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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,

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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, $^{1}H_2{}^{16}O$, evaporates preferentially; and later in the inverse process of vapor condensation, when the isotopically heavy molecules ($^{1}HD^{16}O$ and $^{1}H_2{}^{18}O$) 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ value around 0‰ whereas the adjacent groundwater often is represented by paleowater with $\delta^{18}O$ 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 evapo-transpiration 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 unsat-urated zone if the recharge rate is low (arid conditions) and the thickness of this zone is suffi-ciently 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

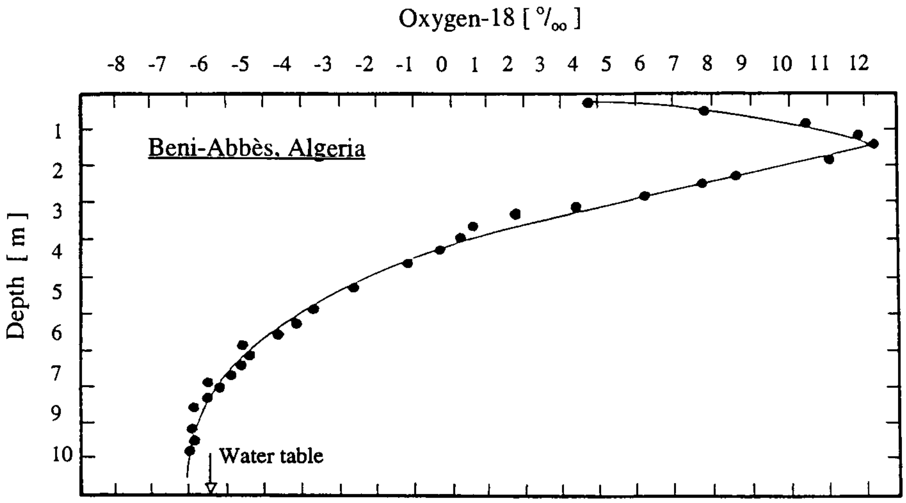

Figure 7.1. Oxygen-18 isotope profile in the unsaturated zone at Beni-Abbès, Algeria (Fontes and Edmunds, 1989, modified).

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 $^{39}\mathrm{K}\rightarrow(\mathrm{n,\ p})^{39}\mathrm{Ar}$. 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 $^{39}\mathrm{Ar} \approx 9\times10^{-5}$ 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).

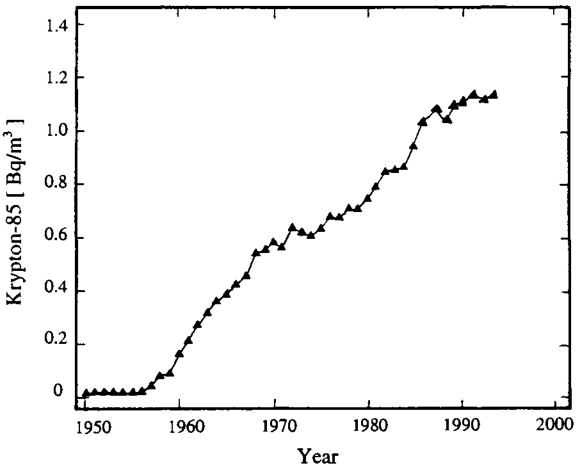

Figure 7.2. The yearly mean values of ^{85}Kr concentration in the lower troposphere of the Northern Hemisphere (data from Weise et al., 1992; Sartorius, 1994).

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:

$$R = \frac{n_f H}{t} \tag{7.1}$$

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 ^{3}He produced by the tritium decay, which remains stored in groundwater (Schlosser et al., 1988, 1989). The tritiogenic ^{3}He concentration, [^{3}He]*, in water is obtained by extracting the total dissolved ^{3}He 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 ^{3}He loss nor a contribution from the deeper aquifer regions, the groundwater age is given by:

$$t = 17.93 \times \ln\left(\frac{[^3He]^*}{[^3H]} + 1\right) \tag{7.2}$$

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}H/^{3}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 ^{3}He in water). However, even in such a case, the identification of the ^{3}H+^{3}He peak remains possible and can be used for dating.

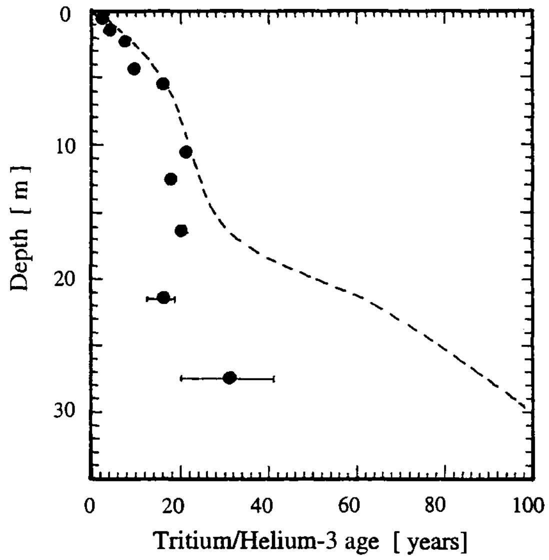

Figure 7.3. The observed (heavy dots) and modeled (broken line) tritium/^{3}He ages of water sampled from multi-level wells located in shallow groundwater system Liedern/Bocholt, Germany (Schlosser et al., 1989, modified). The deviation between the observed and calculated tritium/^{3}He ages most likely 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 Ramspacher 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 Bostwana 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

$\delta^{18}O$ 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 Rimac are -14‰ and -103‰ in $\delta^{18}O$ 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 m^3/s) is about 1.1 m^3/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.

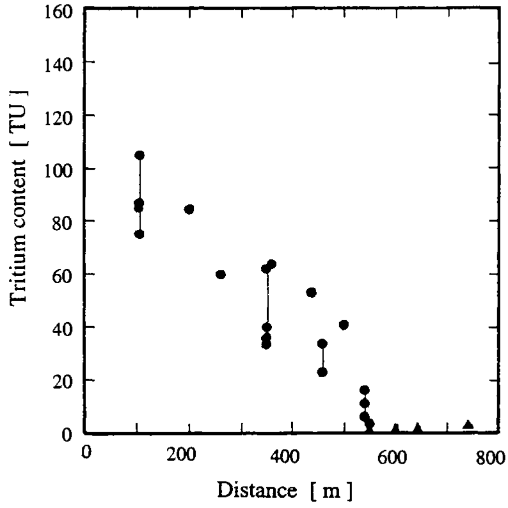

Figure 7.4. Tritium content of groundwater in 1973 versus distance from the Reno River, Italy (Carlin et al., 1975, modified).

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.

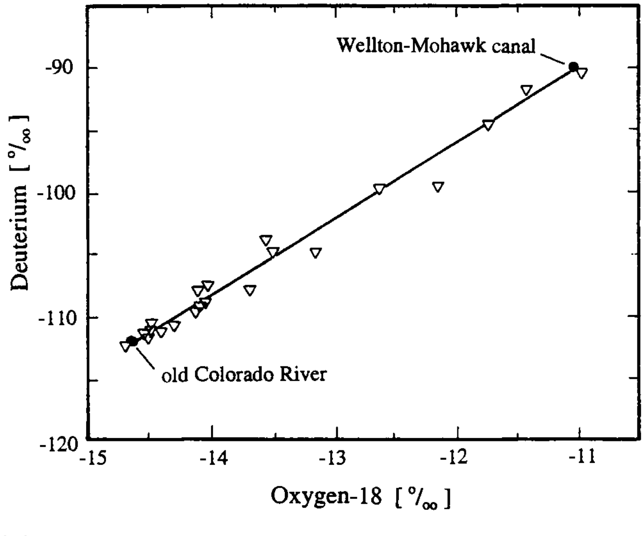

Figure 7.5. Stable isotope composition of groundwater in the Northeast and East Mexicali Valley, Mexico (Payne et al., 1979, modified).

