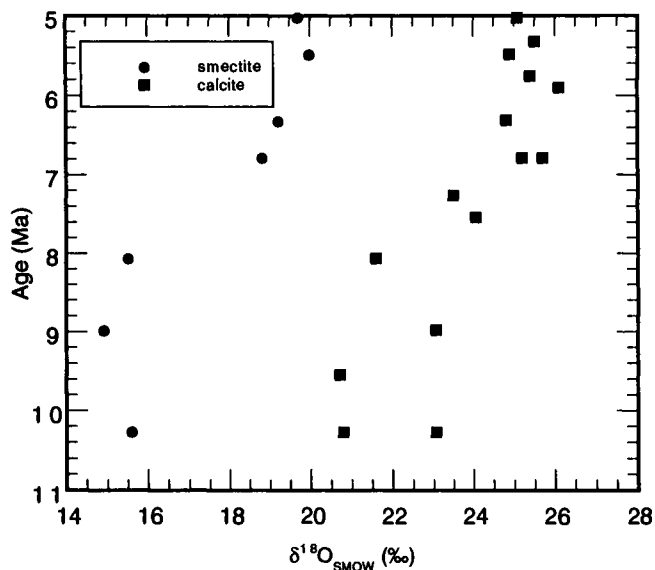


Figure 22.6. $\delta^{18}\text{O}$ values of paleosol minerals versus age from the Siwalik Himalayan molasse, Bhaun, Potwar Plateau, N. Pakistan. Ages determined by magnetostratigraphy (Johnson et al., 1982) and correlation to the magnetic time scale of Cande and Kent (1992). Both the calcite and smectite show a dramatic $\delta^{18}\text{O}$ increase, indicating formation by the same process of pedogenesis. The measured $\Delta^{18}\text{O}_{\text{calcite-smectite}}$ is $\sim 3\text{‰}$ higher than the equilibrium value based on $\Delta^{18}\text{O}_{\text{smectite-water}}$ of Yeh and Savin, 1976 (as reported in Savin and Lee, 1988) and $\Delta^{18}\text{O}_{\text{calcite-water}}$ of O'Neil et al., 1969 (as modified by Friedman and O'Neil, 1977).

the same factors as modern ones. In modern soil carbonates developed on noncalcareous parent material, the carbon isotopic composition is primarily determined by that of soil CO_2 which is a mixture of two components: atmospheric and plant-respired CO_2 . The oxygen isotopic composition of soil carbonate is mainly controlled by that of soil water (Cerling, 1984). When formed at a temperature of 20°C , the soil CaCO_3 phase is enriched by about 10‰ in $\delta^{13}\text{C}$ relative to soil CO_2 and about 30‰ in $\delta^{18}\text{O}$ relative to soil water (O'Neil et al., 1969; Deines et al., 1974).

The carbon isotopic composition of soil carbonate below the zone significantly influenced by atmospheric CO_2 (generally below about 30 cm) is dominated by plant-respired CO_2 . Plant-respired CO_2 , in turn, has a carbon isotopic composition determined by the abundances of local plants using Calvin (C_3) and Hatch-Slack (C_4) photosynthetic pathways. Plants using Crassulacean Acid Metabolism (CAM), such as succulents, may play an important role in some areas (Parada et al., 1983). Pure C_3 plant assemblages, which include trees, most shrubs, and cool-season grasses, respire CO_2 with a mean $\delta^{13}\text{C}$ value of about -27‰ . In contrast, pure C_4 plant assemblages, which include a few annual plants and most warm-season grasses, respire CO_2 with a mean $\delta^{13}\text{C}$ value of about -12‰ . The $\delta^{13}\text{C}$ values of CO_2 respired by CAM plants can switch back and forth between the C_3 and C_4 end members described above, depending on environmental conditions. In general, C_3 and C_4 plants favor different climatic conditions, although they usually are both present in varying proportions depending on a variety of factors such as temperature, soil moisture, and seasonality (Teeri and Stowe, 1976).

The oxygen isotopic composition of soil carbonates is controlled mainly by the $\delta^{18}\text{O}$ of soil water which is derived from atmospheric precipitation and which, in turn, is largely determined by the temperature of cloud formation (see Chapter 3). A strong correlation of decreasing $\delta^{18}\text{O}$ with decreasing mean annual temperature has been observed for modern soil carbonates (Quade et al., 1989a). If paleosol carbonates have not been altered after burial or if soil carbonate horizons on pre-Holocene surfaces have been preserved, the stable isotopic compositions of soil carbonates are useful proxies that can provide paleoclimatic and paleoecological information.

Smith et al. (1993) found that the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonate nodules in paleosols collected from flood plains, channel tracts, and alluvial fans in San Pedro Valley, Arizona, vary with time and with depositional environment. The carbon isotopic variations in depositional facies were attributed to distribution of plants on the paleo-landscape. The $\delta^{13}\text{C}$ variations with time were attributed to the changes of paleoecology and paleoclimate. The changes in oxygen isotopic composition are less well understood, although the $\delta^{18}\text{O}$ values of soil carbonate formed on the flood plains and abandoned fan surfaces are likely to record locally derived water composition (Smith et al., 1993). The $\delta^{13}\text{C}$ values exhibit a minimum (about -6‰ PeeDee Belemnite - PDB) between 2.8 and 3.3 Ma and rise through the late Pliocene to reach uniformly high values (about -1‰ PDB) after 1.6 Ma. Also, $\delta^{18}\text{O}$ decreased after 3.3 Ma and remained relatively low (about -9‰ PDB) until 2.4 Ma before rising concurrently with $\delta^{13}\text{C}$ to about -7‰ PDB in the early Pleistocene. The relatively low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between 2.8 and 3.3 Ma suggest a mixture of C_3 and C_4 plants, an increase in precipitation, and a decrease in seasonality of precipitation with sufficient year-round precipitation to sustain both warm-season and cool-season flora. The comparatively high $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values after 1.6 Ma suggest that the early Pleistocene alluvial fans were vegetated by a nearly pure C_4 grassland and that there was an increase in summer rainfall. In a comparison of their data from the soil carbonates to other continental climate records (e.g. lacustrine histories), Smith et al. (1993) concluded that the stable carbon and oxygen isotopic compositions of paleosol carbonates provide a proxy record of paleoclimate and paleoecosystems.

The $\delta^{13}\text{C}$ of soil carbonate from different-age surfaces in Organ Pipe Cactus National Monument, Arizona (Liu et al., 1996), also show variations with time, but $\delta^{18}\text{O}$ changes little. The $\delta^{13}\text{C}$ values from the last glacial period to Holocene show a significant decrease, from about -6 to about -8‰ (PDB). Mid- to late-Pleistocene (0.7 to 0.2 Ma) soil carbonates are much more enriched in ^{13}C (-4.5‰ PDB). For comparison, the $\delta^{18}\text{O}$ values are invariant at about -6‰ (PDB) for the entire period from the mid-Pleistocene to the Holocene. A similar isotopic distribution pattern for soil carbonate was observed in southern New Mexico and was interpreted to result from expansion of C_3 plants near the end of the last glaciation due to a rapid increase in atmospheric CO_2 concentration rather than to reflect climatic change (Cole and Monger, 1994). However, abundant evidence supports the hypothesis of local and regional warming of at least 5°C at the last glacial termination. Such evidence includes changes in the equilibrium line altitude of glaciers (Porter et al., 1983), lake levels (Markgraf et al., 1984; Phillips et al., 1992; Allen and Anderson 1993; Fleischhauer and Stone 1982), periglacial features (Galloway, 1970; Dohrenwend, 1984), elevational and latitudinal distribution of plants (Betancourt et al. 1990; Van Devender et al., 1987), and noble gas paleothermometer results for groundwater (Stute et al., 1992).

After careful evaluation of geochemical and isotopic processes involved in the formation of the pedogenic carbonate, Liu et al. (1996) attributed the lack of change in the $\delta^{18}\text{O}$ of the soil

carbonate to counteracting effects of the decrease in the $\delta^{18}\text{O}$ of precipitation and the increase in the carbonate-water fractionation factor with decreasing temperature. They proposed that the decrease in the $\delta^{13}\text{C}$ was due to replacement of a glacial-period grassland by Holocene C_3/CAM desert shrubs and succulents. This replacement was probably in response to an increase in temperature and/or a reduction in summer precipitation at the end of the last glacial period. Another contributing factor may be the rapid increase in atmospheric CO_2 concentration at that time. The $\delta^{13}\text{C}$ value of about -4.5‰ for the mid- to late-Pleistocene soil carbonate indicates that the landscape was dominated by C_4 grassland for most of the past 0.7 Ma.

Thus far, many studies have shown the usefulness of $\delta^{13}\text{C}$ of soil carbonates as a paleoecological and paleoenvironmental indicator. The $\delta^{13}\text{C}$ of soil carbonates is linked to paleoclimatic fluctuations, and possibly to changes in atmospheric CO_2 concentrations. The oxygen isotopic composition of soil carbonate is much less sensitive to paleoclimatic changes largely because of counteracting effects of the temperature-induced changes in the $\delta^{18}\text{O}$ of precipitation and the temperature-dependent isotopic fractionation factor.

