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Tracer Techniques in Hydrology

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The paper presents a review of the use of environmental and artificial tracers in studies of surface waters, ground waters and sediments. Both stable and radioactive substances are considered.

The environmental tracers include those whose natural abundance variations allow inference of the origins, movement or depositional history of water or sediments and those whose presence in the environment is due to man's past activities. Examples of the former type are the stable isotopes of hydrogen, oxygen and sulphur, noble gases and the radioactive isotopes carbon-14 and uranium series. The latter type of environmental tracers include radioactive elements from nuclear bomb testing and fluorocarbon compounds.

Artificial tracers, categorized into radioactive, activable, chemical and particulate tracers are described together with their applications in flow measurement, run-off transit-time measurement, lake dynamics and ground water movement studies. Sediment movement studies are briefly described.

Reference is also made to current measurement methods and recent developments in the analysis of environmental isotopes from small samples.

1. Introduction

THE DISCIPLINE of hydrology is quite broad. It embraces all aspects of the earth's water cycle commencing with evaporation of water from the oceans into the atmosphere, the transport of the water vapour by air masses and subsequent precipitation of rain, snow or ice, its direct run-off back to the oceans or its movement through vegetation, soils and rocks to ground water bodies, which may be actively linked to the oceans. A significant contribution to our understanding of the various processes involved in this cycle has resulted from the application of tracer techniques in field and laboratory studies.

Tracers are identifiable substances which, from examination of their behaviour in a flowing medium, may be used to infer the general behaviour of the medium. They may be broadly categorised by their origin. Those substances normally present in the medium are generally termed environmental tracers, and those deliberately introduced into the medium for the purpose of the study are generally termed artificial tracers. Over the past few decades, the use of tracers has expanded considerably mainly owing to advantages in analytical techniques and, with the construction of nuclear reactors, to the availability of radioactive isotopes which provide specificity of detection of the tracer in the presence of the same naturally occurring element.

Particular contribution to the use of tracers have been afforded by past man-made events. These include such things as the use of thermo-nuclear weapons in the atmosphere, causing world-wide spread of radioactivity or the increasing use of fluorocarbon compounds, such as trichlorofluoromethane, as pressurants in aerosol sprays or in refrigeration circuits. Such activities have provided specific tracer substances universally incorporated in modern precipitation that can be used to confirm connections or otherwise with ground water bodies, thereby indicating ground water ages or mixes. The radioactive decay of naturally occurring or enhanced levels of radioactivity provides means of dating waters or lacustrine sediments.

The interpretation of these "passive" tracers is uniquely related to the tracer substance under examination, its origin, physical behaviour in the environment and its measurement. This is not so for artificial tracers which are deliberately introduced into the system to trace movement or dispersion. For these "active" tracers, provided they are physically compatible with the fluid to be studied, interpretation is not a function of the tracer itself. A variety of tracer techniques are used, each consisting of an injection phase, mixing of the tracer with the fluid, sampling, measurement and interpretation of the amounts of tracer recovered or of tracer concentration–time distributions.

Because of this fundamental difference in the interpretation of "passive" and "active" tracers, a review of applications such as this is best achieved by considering each environmental tracer separately. For added tracers, individual techniques, each of which is used with a variety of tracers, are described with their specific operational advantages and disadvantages. It is not intended here to provide a comprehensive review—the scope of the topic would demand a treatment too detailed for the present purpose—but to give a brief description of the methods, present state-of-the-art and some future developments.

2. Environmental Isotopes and Applications

The term "environmental isotopes" generally refer to those isotopes whose natural abundance variations

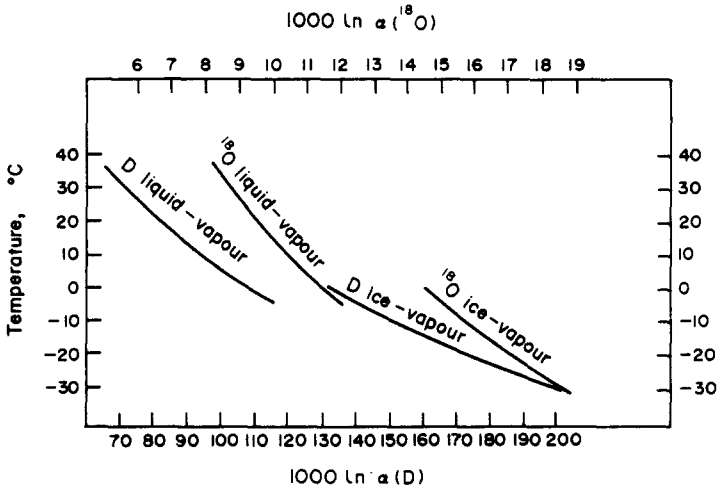

FIG. 1. Deuterium and ^{18}O isotope fractionations between water and vapour and ice and vapour.[1]

can be used in hydrological studies. The stable isotopes of hydrogen and oxygen are commonly used because they form part of the water molecule. Tritium is also included in this category although its presence in the environment is mainly due to nuclear weapons tests. Other isotopes such as ^{34}S, ^{39}Ar, ^{32}Si and those of the uranium and thorium decay series play an important role in understanding particular aspects of the water cycle. Fluorocarbons, released into the atmosphere mainly as pressurants of aerosols, and absorbed in precipitation and surface waters can be used to identify recent water.

The advancement in the use of environmental isotopes has been encouraged by the role of the World Meteorological Organisation and the International Atomic Energy Agency in data co-ordination. Since 1961 more than 120 meteorological stations in 70 countries and territories have been collecting monthly precipitation samples for the WMO/IAEA Isotopes in Precipitation Network (IAEA, 1969–1980). This has allowed an understanding of isotope behaviour on a global scale. Distinct differences have been observed in the amounts of "man-made" isotopes in, and their mixing behaviour between, the Northern and Southern Hemispheres. Common trends in isotopic composition of precipitation have been identified and distinct differences, such as deuterium excess between oceanic and inland seas, have been observed.

2.1 *Stable isotopes of hydrogen and oxygen*

The principal heavy stable isotopic components of water, $HD^{16}O$ and $H_2{}^{18}O$ occur in natural waters in concentrations of about 320 and 2000 ppm respectively. Slight variations in these concentrations occur as a result of fractionation caused by changes of state from ocean water through evaporation, recondensation, precipitation and snow and ice formation. The heavy components, having lower vapour pressures than $H_2{}^{16}O$ are concentrated in the liquid phase. As fractionation is dependent on temperature of condensation, the lower the temperature the greater is the depletion of these heavy isotopes in the vapour phase.

The small variations in isotopic concentrations are measured by mass spectrometry and usually expressed as differences from a standard SMOW (Standard Mean Ocean Water) in parts per thousand (per mille) or δ units defined by:

$$\delta = \frac{R - R_{SMOW}}{R_{SMOW}} \times 1000^{o}_{oo}$$

where R refers to the isotopic ratio D/H or $^{18}O/^{16}O$.

The relative enrichment of isotopes between two phases 1 and 2 for small values of δ is

$$\delta_1 - \delta_2 \simeq 1000 \ln \alpha_{1-2}$$
$$\simeq a + bT^{-1} + cT^{-2}$$

where α_{1-2} is the fractionation factor $R1/R2$. a, b and c are constants and T is absolute temperature.

The sensitivities of isotopic fractionations between water and vapour and ice and vapor are shown in Fig. 1.[1] Thus, moisture evaporated from the ocean is depleted in D and ^{18}O with respect to the surface water. As the vapour moves inland, a Raleigh distillation system occurs with repeated precipitations and the remaining vapour becomes more depleted in its heavy isotopes. The temperature effect results in variations with latitude and altitude of precipitation. The general relationship between δD and $\delta^{18}O$ enrichment for precipitation follows the relationship:[2]

$$\delta D = 8\,\delta^{18}O + d$$

where d is termed the deuterium excess.

The value of d for precipitation from oceans is 10[3] but for inland seas this value is generally greater.[4,5] Regional variations on this relationship exist depending on the source of water vapour. Coastal regions will be influenced by both continental and oceanic air masses and consequently the isotopic content of precipitation will differ from those of inland sites. The

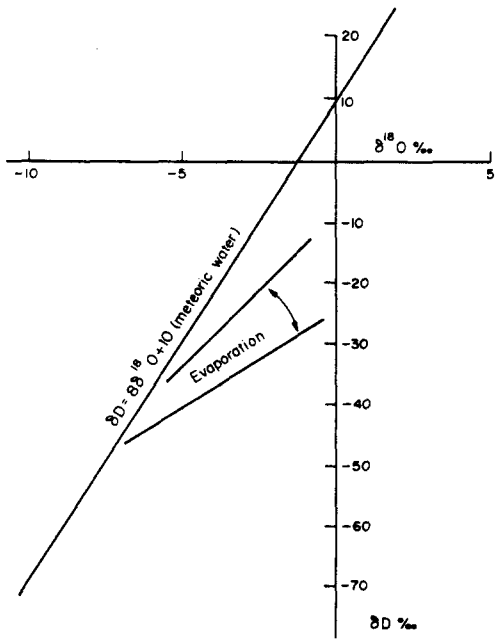

FIG. 2. δD–$\delta^{18}O$ relationships for meteoric and evaporative sources of water.

isotopic compositions of precipitation and ground waters in temperate regions agree reasonably well showing no significant fractionation in the unsaturated zone as infiltration occurs. In the U.K., the slopes of the δD–$\delta^{18}O$ graphs are 6.9 and 6.6 respectively.[6,7] These values are similar to those determined from a number of North European sampling stations where the slope varies from 6 to 7.5,[6] although the measurements represent a narrow range of temperatures. Waters subjected to evaporation (e.g. from lakes and reservoirs) yield much lower slopes of the δD–$\delta^{18}O$ graphs. These may be typically 4–5 and can be readily identified (Fig. 2).

The influence of weather patterns on the composition of ground waters has been clearly demonstrated in comprehensive studies on δD and $\delta^{18}O$ variations in ground waters in North Africa and Europe.[8] Depletion of these isotopes increases in the easterly direction showing the influence of westerly air flows (Fig. 3). When this information is combined with ground water dating, it is clear that even waters older than 20,000 yr BP, have similar deposition histories.

The interpretations of variations in the isotopic composition of waters, either alone or in combination with other isotope data, are of particular importance in studies of interactions of surface waters and ground waters, ground water recharge, the mechanism and components of run-off, aquifer leakage and evaporation studies. Sources of recharge have been identified from comparisons of $\delta^{18}O$ in ground waters with those of precipitations at various altitudes. The dependence of $\delta^{18}O$ values on altitude has been found to be from -0.13 to $0.3‰$ 100 m. This relationship has been used to show, for example, that recharge to a coastal plain was mainly from precipitations on the higher slopes of a nearby mountain range.[9] Similarly, the mean altitude of recharge areas of springs in the Karst regions of the High Alps in Switzerland have been determined.[10]

These techniques are being increasingly applied to mining hydrology, in particular in Poland and Czechoslovakia. Sources of infiltration of mine water in the Lublin and Upper Silesian coal basins have been shown to be old static water from the Carboniferous Series and younger mobile water from infiltration through the overburden, thus inferring that deeper mining would result in less infiltration as the mobile component decreased.[11] Other information, such as the degree of mix of infiltration with connate waters, identification of sea water ingress, and leakage into salt mines have been obtained.