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):

$$t = \frac{nH}{W} \ln \left(\frac{H}{H-x} \right) \tag{7.3}$$

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:

$$t_M = \frac{\displaystyle\int_{x_1}^{x_2} \frac{nH}{W} \ln \left(\frac{H}{H-x} \right) dx}{x_2 - x_1} \tag{7.4}$$

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:

$$t_M = \sum_{i=1}^{n} f_i \, t_i \tag{7.5}$$

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:

$$C_M = \frac{\sum_{i=1}^{n} f_i \, m_i \, C_i}{m_M} \tag{7.6}$$

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:

$$C_M = \sum_{i=1}^{n} f_i \, C_i \tag{7.7}$$

Accordingly, the apparent age computed from C_M with a piston-flow model is:

$$t_{PF} = \frac{1}{\lambda} \ln\frac{C_0}{C_M} \tag{7.8}$$

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:

$$t_M = \sum_{i=1}^{n} f_i\, t_i = \frac{1}{\lambda} \sum_{i=1}^{n} f_i \ln \frac{C_0}{C_i} \tag{7.9}$$

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:

$$t_M = \frac{1}{\lambda} \sum_{i=1}^{n} f_i \ln \frac{C_{0,i}}{C_i} \tag{7.10}$$

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.

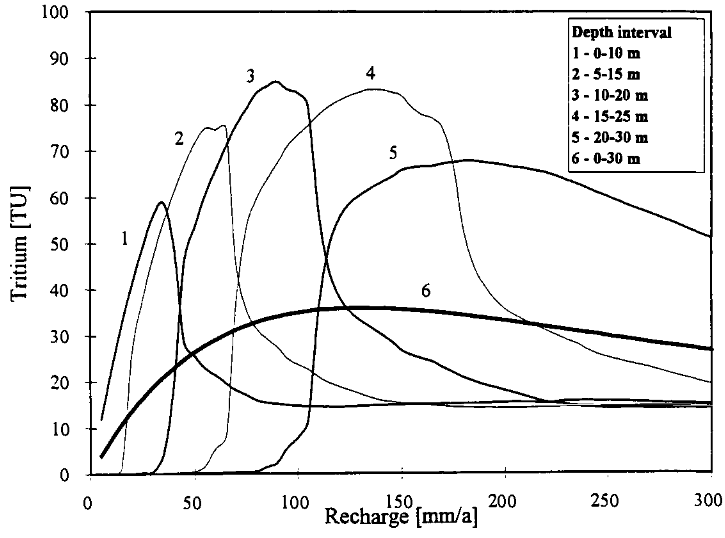

Figure 7.6. Tritium concentration at various depths in a hypothetical unconfined aquifer in 1994, as a function of recharge rate, computed according to Vogel model (Vogel, 1967; 1970). Tritium input function based on Vienna precipitation data.

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:

$$C_{i+1}V_{i+1} = C_iV_i + C_{Pi}P_i + C_{Ii}I_i - C_iE_i - \lambda V_iC_i \qquad (7.11)$$

$$V_{i+1} = V_i + P_i + I_i - E_i \qquad (7.12)$$

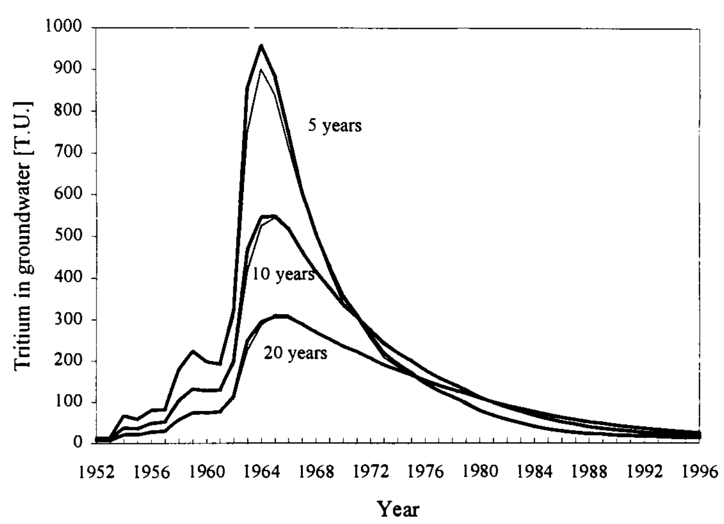

Figure 7.7. Response of one-cell (heavy line) and two-cell (light or dotted line) systems to the tritium input function based on Vienna precipitation data, for three different mean residence times of water in the system.

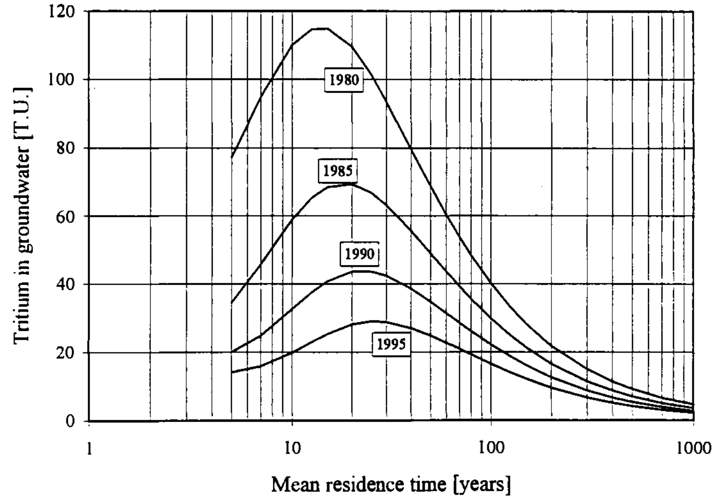

Figure 7.8. Tritium concentration in a well-mixed aquifer in different years and for different residence times. The tritium input function is based on Vienna precipitation data.

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 groundwater 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:

$$C = \left(\frac{C_P}{T_P} + \frac{C_I}{T_I} \right) \frac{T}{1 + \lambda T} \tag{7.13}$$

where T_P and T_I 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:

$$\frac{1}{T_P} + \frac{1}{T_I} = \frac{1}{T} \tag{7.14}$$

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 multicompartment 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 m^3/year or 120 mm/year for lateral recharge, and 27 mm/year for local precipitation. Conventional hydrological estimates give 18×10^6 m^3/year and 70 mm/year, respectively. It is believed that the tritium-based estimate for local recharge is more likely.

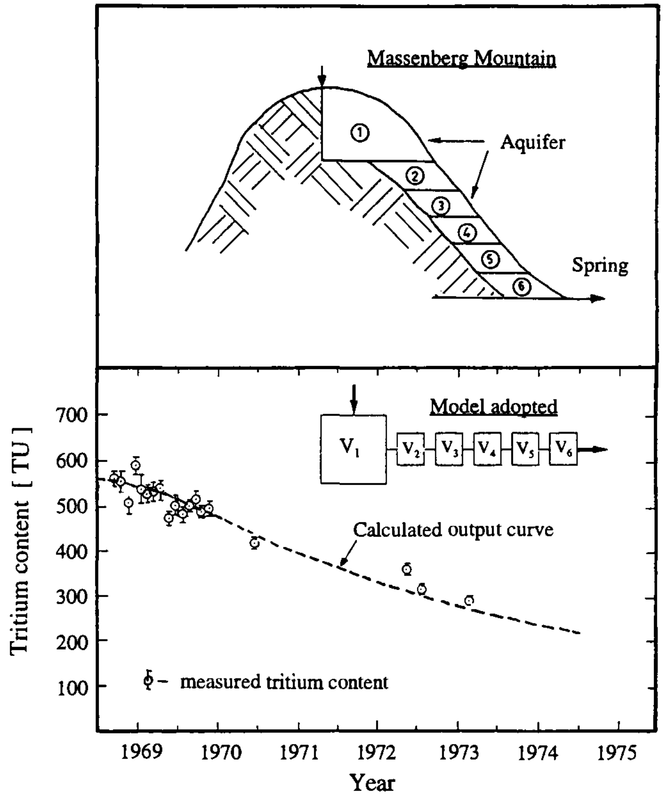

Figure 7.9. Calculated tritium output curve for the Grafendorf spring, southern Austria, using a multi-compartment (Przewlocki and Yurtsever, 1974, modified). The best fit of measured and calculated changes in concentrations of tritium in the spring water was obtained with the model consisting of seven 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.