22.3.5 *Paleoenvironmental reconstruction from stable isotopes in tree rings and plant fossils*

Plant materials provide a valuable source of information for regional paleoclimate reconstruction. Oxygen, hydrogen, and carbon isotopic variations in modern plant cellulose have been related to spatial and temporal patterns in temperature, relative humidity, seasonality and amount of rainfall; carbon isotopic variations in plant cellulose also have been linked to changes in the concentration and isotopic composition of atmospheric CO_2 . Current research is focusing on the underlying physiologic mechanisms responsible for the correlations that have been observed. Although a mechanistic understanding is still evolving, limitations to paleoenvironmental reconstruction due to isotopic variations within plants and populations are being clarified.

Stable isotopes in terrestrial plant matter: introduction

Dendrochronological studies have long exploited visible differences in ring widths for dating and environmental reconstruction, but tree-ring research has evolved to include less obvious differences such as isotopic composition. In many respects, stable-isotope dendrochronology is still in an exploratory stage, with substantial research dedicated to evaluating the areas and limits of application. Many of the results look promising with respect to reconstruction of interannual variations in pollution, atmospheric chemistry, and climate. Useful general reviews of stable isotopes in tree rings have been written by Long (1982), Ramesh et al. (1986b), White (1989), Leavitt (1987, 1993a), and Edwards (1993). To date, much less work has been done utilizing isotopic analyses of plant macrofossils (for example, from packrat middens). The theory and physiologic mechanisms involved in the incorporation of isotopic values into plant cellulose are similar for tree rings and plant macrofossils, with exceptions to be discussed below. For a general review on factors contributing to the isotopic composition of plants, see Lajtha and Marshall (1994).

Abundant and well-preserved leaves of numerous plant species are available from packrat midden deposits found throughout the arid interior of western North America (Betancourt et al., 1990). There are more than 2500 ^{14}C -dated middens spanning the last 40,000 years,

representing the richest source of late Quaternary plant macrofossils in the world (Betancourt et al., 1990). Each deposit contains thousands of identifiable plant fragments typically representing 10 to 40 species. Stable isotopic analyses of fossil plant leaves from middens can focus on isotopic variations for an individual species along environmental gradients (e.g., elevation, latitude) through time. Stable isotope research using packrat midden plant fossils has focused on carbon ($\delta^{13}\text{C}_{\text{cell}}$) and carbon-bound hydrogen ($\delta\text{D}_{\text{cell}}$) of holocellulose. Other preserved plant components (e.g., waxes, lignins) and $\delta^{18}\text{O}$ have yet to be studied in this context.

There are limitations inherent to using fossil plant material from packrat middens aside from those associated with complex, physiologically-mediated, isotopic systems. The first limitation involves dating of the samples. Ideally, radiocarbon dates should be obtained from the actual fossils analyzed for stable isotopic composition, rather than from pellets or other plant material associated with the leaves to be analyzed. Usually, several leaves are required to produce enough CO_2 or H_2O for isotopic analyses. Since these fossils may represent plant growth over a single season, several years or even centuries, the temporal resolution has been uncertain and variable. Recently, accelerator mass spectrometer (AMS) dating has permitted much smaller sample sizes and better resolution. A second limitation is that fossils from a particular sample could represent leaves from a single branch, a single plant, or any number of plants; variations within and between individuals are incorporated but not discriminated.

Stable hydrogen and oxygen isotopes in plant cellulose: theory

The relationships between the isotopic composition of precipitation and temperature (e.g., Dansgaard, 1964; Rozanski et al., 1993) form the basis for analyzing δD and $\delta^{18}\text{O}$ in tree rings to infer climate. The hydrogen in tree rings derives from the local environmental water taken up by roots (White et al., 1994a), and the $\delta^{18}\text{O}$ may derive in part both directly and indirectly (via CO_2 - H_2O isotopic exchange) from local environmental water. The cellulose component of tree rings is preferred for many isotopic studies because of its stability, its well-defined chemical composition, and its non-mobility (it is formed in one year and does not move across tree-ring boundaries).

Cellulose has easily-exchangeable hydrogen bound to oxygen, and non-exchangeable hydrogen bonded to carbon. Epstein et al. (1976) developed nitration techniques to analyze the non-exchangeable hydrogen which have become standard for δD analysis. Yapp and Epstein (1982) analyzed δD in (nitro)cellulose ($\delta\text{D}_{\text{cell}}$) from several species of trees sampled around North America and found a strong relationship to mean annual temperature with a coefficient of $5.8\text{‰ }^{\circ}\text{C}^{-1}$. Gray and Song (1984) analyzed δD in another set of trees from North America and found a strong relationship of $5.5\text{‰ }^{\circ}\text{C}^{-1}$. These early results showed great promise for reconstruction of climate from δD of tree rings because they are quite similar to the temperature coefficient of $5.6\text{‰ }^{\circ}\text{C}^{-1}$ that Dansgaard (1964) found in world-wide precipitation.

Paleoclimatic inferences other than temperature reconstructions have been made from $\delta\text{D}_{\text{cell}}$ in a number of studies such as Yapp and Epstein's (1977) effort to characterize isotopic variation in paleoprecipitation up to 22,000 years B.P. as compared to modern distribution of isotopes in directly-measured precipitation. Dubois and Ferguson (1985) used δD in Scots pine in the Cairngorm Mts. of Scotland to deduce four pluvial (moist) periods in the last 8,000 years. In another study, the δD of submerged logs from Lake Emma, Colorado (Friedman et al., 1988), indicated a shift in moisture or in seasonality of precipitation over the past 10,000 years.

Lack of consistent results in the calibration studies may stem from poor understanding of the mechanisms of incorporation of H isotopes from source water into wood. Complexities of the hydrologic system, such as variable air mass trajectories, evaporation, locally poor drainage, and mixing of waters from different seasons or sources contribute to inconsistent δD results (Long et al., 1990; Friedman et al., 1964). Physiological complexities inherent to biological systems further confound calibration efforts. Although photosynthates (the building blocks of cellulose) are produced in leaves, and leaf water is enriched in δD relative to source water, wood cellulose appears to be more closely related to source water than to leaf water (Terwilliger and DeNiro, 1995). Furthermore, there is evidence that post-photosynthetic modification, such as incorporation of photosynthate stored from prior seasons into wood cellulose, may alter the source water signal to a variable degree (DeNiro and Cooper, 1989; Terwilliger and DeNiro, 1995). According to Yakir (1992), good δD_{cell} -climate relationships from tree rings may result from isotopic exchange of the sugars being translocated in the trunk with the stream of environmental water being drawn up by the roots, which will not yet have been influenced by evaporation at the leaf. Other factors, such as isotopic exchange between leaf water and atmospheric vapor, compartmentalization of leaf water, exchange during carbohydrate transport and metabolism, and species-dependent biochemical fractionation between leaf water and cellulose intermediates, potentially complicate the δD_{cell} - δD_{source} relationship (Yakir, 1992).

Because of rapid equilibration between CO_2 and H_2O in biological systems, water has the greatest influence on $\delta^{18}\text{O}$ of plant cellulose (DeNiro and Epstein, 1979). This link to source water fostered expectations that $\delta^{18}\text{O}$ of cellulose would also have a correspondence with temperature. Gray and Thompson (1976) analyzed cellulose from white spruce tree rings and found a temperature coefficient of $1.3\text{‰ } ^\circ\text{C}^{-1}$. Burk and Stuiver (1981) analyzed $\delta^{18}\text{O}$ in growth rings of trees at various coastal locations where the high relative humidities might limit evaporative effects, and found a temperature coefficient of $0.4\text{‰ } ^\circ\text{C}^{-1}$. These are similar to the temperature coefficient of about $0.6\text{‰ } ^\circ\text{C}^{-1}$ for $\delta^{18}\text{O}$ found in precipitation from temperate regions (Rozanski et al., 1993). The potential influence of relative humidity was shown by Ramesh et al. (1986a), who determined a strong $\delta^{18}\text{O}$ cell-relative humidity coefficient of $-0.19\text{‰ } (\%RH)^{-1}$, although correlations with temperature and rainfall could not be excluded.

Although there are strong correlations of these isotopes in tree rings with source water, the absolute values in the cellulose are not identical to the source water δD and $\delta^{18}\text{O}$. There are fractionation steps between the source water isotopic composition and cellulose composition related to evaporation/transpiration, exchange reactions and biochemical reactions. The recent summary by Ehleringer and Dawson (1992) suggests the biochemical fractionation for δD is "either non-existent for stem tissues or variable within leaf tissues among species;" however, a 27‰ enrichment in $\delta^{18}\text{O}$ in cellulose with respect to source water seems fairly well established and consistent among species (also see Chapter 6).

Quasi-mechanistic models are emerging that link climate variables with physiologically-mediated cellulose isotope values. Edwards and Fritz (1986) and Edwards (1993) developed simultaneous equations for δD and $\delta^{18}\text{O}$ measured in cellulose that could be solved for humidity and the $\delta^{18}\text{O}$ of the environmental water, with assumptions about the various fractionation factors. White et al. (1994a) developed a model for hydrogen isotope fractionation in which δD_{cell} correlates best with source water despite leaf evaporation effects, although they cannot preclude the possibility of re-equilibration of sugars with the sap stream of source water.