Stable isotopes provide a useful means of identifying water bodies and, in some instances of establishing the presence of old water from paleoclimatological data. The growth in their use over the past two decades have placed them in the forefront of current hydrological tracer practice. However, more understanding of ground water behaviour can be obtained from their combined use with other environmental tracers such as tritium and ^{14}C which can provide supporting data on hydrological histories.

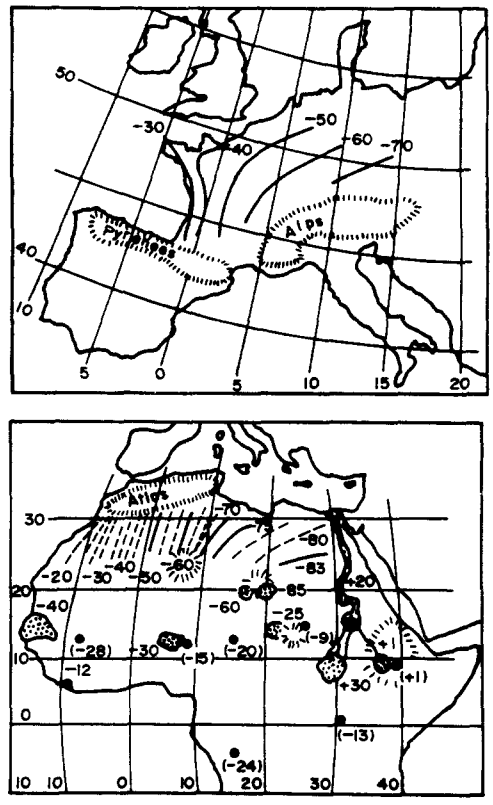

FIG. 3. Preliminary isoline-presentation of δD of modern European and fossil Saharian groundwaters. Mean δD of modern (and fossil) groundwater (in dotted areas) and of mean weighted annual precipitation (black points, numbers in brackets) in Central Africa.[8]

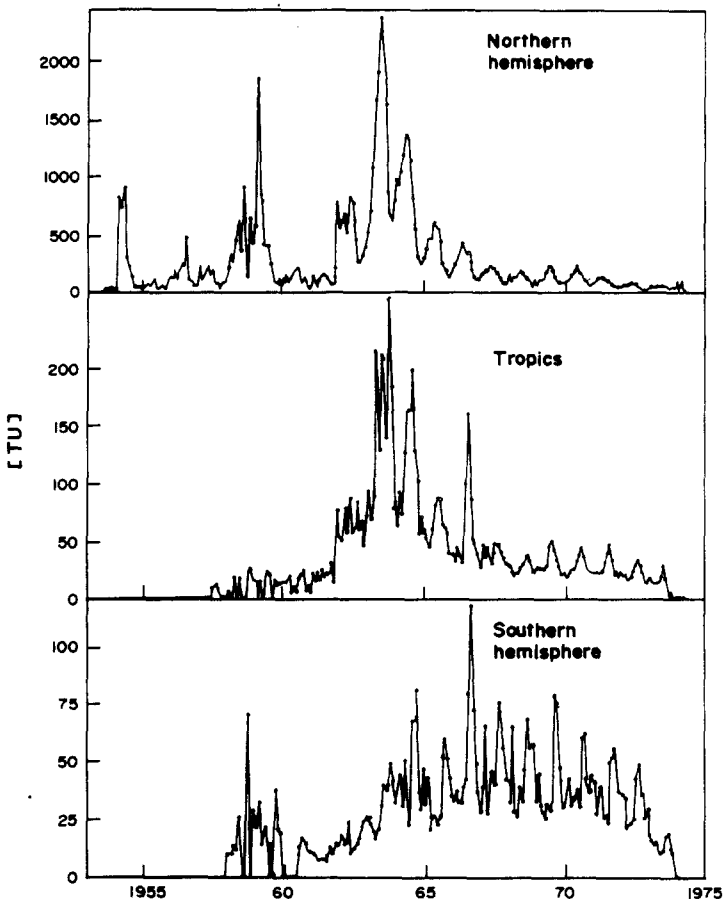

FIG. 4. Average tritium concentration in precipitation in the northern hemisphere, the tropical stations and the southern hemisphere, based on records of IAEA network.[1]

2.2 *Tritium*

Tritium, the radioactive isotope of hydrogen (half-life 12.4 yr), is present in the atmosphere and hydrosphere mainly as a result of thermo-nuclear weapons testing. Little information is available on atmospheric concentrations prior to the first test in 1952 but estimates of the concentrations resulting from cosmic ray reactions range from 4 to 25 TU.[1] The estimated sub-surface production of tritium from uranium fission neutrons is about 1 TU.[12] These values compare with peak values of about 3000 and 120 TU in the Northern and Southern Hemispheres respectively. The pronounced peak in the North occurred in 1963 while the much smaller perturbation in the South occurred three years later due to the release locations and atmospheric mixing. Although mixing in each hemisphere was quite rapid, the tritium signatures have remained quite distinct (Fig. 4).

The main use of environmental tritium in hydrological investigations has been to provide a label for identifying modern waters, that is waters older than 1953 in the Northern Hemisphere and 1957 in the Southern Hemisphere. This has featured in numerous hydrological studies and provides revealing information on ground water mixing when the measurement of tritium is combined with those of stable isotopes and ^{14}C.

The 1963 peak concentration of tritium has been used as a time marker to determine the rate of infiltration through the unsaturated zone of the Chalk.[13] Smith found from tritium measurements of pore water in extracted cores that the peak concentration was clearly identifiable. A large fraction of the tritium which entered the Chalk from rainfall since 1954 is stored in the upper 15 m of the unsaturated zone. Measurements show a downward movement of about 1 m/yr and implied intergranular seepage as the main transport mechanism. This simple piston-type movement approach was contested by some hydrologists and an alternative qualitative description of the flow is that bulk infiltration is through fissures with continuous diffusion of the tritium between waters in the fissures and in the pores.[14,15] The significance of the movement of tritium to that of nitrate was apparent. Because of the association of nitrates with methaemoglobinaemia and gastric cancer, considerable studies on chalk and sandstones have been carried out on this aspect of hydrology.[16,17] Typical measurements are shown in Fig. 5.[18]

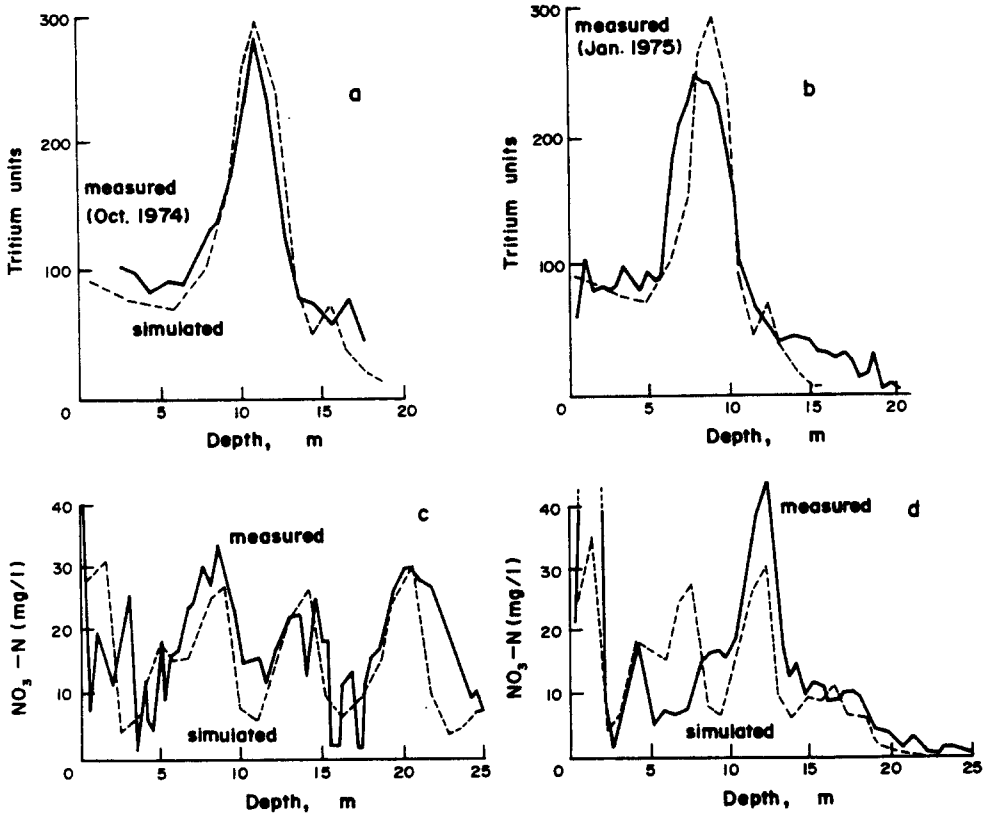

FIG. 5. Comparison of numerical models and field observations. (a) and (b)—tritium; (c) and (d)—nitrate.[18]

Mathematical models representing relatively fast flow through fissures with diffusion into dead-end pores of the rock matrix have shown that considerable delays can be experienced in the movement of a tracer substance in the flow.[19] This approach, when applied to the water movement through the Chalk has shown that although the downward movement of tritium is about 1 m/yr, the water velocities in the fissures are approximately two orders of magnitude greater.

Apart from the identification of obvious peaks in the tritium profile, attempts have been made to determine the residence time distribution of infiltration from correlation of observed variations in the inlet and outlet concentrations. The relationship between the inlet (C_i) and outlet (C_0) concentrations is:

$$C_0(t) = \int_0^\infty C_i(t-\tau)h(\tau)\exp(-\lambda\tau)\,d\tau$$

where $h(\tau)$ is a weighting function determined by the impulse response of the flow system and λ is the decay constant of tritium (0.056 yr^{-1}).

The solution of this equation, termed de-convolution, may be achieved by matrix methods but for systems with large dispersion and relatively small input variations, these methods are unstable. A more commonly used method is to calculate the output functions from the known input variations assuming different flow models and impulse responses. The model providing the best fit of measured and calculated output data is then adopted to describe the flow system. A number of models such as 'piston-flow", completely mixed reservoir and mixed cells have been used to describe aquifer behaviour.[20,21]

A more recent use of tritium for residence time studies has been utilization of the decay of tritium to ^3He. Improvements in mass-spectrometric techniques now enable accurate measurements of small concentrations of ^3He to be made. The ratio of tritium to ^3He in a closed system is a measure of the period over which the tritium has decayed. This fact has been applied to the measurements of relatively short (a few years) residence times of water layers in lakes.[22] The methods may also have applications in ground water dating but a number of complications are introduced by possible variations in the composition of any added helium from the atmosphere or from α-decay of uranium and possible ground water mixing.