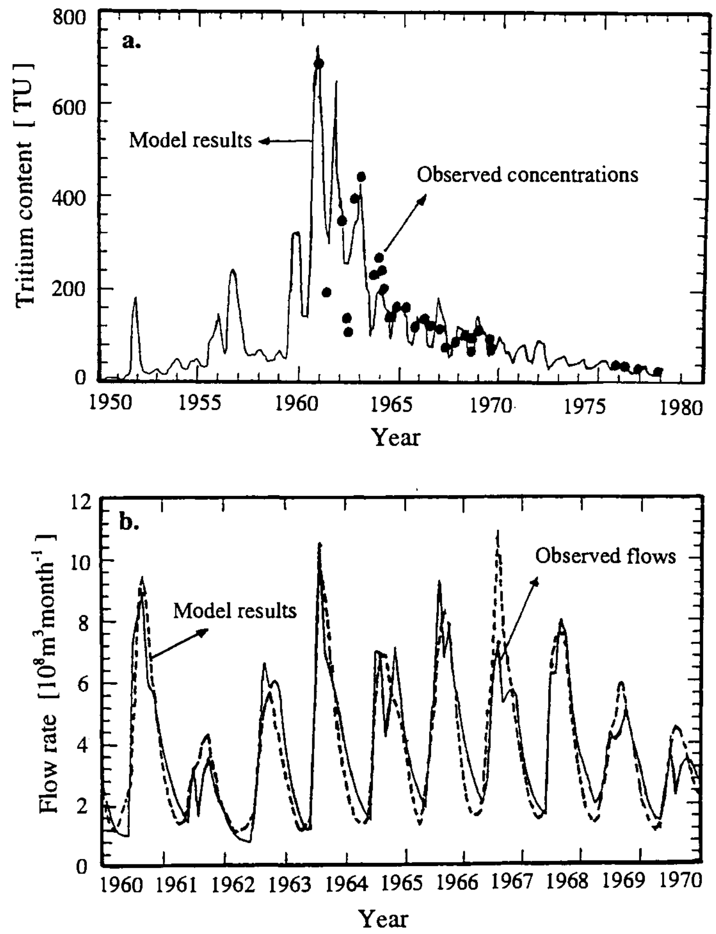

Figure 7.10. a) Comparison of model calculated tritium output concentrations with actual observed values in Manavgat river, southern Turkey. b) Comparison of model calculated flows with actual observed flows in Manavgat river. (Yurtsever and Payne, 1986, modified).

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 $^{36}Cl/Cl$ 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

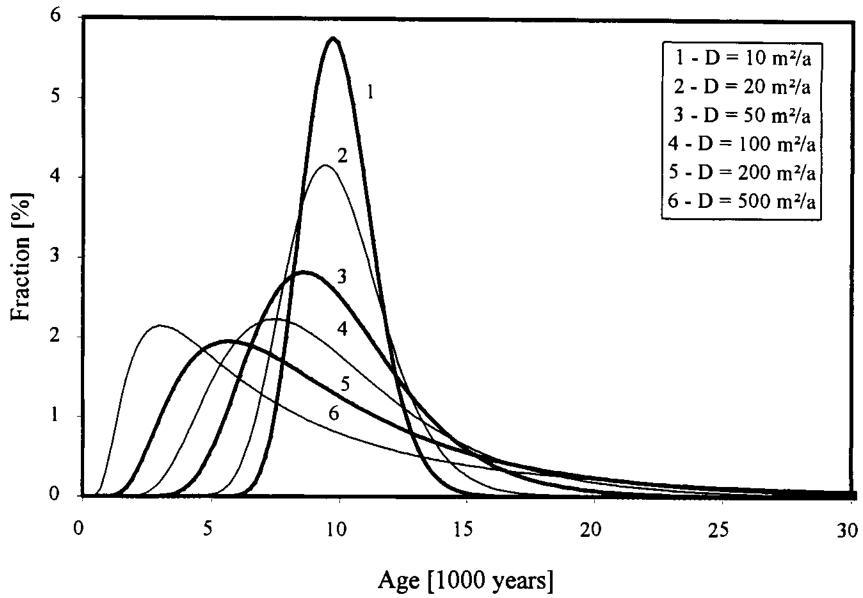

Figure 7.11. Groundwater age distribution at a distance of X = 10,000 m from the recharge area, flowing with Darcy velocity of 0.1m/a in a porous aquifer with effective porosity of 10%. The age percent fractions are computed over a 200 years time interval. The retardation coefficient has been taken equal to 1 (no retardation).

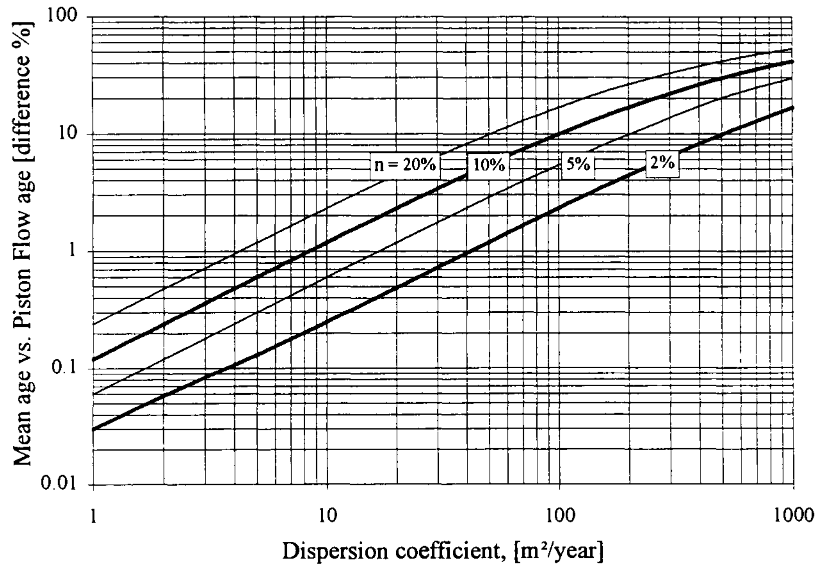

Figure 7.12. Effect of dispersion on the C-14 piston flow age of groundwater flowing with Darcy velocity of 0.1 m/yr. The difference between the mean age and the piston flow carbon-14 age of groundwater is plotted as a function of the dispersion coefficient, for selected effective porosities. In this computation the DIC concentration has been assumed constant, and the interaction with the matrix negligible.

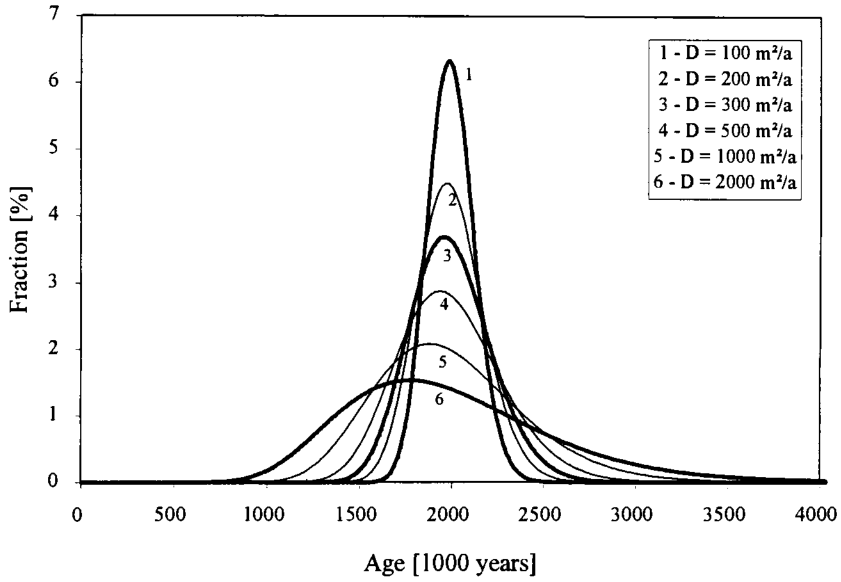

Figure 7.13. Distribution of water age at a distance of X =1,000 km from the recharge area, for different dispersion coefficients. Water is flowing with a Darcy velocity of 0.05 m/yr in a porous aquifer with effective porosity of 10%. The age percent fractions are computed over a 20,000 years time interval. 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 20-30 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:

$$t_M = \frac{1}{\lambda}\left(\frac{C_0}{C} - 1\right) \qquad (7.15)$$

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:

$$t_M = \frac{nH}{R} \tag{7.16}$$

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.