Case study: lake levels inferred from δD in tree rings

The long-term isotopic composition of lakes reflects the effects of dry periods (when lake waters become enriched) and wet periods (when lake waters become depleted). Krishnamurthy and Epstein (1985) analyzed δD of nitrocellulose from tree rings of a juniper tree (*Juniperus procera*) from a forest (elevation 2700 m) near Lake Victoria in Kenya as a measure of aridity. In tree rings subdivided into 5-year groupings from 1834 to 1979, δD averaged ca. -10‰ . Based on previous studies (Epstein et al., 1977) indicating that δD of environmental water (i.e., water utilized by the plants in photosynthesis) is about 22‰ heavier than δD of the nitrocellulose, Krishnamurthy and Epstein (1985) inferred a fairly "heavy" source water of ca. $+12\text{‰}$ from the tree-ring values. This δD value for source water is consistent with δD from other lakes in the area.

The unusual features of the δD chronology, however, were a period of elevated values between 1918 and 1933, and a dramatic negative excursion of ca. 20‰ in the 1959-1963 period. The first period encompasses 1919-1923, when Lake Victoria water levels were the lowest in recorded history. Presumably this was a period of high aridity with greater evaporative effects leaving the source water enriched in deuterium. The second period includes 1961, when rainfall was three times the average and water levels of Lake Victoria rose 1-2 m above previous levels. Although storm tracks -- and thus the δD of precipitation -- might have changed during these climatic excursions, the most probable cause of the δD_{cell} variations is the degree of evaporative enrichment of the source water.

Case study: paleoclimate of the Southwestern USA reconstructed from δD in fossil plant cellulose

In the most comprehensive study to date using δD of packrat midden plant fossils, Long et al. (1990) obtained δD_{cell} -temperature relations from leaves of two modern *Juniperus* spp. growing from northern Nevada to southeastern New Mexico to calibrate δD in fossils spanning the last glacial cycle. Regression using growing season temperatures yielded a slope of $4.5\text{‰ }^{\circ}\text{C}^{-1}$ ($r^2 = 0.67$), whereas mean annual temperature gave a slope of $5\text{‰ }^{\circ}\text{C}^{-1}$ ($r^2 = 0.66$). The annual temperature coefficient is reasonably close to the expected value of $5.6\text{‰ }^{\circ}\text{C}^{-1}$. A less significant correlation was found between δD and summer precipitation (as percentage of annual precipitation), which reflects growing season relative humidity. The modern temperature correlation was applied to fossil leaves found in packrat middens dated from $>40,000$ ^{14}C yr B.P. to present to estimate past temperature.

Midden data were collected from 7 fossil species occurring at elevations ranging from about 1400 to 2100 m, at sites up to 800 km apart. δD_{cell} values corrected for elevation and site location effects are shown in Figure 22.7. Using the linear relationship between δD and temperature obtained from modern junipers, a paleotemperature trend was reconstructed that approximated temperatures generated by the NCAR (National Center for Atmospheric Research) Community Climate Model (Kutzbach, 1987). As expected, lowest temperatures (and δD_{cell} values) occurred prior to about 12,000 ^{14}C yr B.P., temperatures were warmest between 5000-8000 ^{14}C yr B.P., and temperatures moderated to intermediate values during the last few thousand years.

In another study, packrat middens containing pinyon pine (*Pinus edulis*) from the Sevilleta Long Term Ecological Research (LTER) site in central New Mexico were analyzed for δD_{cell}

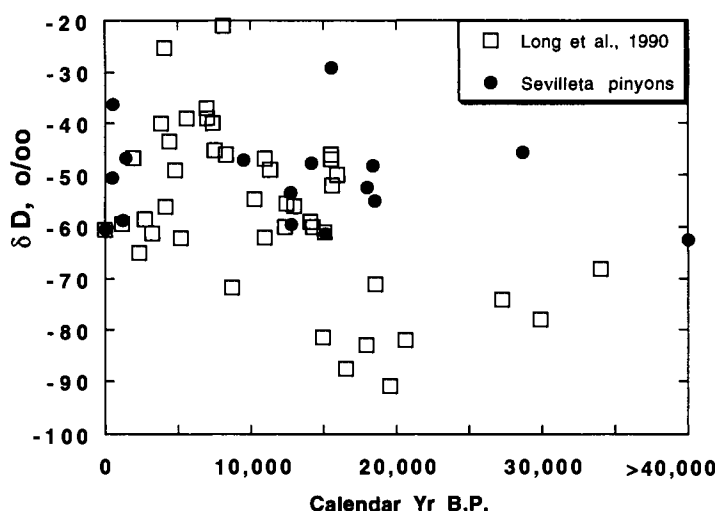


Figure 22.7. Deuterium in fossil and modern leaves as a function of age. Radiocarbon years B.P. were converted to calendar years B.P. following Stuiver and Reimer (1993) back to 17,500 radiocarbon years B.P. Beyond that age, dates are reported as radiocarbon years B.P. Deuterium data from the Sevilleta were corrected for latitude and altitude in the same way as in Long et al. (1990), with modern values falling at -60‰ .

in an attempt to detect environmental changes on a local scale (Pendall, 1997). Midden locations were separated by at most 30 km and 200 m elevation, and only pinyon needles were analyzed. Single-year cohorts of modern needles from the last 10 years had δD_{cell} most strongly correlated with growing season precipitation amount ($r^2 = 0.67$) and growing season relative humidity ($r^2 = 0.50$). Despite controlling for variables except climate, δD_{cell} in Pleistocene middens was not significantly different than that in Holocene middens and modern trees (Figure 22.7). A gap in the record during the middle Holocene was due to the lack of middens during that time, possibly due to drier conditions that reduced ecosystem productivity and packrat activity (Betancourt et al., 1993).

The unexpectedly high δD_{cell} values prior to 10,000 ^{14}C yr B.P. at Sevilleta suggest that late Pleistocene summers were as moist as today; the cold Pleistocene signal found in Long et al.'s (1990) data is not seen in Sevilleta pinyon δD_{cell} . Apparently, pinyons at the Sevilleta used mainly summer rain or soil water that was enriched by evaporation rather than isotopically depleted winter precipitation. Alternatively, low growing season relative humidity may have increased transpiration rates and evaporative enrichment of leaf water. In any case, it appears that changes in seasonality or storm tracks at the Sevilleta could have compensated for lower temperatures and lower δD source values, during the Pleistocene. Continued study of modern $\delta D_{\text{cell}} - \delta D_{\text{source}}$ relationships, such as the study by Terwilliger and DeNiro (1995), is necessary to interpret fossil plant material δD .

Stable-carbon isotopes in plant cellulose: theory

Early studies of $\delta^{13}\text{C}$ in tree rings attempted either to extract climate information by developing empirical climate- $\delta^{13}\text{C}$ relationships (e.g., Wilson and Grinsted, 1977; Pearman et al., 1976),

or to use the $\delta^{13}\text{C}$ of tree rings as a proxy for atmospheric $\delta^{13}\text{C}$ (e.g., Peng et al., 1983; Stuiver et al., 1985; Leavitt and Long, 1988, 1989a) because the only source of carbon fixed into plant matter is atmospheric CO_2 . It became apparent, however, with the carbon isotope fractionation model of Farquhar et al. (1982) (first applied to tree rings by Francey and Farquhar (1982)) that the relation is more complicated:

$$\delta^{13}\text{C}_{\text{plant}} = \delta^{13}\text{C}_{\text{air}} - a - (b-a) C_i/C_{\text{air}} \quad (22.1)$$

where a is a constant representing fractionation as CO_2 diffuses through the stomata (4.4‰), and b is a constant representing fractionation by the photosynthetic enzyme RuBP (29‰). The term C_i is the intercellular CO_2 concentration and C_{air} is the CO_2 concentration of the ambient air. When the ratio of C_i/C_{air} is high, then the plant shows the greatest departure from atmospheric $\delta^{13}\text{C}$ (currently about -8‰) and the greatest ^{13}C depletion. When the ratio is very small, the difference between $\delta^{13}\text{C}$ of the air and the plant is minimum. The rate of carbon fixation and the rate of stomatal conductance are the two primary factors that determine C_i/C_{air} , with high rates of conductance and low rates of fixation promoting high C_i/C_{air} (more negative $\delta^{13}\text{C}$). Environmental conditions that may influence these processes include relative humidity (Saurer and Siegenthaler, 1989), humidity and cloud cover (Ramesh et al., 1986a), light levels (Francey and Farquhar, 1982), drought and moisture stress (Leavitt and Long, 1989b), pollution such as ozone and sulfur dioxide (Martin et al., 1988; Martin and Sutherland, 1990), and nutrient levels (Francey and Farquhar, 1982). Empirical results from field studies (Leavitt and Long, 1991; Leavitt, 1993b) suggest that soil water status, as related to stomatal conductance, may be a primary driving mechanism for the seasonal $\delta^{13}\text{C}$ observed in tree rings. This formidable assortment of environmental variables that could influence $\delta^{13}\text{C}_{\text{cell}}$ confounds attempts to reconstruct changes in $\delta^{13}\text{C}_{\text{air}}$ and/or climate variables from measurements on tree rings.