2.3 *Carbon isotopes*

A major contribution to the study of ground water movement resulted from the proposal to apply radiocarbon dating to the carbonate contents of the waters,

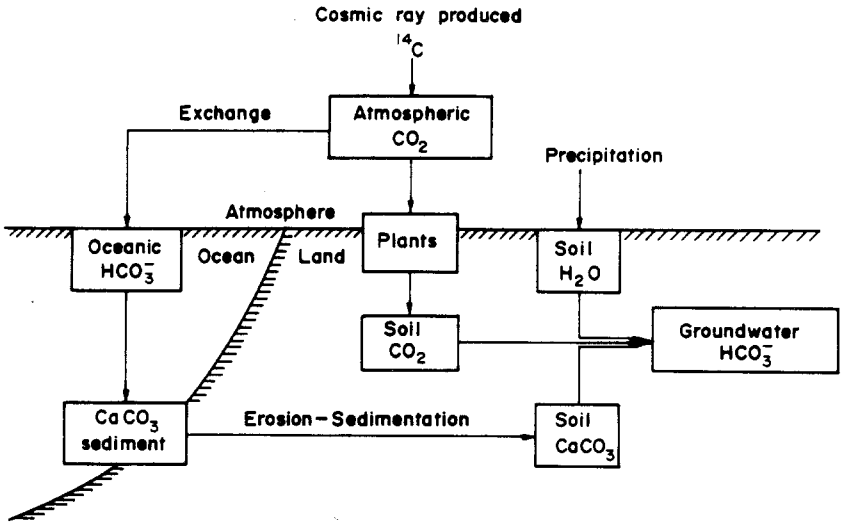

FIG. 6. A part of the natural carbon cycle, relevant to the origin of ^{14}C in groundwater.[1]

allowing a measurement of "age" of the waters over many thousands of years.[23] ^{14}C is incorporated into the ground waters from dissolved carbon dioxide occurring from root respiration of plants and decaying humus at the biologically active layers of soil. The most common origin of the bicarbonate is the solution of the limestone according to the equation:

$$CO_2 + H_2O + CaCO_3 \rightleftharpoons Ca(HCO_3)_2. \quad (1)$$

The radioactive decay of ^{14}C (half-life 5730 yr), present in the total dissolved carbonate in the water, from its initial value gives a measure of the "age" of the water according to the relationship:

$$t = \frac{5730}{\ln 2} \ln \frac{A_0}{A}$$

where A_0 is the initial amount of ^{14}C in the carbonates when exchange of carbon with the biogenic component has ceased and A is the amount of ^{14}C present at the time of measurement.

The presence of ^{14}C in ground waters originates from atmospheric carbon dioxide through the various routes shown in Fig. 6.[1] The natural specific activity of atmospheric CO_2, oceanic bicarbonate, living plants and animals is about 0.23 Bq/g of carbon (13.6 dpm) and the internationally accepted standard of modern carbon referred to 1950 is taken as 95% of that of NBS oxalic acid. However, unlike archaeological dating, where the initial activity of the material to be dated is considered to be 100% of modern CO_2 activity (denoted as 100 pmc) uncertainties surround the initial levels of ^{14}C in the dissolved carbonates. The radioactive carbon from the soil is diluted with the old, inorganic carbon of the rock which contains no ^{14}C. Various geochemical models have been developed to describe the initial conditions of ^{14}C and its subsequent behaviour as the water moves through various chemical conditions through to equilibrium states. Comprehensive reviews of these models have been presented.[25,26]

The earliest and simple method proposed was to use a value for A_0 of 85 ± 5 pmc derived from many measurements of ^{14}C in ground waters from North West Europe. A model later used the molalities of CO_2 and HCO_3 in the waters assuming perfect stoichiometry for the various chemical reactions involving carbon and gave an initial value of 55 pmc. This gives differences in ages of 3600 yr. Other values[26] suggested 0.65–0.75 for karst systems, 0.75–0.90 for sediments such as loess and 0.9–1.00 for crystalline rocks.

A more analytical approach was to use the stable isotope ^{13}C (natural abundance 1.11%) to determine the degree of isotopic mix between biogenic carbon and that of the solid carbonate which possess distinctly different ratios of $^{13}C/^{12}C$. One technique which has been widely used is to consider a simple mass balance of ^{13}C in equation (1).[27] When the ^{14}C levels of rock and biogenic carbon are taken as 0 and 100 pmc respectively, the ground water age is given as

$$t = \frac{5730}{\ln 2} \ln \frac{100}{A} \left[\frac{\delta^{13}Cs - \delta^{13}Cr}{\delta^{13}Cb - \delta^{13}Cr} \right]$$

where the italic suffixes s, r and b refer to solution, rock and biogenic components respectively; and

$$\delta C = \left[\frac{(^{13}C/^{12}C)}{(^{13}C/^{12}C)_{standard}} - 1 \right] \times 1000‰.$$

The value of $\delta^{13}C$ of the biogenic carbon depends on the particular photosynthetic process undergone by the plants in the fixation of carbon. Three groups have been identified. These are the Calvin (C3), Hatch Slack (C4) and the Crassulacean-Acid Metabolism (CAM), the first two main types having distinctive $\delta^{13}C$ range of values. The standard for ^{13}C measurement is usually taken as that of carbon dioxide pre-

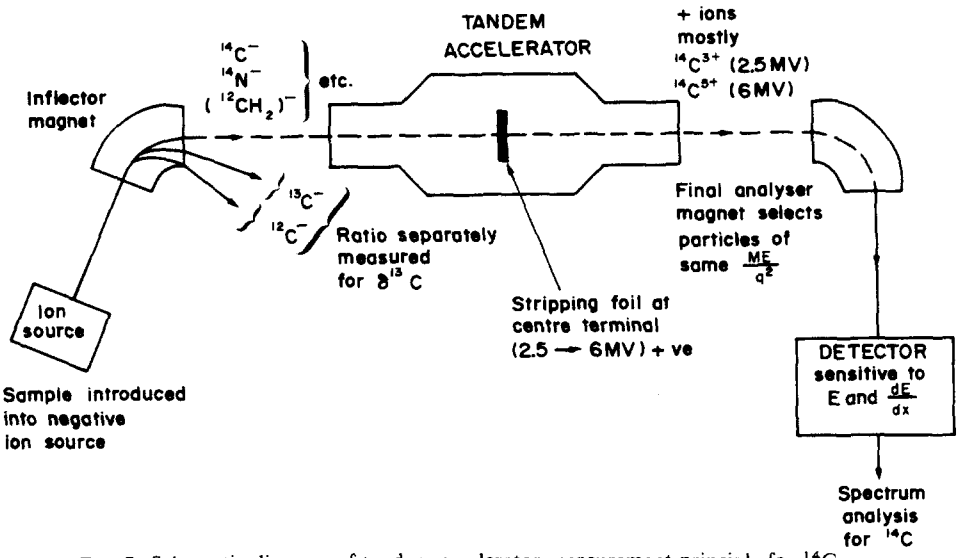

FIG. 7. Schematic diagram of tandem accelerator measurement principle for ^{14}C.

pared from belemnites (Belemnitella americana) collected from the Peedee formation of South Carolina (known as PDB standard).

In this stage of dissolution it is assumed that no precipitation of carbonate occurs. Where precipitation and dissolution of different carbonates occur, such simple representation of balance is inapplicable. Correction must also be made for the combined effects of isotopic fractionation occuring in the precipitation and redissolution of carbonate resulting in dilution of ^{14}C in solution. Computer modelling of ground water chemistry and isotope compositions enable ^{14}C measurements to be interpreted in terms of ground water ages. A simple physical model which has been shown to give values of ground water age very similar to computer models gives the following expression for ground water age.[6]

$$t = 8270 \ln\left[\frac{50}{A}\left(\frac{K - \delta^{13}Cs}{K - \delta^{13}Ci}\right)^{1+\epsilon_{13}\,1000}\right]$$

where $\delta^{13}Ci$ is

$$\frac{\delta^{13}Cr + \delta^{13}Cb}{2}.$$

ϵ_{13} is the fractionation factor and is the difference between the $\delta^{13}C$ values of the precipitate and solution; and K is the $^{13}Cr - \epsilon_{13}$.

Unfortunately, the monitoring of exchanges of carbonate and hence dilutions of ^{14}C in solution by measurements of $\delta^{13}C$ of the components cannot be made in the limiting conditions when the $\delta^{13}C$ of the precipitate equals that of the rock. Where they can be used, differences in derived "ages" using the various corrections may be quite small. Ground water velocities computed by differences in ^{14}C measurements in aquifer are almost independent of the models selected.

Recent advances in ^{14}C measurement enable dating to be achieved from extremely small samples of carbon. These methods allow the dating of ground waters bearing low levels of carbonate and when large volume samples are not available. A relevant area of study is investigation of options for the disposal of highly radioactive waste in geological formations. The main mechanism by which radionuclides can be transported from the site of deposition is by ground water movement. Consequently, the behaviour of deep ground waters in granitic formations, where there is a combination of low water volumes and low carbonate content, is of considerable interest.

One such advance is the use of high energy accelerators as ultra-sensitive mass spectrometers capable of directly measuring the ratio of ^{14}C to ^{12}C nuclei. The number of ^{14}C nuclei present for every dpm occurring is approximately 4×10^9 and modern carbon contains 6×10^{10} per gramme of carbon. This large factor provides considerable potential for improvement in sensitivity over counting methods. Both tandem accelerators and cyclotrons have been used, but, as nitrogen does not form a stable negative ion, whereas carbon does readily, tandem accelerators are preferred since this major atmospheric contaminent is considerably reduced An outline diagram of a tandem accelerator measurement scheme now commercially available is shown in Fig. 7. Features of the new machine which make possible measurements from milligram quantities of carbon are:

(1) Large initial negative ion beams obtained from solid "sputter" ion sources.

(2) Separation of extraneous molecular ions by passing the beam through a "stripping" foil.

(3) Further selection using a crossed-field mass filter.

(4) Energy and loss discrimination of residual ions at the detection stage which enables their separation (electronically) from any residual ions of the same mass.