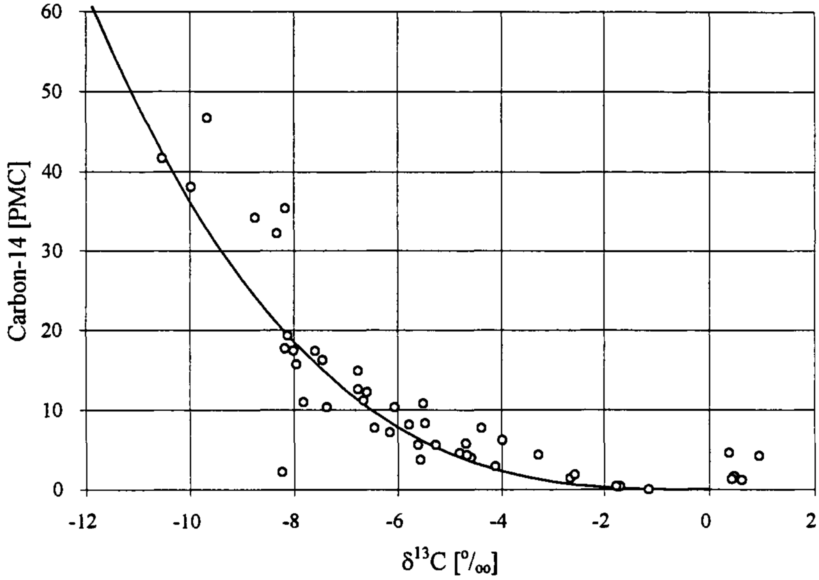

Figure 7.14. Carbon-14 versus carbon-13 content in bicarbonate dissolved in groundwater of Cyrenaica aquifer, northern Libya (Gonfiantini, 1988, modified).

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 nth cell is given by:

$$t_M = \sum_{i=1}^{n} t_i = \frac{1}{\lambda}\left(\sum_{i=1}^{n} \frac{C_{i-1}}{C_i} - 1 \right) \tag{7.17}$$

Assuming now for simplicity that the mean residence time of water is the same in all the cells or compartments: $t_1 = t_2 \ldots = t_n$, 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:

$$\ln\frac{C_0}{C_n} = \frac{t_M}{t_1}\ln(1+t_1\lambda) \tag{7.18}$$

where t_1 is the mean residence time in each cell. In other words, the logarithm of the ^{14}C content in the nth 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.

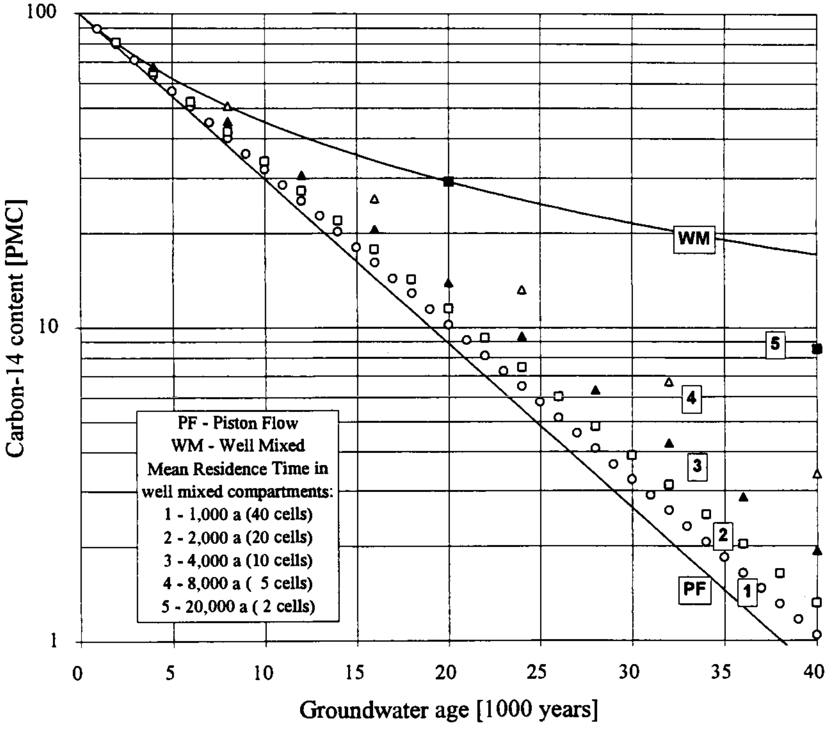

Figure 7.15. Difference between groundwater ages computed from the same carbon-14 content, with different models: piston flow, well mixed reservoir, and multicompartment models with different number of equal cells in cascade.

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 $\delta^{18}O$ 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 $\delta^{18}O$ (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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 δ^{18}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 km^2 plain, situated within a graben between two Eocene karst anticlinoriums. 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 µS·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 Albero et al. (1987). This valley, about 200 km east of the Andean Cordillera, extends over 440 km^2. 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 ($\delta^{18}O$ = -16.0 ‰), and by streams fed by rains on the hills surrounding the valley which are less depleted in heavy isotopes: $\delta^{18}O$ 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 km^2. 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 km^2 within the 3825 km^2 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 Harrysburg, 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 km^2 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 ^{14}C 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 $\delta^{18}O = -6.6$ ‰) is generally depleted in heavy isotopes with respect to groundwater ($\delta^{18}O$ from -6.8 to -4.1 ‰), whereas rivers are enriched ($\delta^{18}O$ 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 ^{14}C, 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 $^{18}O/^{16}O$ 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 $^{18}O/^{16}O$ 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 $^{11}B/^{10}B$, $^{37}Cl/^{35}Cl$, $^{87}Sr/^{86}Sr$ 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.

References

Adar, E.M., Rosenthal, E., Issar, A.S. and Batelaan, O., 1992. Quantitative assessment of the flow pattern in the southern Arava Valley (Israel) by environmental tracers and a mixing cell model. Jour. of Hydrol., 136: 333-352.

Adar, E.M., 1994. Assessment of groundwater fluxes and transmissivities by environmental tracers: Summary of theory, application and sensitivity analysis. In: Mathematical models and their applications to isotope studies in groundwater hydrology. IAEA, Vienna, pp. 93-122.

Albero, M.C., Levín, M:, Panarello, H.O., Lohn, P. and García, E., 1987. Isotopic evidence for the different origins of the Tulum Valley groundwaters (San Juan, Argentina). In: Isotope Techniques in Water Resources Development, IAEA, Vienna, pp. 287-299.

Albero, M.C., Levín, M., Panarello, H.O., García, E. and Lohn, P., 1989. Estudio isotópico de los acuíferos de los valles de Tulum y Ullum-Zonda, San Juan, Argentina. In: Estudios de Hidrología Isotópica en América Latina, IAEA-TECDOC-502. IAEA, Vienna, pp. 11-32.

Allison, G.B. and Barnes, C.J., 1983. Estimation of evaporation from non-vegetated surfaces using natural deuterium. Nature, 301: 143-145.

Allison, G.B. and Hughes, M.W., 1972. Comparison of recharge to groundwater under pasture and forest using environmental tritium. Jour. of Hydrol., 17: 81-95.

Allison, G.B. and Hughes, M.W., 1975. The use of environmental tritium to estimate recharge to a South-Australian aquifer. Jour. of Hydrol., 26: 245-254.

Alvarado, J., Seiler, K.P. and Trimborn, P., 1995. Investigación hidrogeológica, isotópica e hidroquímica en la cuenca del lago de Valencia, Venezuela. In: Nuevos Estudios de Hidrología Isotópica en América Latina, IAEA-TECDOC-835. IAEA, Vienna, pp. 315-337.

Andres, G. and Egger, R., 1985. A new tritium interface method for determining the recharge rate of deep groundwater in the Bavarian Molasse basin. Jour. of Hydrol., 82: 27-38.

Andrews, J.N. and Fontes, J.Ch., 1992. Importance of the in situ production of ^{36}Cl, ^{36}Ar and ^{14}C in hydrology and hydrogeochemistry. In: Isotope Techniques in Water Resources Development. IAEA, Vienna, pp. 245-269.