The plant's water use efficiency (WUE) may link $\delta^{13}\text{C}_{\text{cell}}$ to variations in atmospheric CO_2 concentration (Beerling, 1994; Van de Water et al., 1994). WUE, the ratio of CO_2 assimilation to H_2O transpiration, is directly proportional to the difference between C_{air} and C_i , and inversely proportional to water vapor pressure gradient divided by total atmospheric pressure (v) (Ehleringer, 1991). When plants using the C_3 photosynthetic pathway restrict water loss by reducing stomatal apertures, continued CO_2 assimilation reduces. This decreases C_i , causing the plant to be less selective against $^{13}\text{CO}_2$ than it would under less water-stressed conditions. Larger $C_{\text{air}} - C_i$ leads to greater WUE and more positive $\delta^{13}\text{C}$. If $\delta^{13}\text{C}_{\text{air}}$ effects are removed, $\delta^{13}\text{C}_{\text{cell}}$ may be a drought indicator (Leavitt and Long, 1989b). If $\delta^{13}\text{C}_{\text{air}}$, temperature and relative humidity are constrained, $\delta^{13}\text{C}_{\text{cell}}$ may be used to estimate atmospheric CO_2 concentration (White et al., 1994b). These relationships are dependent on stomatal response to environmental conditions, which varies among, and possibly even within, species (Terashima et al., 1988).

Case study: soil moisture conditions correlated with $\delta^{13}\text{C}$ in tree rings

Empirical modeling of tree-ring $\delta^{13}\text{C}$ series at a site with long, detailed climate records suggests that, indeed, soil moisture plays a key role, even in relatively mesic environments. Dupouey et al. (1993) investigated $\delta^{13}\text{C}$ in tree rings at an experimental beech (*Fagus sylvatica* L.) forest 18 km from Nancy, France. Rings for each year from 1950-1990 were pooled from these 16

cores, and the holocellulose component was extracted after grinding (Leavitt and Danzer, 1993). A bioclimatic model of total evapotranspiration in forests (Chassagneux and Choiseul, 1986) was used with climate data from Nancy to estimate soil water content and percent remaining extractable water (PREW) from 1950-1990. Tree-ring $\delta^{13}\text{C}$ was highly correlated with stand basal area increment (BAI) ($r = -0.59$) and more strongly correlated to BAI than to ring width. The $\delta^{13}\text{C}$ values could be modeled quite well ($r^2 = 0.71$) by the relation:

$$\delta^{13}\text{C} = -13.39 - 0.033\text{PREW}_{(\text{July})} + 0.39 \delta^{13}\text{C}_{(n-1)} \quad (22.2)$$

The $\delta^{13}\text{C}$ correlation with PREW alone is high ($r = -0.77$), but the extra term above for $\delta^{13}\text{C}_{(n-1)}$ suggests carbon contributed from the end of the previous year is stored and contributes to the current year's value. A model of BAI using PREW produced a weaker relationship ($r^2 = 0.38$) than the above model with $\delta^{13}\text{C}$. Dupouey et al. (1993) concluded that $\delta^{13}\text{C}$ best integrates variation in transpiration during the growing season, and is a reliable indicator of past interannual variations of water availability.

Livingston and Spittlehouse (1993) also found $\delta^{13}\text{C}$ strongly correlated with modeled April to August accumulated growing-season transpiration in Douglas-fir (*Pseudotsuga menziesii*) trees in British Columbia over a 17-year period ($r^2 = 0.61$, significant at 99.9%), but in this study BAI had a somewhat stronger relationship with accumulated transpiration ($r^2 = 0.55$ or $r^2 = 0.75$ with one outlier removed). The study found differences in strength of these relationships for two nearby sites as a function of different soils, and determined accumulated transpiration was a more useful parameter than accumulated water deficit, although most correlations with water deficit were still significant.

Case study: environmental change detected in $\delta^{13}\text{C}$ of fossil plant cellulose

If other environmental variables are held constant (or assumed), $\delta^{13}\text{C}$ of leaf cellulose may reflect atmospheric CO_2 concentration (White et al., 1994b). Van de Water et al. (1994) analyzed $\delta^{13}\text{C}_{\text{cell}}$ of limber pine (*Pinus flexilis*) needles from middens in the southwestern USA from 40,000 yr B.P. to present. A pattern emerged of decreasing $\delta^{13}\text{C}_{\text{cell}}$ during deglaciation that paralleled a pattern of decreasing leaf stomatal density over the same period. Because the authors attempted to hold climate constant by selecting glacial-age middens from more southerly locations and post-glacial age middens from more northerly locations, they inferred these changes were largely a consequence of atmospheric CO_2 concentration increasing ~ 70 - 80 ppm during deglaciation. Using C_{air} from ice core data and $\delta^{13}\text{C}_{\text{air}}$ from C_4 plants and ice core measurements, they inferred a 15% increase in water-use efficiency (WUE) for limber pine during deglaciation. The increase in WUE with higher CO_2 levels, however, was not enough to offset the effect of increased aridity occurring at this time (Betancourt et al., 1990).

It is likely that the exact physiological response to shifting CO_2 concentrations will be species-specific. For example, Leavitt and Danzer (1992) report a $\delta^{13}\text{C}_{\text{cell}}$ decrease of 0.44‰ in *Juniperus* spp. during deglaciation. Pinyon pine $\delta^{13}\text{C}_{\text{cell}}$ from middens at the Sevilleta LTER increased by ~1.5‰ over a similar time period; no attempt was made to hold climate constant through site selection. At Sevilleta, enrichment may be a function of increasing aridity into the Holocene (Pendall, 1997).

The physiology of plants using the C_4 photosynthetic pathway allows them to take up atmospheric CO_2 with less effective carbon isotopic fractionation than in C_3 plants, by maintaining more constant C_i/C_{air} ratios (Marino and McElroy, 1991). This results in $\delta^{13}C_{cell}$ that closely reflects $\delta^{13}C_{air}$. Hence, estimates of $\delta^{13}C_{air}$ variations from $\delta^{13}C_{cell}$ of fossil C_4 cellulose could be used to constrain hypotheses about past atmospheric CO_2 variations, or to estimate WUE for C_3 plants (Marino et al., 1992; Toolin and Eastoe, 1993; Van de Water et al., 1994; Beerling, 1994). $\delta^{13}C_{cell}$ in leaves from the C_4 shrub, shadscale (*Atriplex confertifolia*), found in packrat middens gave an estimated $\delta^{13}C_{air}$ increase of $\sim 0.7\text{‰}$ during deglaciation (Marino et al., 1992). However, these *Atriplex* samples occurred in middens containing species that indicated a shift from cool, humid conditions during the last glacial to warm, dry conditions in the Holocene. Thus, the shift in isotopic composition may merely be a response to increasing aridity. Both light and water supply have been shown to influence isotopic composition in modern C_4 grasses (Tieszen and Boutton, 1989; Buchmann et al., 1996). Clearly, additional stable carbon isotope data are needed from a variety of C_4 species that occur in the fossil record, especially in cases where climate can be held constant by site selection.

Stable isotopes in tree rings and plant fossils: summary

There is a considerable potential for accurate and well-quantified reconstruction of past environmental parameters from stable isotopes in plant matter such as tree rings and packrat midden fossils. In this emerging subfield, studies with unexpected or contradictory results can be useful for evaluating previously disregarded influences. Additional study on modern systems to assess the effects of single environmental parameters by measuring or holding other factors constant will help elucidate the physical and physiological bases, and thus provide a stronger foundation, for isotopic reconstructions.

22.3.6 Lacustrine environments: organics

Coupled oxygen and carbon isotope analyses on the fine-grained ($<500\text{ }\mu\text{m}$) cellulose fraction of lacustrine organic matter have recently emerged as an effective tool for reconstructing hydrological conditions and carbon cycle pathways in lake watersheds (e.g. Edwards and McAndrews, 1989; Edwards, 1993; MacDonald et al., 1993; Duthie et al., 1996; Wolfe et al., 1996; Wolfe and Edwards, 1997; Beuning et al., 1997). Although studies thus far have been limited, this approach holds much promise, especially for lakes that lack continuous records of inorganic or biogenic carbonate, the more traditional lacustrine archives of isotopic data.

An important condition for using this technique is that the cellulose in the fine-grained lake sediment have a lacustrine origin. Results from eastern and northern Canada (Wolfe et al., 1996), western Canada (Padden, 1996) and northern Russia (Wolfe et al., 1997), suggest that this requirement is often met in many different hydrologic and ecologic settings. The rationale for interpreting oxygen isotopic composition of lacustrine-derived lake sediment cellulose can be summarized in the following equation:

$$\delta^{18}O_{cell} = \delta^{18}O_{lw} + \epsilon_{cell-lw} \quad (22.3)$$

$\epsilon_{cell-lw}$ represents the isotopic separation between cellulose and lake water and is essentially constant, apparently unaffected by changes in temperature and plant species (Epstein et al.,

1977; DeNiro and Epstein, 1981; Sternberg and DeNiro, 1983; Sternberg et al., 1984; Sternberg et al., 1986; Sternberg, 1989; Yakir and DeNiro, 1990). Therefore lake water $\delta^{18}\text{O}$ histories, which can provide information on changes in catchment hydrology, can be directly inferred from the $\delta^{18}\text{O}$ of cellulose in sediment cores. This is in sharp contrast to oxygen isotope studies of lacustrine carbonates which require assumptions on the temperature of mineral or biogenic precipitation to reconstruct lake water $\delta^{18}\text{O}$. Assuming a lacustrine origin and constant $\epsilon_{\text{cell-lw}}$, interpretation of $\delta^{18}\text{O}$ in lake sediment cellulose is reduced to distinguishing the degree of influence of (1) the isotopic composition of input waters determined by surface and subsurface inflow, and precipitation falling directly on the lake and (2) hydrologic factors, principally the inflow:evaporation ratio, which can modify the input isotopic signature.