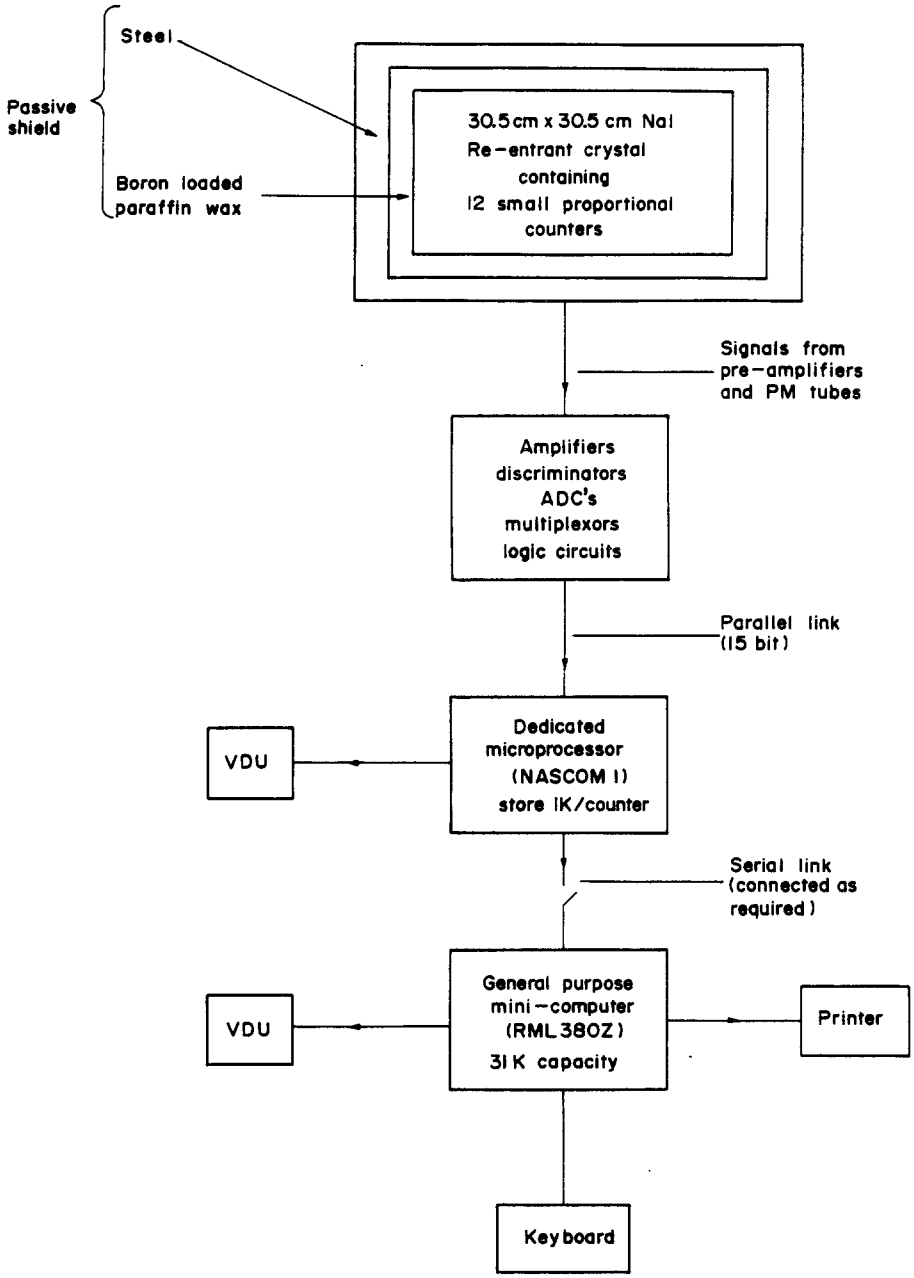

FIG. 8. Schematic diagram of Harwell Small Counter Facility.

These high energy machines allow the use of the other naturally occurring isotopes in hydrology, notably ^{36}Cl (half-life 3.1×10^5 a) for ground water studies and ^{10}Be (half-life 1.6×10^6 a) and ^{26}Al (half-life 7.2×10^5 a) in sedimentation dating.

The other major development in ^{14}C measurement is the use of small proportional counters within large NaI anti-coincidence shields. Measurements are made from carbon dioxide filling gas prepared from the ground water carbonate and measurement periods of up to several months can be achieved with stable operation. Samples as small as 10 mg carbon can be measured in this fashion. The Harwell Small Counter Facility[29] incorporates 12 small counters and an outline schematic of the shield, counter system electronics and data management is shown in Fig. 8.

2.4 *Uranium and thorium series*

Variations in the content and composition of uranium and thorium isotopes in ground water, derived from dissolution of these elements from the host rock, have been used in studies of the evolution and movements of ground waters.[30] As this topic is dealt with in detail in this edition by the main proponents of these methods, only a brief description is given here.

Both uranium concentrations and $^{234}U/^{238}U$ ratios can be used as natural tracers in ground and surface

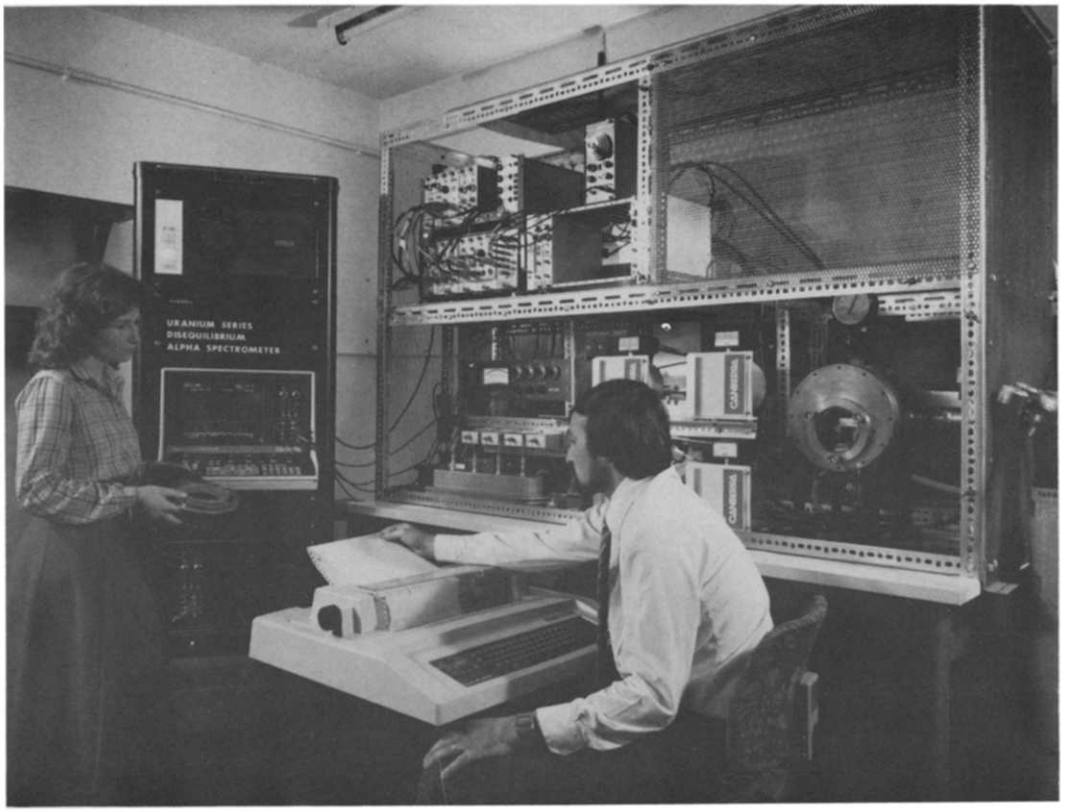

FIG. 9. Typical spectrometer for α-particle measurement.

waters. Values of $^{234}U/^{238}$ greater than unity generally exist in waters mainly owing to the recoil of the ^{234}Th during transmutation from ^{238}U. The thorium decays quickly to ^{234}U which has a half-life of about 250,000 yr. The α-recoil may result in direct injection of the atom from the rock into the ground water contained within pores in the rock or result in damage to the crystal lattice allowing preferential leaching to occur. Re-establishment of equilibrium from the initial disequilibrium state provides a means of dating the water or at least determining delay periods between two points in the flow direction from the point of establishment of disequilibrium conditions. The decay of ^{234}U to ^{230}Th (half-life 75,000 yr) is used for the dating of speleothems and sediments but its use in ground water dating is restricted by the high ionic potential of the thorium 4^+ ion causing rapid adsorption onto particulate matter or precipitation when in solution.

Uranium "signatures" in the form of concentrations and activity ratios $^{234}U/^{238}U$ have been used to identify separate water bodies and the extent of their mixing. Studies of aquifers in the U.K. and in crystalline rocks are in progress. Measurements of uranium and thorium isotopes in the host rock, particulate matter and ground waters have been made to provide a more complete understanding of the geo-chemistry of the ground water evolution. These methods also form part of an on-going intercomparison study coordinated by the IAEA, of ground water dating methods in a triassic sandstone aquifer in England.

Measurement of the separated components of uranium and thorium may be made by mass spectrometry but the more common practice, requiring less expensive equipment, is to use α-spectrometry with ion chamber or surface barrier detectors. A typical set-up is shown in Fig. 9. Uniformity of measurement procedures and a cross-checking of measurement capabilities of over 30 laboratories throughout the world have been provided by a series of "workshops" of the Uranium-Series Intercomparison Project (USIP).[31]

2.5 *Other environmental isotopes*

As measurement capabilities increase, other isotopes normally present in the environment can be used to provide more information in hydrology. Low level counting methods have been used to measure ^{32}Si and ^{32}Ar for dating ice cores.[32,33] These isotopes are produced in the atmosphere by cosmic ray spallation and incorporated into precipitation. As levels of ^{32}Si and ^{39}Ar activities are less than 10^{-2} Bq t and 10^{-3} Bq/t respectively, very large samples (typically 10–20 t) are required. Good agreement has been obtained with these methods and stable isotope measurements in ice core dating. This is not so in ground water dating studies where considerable discrepancies exist between dates derived from ^{39}Ar and ^{14}C measurements.[34] Some of this discrepancy is due to underground production of ^{39}Ar from the ^{39}K (n, p) ^{39}Ar reaction with neutrons originating from (α, n) processes. Large excesses have been found in granitic environments, for example. However, not all the questions of discrepancy have been answered and studies are in progress to compare various dating methods and to understand more fully the processes involved in the behaviour of these isotopes in ground water.

Accelerators have been used to measure ^{36}Cl (half-life 3.08×10^5 a), ^{10}Be (half-life 1.6×10^6 a) and ^{32}S. Although they have not yet been applied widely to hydrological problems, the potential exists for dating studies of ground waters and sediments beyond the range of ^{14}C measurements. Even this range has extended by the use of accelerators from about 40,000 to 100,000 years.

The accumulation of helium in ground waters from the decay of uranium and thorium in the host rock has been used as a dating method.[7,35] The annual rate at which ^4He increases is given by the expression:

$$\rho\phi^{-1}\,[1.19 \times 10^{-13}\,(U) + 0.288 \times 10^{-13}\,(Th)]\ cm^3/cm^3\ water$$

where ρ is the bulk density of the rock, ϕ is fractional porosity and U and Th are the uranium and thorium contents in ppm.