Aranyossy, J.F. and Gaye, C.B., 1992. La recherche du pic thermonucléaire en zone non saturée profonde sous climat semi aride pour la mesure de la recharge des nappes: première application au Sénégal. C.R. Acad. Sci. Paris, 315, série II, pp. 637-643.

Baldizón, R., Seiler, K.P. and Trimborn, P., 1995. Investigaciones isotópicas ambientales, químicas e hidrogeológicas en la cuenca del lago Atitlán, Guatemala. In: Nuevos Estudios de Hidrología Isotópica en América Latina, IAEA-TECDOC-835. IAEA, Vienna, pp. 225-236.

Barnes, C.J. and Allison, G.B., 1983. The distribution of deuterium and ^{18}O in dry soils. I. Theory. Jour. of Hydrol., 60: 141-156.

Barnes, C.J. and Allison, G.B., 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. Jour. of Hydrol., 100: 143-176.

Bath A., 1983. Stable isotopic evidence for palaeo-recharge conditions of groundwater. In: Paleoclimates and Palaeowaters. A Collection of Environmental Isotope Studies. IAEA, Vienna, pp. 169-186.

Bentley, H.W., Phillips, F.M., Davis, S.N., Habermehl, M.A., Airey, P.I., Calf, G.E., Elmore, D., Gove, H.E. and Torgersen, T., 1986. Chlorine-36 dating of very old groundwater. I. The Great Artesian Basin. Water Resour. Res., 22: 1991-2001.

Bertleff, B., Ellwanger, D., Szenkler, C., Eichinger, L., Trimborn, P. and Wolfendale, N., 1993. Interpretation of hydrochemical and hydroisotopical measurements on paleogroundwaters in Oberschwaben, South German Alpine foreland, with focus on Quaternary geology. In: Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. IAEA, Vienna, pp. 337-357.

Blavoux, B., 1978. Etude du cycle de l'eau au moyen de l'oxygène 18 et du tritium. Thèse de Doctorat d'Etat ès Sciences Naturelles. Université Pierre et Marie Curie, Paris, 333 p.

Blavoux, B., Dray, M., Fehri, A., Olive, P., Gröning, M., Sonntag, C., Hauquin, J-P., Pelissier, G. and Pouchan P., 1993. Paleoclimatic and hydrodynamic approach to the Aquitaine basin deep aquifer (France) by means of environmental isotopes and noble gases. In: Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. IAEA, Vienna, pp. 293-305.

Brown, R.M., 1961. Hydrology of tritium in the Ottawa valley. Geochim. et Cosmochim. Acta, 21: 199-216.

Brown, R.M., 1970. Distribution of hydrogen isotopes in Canadian waters, In: Isotope Hydrology 1970. IAEA, Vienna, pp. 3-21.

Carlin, F. Magri, G., Cervellati, A. and Gonfiantini R., 1975. Use of environmental isotopes to investigate the interconnections between the Reno River and groundwater (Northern Italy). In: Isotope Ratios as Pollutant Source and Behaviour Indicators. IAEA, Vienna, pp. 179-194.

Carreira, P.M., Monge Soares, A.M., Marques da Silva, M.A., Araguás Araguás, L. and Rozanski K., 1996. Application of environmental isotope methods in assessing groundwater dynamics of an intensively exploited coastal aquifer in Portugal. In: Isotopes in Water Resources Management. IAEA, Vol. II, Vienna, pp. 45-58.

Celico, P., Gonfiantini, R., Koizumi, M. and Mangano, F., 1984. Environmental isotope studies of limestone aquifers in Central Italy. In: Isotope Hydrology 1983. IAEA, Vienna, pp. 173-192.

Clarke, W.B., Jenkins,W.J. and Top, Z., 1976. Determination of tritium by mass spectrometric measurements of $^3He^+$. Int. J. Appl. Radiat. Isotopes, 27: 515-522.

Ciezkowski, W., Gröning, M., Lesniak, P.M., Weise, S.M. and Zuber, A., 1992. Origin and age of thermal waters in Cieplice Spa, Sudeten, Poland, inferred from isotope, chemical and noble gas data. Jour. of Hydrol., 140: 89-117.

Colville, J.S., 1984. Estimation of aquifer recharge and flow from natural tritium content of groundwater. Jour. of Hydrol., 67: 195-222.

Cook, P.G., Jolly, I.D., Leaney, F.W., Walker, G.R., Allan, G.L. Fifield, L.K. and Allison, G.B., 1994. Unsaturated zone tritium and chlorine -36 profiles from southern Australia: Their use as tracers of soil water movement. Water Resour. Res., 30(6): 1709-1719.

Coplen, T.B., Wildman, J.D. and Chen, J., 1991. Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope ratio analysis. Anal. Chem., 63(9): 910-912.

Craig, H., 1961. Isotopic variations in meteoric waters. Science, 133: 1702-1703.

Davisson, M.L. and Criss, R.E., 1996. Stable isotope and groundwater flow dynamics of agricultural irrigation recharge into groundwater resources of the Central Valley, California. In: Isotope Techniques in Water Resources Management. IAEA, Vol. I, Vienna, pp. 405-418.

Degens, E.T., 1962. Geochemische Untersuchungen von Wassern aus der Aegyptischen Sahara. Geol. Rundsch., 52: 625-639.

Delcore, M.R., 1989. Determinación del promedio anual de la recarga a base de la profundidad del tritio termonuclear en la zona saturada. In: Estudios de Hidrología Isotópica en América Latina, IAEA-TECDOC-502. IAEA, Vienna, pp. 451-456.

De Marsily, G., 1981. Hydrogéologie quantitative. Masson, Paris, 215 p.

Dinçer, T., Al-Mugrin, W. and Zimmermann, V., 1974. Study of the infiltration and recharge through the sand dunes in arid zone with special reference to the stable isotopes and thermonuclear tritium. Jour. of Hydrol., 23: 79-109.

Dinçer, T., Hutton, L.G. and Kupee, B.B.J., 1979. Study, using stable isotopes, of flow distribution, surface-groundwater relations and evapotranspiration in the Okawango Swamp, Botswana. In: Isotope Hydrology 1978, Vol. I. IAEA, Vienna, pp. 3-26.

Dörr, H. and Münnich, K.O., 1987. Annual variation in soil respiration in selected areas of the temperate zone, Tellus, 39B, 114-122.

Dray, M., Gonfiantini, R. and Zuppi, G.M., 1983. On the isotopic composition of groundwater in Southern Sahara. In: Palaeoclimates and Palaeowaters. A Collection of Environmental Isotope Studies. IAEA, Vienna, pp. 187-199.

Edmunds, W.M. and Walton, N.R.G., 1980. A geochemical and isotopic approach to recharge evaluation in semi-arid zones: Past and present. In: Arid-Zone Hydrology: Investigations with Isotope techniques. IAEA, Vienna, pp. 47-68.

Ekwurzel, B., Schlosser, P., Smethie, W.M., Plummer, L.N., Busenberg, E., Michel, R.L., Vappering, R. and Stute, M., 1994. Dating of shallow groundwater: comparison of the transient tracers ^{3}H/ ^{3}He, chlorofluorocarbons and ^{85}Kr. Water Resour. Res., 30(6): 1693-1708.

Eriksson, E., 1963. Atmospheric tritium as a tool for the study of certain hydrologic aspects of river basins. Tellus, XV(3): 303-308.

Fabryka-Martin, J., Bentley, H., Elmore, D. and Airey, P.L., 1985. Natural iodine-129 as an environmental tracer. Geochim. et Cosmochim. Acta, 49: 337-347.

Fabryka-Martin, J., Davis, S.N. and Elmore, D., 1987. Applications of ^{129}I and ^{36}Cl in hydrology. Nucl. Instr. and Methods in Physics Res., B29: 361-371.

Flora, O. and Longinelli, A., 1989. Stable isotope hydrology of a classical karst area, Trieste, Italy. In: Isotope Techniques in the Study of Hydrology of Fractured and Fissured Rocks. IAEA, Vienna, pp. 203-213.

Florkowski, T. and Rozanski, K., 1986. Radioactive noble gases in the terrestrial environment. In: P. Fritz and J.Ch. Fontes (Editors), Handbook of Environmental Isotope Geochemistry. The terrestrial environment B., Elsevier, Amsterdam, pp. 481-506.