Many researchers continue to utilize carbon isotopes in bulk organic lake sediments ($\delta^{13}\text{C}_{\text{org}}$) to acquire paleolimnologic information, as pioneered by Oana and Deevey (1960), but interpretation is hampered for several reasons. Early reviews by Stuiver (1975) and Hakansson (1985) showed that many different processes can invoke similar shifts in the $^{13}\text{C}/^{12}\text{C}$ ratio. For example, increased lake productivity, reduced contribution of respired $\text{CO}_2(\text{aq})$ from bottom waters or sediment to the dissolved inorganic carbon (DIC) pool, lake water $\text{CO}_2(\text{aq})$ equilibration with the atmosphere, and decreased supply of DIC from non-carbonate bedrock catchments can all result in ^{13}C -enrichment trends in profiles of bulk organic lake sediment. Second, delivery of both aquatic and terrestrial material to lake sediment can complicate the $\delta^{13}\text{C}_{\text{org}}$ record. Consequently, additional analyses such as isotopic measurement of macrofossils of known origin and carbon/nitrogen ratios are required to ascertain the importance of autochthonous and allochthonous contributions (e.g. Aravena et al., 1992; Meyers, 1990). Third, major components of plant matter have varying carbon isotopic composition (Deines, 1980) and a change in the relative proportion of these constituents preserved in lake sediments (e.g., as a result of selective degradation of labile fractions) may cause a shift in $\delta^{13}\text{C}_{\text{org}}$ that is unrelated to any climate-induced isotopic effect (Epstein et al., 1976). Although interpretation remains qualitative and often speculative, fine-grained cellulose offers an alternative to bulk organic matter because it frequently appears to be aquatic in origin, is resistant to degradation, and can be isolated using a well-established technique (Edwards and McAndrews, 1989). As a result, analysis of $\delta^{13}\text{C}_{\text{cell}}$ generally provides a better isotope record of DIC, the carbon source for particulate aquatic organic carbon.

Recent investigations of paleohydrological change have been performed at the central Canadian northern treeline (MacDonald et al., 1993; Wolfe et al., 1996). Queen's Lake and Toronto Lake are located on the tundra, although paleobotanical evidence has indicated that the terrestrial landscape in this region supported forest-tundra vegetation during the mid-Holocene (MacDonald et al., 1993; Wolfe et al., 1996). Carbon and oxygen isotope analyses on cores of organic sediment from these lakes provide insight to changes in catchment hydrology during this period of climate amelioration (Figure 22.8).

Studies of modern hydrology in northern Canada demonstrate that changes in lake water isotopic composition in basins with low inflow:evaporation ratio are mainly related to changes in water balance (Bursey et al., 1991; Gibson et al., 1993; Taal, 1994). Therefore marked fluctuations in $\delta^{18}\text{O}_{\text{cell}}$ (Figure 22.8), particularly evident at Toronto Lake, are likely due to shifts between closed basin, strongly evaporative conditions (enriched $\delta^{18}\text{O}$) and intervals of open basin hydrology when the inflow:evaporation ratio was high (depleted $\delta^{18}\text{O}$). Both the Queen's Lake and Toronto Lake $\delta^{18}\text{O}_{\text{cell}}$ records show that relatively moist conditions (i.e.,

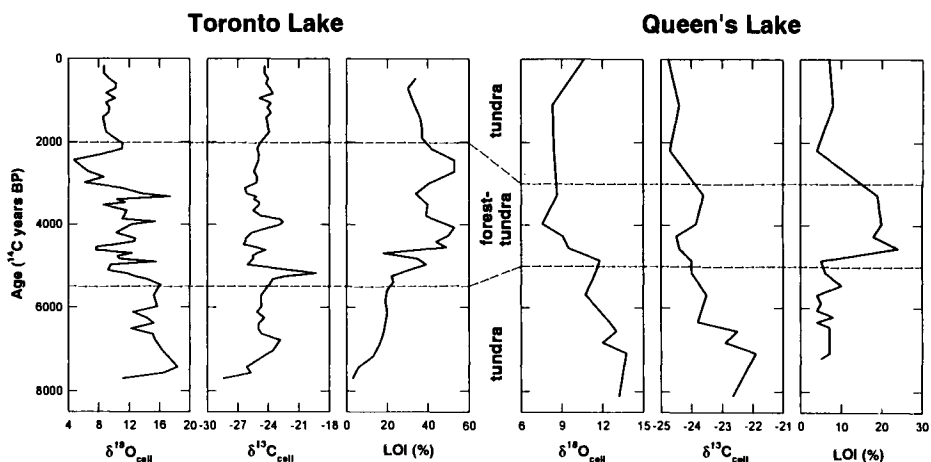


Figure 22.8. Isotope and loss-on-ignition (LOI) records from tundra sites, Toronto Lake (T) and Queen's Lake (Q), located in central Canada (see MacDonald et al., 1993 and Wolfe et al., 1996 for methods). Extrapolation between conventional radiocarbon dates on bulk organic sediment provide chronological control for the cores; vegetation zones are based on pollen records from Toronto Lake and Queen's Lake (MacDonald et al., 1993). Note that Toronto Lake contains a longer forest-tundra interval because it is closer to this ecotone.

depleted $\delta^{18}\text{O}$) occurred during the forest-tundra interval, particularly during peak periods of forest development (MacDonald et al., 1993; Wolfe et al., 1996), yet hydrologic change was much more rapid and frequent at Toronto Lake. Although the apparent higher frequency of hydrologic response might be an artifact of the better temporal resolution at Toronto Lake, a more likely explanation is the contrasting hydrologic settings of the two lake-catchments. Queen's Lake drains a considerably smaller catchment (ca. 200 ha) than Toronto Lake (ca. 2900 ha) and thus contains a $\delta^{18}\text{O}_{\text{cell}}$ record that is largely dependent on the hydrologic sensitivity of this single lake. Toronto Lake, in contrast, is downstream of two subcatchments that under present climatic conditions have markedly different hydrologic budgets. The larger of the two subcatchments (ca. 2100 ha) yields continuous outflow during the thaw season, whereas the smaller subcatchment (ca. 650 ha) apparently discharges only intermittently following spring freshet. Abrupt changes in the size of the contributing drainage basin area, in response to changes in moisture conditions in the past, would have strongly influenced residence time and degree of evaporative enrichment. These events were recorded downstream at Toronto Lake as rapid, several permil oscillations in the $\delta^{18}\text{O}_{\text{cell}}$ profile.

The tundra to forest-tundra transition was also marked by increased lake productivity at both Queen's Lake and Toronto Lake. This is reflected by increased organic content (i.e. high loss-on-ignition) and positive trends in $\delta^{13}\text{C}_{\text{cell}}$ (Figure 22.8) caused by productivity-driven enrichment in DIC and perhaps decreased fractionation between the DIC and phytoplankton due to low concentration of $\text{CO}_2(\text{aq})$. The rapid changes in hydrologic status of the Toronto Lake catchment from relatively closed to open-basin conditions also significantly influenced the $\delta^{13}\text{C}_{\text{cell}}$ record. Depleted $\delta^{18}\text{O}_{\text{cell}}$ peaks (i.e. open-basin conditions) correlate with the termination of $\delta^{13}\text{C}_{\text{cell}}$ enrichment trends, including at 5100, 4500, and 3500 yr B.P. during the forest-tundra interval. Increased flow rate through the lake during these intervals caused a flushing out of ^{13}C -enriched DIC with ^{13}C -depleted DIC and, likely, replenished the $\text{CO}_2(\text{aq})$

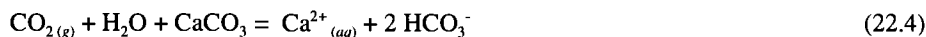
supply to thriving phytoplankton. In spite of high levels of productivity, as suggested by continued increased deposition of organic matter at these strata, $\delta^{13}\text{C}_{\text{cell}}$ became more negative. During the most recent period of increased productivity at about 2700 yr B.P., the carbon isotopic record remains constant probably because productivity-driven enrichment in DIC was offset by the supply of ^{13}C -depleted DIC and rapid lake water renewal.

Oxygen and carbon isotope analyses on lake sediment cellulose from Queen's Lake and Toronto Lake indicate that in catchments of north-central Canada, both water and carbon balance changed rapidly during the mid-Holocene interval of northward treeline migration. More humid conditions accompanied natural climate warming, thus providing data critical for testing models of projected climate change and its impact on northern regions. $\delta^{18}\text{O}_{\text{cell}}$ and $\delta^{13}\text{C}_{\text{cell}}$ combine to form a powerful approach for paleoenvironmental reconstruction and are a recommended component in multidisciplinary research strategies of lake sediment coring programs.

22.3.7 *Lacustrine environments: authigenic carbonates*

Many lakes around the world have chemistries that allow the precipitation and preservation of authigenic carbonates. The stable-isotopic composition of these carbonates in stratigraphic sequences can be used as proxies of both climatic and environmental changes through time. Since Stuiver (1968, 1970) first applied the method to lake sediments, carbonate isotope research has documented temperature changes, moisture-source variations, and fluctuations in the hydrologic balance of lakes.