Up to 10^5 times the ^4He contribution from the atmosphere has been found in some ground waters. This has been used to "date" ground waters in radioactive waste disposal and water resource studies.

Other gases have been incorporated into ground waters as a result of man's activities and can be used as a tracer of "modern" water. ^{85}Kr, a nuclear fission product, has increased steadily in concentration since the advent of nuclear weapons testing, Fig. 10.[36] Also, the increasing use of fluorocarbon compounds such as trichlorofluoromethane CCl_3F (Freon 11) has also provided us with a tracer which can be measured in the field by electron-capture devices.[37]

Sources of ground water may be determined from analysis of the isotopic composition of its sulphur bearing minerals such as anhydrite ($CaSO_4$) or gypsum ($CaSO_4\ 2H_2O$). The $^{34}S/^{32}S$ ratios in various natural sulphur compounds vary greatly. Basically, there are two types of sulphate—those derived from evaporite materials are enriched in ^{34}S and those from sulphide are relatively depleted. Sulphates in coastal precipitation are similar to oceanic compositions, but inland, where terrestrial sulphur sources may exist, particularly in arid climates or near industrialised, coal burning areas, the composition changes. Consequently, much information may be obtained from analysis of the isotopic composition of surrounding strata, precipitation and the minerals present in the ground water.[1]

The use of amino acids to date old ground waters has been considered to have strong possibilities.[38] This method is based on a chemical reaction, known as racemization, of amino acid isomers. When an

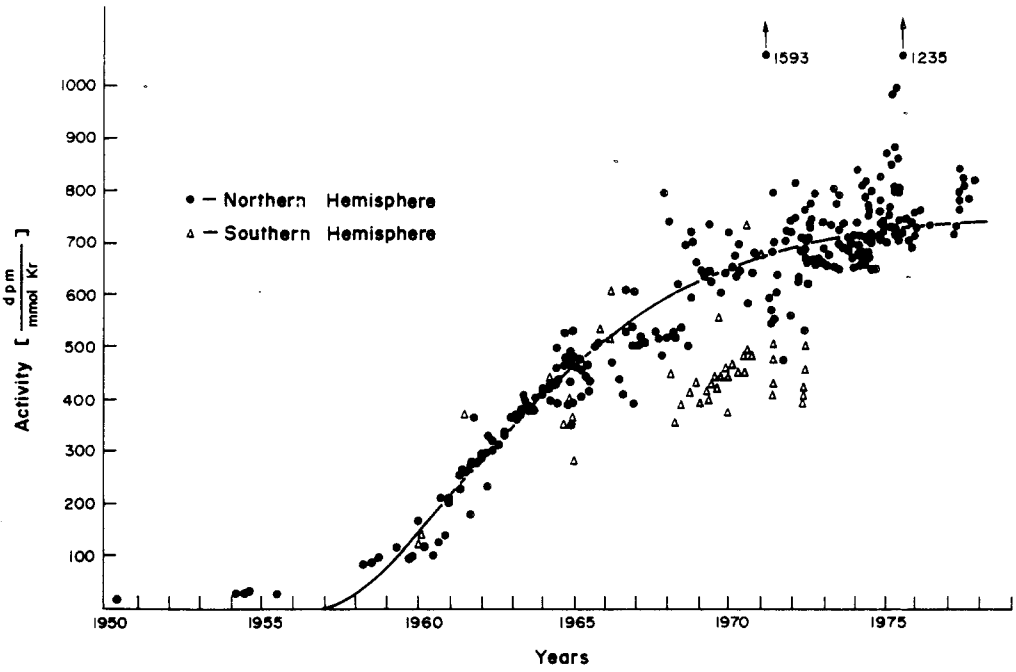

FIG. 10. ^{85}Kr in the atmosphere, 1950–1977.[36]

organism dies its amino acids, which are predominently as the L isomer, are converted to the D isomer at a rate depending on temperature, until equilibrium is achieved and the number of D and L isomers are equal. Hence, from a measurement of the ratio of the two isomers and the knowledge of the rate of racemization, it is possible to estimate the age since the death of the organism. The most likely source of dissolved amino acids in ground waters from igneous, metamorphic and many sedimentary aquifers is soil organic matter which has very low ratios of D/L amino acids. Studies on samples of bone and shell have proved reasonably reliable but ground water dating may be affected by possible leaching of amino acids from sedimentary rocks. Also, the intermediate temperature history of the ground water is important as racemization rates approximately double for every 4–5°C increase in temperature. Nevertheless, age ranges exceeding 300,000 yr are postulated for this method.

3. Artificial Tracers

3.1 *Selection*

Artificial tracers may be defined as those elements deliberately introduced into the hydrologic system to follow movement. Measurement of the tracer movement is then used to infer the behaviour of the flowing medium and hence determine some physical parameter of the system, such as the permeability of an aquifer.

The ideal tracer is one which:

(a) follows completely the movement of flow under study without loss from the flow by physical or chemical processes such as adsorption onto sediments or strata.

(b) is of negligible toxicity allowing safe usage with little administrative or legislative requirements.

(c) can be detected with high sensitivity and measured accurately *in situ* in the field.

(d) does not contaminate the site of the measurements thus affecting the results of further tests.

(e) is inexpensive and has low cost of analysis.

Unfortunately, no ideal tracer exists and selection must be based on optimum considerations of the above characteristics.

This will depend on the nature of the proposed investigation and the major factors affecting the movement under study. For example, where convective movements dominate and diffusion is negligible, attention would be given to matching the chemical compatibility and the physical transport properties of the tracer with that of the fluid to be studied. However, in diffusive flow through a porous medium, attention would have to be given to the diffusion constants and molecular size of the tracer. The behaviour of a sediment may be followed by use of a completely different substance, such as crushed glass, of such a size distribution as to behave hydraulically the same as the sediment particles. It is, therefore, important to consider carefully the relative contribution of factors affecting the flow under study and if possible to vary test conditions or tracers to check the degree of representation of the tracer data.

For convenience, tracers may be broadly categorised according to the means of analysis adopted. These are:

(i) *Radioactive tracers.* These are elements made radioactive prior to use and detected by means of their radioactive emissions.

TABLE 1. Radioactive tracers used in ground water studies

Isotope	Half-life	Chemical form	Principal γ-energies (MeV)
^{3}H	12.4 a	HTO	0.018(β)
^{24}Na	15 h	$NaHCO_3$	1.37, 2.75
^{46}Sc	84 days	$ScCl_3$	0.89, 1.12
^{51}Cr	28 days	$CrCl_3$, EDTA complex	0.32
^{57}Co	270 days		0.122
^{58}Co	71 days	$Co(CN)_6^{3-}$ or EDTA	0.81
^{60}Co	5.2 a		1.17, 1.33
^{82}Br	35.4 h	KBr, NH_4Br	0.55, 0.78, 1.32
^{103}Ru	39.5 days	$RuCl_3$	0.5, 0.61
^{114m}In	50 days	EDTA	0.19, 0.56, 0.72
^{131}I	8 days	NaI, KI	0.36, 0.64
^{134}Cs	2.06 a	CsCl	0.61, 0.80
^{153}Gd	242 days	EDTA	0.103
^{198}Au	2.6 days	$HAuCl_4$, $AuCl_3$	0.41

(ii) *Activable tracers.* These elements are stable during use but made radioactive for analysis by detection of their radioactive emissions.

(iii) *Chemical tracers.* The detection of chemical tracers may be based on their mass (mass spectrometry) orbital electron arrangements (chemical reactions) or shell binding energies (energy absorption or emission properties).

(iv) *Particulate tracers.* While all the above-mentioned tracers may be in particulate form, this category refers to those tracers detected by collection and weighing or counting of individual particles.

3.2 *Radioactive tracers*

Although an element may be made radioactive to provide a tracer with a suitable half-life and radiation properties for easy detection for the duration of the test, its behaviour in the flow system depends on its chemical form. The radioactive tracer may be obtained as a labelled compound such as tritiated water (HTO) or from a soluble radioactive salt such as potassium bromide solution ($K^{82}Br$), by nuclear irradiation of some of the material to be traced or of a compatible additive such as iron bearing sediments, or by coating the material with the radioactive substance.

Labelled compounds are by far the most used radioactive tracers in hydrology as they relate to tracing water movement. Tritium is commonly used as it forms part of the water molecule and will faithfully follow the water. Because the vapour pressure of HTO is only 10% lower than that H_2O, it is used extensively in evaporation studies as well as those of aquifer recharge, dam leakage, river flow measurement and residence times. Although its chemical characteristics make it near to ideal, its radioactive emissions of low energy β-particles (0.018 MeV E_{max}) cannot be measured adequately *in situ*. Samples must be returned to the laboratory for measurement by liquid scintillation counting or gas counting. Considerable effort has been expended in seeking alternative ground water tracers which emit γ-radiation and do not adsorb or chemically interact with any surrounding medium.

A list of radioactive tracers commonly used in ground water studies is given in Table 1. For relatively short transit times ($\sim$ several days), the halides ^{82}Br (half-life 35.4 h) and ^{131}I (half-life 8.05 days) are commonly used in the form of bromide or iodide respectively. These tracers have been used extensively in borehole tests of ground water movement and river flow studies and yield very similar results to those obtained using tritium.[39] Other anionic tracers in the form of metal complex compounds, such as EDTA, have been used for long-term experiments. These ions suffer considerably less loss by sorption than the cations. Their suitability in particular strata is determined by comparison with tritium. For example, ^{51}Cr EDTA has been shown to behave the same as tritium in tests extending over 2 months duration in glacifluvial sands and gravels.[40] Cobalt in the form of cyanide compounds is also satisfactory in low clay media.[41] However, retardation of complexes generally occur in clay environments.

Sediment tracing may be achieved by the use of scandium loaded glass size-matched to the sediment and irradiated in a neutron flux to yield ^{46}Sc (half-life 84 days). Alternative methods are to coat the sediment with a complex cation such as $[^{198}Au(NH_3)_4]$ (half-life 2.7 days) or $[^{110m}Au(NH_3)_2]$ (half-life 253 days) for particles with a negative surface or $[AuCl_4]$ for particles with a positive charge.[42] The main disadvantage of surface labelling is that the amount of tracer in a sample is not proportional to the mass of labelled sediment but to its surface area. This can lead to considerable errors of interpretation when the variation in particle size is large unless correction is made.

All radioactive tracers suffer from the fact that their use in most countries is governed by legislation and some form of administrative procedure may have to be undertaken before they can be used. This is not so

for most chemical tracers although their toxicity may exceed those of radioactive tracers and their concentrations do not diminish due to radioactive decay. Previous concepts of maximum permissible concentrations (MPC) of radioactive materials used to assess the acceptability of using certain quantities of tracer have now been replaced by annual limits of intake (ALI)[43] and allow more realistic assessments of effects of infrequent use of radioactive substances in the environment.