Fontes, J.Ch., 1981. Palaeowaters. In: J.R. Gat and R. Gonfiantini (Eds), Stable Isotope Hydrology. Deuterium and Oxygen-18 in the Water Cycle, IAEA, Vienna, pp. 273-302.

Fontes, J.Ch., 1983. Dating of groundwater. In: Guidebook on Nuclear Techniques in Hydrology, 1983 Edition. IAEA, Vienna, pp. 285-317.

Fontes, J.Ch., 1992. Chemical and isotopic constraints on ^{14}C dating of groundwater. In: R.E. Taylor, A. Long and R.S. Kra (Eds), Radiocarbon After Four Decades, Springer-Verlag, New York, pp. 242-261.

Fontes, J.Ch. and Edmunds, W.M., 1989. The use of environmental isotope techniques in arid zone hydrology. A critical review. Technical Documents in Hydrology, UNESCO, Paris.

Fontes, J.Ch., Andrews, J.N., Edmunds, W.M., Guerre, A. and Travi Y., 1991. Paleorecharge by the Niger River (Mali) deduced from groundwater geochemistry. Water Resour. Res., 27: 199-214.

Forster, M., Ramm, K. and Maier, P., 1992. Argon-39 dating of groundwater and its limiting conditions. In: Isotope Techniques in Water Resources Development 1991, IAEA, Vienna, pp. 203-214.

Fritz, P., 1981. River waters. In: Stable Isotope Hydrology. Deuterium and Oxygen-18 in the Water Cycle. IAEA, Vienna, pp. 177-201.

Fritz, P., Cherry, J.A., Weyer, K.W. and Sklash, M., 1976. Storm runoff analyses using environmental isotope and major ions. In: Interpretation of environmental isotope and hydrochemical data in groundwater hydrology. IAEA, Vienna, pp. 111-130.

Fritz, P., Drimmie, R.J. and Render, F.W., 1974. Stable isotope content of a major prairie aquifer in Central Manitoba, Canada. In: Isotope Techniques in Groundwater Hydrology, Vol. I. IAEA, Vienna, pp. 379-398.

Fritz, P. and Stichler, W., 1983. Runoff analysis. In: Guidebook on Nuclear Techniques in Hydrology, 1983 Edition. IAEA, Vienna, pp. 81-86.

Fröhlich, K., Franke, T., Gellermann, R. and Hebert, D. 1987. Studies of ^{32}Si in different aquifer and implications for groundwater dating. Isotopenpraxis, 24(9): 355-362.

Fröhlich, K. and Gellermann, R., 1987. On the potential use of uranium isotopes for groundwater dating. Chem. Geol. (Isotope Geoscience Section), 65: 67-77.

Gat, J.R. and Tzur, Y., 1967. Modification of the isotopic composition of rainwater by processes which occur before groundwater recharge. In: Isotopes in Hydrology, IAEA, Vienna, pp. 49-60.

Geyh, M.A., 1992. The ^{14}C time-scale of groundwater. Correction and linearity. In: Isotope Techniques in Water Resources Development 1991, IAEA, Vienna, pp. 167-177.

Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: P. Fritz and J.Ch. Fontes (Eds), Handbook of Environmental Isotope Geochemistry, The Terrestrial Environment B, Vol. II. Elsevier, Amsterdam, pp. 113-168.

Gonfiantini, R., 1988. Carbon isotope exchange in karst groundwater. In: Proceedings of the IAH 21st Congress on Karst Hydrogeology and Karst Environment Protection (Guilin, China, 10-15 October 1988), pp. 832-837.

Gonfiantini, R., Conrad, G., Fontes, J-Ch., Sauzay, G. and Payne, B.R., 1974. Etude isotopique de la nappe du Continental Intercalaire et de ses relations avec les autres nappes du Sahara septenrional. In: Isotope Techniques in Groundwater Hydrology, Vol. I. IAEA, Vienna, pp. 227-241.

Gonfiantini, R. and Simonot, M., 1987. Isotopic investigations of groundwater in the Cul-de-Sac plain, Republic of Haiti. In: Isotope Techniques in Water Resources Development. IAEA, Vienna, pp. 483-504.

Gonfiantini, R., Araguás-Araguás, L. and Rozanski, K., 1990. Tritium in precipitation: comparison between the years of high tritium (1963-67) and recent years. Bulletin of Radiation Protection, 13: 1-6.

Hinkle, M.E., 1994. Environmental conditions affecting concentrations of He, CO_2, O_2 and N_2 in soil gases. Appli. Geochem., 9: 53-63.

Hoehn, E. and von Gunten, H.R., 1989. Radon in groundwater. A tool to assess infiltration from surface waters to aquifers. Water Resour. Res., 25: 1795-1803.

Horita, J., 1988. Hydrogen isotope analysis of natural waters using an H_2 - water equilibration method: a special implication to brines. Chem. Geol., 72: 89-94.

Hötzl, H., Reichert, B., Maloszewski, P., Moser, H. and Stichler, W., 1989. Contaminant transport in bank filtration. Determining hydraulic parameters by means of artificial and natural labeling. In: H.E. Kobus and W. Kinzelbach (Eds), Contaminant Transport in Groundwater. Balkema, Rotterdam, pp. 65-71.

International Atomic Energy Agency, 1992a. Statistical Treatment of Data on Environmental Isotopes in Precipitation, Technical Reports Series. No. 331. IAEA, Vienna, 784 p.

International Atomic Energy Agency, 1992b. Isotopes of Noble Gases as Tracers in Environmental Studies, Panel Proceedings Series, STI/PUB 859. IAEA, Vienna, 308 p.

Ivanovich, M., Fröhlich, K., Hendry, M.J., Andrews, J.N., Davis, S.N., Drimmie, R.J., Fabryka-Martin, J., Florkowski, T., Fritz, P., Lehmann, B.E., Loosli, H.H. and Nolte, E., 1992. Evaluation of isotopic methods for the dating of very old groundwaters: a case study of the Milk River Aquifer. In: Isotope Techniques in Water Resources Development 1991. IAEA, Vienna, pp. 229-244.

Jean-Baptiste, P., Mantisi, F., Dapoigny, A. and Stievenard M., 1992. Design and performance of a mass spectrometric facility for measuring helium isotopes in natural waters and for low-level tritium determination by the ^{3}He ingrowth method. Appl. Radiat. Isot., 43: 881-891.

Krimissa, M., Chery, L. and Fouillac, C., 1993. Isotopic study of thermomineral springs in the Eastern Pyrenees: correlation with the origin of the air masses and the altitude of recharge. In: Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. IAEA, Vienna, pp. 583-586.

Lehmann, B.E., Loosli, H.H., Rauber, D., Thonnard, N. and Willis, R.D., 1991. ^{81}Kr and ^{85}Kr in groundwater, Milk River Aquifer, Alberta, Canada. Appl. Geochem., 6: 419-424.

Leopoldo, P.R., Martinez, J.C. and Mortatti, J., 1992. Estimation using ^{18}O of the water residence time in small watersheds. In: Isotope Techniques in Water Resources Development 1991. IAEA, Vienna, pp. 75-84.

Liu, B., Phillips, F., Heines, S., Campbell, A.R. and Sharma, P., 1995. Water movement in desert soil traced by hydrogen and oxygen isotopes, chloride and chlorine-36, southern Arizona. Jour. of Hydrol., 168: 91-110.

Loosli, H.H., 1992. Applications of ^{37}Ar, ^{39}Ar and ^{85}Kr in hydrology, oceanography and atmospheric studies: Current state of art. In: Isotopes of Noble Gases as Tracers in Environmental Studies. IAEA, Vienna, pp. 75-84.

Loosli, H.H., Lehmann, B.E., Thalmann, C., Andrews, J.N. and Florkowski, T., 1992. Argon-37 and argon-39: measured concentrations in groundwater compared with calculated concentrations in rock. In: Isotope Techniques in Water Resources Development 1991. IAEA, Vienna, pp. 203-214.

Maloszewski, P., Rauert, W., Stichler, W. and Hermann, A., 1983. Application of flow models in an Alpine catchment area using tritium and deuterium data. Jour. of Hydrol., 66: 319-330.