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of lake carbonates are intrinsically related to the seasonal timing and conditions of crystallization. Calcite precipitation occurs primarily in the epilimnion of hardwater lakes and is described by the equation:



Processes that remove CO_2 from the water, such as degassing or photosynthetic uptake by phytoplankton, can increase the pH. In temperate lakes, Ca^{2+} and HCO_3^- concentrations reach supersaturation during summer (Dean and Megard, 1993). Tropical and sub-tropical lakes that do not experience ice cover can precipitate calcite year-round.

The source of carbon incorporated into calcite is dissolved inorganic carbon (DIC) in the lake. Within the DIC pool, carbon is distributed between CO_2 , CO_3^{2-} , and HCO_3^- . Although the isotopic fractionation between these ionic species was experimentally determined by Mook et al. (1974), the overall $\delta^{13}\text{C}$ of the DIC reflects a variety of sources, which may vary in importance through time. These sources include root respiration in the catchment, types of vegetation and their related photosynthetic pathways (e.g., C_3 , C_4 , and CAM), dissolution of limestone or dolostone, atmospheric exchange, photosynthetic uptake by algae, and oxidation of organic debris in the sediment.

The greater natural variability of $\delta^{18}\text{O}$ in lakes compared to oceans makes it much more sensitive to climate change in lakes, but also more difficult to interpret. The links between climate and lacustrine carbonates are expressed in the fractionation equation for oxygen between calcite (c) and water (w) from 0 to 500°C given by Friedman and O'Neil (1977):

$$10^3 \ln(a_{c-w}) = 2.78(10^6 T^{-2}) - 2.89 = \delta^{18}O_c - \delta^{18}O_w \quad (22.5)$$

where a is the fractionation factor. This equation shows that the $\delta^{18}O_c$ depends on both the temperature of calcite formation ($-0.24\text{‰ } ^\circ\text{C}^{-1}$; Epstein et al., 1953) and the $\delta^{18}O$ of the water, which is controlled by hydrologic factors. Since the temperature of calcite formation is related to water temperature, it can be limited to a range between approximately 3 and 30°C . The actual range will be much smaller, especially in temperate regions where calcite precipitates only in summer. According to the above equation, a long-term increase in temperature would result in a decrease in $\delta^{18}O_c$. However, the hydrology of the lake may produce the opposite relationship in $\delta^{18}O_c$ by affecting the $\delta^{18}O_w$.

A number of early paleoclimate studies made unrealistic assumptions about the hydrology of lakes, almost treating them as passive "buckets" in the landscape whose isotopic composition reflected that of mean annual precipitation. As shown by Chapter 14, groundwater/stream/lake interactions can be very complex; a number of hydrologic factors may further compromise the air temperature- $\delta^{18}O_c$ relation, as briefly discussed below.

Hydrologic inputs

1. *Precipitation:* As presented in Chapter 3, the $\delta^{18}O$ of precipitation increases with mean air temperature at a rate of $0.6\text{‰ } ^\circ\text{C}^{-1}$. The application of the air-temperature/precipitation isotopic relation to trends in lake $\delta^{18}O_w$ requires several assumptions (minimal rain-out effects, minimal recycled water added to airmass, and constant moisture source for precipitation) which cannot always be verified for paleoclimatic studies. Although fairly constant for the last 8000 years or so, the $\delta^{18}O$ of ocean water was as much as 1.2‰ greater during the last glacial period (Shackleton, 1967; Fairbanks, 1989).

2. *Streamflow:* The $\delta^{18}O$ of inflowing streamwater is an important control on $\delta^{18}O_w$ in many lakes. Paleoclimatic reconstructions often assume that streamflow is either a minor component or that its $\delta^{18}O$ is the same as meteoric water. However, in a chain of lakes, the inflow might actually represent enriched water derived from the lake upstream (e.g. Pyramid Lake, Nevada; Benson, 1994). In certain instances, the diversion of a stream into a lake can alter the $\delta^{18}O$ of the lake water significantly, producing a "false" climatic signal (Schwalb et al., 1994). In many temperate and sub-arctic lakes, spring runoff from snowmelt, which has depleted $\delta^{18}O$ values, is the most important hydrologic event of the year. Depending on the amount of snowmelt and the hydraulic residence time, the effect of this large input of depleted $\delta^{18}O$ may persist into the calcite-forming season.

3. *Groundwater:* The amount of groundwater that enters a lake is site-specific and depends on the recharge area, hydraulic gradient, and hydraulic conductivity of the surrounding material. The isotopic composition of groundwater may plot near the MWL in areas of rapid recharge or may be enriched in arid regions or areas of slow recharge. In addition, the lag in travel time between the point of recharge and the lake may be days to thousands of years. In the latter case, the proportion of groundwater discharge must be critically assessed. Early climatic reconstructions from carbonates tended to ignore the groundwater component. More recent studies (Smith et al., 1997; Schwalb et al., 1995) have begun to focus on this component in greater detail.

Hydrologic outputs

1. *Evaporation:* The effect of evaporation is to increase the $\delta^{18}\text{O}_w$ (Craig et al., 1963). Evaporative concentration in lakes depends on temperature, the relative humidity gradient, and wind speed. Although absolute amounts of evaporation cannot be determined, the evaporative history can be very useful in reconstructing past climates. In lakes where the primary or only output is evaporation, isotopic changes are related to the local climate (warm and dry, cool and wet) and may completely overprint the original composition of the precipitation that was the source of the water.

2. *Outflow:* Groundwater flow and streamflow out of a lake do not alter the isotopic composition of the lake directly. They do affect the composition indirectly by controlling the residence time of the water. Lakes with long residence time may undergo considerable evaporative concentration of ^{18}O , whereas open lakes with shorter residence times may have less evaporative concentration due to the high flushing rate.

In-lake processes

In addition to hydrologic considerations, there are some in-lake processes that may affect climatic interpretations: (1) Other carbonate minerals including Mg-calcite, aragonite, siderite, rhodochrosite, kutnohorite, and dolomite can also precipitate from lake water. Because of fractionation differences, admixtures in the sediment can complicate climatic reconstruction efforts. This problem also applies to detrital mixing between two carbonates that were formed in different environmental conditions. (2) Once calcite crystals are stored in the sediment, exchange with the pore water will be minimal. However, methanogenesis and sulfate reduction can increase the bicarbonate in pore water and induce precipitation of a secondary set of carbonate minerals, which would have a different isotopic signature from those precipitated in the epilimnion.

In summary, the net value of $\delta^{18}\text{O}_c$ reflects (1) the $\delta^{18}\text{O}$ of lake water, which increases with increasing air temperature and/or aridity, and (2) the temperature dependence of the fractionation factor, which characterizes the decrease in $\delta^{18}\text{O}_c$ with an increase in water temperature. Because the $\delta^{18}\text{O}$ of lake carbonates is linked to climate via $\delta^{18}\text{O}_w$, the hydrologic balance of each site must be studied to determine which factor (temperature of atmospheric precipitation or aridity) controls the isotopic composition of the water now and in the past.

Case studies

Paleoenvironmental reconstructions from the stable-isotopic records in lake sediments focus mainly on fluctuations in air temperature and effective moisture (precipitation - evaporation). Air temperature is a dominant control on the isotopic composition of atmospheric precipitation and thus directly affects the isotopic composition of the lake water. Variations in effective moisture may cause changes in water residence time that can be related to changes in lake level. The isotopic composition of calcite will record the longer residence time as an increase in $\delta^{18}\text{O}$, as ^{16}O is preferentially removed. The following two case studies serve as separate examples of the application of isotopes to reconstruct (1) temperature change, and (2) fluctuations in effective moisture.

Red Bog, Ireland. The isotopic record from sediments at Red Bog in southwestern Ireland (Ahlberg et al., 1996) reflects fluctuating air temperature at the transition from cold glacial to

warm Holocene conditions. The climate at Red Bog is dominated by the North Atlantic Drift and by westerly circulation, which brings warm winds and moisture from the Atlantic. During the Younger Dryas cold interval (11,650 to 12,850 years B.P.; Alley et al., 1993) at the end of the last glaciation, the North Atlantic Drift and polar front were displaced to the south. Colder temperatures at the site of evaporation (due in part to icebergs) produced a lower $\delta^{18}\text{O}$ signal in the northwestern air mass. Temperatures were also cooler along the track of the air mass, resulting in an additional decrease in the $\delta^{18}\text{O}$ of atmospheric precipitation over the lake site.

The relatively high $\delta^{18}\text{O}$ of the marl (-1 to -3‰) between 610-550 cm (Figure 22.9) indicates warmer temperatures at the end of the full glacial. A temperature decrease associated with the onset of the Younger Dryas and the southward shift of the North Atlantic Drift (Ruddiman and McIntyre, 1981) resulted in lighter $\delta^{18}\text{O}$ (-5 to -6‰) between 500-425 cm. The abrupt shift back to higher $\delta^{18}\text{O}$ at 400 cm is concurrent with the rapid increase in temperature at the end of the Younger Dryas. $\delta^{18}\text{O}_c$ values remain fairly constant for the remainder of the sequence, signifying a single moisture source and fairly constant temperatures, associated with the milder Holocene climate. Similar isotopic patterns in lake sediments around the world have been interpreted as representative of temperature fluctuations and include records from Gerzensee, Switzerland (Eicher and Siegenthaler, 1976), Rotsee, Switzerland (Lotter and Zbinden, 1989), Lake Zurich (Lister, 1988a), Lake Gosciarz, Poland (Rozanski et al., 1992), Elk Lake, USA (Dean and Stuiver, 1993), and Lake Mina, USA (Stevens, 1997).