Approval for such use in the U.K. is given by the Department of the Environment following their satisfaction of the need and safety of the use. This requirement and the general public reaction to the use of radioactivity provide the main disadvantage of using radioactive tracers. Other disadvantages relate to its transport in approved containers, the use of specialised personnel and limitations on the duration of measurements imposed by the half-life of the isotope used. Against these, considerable advantages accrue from their use.

These may be listed as follows:

(a) uniqueness of tracer substance (i.e. absence of considerable background interference from naturally occurring elements).

(b) high sensitivity and precision of detection.

(c) for γ-emitting tracers the capability of being measured easily *in situ* in the field (e.g. down boreholes).

(d) small volume of injected tracer due to (b) thus minimising disturbance to the flow system.

(e) specificity of detection by energy discrimination thus allowing several different tracers to be used simultaneously.

3.3 *Activable tracers*

Stable elements, capable of short-term neutron irradiation to yield a radioactive isotope, are used to trace ground waters. There are generally used in the form of anionic complexes and samples passed through ion exchange filters which are irradiated and measured with a high resolution Ge(Li) detector and pulse height analyser. A list of the major activable tracers used in hydrology is given in Table 2. Field studies with ^{165}Dy, ^{116}In and ^{176}Lu have shown that only small amounts are naturally present in the environment and that, as EDTA complexes, remain stable and are negligibly adsorbed.[44] Inactive bromine compounds may also be used as activable tracers but background concentrations may be considerable. This fact and the variations experienced in the extraction and irradiations of the tracer from the sample make the measurement of activable tracers less reliable than radioactive tracers.

For high sensitivities of measurement, large neutron fluxes from a nuclear reactor are required necessitating off-site analysis. Alternatively, heavily shielded isotopic neutron sources or neutron tubes may be used for *in-situ* measurements. Their main attractions are that no authorisation is required for their use in the former mode of operation and high sensitivity ($<10^{-12}$) can be achieved.

TABLE 2. Principal activable tracers used in hydrological studies

Isotopes	Half-life	Radiation of interest (MeV)
^{99m}Tc	6 h	γ:0.142
^{116m}In	54 min	γ:1.27 :2.09
^{140}La	40.2 h	γ:1.60 β:1.4
^{152m}Eu	9.2 h	γ:0.84 β:1.87
^{165}Dy	2.3 h	γ:0.71 β:1.31
^{166}Ho	27 h	γ:0.08 :1.38 β:1.84
^{176m}Lu	3.7 h	γ:0.089 β:1.1
^{177}Lu	6.75 days	γ:0.21 β:0.50
^{192}Ir	74.4 days	γ:0.315 :0.605
^{198}Au	2.7 days	γ:0.412 β:0.96

3.4 *Chemical tracers*

The chemical compounds present in ground waters are frequently used as tracers to identify zones of different ground water bodies and their mixture in a region. Ground waters are analysed for major ions which assist in determining the chemical evolution and hence ground water directions. These tracers are more appropriately grouped under environmental tracers. However, added tracers in the form of soluble salts such as NaCl and KBr are frequently used for ground water movement studies and ions are generally measured by ion-selective electrodes. Although the number of different ions which may be used is large, cations are usually lost from the water by exchange.

Although iodide tends to be sorbed to a greater extent than the bromides or chlorides, natural concentrations are generally less than 10 μg/L compared with 100 μg/L for bromide and 30 mg/L for chloride. Metallic compounds such as EDTA have been used with detection by established analytical techniques such as atomic absorption spectrometry. This method of detection has been used to measure lithium chloride tracer used in the measurement of river flows and potable water supplies. Other metallic compounds can be analysed *in-situ* by means of energy dispersive x-ray fluorescence (XRF) and some elements are listed in Table 3 with corresponding detection limits.[45] The ions are extracted from water samples by ion

TABLE 3. Comparison of detection limits of elements analysed by XRF with isotopic and x-ray tube sources

Element*	Radioisotope source ^{238}Pu/100 mCi (ppl0^9)	x-Ray tube† (ppl0^9)
Cr K_α	6.0	1.6
Mn K_α	3.2	1.4
Fe K_α	4.4	1.6
Ni K_α	2.0	0.5
Cu K_α	2.6	0.7
Zn K_α	1.8	0.8
Pb L_α	2.6	0.8

* 500 ml sample precipitated with sodium diethyldithiocarbamate (DDTC) and 2000s counting time.
† Measured with low-power x-ray tube with Ag target operated at 30 kV and 150 μA.

exchange, precipitation with organic reagents or collection on activated charcoal. However, even with preliminary enrichment on filters, energy dispersive XRF is not as sensitive as the atomic absorption method of analysis.

Organic dyes are frequently used as ground water tracers but their major disadvantage is that they are not wholly conservative tracers and tend to be lost from the water by adsorption, particularly in clays. Analysis is generally by filter fluorimeters or colorimeters which are sufficiently robust for field operation. Alternatively, higher sensitivities may be achieved by laboratory analysis of the dyes and their derivatives by means of mass spectrometry. Typical sensitivities with field equipment are shown in Table 4.[46]

High sensitivities of detection can be obtained for fluorocarbon compounds in water. Compounds such as CCl_3F, CCl_2F_2 and CBr_2F_2 can be easily detected at concentrations of 0.001–0.1 μg/L using electron-capture detectors as used in gas chromatography. With these sensitivities of detection, initial concentrations of only a few ppm may be used thus providing a convenient non-toxic tracer. Unfortunately, however, the tracer is easily lost from samples by gaseous exchange with the atmosphere so that care must be taken to exclude atmospheric contact during sampling and with gas-stripping treatment for analysis. A further disadvantage is that tracer tests on water flowing through a quartz sand column showed that CBr_2F_2, for example, moves at only about 70% of the water velocity.[47] Consequently, although this tracer can be used in extremely small quantities, the movement difficulties and adsorptive delays make it most unattractive as a quantitative long-term ground water tracer.

The main disadvantage of chemical tracers are:

(a) adsorption onto strata and or equipment.
(b) analysis may require sample treatment and transfer to a laboratory.
(c) possible variations in background concentrations due to previous tracer injections.
(d) analysis may require sample treatment and transfer to a laboratory.
(e) direct measurement of concentrations in boreholes is restricted.

The advantages are:

(i) they can be used without specific authorisation.
(ii) a high detection sensitivity can be obtained.
(iii) field detection equipment (especially for dyes) is readily available.

These advantages justify the large role played by chemical tracers in hydrological applications, particularly when slight adsorption can be tolerated such as in investigations of leakage or hydraulic connections between swallow holes and issues. However, in situations where adsorption can occur, the absence of tracer at the sampling positions must still be treated with suspicion.

3.5 *Particulate tracers*

While the use of particle tracers is generally associated with sediment movement studies, they have been used in a number of hydrological applications where large convective movements of water are involved. The particles may be of biological, botanical, geological or man-made origin and may be detected by sampling and counting, fluorimetry or by incorporation of radioactivity.

Micro-organisms such as *Serratia marcescens* are used to trace movements in surface and karst waters. *Serratia* produces red pigmented colonies which are readily identifiable and a strain has been selected which has resistance to certain antibiotics.[48] Samples are filtered and incubated to increase the colonies of *Serratia* while the growth of other organisms is reduced by the use of the antibiotics. Bacteriophages, bacteria destroying agents, have also been used for water tracing and simple baker's yeast (*saccharomyces cerevisiae*) has been used in sand/gravel environ-

TABLE 4. Typical sensitivities of organic dyes obtained with field operated equipment

Dye	Sensitivity* (μg l^{-1}/scale unit)	Background reading† (scale units 0–100)	Minimum detectability‡ (μg l^{-1})
Amino G acid	0.27	19.0	0.51
Photine CU	0.19	19.0	0.36
Fluorescein	0.11	26.5	0.29
Lissamine FF	0.11	26.5	0.29
Pyranine	0.033	26.5	0.087
Rhodamine B	0.010	1.5	0.010
Rhodamine WT	0.013	1.5	0.013
Sulpho Rhodamine B	0.061	1.5	0.061

For a Turner III filter fluorometer with high-sensitivity door and recommended filters and lamp at 21°C.
* At a pH of 7.5; † For distilled water; ‡ For a 10% increase over background reading or 1 scale unit, whichever is larger.

ments.[49] All these methods rely on filtration of samples and microscopic (with or without cultivation) or fluorimetric analysis. Spores of the club moss, Lycopodium, which are only slightly denser than water and ~30 μm diameter have been used for tracing water through karst regions. The spores are dyed for identification and water samples are filtered for analysis.

When particulate tracers are used to study sand or sediment movements, attention is given to the matching of their hydraulic properties. Artificial glass incorporating a radioactive element is generally favoured. Typical tracers incorporated in glass are ^{24}Na (half-life 15 h), ^{140}La (40.2 h), ^{86}Rb (19 days), ^{192}Ir (74 days), ^{46}Sc (84 days) and ^{65}Zn (245 days). As discussed previously, an alternative approach is the adsorption of radioactive ions such as ^{198}Au or ^{110m}Ag from solution onto natural particles. This method was used in an early investigation of shingle movement but the current preferred method is to label individual pebbles by inserting a small piece of radioactive wire into a hole drilled in the pebble and sealing with epoxy resin. Usually up to 1000 pebbles are labelled in this fashion for an investigation.

In particulate tracing work, consideration must be given to the number of tracer particles used. A sufficient number must be used so that the samples contain enough particles to provide a statistically significant result. In some studies, this may be the limiting factor to the accuracy of the result. Cultivation of bacteria tracers in samples cannot improve on the limits set by the initial numbers of particles in the sample.

4. Applications of Artificial Tracers

4.1 *Surface waters*

4.1.1 *Flow measurement.* Tracer methods of flow measurement are used when only occasional measurements are required on streams or rivers where no gauging stations exist, or for the periodic calibration of such stations. The measurement principle is based on the dilution of a known amount of tracer injected into the flow and the determination of a tracer mass or activity balance between the point of injection and the sampling station. Since the first use of these methods in the last century,[50] dilution methods have developed into a convenient tool of the hydrologist, providing him with a means of accurate measurement. The use of tracers capable of measurement at extremely low concentrations enable very large flow rates (>100 m^3/s) to be measured with injection volumes of tracer of less than 1 L.

The dilution methods used are commonly termed the constant rate injection and the integration or gulp-injection methods. Briefly, the principles of the methods are that tracer is injected into the flow, either at a constant rate or, in the case of the integration methods as a known quantity. At some distance downstream, where the tracer is completely mixed with the flow, its concentration in the flow is determined. From a balance of the tracer mass or activity at the injection and sampling points, the flow rate Q (m^3/s) is given by the expression

$$Q = q\left(\frac{C_0 - C_1}{C_1 - C_2}\right)$$

where q is the injection rate of the tracer (m^3 s), C_0 is the concentration of the injected tracer, C_1 is the tracer concentration at the sample point, C_2 is the tracer concentration in the stream prior to injection, and all the concentrations are expressed in the same units.