Maloszewski, P. and Zuber, A., 1991. Influence of matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate aquifers. Water Resour. Res., 27(8): 1937-1945.

Mazor, E., 1972. Paleotemperatures and other hydrological parameters deduced from noble gases dissolved in groundwaters, Jordan Rift Valley, Israel. Geochim. et Cosmochim. Acta, 36: 1321-1336.

Mazor, E. and Bosch A., 1992. Helium as a semiquantitative tool for groundwater dating in the range of 10^{4}-10^{8} years. In: Isotopes of Noble Gases as Tracers in Environmental Studies. IAEA, Vienna, pp. 163-178.

Mazor, E., 1995. Stagnant aquifer concept. Part I. Large-scale system - Great Artesian Basin, Australia. Jour. of Hydrol., 173: 219-240.

Michel, R.L., 1992. Residence times in river basins as determined by analysis of long-term tritium record. Jour. of Hydrol., 130: 367-378.

Miró, R. and Gonfiantini, R., 1981. Isotopic investigation of groundwater in the area of Santiago del Estero, Republic of Argentina. In: Proceedings of the Interamerican Symposium on Isotope Hydrology. Instituto de Asuntos Nucleares, Bogotá, pp. 149-161.

Münnich, K.O., 1983. Moisture movement in the unsaturated zone. In: Guidebook on Nuclear Techniques in Hydrology, 1983 Edition. IAEA, Vienna, pp. 203-222.

Nguyen T.V., Nguyen K.C., Huynh L., Nguyen D.M., and Phan T.T., 1994. Preliminary geochemical and isotopic study of the South Trungbo geothermal area in Central Vietnam. In: Isotope and Geochemical Techniques Applied to Geothermal Investigations, IAEA- TECDOC-788. IAEA, Vienna, pp. 249-269.

Nir, A., 1964. On the interpretation of tritium age measurement in groundwater. J. Geophys. Res., 69: 2589-2595.

Osenbrück, K., Weise, S.M., Zuber, A., Grabczak, J. and Ciezkowski, W., 1993. Noble gas temperatures and ages of some glacial and buried brine waters in Poland. In: Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. IAEA, Vienna, pp. 319-336.

Payne, B.R., Quijano, L. and Latorre, C., 1979. Environmental isotopes in a study of origin of salinity of groundwater in the Mexicali Valley. Jour. of Hydrol., 41: 201-215.

Payne, B.R., Quijano, L. and Latorre, C., 1980. A study of the leakage between two aquifers in Hermosillo, Mexico, using environmental isotopes. In: Arid Zone Hydrology: Investigations with Isotope Techniques. IAEA, Vienna, pp. 113-130.

Payne, B.R. and Schroeter, P., 1979. Importance of infiltration from the Chimbo River in Ecuador to groundwater. In: Isotope Hydrology 1978, Vol. I. IAEA, Vienna, pp. 145-158.

Pearson, F.J. Jr. and Hanshaw, B.B., 1970. Sources of dissolved carbonate species in groundwater and their effects on carbon-14 dating. In: Isotope Hydrology 1970. IAEA, Vienna, pp. 271-286.

Phillips, F.M., Mattick, J.L., Duval, T.A., Elmore, D. and Kubik, P.W., 1988. Chlorine 36 and tritium from nuclear weapons fallout as tracers for long-term liquid and vapor transport movement in desert soils. Water Resour. Res., 24(11): 1877-1891.

Plummer, L.N., 1993. Stable isotope enrichment in paleowaters of the Southeast Atlantic coastal plain, United States. Science, 262: 2016-2020.

Przewłocki, K. and Yurtsever, Y., 1974. Some conceptual mathematical models and digital simulation approach in the use of tracers in hydrological systems. In: Isotope Techniques in Groundwater Hydrology 1974, Vol. II. IAEA, Vienna, pp. 425-450.

Ramspacher, P., Zojer, H., Fröhlich, K. and Stichler, W., 1992. The recharge of large springs from a carbonate aquifer near Innsbruck applying environmental tracers. In: H. Hötzl and A. Werner (Eds), Tracer hydrology. A.A. Balkema, Rotterdam, Brookfield, pp. 251-257.

Richter, J., Szymczak, P. and Jordan, H., 1993. Use of combination of lumped parameter models to interpret groundwater isotopic data. J. Contam. Hydrol., 14: 1-13.

Robertson, W.D. and Cherry, J.A., 1989. Tritium as an indicator of recharge and dispersion in a groundwater system in Central Ontario. Water Resour. Res., 25: 1097-1109.

Rozanski, K., 1985. Deuterium and oxygen-18 in European groundwaters - links to atmospheric circulation in the past. Chem. Geol. (Isotope Geoscience Section), 52: 349-363.

Rozanski, K., Gonfiantini, R. and Araguás-Araguás, L., 1991. Tritium in the global atmosphere: distribution patterns and recent trends. J. Phys. G: Nucl. Part. Phys., 17: 523-536.

Rozanski, K., Araguás-Araguás, L. and Gonfiantini, R., 1992. Relation between long-term trends of oxygen-18 isotope composition of precipitation and climate. Science, 258: 981-985.

Rozanski, K., Araguás-Araguás, L. and Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: P.K. Swart, K.C. Lohmann, J. McKenzie and S. Savin (Eds), Climate Change in Continental Isotopic Records. Geophysical Monograph 78, American Geophysical Union, Washington, D.C, pp.1-36.

Ruiz, J.C. and Rojas Molina, R., 1995. Estudio hidrológico del acuífero de Lima (Perú) aplicando técnicas isotópicas. In: Nuevos Estudios de Hidrología Isotópica en América Latina, IAEA-TECDOC-835. IAEA, Vienna, pp. 277-305.

Salomons, W. and Mook, W.G., 1986. Isotope geochemistry of carbonates in the weathering zone In: P. Fritz and J.Ch. Fontes (Eds), Handbook of Environmental Isotope Geochemistry. Vol. 2 The Terrestrial environment B. Elsevier, Amsterdam-Oxford-New-York-Tokyo, pp. 239-265.

Sartorius, H., 1994. Spuren-analyse: 20 Jahre Kr-85-messung in Freiburg; Bundamt für Strahlenschutz, Jahresbericht 1993, pp. 122-123.

Schlosser, P., Stute, M., Dörr, H., Sonntag, C. and Münnich, K.O., 1988. Tritium/^{3}He dating of shallow groundwater. Earth Plan. Sci. Letters, 89: 353-362.

Schlosser, P., Stute, M., Sonntag, C. and Münnich K.O., 1989. Tritiogenic ^{3}He in shallow groundwater. Earth Plan. Sci. Letters, 94: 245-256.

Schotterer, U., Fröhlich, K., Stichler, W. and Trimborn, P., 1993. Temporal variation of ^{18}O and deuterium excess in precipitation, river and spring waters in Alpine regions of Switzerland. In: Isotope Techniques in the study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. IAEA, Vienna, pp. 53-64.

Schotterer, U., Stocker, T., Hunziker, J., Buttet, P. and Tripet, J.P., 1995. Isotope im Wasserkreislauf. Schweizerischen Vereins des Gas- und Wasserfaches (SVGW), gwa 9, Sonderdruck Nr. 1348, pp. 2-8.

Shackleton, N.J., 1987. Oxygen isotopes, ice volume and sea level. Quat. Sci. Rev., 6: 183-190.

Smethie, W.M., Solomon, D.K., Schiff, S.L. and Mathieu, G.C., 1992. Tracing groundwater flow in Borden aquifer using krypton-85. Jour. of Hydrol., 130: 279-297.

Smith, D.B., Wearn, P.L., Richards, H.J. and Rowe, P.C., 1970. Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium. In: Isotope Hydrology 1970. IAEA, Vienna, pp. 73-87.

Solomon, D.K. and Sudicky, E.A., 1991. Tritium and helium-3 isotope ratios for direct estimation of spacial variations in groundwater recharge. Water Resour. Res., 27: 2309-2319.

Solomon, D.K., Schiff, S.L., Poreda, R.J. and Clarke, W.B., 1993. A validation of the ^{3}H/^{3}He method for determining groundwater recharge. Water Resour. Res., 29: 2951-2962.