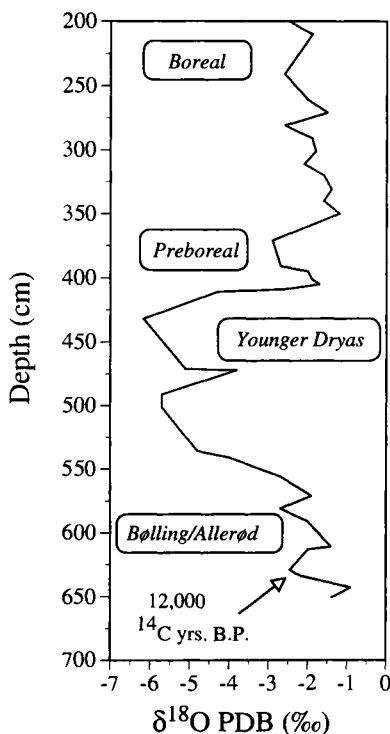


Figure 22.9. $\delta^{18}\text{O}$ as a function of depth, Red Bog, Ireland. Modified from Ahlberg et al., 1996.

Lake Mina, Minnesota, USA. In regions with significant seasonal moisture deficits, the isotopic composition of lake carbonates may preserve a record of the hydrologic balance (i.e. water residence time) of the lake. Lake Mina is a deep, freshwater lake at the transition from positive effective-moisture in the Midwest to negative effective-moisture in the Great Plains. Interannual shifts in the position of this transition zone are common. As a result, the isotopic composition of Lake Mina and its carbonates should be more sensitive to fluctuations in the hydrologic balance than to temperature changes.

Because of the depth of the lake, organic varves (sedimentary layers that consist of a summer calcite layer and winter organic layer) are preserved. These couplets were assigned a calendar date (error of 2 - 3 years). The $\delta^{18}\text{O}$ profile constructed from these layers is compared to the Palmer Hydrologic Drought Index (PHDI) (Figure 22.10). Negative values of the drought index (black shading) indicate dry conditions. During the dust-bowl drought of the early 20th century, an increase in aridity due to decreased precipitation and increased temperatures caused reduced surface-water inflow and groundwater recharge, resulting in lowered lake levels and longer water residence times. These factors culminated in an increase in $\delta^{18}\text{O}_c$ by as much as 3‰ during the 1920's and by 2.2‰ in the 1930's (Stevens, 1997). Other less severe droughts are also indicated in the isotopic record as an increase in $\delta^{18}\text{O}_c$. The offset between the PHDI and $\delta^{18}\text{O}_c$ may result from errors in dating or from a natural lag in the hydrologic response to drought. Additional isotopic records have been interpreted as a function of an effective moisture signal in other lakes including Medicine Lake, USA (Valero-Garcés et al., 1994), Lake Bosumtwi, Ghana (Talbot, 1990), Magadi, Kenya (Hillaire-Marcel and Casanova, 1987), Lake Turkana, Kenya (Johnson et al., 1991), and Lake Van, Turkey (Schoell, 1978).

22.3.8 *Lacustrine environments: ostracodes*

Ostracodes are microscopic crustaceans with calcite carapaces that are common in marine and in continental aquatic environments. Continental ostracodes usually live in, on, or near the substrate, and require oxygenated conditions at the sediment-water interface, at least during part of the year. They generally are absent from highly ephemeral water bodies such as playa lakes (Forester 1987, Delorme 1990).

Continental ostracodes are valuable for modern and past hydrologic studies, because each species has characteristic environmental sensitivities. They are often restricted to particular environmental settings such as springs, streams, lakes, wetlands, or aquifers. Within those settings each species is limited to certain ranges of physical (e.g. temperature) and chemical (e.g. total dissolved solids (TDS) or solute composition) properties. Thus, some or all of the ostracodes living in a cold freshwater spring will differ from those in a cold freshwater lake, or from those in a warm saline spring. Moreover, aquifer taxa, though poorly known ecologically, differ in shell form from surface-water taxa. Because many of the climate-linked aquatic parameters limit ostracode viability, a species' biogeographic range may be described in climatic terms. Ostracode biogeographic ranges expand or contract rapidly (months to years) as climate and the commensurate aquatic properties change. Thus ostracodes also offer insights into climate driven hydrological changes on the landscape, whether within a time scale of human records or of changes in climate state such as those from the last glacial to interglacial period (10 to 12 ka) (Forester, 1991; Forester et al., 1994; Smith and Forester, 1994).

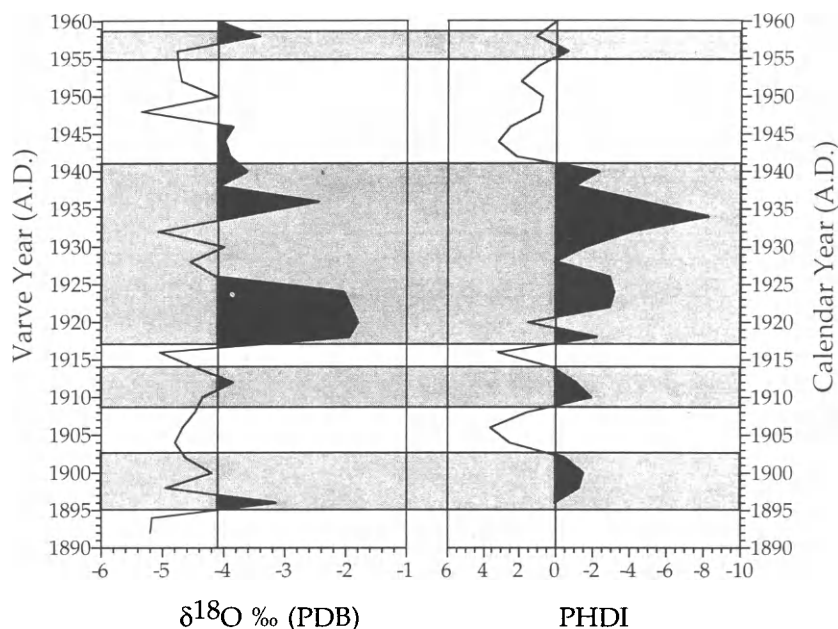


Figure 22.10. $\delta^{18}\text{O}$ (PDB) of lacustrine carbonate and Palmer Hydrologic Drought Index (PHDI) profiles, Lake Mina, Minnesota. Periods of drought are denoted on the PHDI profile as negative numbers (black areas). The droughts in the 1920's and 1930's resulted in a $\delta^{18}\text{O}$ increase in the isotopic profile.

The ostracode valve offers another advantage for recognition of various environmental properties, through an isotopic and geochemical record of the environment in which it calcified. Ostracode valve composition, e.g. Sr/Ca or Mg/Ca ratios, may identify changes in total dissolved solids (TDS) or temperature, or mixing of different water sources. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of ostracode valves from a stratigraphic sequence, such as a sediment core, provide a way to identify changes in the properties of the source waters whether those changes are due to climate or local hydrologic change. Similarly, strontium isotopes from the valves may reveal solute sources in the water body, and water-rock interactions along flow paths (DeDeckker and Forester, 1988; Last et al., 1994).

Collection of stable isotope data from continental ostracodes is now common, but is a recent paleohydrological and paleoclimate tool (Lister, 1988b). Heaton et al. (1995) summarize applications as well as the systematic properties of ostracode stable isotope data. Whereas ostracode stable isotopes appear to be relatively precise recorders of their environment, a number of studies note that stable oxygen isotope values are higher than values expected for inorganic calcite in equilibrium (Heaton et al., 1995, references therein). A similar relationship was observed in springs from southern Nevada (R. Forester, unpublished data). In two examples, ostracode stable oxygen isotope values average 2.23 and 1.07‰ higher than expected for equilibria. Temperature differences between the springs, 33 and 17 °C, respectively, do not explain the disequilibria. Other factors that might affect calcification rates, such as the availability of Ca, may explain the disequilibria, but would require that calcification was at a slower than equilibrium rate, which is atypical of biogenic carbonate.

Case study: Pahrnagat marshes

The southern Pahrnagat Lake in southern Nevada (37.22° N, 115.08° W) is a saline wetland in the White River channel, which contains many fresh and saline wetlands and marshes along its course. A 5-m sediment core, with a basal age of about 2000 radiocarbon years, was taken by the Desert Research Institute of Reno, Nevada, and sampled at 4-cm intervals for ostracodes and pollen. The profile of ostracode species indicates that in the recent past the site has alternated between a saline wetland and a freshwater, spring-discharge dominated marsh. The profile indicates that the White River has had no sustained flow recently. The wetlands probably receive subsurface flow via the White River channel sands and gravel. They also receive discharge from shallow springs (temperatures about 12 to 20 °C), and limited discharge from deep aquifers (temperatures about 28 to 36 °C). Starting near the beginning of this century, human influences on local hydrology, such as periodic flushing of the southern wetland with freshwater from other nearby wetlands, are also evident in the ostracode and pollen record (P. Wigand, written communication, 1994).