In the integration methods, the tracer concentration at the sampling cross-section will vary spatially and temporally owing to the mode of injection and the non-uniform velocity distribution across the stream. In this case, the flow rate Q is given by the expression:

$$Q = \frac{A}{\int_0^\infty C\,dt}$$

where A is the amount of tracer injected (activity or mass units) C is the tracer concentration at time t (activity or mass units/m^3) and dt is the time increment (s).

For these methods, complete mixing is achieved when $_0\int^x C\,dt$ is constant over the entire stream cross-sectional area. Variations in these methods relate to the means of determining the integration term.[51]

The minimum distance required to achieve complete mixing, termed the mixing distance, depends on the degree of turbulence of the flow, linear velocity and the extent of "dead-water" regions. Various formulae have been proposed to estimate the mixing distance[52] relating to velocity and bed roughness. These are not very reliable and the preferred procedure is to carry out a preliminary tracer test to establish the degree of mixing. Then an assessment of the error due to mixing may be made by sampling simultaneously from several parts of the sample cross-section or at different distances from the injection position and comparing the results.

For large flows, the integration methods are used because they require less tracer than the constant rate injection method. Although routine use of these methods with radioactive tracers is not considered to be convenient because of handling and transportation of the tracer,[53] high accuracy can be achieved. Measurement uncertainties of less than ±1% are obtained with good mixing.[54,55] The accuracy with chemical tracers is not so good. A study of 409 injections of salt over 39 flow rates gave the median of the probable errors of ±5.4% with variations in the range ±0.9% to 15.4%. Tracer methods are most appropriate for occasional measurements, such as for flood flow determinations or measurements in remote locations. Examples of such uses are in the measurement with tritium of flood flows of the River Trent

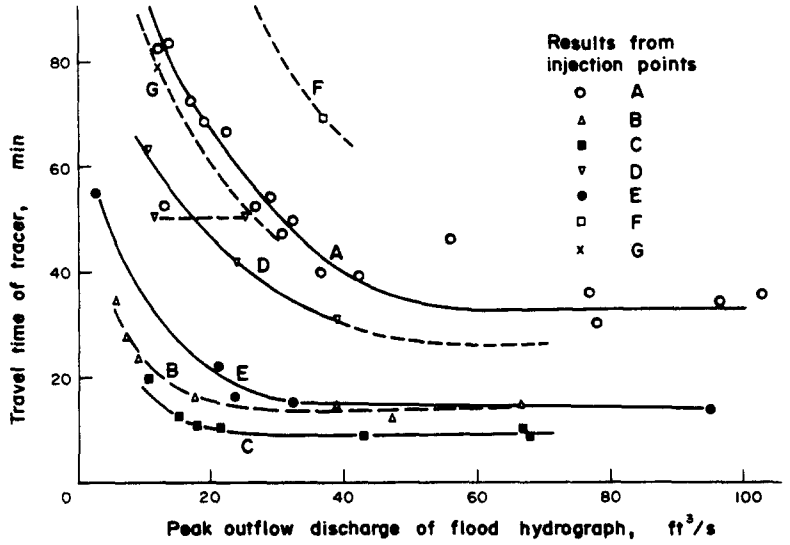

FIG. 11. Relation of travel time of tracer and peak discharge in flood studies.[64] (Note constant travel times at larger flow rates).

(330 m^3/s) in England,[56] and the River Tana (550 m^3/s) in Kenya.[57] Also it has been shown that gauging can be successfully carried out with tracers where most gauging methods are unsuitable or difficult to apply. In particular, low river flows with long residence times and dense weed growth have been measured using ^{82}Br as a tracer.[58] These methods are now well developed and their use is fully described in International Standards for both pipe flow[59] and rivers.[60]

4.1.2 *Transit time studies.* The time of travel of water run-off from a basin is of interest in flood storage studies. The transient response of the basin to a specified rainfall may be determined from its characteristic impulse response. This response, the instantaneous unit hydrograph, is generally determined from records of precipitation and flood flows for the area. However, where suitable records are not available, tracer tests may be used to correlate the distribution of travel times with physical characteristics of the basin such as surface area, channel lengths, slopes and roughness and hence derive the basin response.

Tracer methods have been used to study the dynamics of a small watershed in Australia over a period of eight years.[61–64] The radioisotopes ^{51}Cr EDTA and ^{198}Au were injected at 7 sites for a total of 45 tracing runs. Travel times were measured for peak out-flow discharges (Fig. 11) and correlations with various geomorphological parameters of the streams, such as functions of length of reach and hydraulic radius, were made to establish the best basis for estimating the spacing of the isochrones and the distribution of flood storage. This showed that while the best method of estimating the spacing of isochrones relied on field inspection of channel roughness coefficients and mean depths, simple parameters based on stream length also gave good results. However, the study did not include "overland" water movement but only the movement in the drainage channels. While this might have been an appropriate approximation for the study area, the extrapolation of the results to other areas should be made with caution.

The movement and dispersion of a pollutant discharged into a water course may be predicted from tracer measurements. The basic one-dimensional differential equation for diffusion in channel flow is

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} = D\frac{\partial^2 C}{\partial x^2} \tag{2}$$

where D is the diffusion coefficient, C is the tracer concentration, x is the distance from the source, v is the mean velocity and t is the time from tracer release.

For an instantaneous release of tracer uniformly across the flow cross-section, the following solution is given:

$$C = At^{-1/2}\exp\left[-\frac{(x-vt)^2}{4Dt}\right] \tag{3}$$

where A is a constant proportional to the amount of diffusing material.

This treatment may not be appropriate to natural channels where "dead water" zones exist. Tracer tests using common salt with conductivity measurements have shown that the effective dispersion coefficient increases with distance down the channel.[65] Rivers receiving industrial effluent discharges may be modelled by tracer measurements. Numerous examples exist but one of the most recent is the injection of tritium and ^{82}Br into one of the largest rivers in Spain, the Guadalquivir, to prepare a mathematical model.[66] Seawater penetration into the estuary was followed by tracers for a distance exceeding 100 km. Delayed mud flow along the estuary bed was thought to account for an apparent loss of tritium over the three month test although evaporation would have been a contributory factor.

Transit time methods are frequently used for the measurement of flows in closed conduits. Their use for this purpose in open channels and rivers is restricted because of the greater longitudinal dispersion, usually existing in natural flow systems, and the presence of a free surface. However, ^{51}Cr EDTA has been used to measure the transit times of two rivers in north Morovia in frozen and unfrozen states and showed that fluid velocities in the iced channel were generally greater than the free-surface channel under the same hydraulic conditions.[67]

4.1.3 *Lake dynamics.* Apart from the use of such environmental isotopes as tritium to measure residence times, stable isotopes for water budgets or ^{210}Pb to measure sedimentation rates,[68] artificial tracers are used in lake studies to measure local movements, vertical mixing, dilution effects on pollutants discharges from supply streams or investigations of leakages.

Investigations of vertical and horizontal mixing rates were made in two Canadian lakes by injections of up to 1.5 TBq (40 Ci) of tritium into the thermocline and hypolimnion regions.[69] Samples, measured in a laboratory by liquid scintillation counting, showed that vertical diffusion rates in the stratified thermocline were less than molecular diffusion of heat while in the epilimnion, horizontal diffusion, more appropriately "dispersion", was over seven orders of magnitude greater.

The flow patterns in lake waters are determined by releasing tracer and following the tracer cloud. Dyes are convenient tracers and measurements can be made by continuously pumping a sample stream through filter fluorimeters operated from boats. Radioactive tracers such as ^{82}Br, ^{131}I and $^{60}Co(CN)_6^{3-}$ have been used with detection by NaI scintillation detectors suspended from boats traversing the tracer cloud. This method has the advantages of measuring a large volume of water, determined by the energy of the γ-rays emitted, and easy acquisition and recording of data thus allowing optimum traverses over the tracer cloud which varies spatially and temporally.

Leakages from lakes may occur through containing hydraulic structures, foundations or through the ground. Confirmation that seepages were due to leakage has been obtained in Cornwall where an artificial lake used for precipitation of china clay waste was labelled continuously with tritium during filling. Samples taken from springs and drainage channels confirmed the presence of a leak and the contribution to seepage of natural ground water was determined.[70] A number of methods have been adopted for the location of leakage zones.[71] The principles involve either the injection of a radioactive tracer, which adsorbs onto sediment or is incorporated in an emulsion,[72] that can be measured in greater quantities at the sites of leakage where filtration of the labelled particles occur, or injection of tracer near the bottom of the lake to identity movement towards the leak or correlate its arrival at the bottom with its appearance in drainage channels.[73]

4.2 *Ground waters*

4.2.1 *General tracing.* Studies of the movement of ground waters represent the largest area of use of artificial tracers in hydrology. It may simply be required to prove connections between stream sinks and emergent springs of ground water or, more quantitatively, to determine from movement studies some parameters of the storage area such as volume or rock porosity, mean permeability or the location of high permeability zones. The former studies are often related to the subterranean movement of water in karst limestone areas or to areas subjected to mining where old workings may provide short circuit routes to ground waters.

Generally dyes or lycopodium spores are used and a comprehensive map of connections can be established. Fig. 12 shows the ground water interconnections found for the Mendip Hills in England.[74] A review of this type of study in the tropical regions and tests in Jamaica, showed that the use of lycodium spores are preferred mainly because more sites can be investigated simultaneously and they are unaffected by water chemistry and pollutants.[75]

Tritium is commonly used for these studies because of the ease of handling in the field, sensitivity of measurement possible and its reliability as a water tracer over extended periods. Generally, samples (only a few cm^3 volume) are taken at regular intervals and returned to the laboratory where only occasional samples are measured until a positive result is obtained. Then, intermediate samples may be measured to obtain a concentration–time distribution. The storage volume V (cm^3) may be determined from the relationship:

$$V = \frac{\int_0^\infty C v \, dv}{\int_0^\infty C \, dv}$$

where v is the accumulated volume of discharge (m^3).

As it is likely that the sampled streams may not represent the total discharge, this volume must be considered the minimum. Correction can be made by comparing the activities of recovered tracer with that injected.

This method was used to investigate water movement in a karstic region of Greece where injections of up to 37 TBq (1000 Ci) of tritium were used to identify a large storage volume.[76] Many investigations require only a small fraction of this amount of tracer, typically 0.04–4 TBq ($\sim$1–50 Ci). Leakages from canals and reservoirs have been identified by this means.