Sonntag, C., Neureuther, P., Kalinke, Ch., Münnich, K.O., Klitzsch, E. and Weistroffer, K., 1976. Zur Paleŏklimatik der Sahara. Kontinental Effekt in D- und ^{18}O-Gehalt pluviales Saharwasser. Naturwissenschaften, 63: 479.

Sonntag, C., Klitsch, E., Löhnert, E.P., El-Shazly, E.M., Münnich, K.O., Junghans, Ch., Thorweihe, U., Weistroffer, K. and Swailem, F.M., 1979. Palaeoclimatic information from deuterium and oxygen-18 in carbon-14 dated North Saharian groundwaters. In:Isotope Hydrology 1978, Vol. II. IAEA, Vienna, pp.569-581.

Sonntag, C., Thoma, G., Münnich, K.O., Dinçer, T. and Klitzsch, E., 1980a. Environmental isotopes in North African groundwaters; and the Dahna sand-dune study, Saudi Arabia. In: Arid-zone Hydrology: Investigations with Isotope Techniques. IAEA, Vienna, pp. 77-84.

Sonntag, C., Thorweihe, U., Rudolph, J., Löhnert, E.P., Junghans, Ch., Münnich, K.O., Klitzsch, E., Shazly, E.M. and Sweilem, F.M., 1980b. Paleoclimate evidence in apparent ^{14}C of Saharan groundwater. Radiocarbon, 22(3): 871-878

Sonntag, C., Christmann, D. and Münnich, K.O., 1985. Laboratory and field experiments on infiltration and evaporation of soils by means of deuterium and oxygen-18. In: Stable and Radioactive Isotopes in the Study of the Unsaturated Zone, IAEA-TECDOC-357. IAEA, Vienna, pp. 145-159.

Srdoc, D., Sliepcevic, A., Obelic, B., Horvatincic, N., Moser, H. and Stichler, W., 1980. Isotope investigations as a tool for regional hydrogeological studies in the Libyan Arab Jamahiriya. In:Arid-Zone Hydrology: Investigations with Isotope Techniques. IAEA, Vienna, pp. 153-164.

Stichler, W., Maloszewski, P. and Moser, H., 1986. Modelling of river water infiltration using oxygen-18 data. Jour. of Hydrol., 83, 355-365.

Stute, M., Clark, J.F., Phillips, F.M. and Elmore, D., 1993. Reconstruction of the late glacial climates from the groundwater archive: Cl$^-$ and ^{36}Cl in the Carrizo aquifer, Texas. In: Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. IAEA, Vienna, pp. 259-270.

Stute, M. and Schlosser, P., 1993. Principles and applications of the noble gas paleothermometer. In: P.K. Swart, K.C. Lohmann, J. McKenzie and S. Savin (Editors), Climate Change in Continental Isotopic Records. Geophysical Monograph 78, American Geophysical Union, Washington, D.C, pp. 89-100.

Stute, M., Clark, J.F., Schlosser, P., Broecker, W.S. and Bonani, G., 1995a. A 30,000 yr continental paleotemperature record derived from noble gases dissolved in groundwater from the San Juan basin, New Mexico. Quaternary Research, 43: 209-220.

Stute, M., Forster, M., Frischkorn, H., Serejo, A., Clark, J.F., Schlosser, P., Broecker, W.S. and Bonani, G., 1995b. Cooling of tropical Brazil (5°C) during the Last Glacial Maximum. Science, 269: 379-383.

Stute, M., Schlosser, P., Clark, J.F. and Broecker, W.S., 1992. Paleotemperatures in the Southwestern United States derived from noble gases in ground water. Science, 256: 1000-1003.

Stuyfzand, P.J., 1989. Hydrology and water quality aspects of Rhine bank groundwater in The Netherlands. Jour. of Hydrol., 106: 341-363.

Tandia, A.A., Aranyossy, J-F. and Gaye, C.B., 1993. Evaluation de la recharge des nappes phréatiques sous climat semi-aride. Exemple du Nord-Sénégal. In: Les ressources en eau au Sahel, IAEA-TECDOC-721. IAEA, Vienna, pp. 39-51.

Taylor, C.B., Wilson, D.D., Brown, L.J., Stewart, M.K., Burden, R.J. and Brailsford, G.W., 1989. Sources and flow of North Canterbury Plains groundwater. Jour. of Hydrol., 106: 311-340.

Taylor, C.B., Brown, L.J., Cunliffe, J.J. and Davidson, P.W., 1992. Environmental tritium and ^{18}O applied in a hydrological study of the Wairau Plain and its contributing mountain catchments, Marlborough, New Zealand. Jour. of Hydrol., 138: 269-319.

Thilo, L. and Münnich, K.O., 1970. Reliability of carbon-14 dating of groundwater: effect of carbonate exchange. In: Isotope Hydrology 1970. IAEA, Vienna, pp. 259-270.

Torgersen, T., 1992. Helium-4 model ages for pore fluids from fractured lithologies. Discussion and application. In: Isotopes of Noble Gases as Tracers in Environmental Studies. IAEA, Vienna, pp. 179-201.

Torgersen, T., Clarke, W.B. and Jenkins, W.J., 1979. The tritium/helium-3 method in hydrology. In: Isotope Hydrology 1978, Vol. II. IAEA, Vienna, pp. 917-930.

Urbka, P., Jacob, H., Fröhlich, K. and Salih, M.K., 1993. Identification of groundwater recharge source in Northern Sudan by environmental isotopes. Journal of Environmental Hydrology, 1(4): 8-16.

Vogel, J.C., 1967. Investigation of groundwater flow with radiocarbon. In: Isotopes in Hydrology. IAEA, Vienna, pp. 355-369.

Vogel, J.C., 1970. Carbon-14 dating of groundwater. In: Isotope Hydrology 1970. IAEA, Vienna, pp. 225-239.

Vogel, J.C., Talma, A.S. and Heaton, T.H.E., 1982. The age and isotopic composition of groundwater in Stampriet Artesian Basin, SWA. Report to the Steering Committee for Water Research in SWA. National Physical Research Laboratory, Pretoria, 90 p.

Walker, G.R., Jolly, I.D., Stadter, M.H., Leaney, F.W., Davie, R.F., Fifield, L.K., Ophel, T.R. and Bird, J.R., 1992. Evaluation of the use of ^{36}Cl in recharge studies. In: Isotope Techniques in Water Resources Development 1991. IAEA, Vienna, pp. 19-29.

Wang Ji-yang and Pang Zhong-he, 1994. Application of isotope and geochemical techniques to geothermal exploration in Southeast China. In: Isotope and Geochemical Techniques Applied to Geothermal Investigations. IAEA-TECDOC-788. IAEA, Vienna, pp. 9-21.

Wassenaar, L.I., Aravena, R. and Fritz, P., 1992. Radiocarbon contents of dissolved organic and inorganic carbon in shallow groundwater systems. Implications for groundwater dating. In: Isotope Techniques in Water Resources Development 1991. IAEA, Vienna, pp. 143-151.

Weise, S.M. and Moser, H., 1987. Groundwater dating with helium isotopes. In: Isotope Techniques in Water Resources Development. IAEA, Vienna, pp. 105-126.

Wigley, T.M.L., Plummer, L.N. and Pearson, F.J., 1978. Mass transfer and carbon isotope evolution in natural water systems. Geochim. et Cosmochim. Acta, 42: 1117-1139.

Yurtsever, Y. and Buapeng, S., 1992. Compartmental modelling approach for simulation of spacial isotopic variation in the study of groundwater dynamics. A case study of a multi-aquifer system in the Bangkok Basin, Thailand. In: Isotope Techniques in Water Resources Development 1991. IAEA, Vienna, pp. 291-308.

Yurtsever, Y. and Payne, R.B., 1986. Matemathical models based on compartmental simulation approach for quantitative interpretation of tracer data in hydrological systems. In: Proc. 5th International Symposium on Underground Water Tracing. IGME, Athens, pp. 341-353.

Zuber, A., 1986. Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. In: P. Fritz and J.Ch. Fontes (Editors), Handbook of Environmental Isotope Geochemistry, Vol. 2. The Terrestrial Environment B. Elsevier, Amsterdam, pp. 1-59.