The wetland ostracode assemblage is dominated by *Limnocythere sappaensis*, a salt loving ostracode, which requires a (bi)carbonate-enriched, calcium-depleted solute composition (Forester, 1986). The observed TDS range of *L. sappaensis* is 0.7 to 110 g/L (mean = 12 g/L; R. Forester, unpublished data). The marsh freshwater ostracode assemblage includes *Candona caudata*, *C. acuminata*, and *Cypridopsis vidua*, which indicate that (bi)carbonate and calcium dominate or comprise an important part of the solute composition. The observed TDS range of *C. caudata*, the most common marsh species, is 70 to 5000 mg/L (mean 780 mg/L; R. Forester, unpublished data).

Based on pollen data, regional precipitation shifts from winter-dominated during the wetland phases to summer-dominated during the marsh phases (Peter Wigand, written communication, 1994), which correlates with wet years and drought years, respectively. Thus the existence of a wetland or a marsh covaries with the seasonality of precipitation. Conversely, as the ostracodes show, wet years result in saline conditions, whereas dry years result in freshwater conditions.

Stable isotope values were determined for *L. sappaensis* and *C. caudata* valves taken from many samples throughout the core (Figure 22.11). *L. sappaensis* generally had low $\delta^{18}\text{O}$ values (range -9.3 to +3.2‰, mean - 5.13‰), whereas *C. caudata* had high $\delta^{18}\text{O}$ values (range -7.78 to +9.22‰, mean +1.98‰). The relation between $\delta^{18}\text{O}$ and TDS inferred from the ostracodes is the opposite of what might be expected, but $\delta^{18}\text{O}$ values and climate inferred from the pollen show positive covariance with wet/dry episodes. The discrepancy may indicate that the wetland was supported by isotopically unevolved source water derived from local snow melt, alluvial fan runoff, and subsurface flow in the channel that dissolves salts in the basin. By contrast, the freshwater with high $\delta^{18}\text{O}$ values may result from evaporative fractionation along shallow aquifer flow paths originating in the surrounding mountains (Smith et al., 1997). Alternatively, the difference between the $\delta^{18}\text{O}$ values in the dataset may simply reflect the dominance of winter (low $\delta^{18}\text{O}$) versus summer (high $\delta^{18}\text{O}$) air mass sources for the precipitation.

The $\delta^{13}\text{C}$ values from the two ostracode species covary with the $\delta^{18}\text{O}$ values (see inset, Figure 22.11) indicating that DIC content of the waters was also partitioned into low and high values. The distribution may indicate different source rocks, but more likely, the low $\delta^{13}\text{C}$ values associated with winter precipitation indicate C_3 plant dominance versus C_4 plants for the high

$\delta^{13}\text{C}$ values associated with summer precipitation. If C_3 and C_4 plant communities are responsible for the overall $\delta^{13}\text{C}$ DIC composition of the water, then precipitation source becomes the likely explanation for the $\delta^{18}\text{O}$ patterns. The very high $\delta^{13}\text{C}$ values (5 to 10‰) may indicate methanogenesis or some other carbon-isotope enrichment process.

This record is interesting from at least two perspectives. First, the wetlands contain an evolved solute composition with saline water, but produce low carbonate $\delta^{18}\text{O}$ values (modern ostracode $\delta^{18}\text{O}$ value -7.07‰ PDB). Second, the present day wetland does not represent climate-hydrologic linked changes common to the site as recently as a century ago; in other words, historic records only identify part of the system's natural hydrological variability.

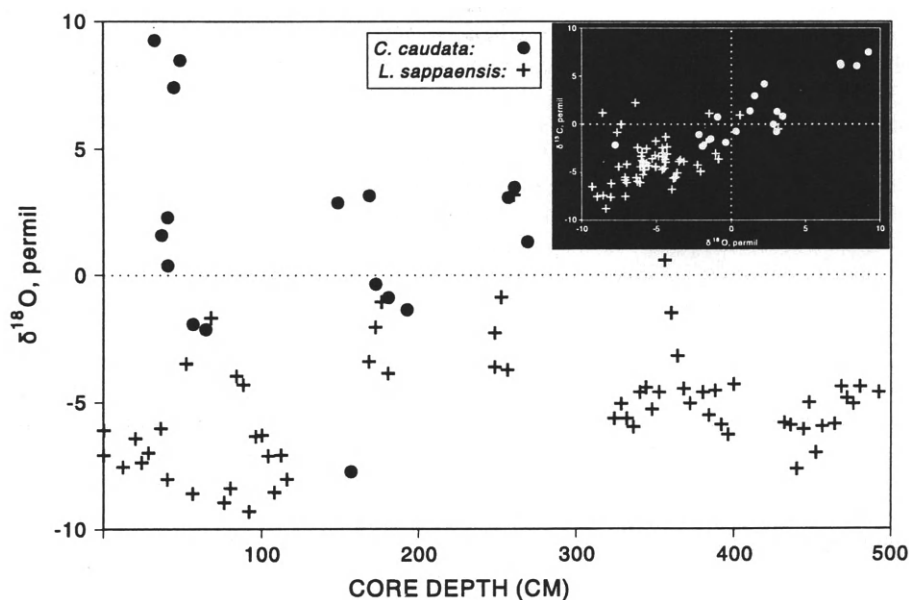


Figure 22.11. $\delta^{18}\text{O}$ (PDB) in ostracodes as a function of core depth in Lower Pahranaagat Lake, Nevada. Inset: $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$.

22.4 New Research Directions

Environmental change research is advancing rapidly on many fronts, and isotopes are playing a leading role. The application of isotopic techniques to the reconstruction of continental paleoclimates undoubtedly will continue to grow steadily in the 21st century. Established procedures such as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ determinations on soil and lacustrine carbonates are increasingly being augmented by novel techniques, e.g. determinations of δD in surficial minerals or $\delta^{18}\text{O}$ of phosphate in animal teeth, to provide an ever more comprehensive spatial and temporal record of continental paleoclimate. Because of the role of carbon in global warming, increased study will be directed toward carbon cycling in different ecosystems (Chapter 17). Interest will also grow in tracers of erosion rates and sediment sources (Chapter

19) as a consequence of deforestation, transport of particle-associated herbicides and pesticides in agricultural areas, clogging of rivers, destruction of productive coastal fisheries, nuclear accidents, and other byproducts of "human enterprise".

Rapid advances in technology fuel advances in science, and vice versa, in an age-old synergy. The decreased costs of new automated, sometimes micro-sample, on-line preparation systems (e.g., for waters, carbonates, or organic samples) for mass spectrometers is greatly expanding our ability to provide detailed timelines in the isotopic records of lacustrine sediments and fossils. Analyses that once required hours per sample are now being achieved at a rate of many samples per hour. A particularly good example of a recent technological advance in the field of environmental isotope geochemistry is the replacement of conventional dual inlet stable isotope mass spectrometers by new "continuous flow" mass spectrometers in which samples are introduced automatically into a helium stream that flows continuously through the instrument. While technological advances have fostered valuable data generation and taken the field in new directions, technology may not be the rate-limiting step to advancement of the discipline. In so many environmental change studies, formidable uncertainties persist regarding multiple interpretations for the observed interannual variations in isotopic signatures. Reducing these uncertainties through focused interdisciplinary research is a foremost need. Success for this goal depends in part on better documentation of isotopic patterns in the modern hydrologic cycle, and understanding of the patterns of local variability.

22.5 Summary

Global environmental change - encompassing a diverse array of issues such as climate change, changes in atmospheric chemistry, increases in erosion rates, land-use shifts, and decreases in biodiversity - has a sweeping and often adverse impact on our environment. Many recent changes are a direct consequence of anthropogenic activities. Isotopic analysis serves as a valuable tool for distinguishing between natural variations in long-term climatic patterns and anthropogenic effects, yielding improved understanding of natural feedback mechanisms and the development of realistic remediation strategies. Although this multi-authored chapter is by no means comprehensive, it is intended to provide a flavor for how isotopic indicators are being applied in investigations of environmental change in continental settings.

Keeping in mind the adage "the present is the key to the past", the chapter begins with examples of isotopic techniques that have been applied to understanding several types of ongoing and recent environmental changes, and finishes with examples of isotopic techniques applied in paleo-environmental studies. Studies of recent environmental change have the advantage that direct records of environmental conditions are obtained from samples of well-constrained age (e.g., CFC-dated groundwater, tree cellulose, etc.), and that isotopic results often can be supported by historic information (e.g., weather records, land use histories). While some paleoenvironmental studies obtain direct records (glacial ice cores, ancient groundwater), most rely on ancient material, such as soil and lacustrine carbonates, and fossil plants, which preserve an indirect or "proxy" record of the isotopic compositions of local waters ($\delta^{18}\text{O}$, δD) and solutes (often $\delta^{13}\text{C}$) at the time of formation. The material is dated independently, most often by isotopic techniques as well. Under favorable conditions, long time series of climatic or hydrologic conditions can be reconstructed, thus providing a framework within which recent environmental change can be evaluated. However, the development of modern-day atmospheric

climate models and the reconstruction of ancient climatic and hydrologic models based on proxy isotopic records is severely hampered by limited information about current isotopic patterns in the modern hydrologic cycle. This book is an attempt to help remedy this situation.

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