The infiltration of water through the unsaturated zone to the water table has been studied using radioactive tracers. Added γ-emitting $K_3 Co(CN)_6$ has been

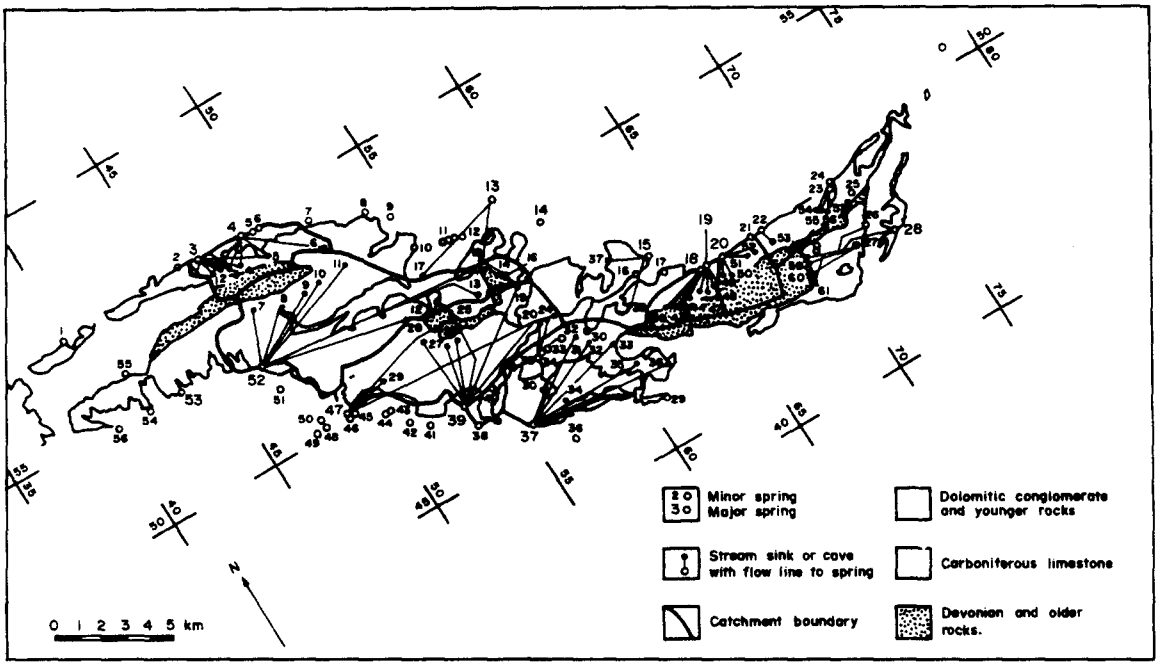

FIG. 12. Ground water connections identified by tracers in the Mendip Hills.[74]

used to measure the movement of moisture through soils in arid regions. A similar study of water movement in the unsaturated zone has already been discussed in relation to atmospheric tritium. Estimates of recharge have been made in the Rhine Valley and more recently in the Lower Maner Basin which forms part of the Godavari Rift Valley in India[77] by the addition of tritium. In this investigation, some 28 sites covering an area of 1600 km^2 were examined. Tritium, typically 1 MBq, was injected just below the root zone of crops and samples of soil core were taken eight months after injections and following the monsoon period. The variation in tritium and moisture content with core depth was used to estimate a recharge during the 1976 monsoon season of over 150 million m^3 or 8% of the average rainfall in the basin.

4.2.2 *Single borehole techniques.* As their name implies, these techniques relate to the use of a borehole to achieve penetration to the ground water. The techniques, which may be concerned with the determination of water movement up or down the borehole, its exit from the borehole or to properties of the aquifer matrix surrounding the borehole, are long established and have been the subject of periodic review.[78,79]

The point dilution method used for measuring the filtration velocity of the ground water has been subjected to comprehensive laboratory testing thus allowing suitable calibration of the method. Basically, the method consists of injecting a tracer into a region of the borehole, usually isolated by inflatable packers and measuring the concentration–time distribution. The injection, mixing and measurement device is constructed within a borehole probe.

The "dilution velocity" (v_g) is given in the expression:

$$v_g = \frac{\pi r \beta}{2t} \ln \frac{C_0}{C}$$

and the filtration velocity v_f is

$$v_f = \frac{v_g - [v]}{\alpha\gamma}$$

where r is the internal radius of the filter tube, C is the tracer concentration at time t, C_0 is the initial tracer concentration, α, β, γ are correction factors and $[v]$ is the sum of dilution velocities not dependent on horizontal ground water flow.

These laboratory studies have revealed that the instrument should be used in homogeneous permeability and that vertical currents should be avoided. Filtration velocities of between 0.01 and a few hundred metres per day may be measured. Hence, the permeability of the surrounding medium may be determined. A comparison of permeability values derived from the use of tracers and those obtained from pumping tests (Dupuit Method) is shown in Table 5 and shows agreement within measurement uncertainties of both methods. An advantage of the tracer method over pumping tests is that more detailed information can be obtained from layered aquifers of different permeabilities.

The flow direction in the borehole may be determined by release of tracer and measurement of its movement or its preferential adsorption at the sites of water exit. γ-Emitting radioactive tracers are generally used and the borehole is logged with a scintillation detector. The direction of flow across the borehole

TABLE 5. Comparison of permeability values determined by single-borehole tracer techniques and pumping tests[79]

Test area	Aquifer composition	Permeability (m s)	
		From pumping tests	From tracer method
Mangfall Upper Bavaria	Gravely sands	$4 \cdot 10^{-3}$	$4 \cdot 10^{-3}$
Munich-Pasing	Gravely sands	$7 \cdot 10^{-3}$	$9 \cdot 10^{-3}$
Munich-Gravel Plain-Arget	Gravely sands	$2.4 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$
Munich-Gravel Plain-Perlach	Gravely sands	$2 \cdot 10^{-2}$	$2.4 \cdot 10^{-2}$
Loisach-Valley Upper Bavaria	Gravely sands	$1–2.6 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$
Erdinger Moos Upper Bavaria	Gravely sands	$5 \cdot 10^{-3}$	$8 \cdot 10^{-3}$
Neufahrn Upper Bavaria	Gravely sands	$6 \cdot 10^{-3}$	$9 \cdot 10^{-3}$
Erolzheim Swabia	Gravely sands	$2.5 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$
Tannheim Swabia	Gravely sands	$1.5 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$
Danube Valley, near Moos, Lower Bavaria	Gravely sands	$9 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
Danube-Lech area	Gravely sands	$8 \cdot 10^{-3}$	$9 \cdot 10^{-3}$
Nuremberg	Sandy gravels	$4 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
Rhine-bend at Hockenheim	Sandy gravels	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$
Frankfurt Stadtwald	Sands	$2 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Hagen-Westhofen	Sandy gravels	$3 \cdot 10^{-3}$	$4 \cdot 10^{-3}$
Lippstadt	Sands	$2 \cdot 10^{-4}$	$3 \cdot 10^{-4}$
Jülich	Sands	$9 \cdot 10^{-4}$	$9.3 \cdot 10^{-4}$
Esenchenlohe Upper Bavaria	Gravely sands	$1.6 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$

may be determined by the use of an eccentrically shielded detector either suspended on a rod and rotated or with a direction indication device, such as a magnetic compass. Flow direction along the borehole may be determined from a probe consisting of a detector either side of the injection volume or by traversing the detector.

These methods have been used to locate fractures in metamorphic rocks as part of a study on the disposal of radioactive waste in crystalline rocks.[80] ^{131}I, of 3–15 MBq activity depending on duration of test, was injected at various levels in a 600 m borehole and their movement monitored over some 9 days (Fig. 13a). Following this period, movement of a tracer pulse in the upper cased section of the borehole was compared with those in the uncased section when water was added to the borehole. Graphs of the two movements showed from their change of slope, the positions of major fractures (Fig. 13b).

Ground water velocity may be determined by injecting tracer into a well, allowing it to drift with the ground water flow for a known time and then pumping the well and monitoring the tracer concentration–time distribution. The ground water velocity (m/s) is obtained from the relationship:

$$= \frac{1}{\tau}\sqrt{\frac{Qt}{\pi bn}}$$

where τ is the time between injection of the tracer and start of pumping (s), Q is the pumping rate (m^3/s), t is the time corresponding to the centre of gravity of the concentration–time distribution (s), b is the aquifer thickness (m) and n is the effective porosity.

4.2.3 *Two-well technique.* A more commonly used method of determining the permeability of an aquifer is to inject tracer into one borehole situated within the draw-down cone of a second, pumped well. The movement of tracer injected into the aquifer has been described by models derived from the Fick diffusion equation.[81] For one-dimensional dispersion in an infinite medium and instantaneous uniform planar injection the solution is:

$$C(x, t) = \frac{M}{nS}\frac{1}{\sqrt{4\pi Dt}}\exp\left[-\frac{(x - vt)^2}{4Dt}\right]$$

where M is the mass or activity of the tracer; x is the distance between boreholes (m); t is the time from injection (s); D is the dispersion coefficient (m^2/s); v is the mean interstitial velocity of water (m/s); S is the cross-sectional area of the flow (m^2), and n is the effective porosity.

The mean time of the tracer pulse $\bar{t}$, defined as the time corresponding to the centre of gravity of the observed concentration–time distribution at the sampling position, is not equal to the mean time (t_0)

of the water (viz x/v). For large dispersion the relationship is:

$$\bar{t} = t_0\left(1 + 2\frac{D}{vx}\right).$$

When the boundary conditions of the model are changed so that the injection and sampling of the tracer is proportional to the flux or volume across the flow section, the solution becomes[82]:

$$C(x, t) = \frac{M}{nS\sqrt{4\pi Dt^3}} x \exp\left[-\frac{(x - vt)^2}{4Dt}\right].$$

In this case $\bar{t}$ is equal to t_0. This demonstrates mathematically that correct interpretation of tracer experiments depends upon the employment of suitable boundary conditions relating to the injection and sampling of the tracer and the establishment of steady state conditions.

The permeability of the aquifer is determined from Darcy's law relating the superficial velocity ($\bar{v}$) to the hydraulic gradient, viz.

$$\bar{v} = nv = k\frac{d\phi}{dx}$$

where k is the permeability (m/s), and ϕ is hydraulic head.

This method has been applied in both single and layered aquifers mainly using radioactive tracers.[83,84] Evidence for the number of flow paths is obtained from geological surveys and determining the best fit of theoretical models with the measurement data using three parameters (quantity of tracer, velocity and dispersion) per flow path. This approach can result in more than one path being identified from the model but not supported by geological evidence.[83] Glueckauf has drawn attention to this and has developed a theoretical model based on previous chromatographic theory with diffusion into the rock matrix.[19] His model, when applied to the above data, fitted a single flow path and gave a result more consistent with geological evidence (Fig. 14). In an artificially fractured granite, tracer tests have been interpreted on the basis of five separate paths[85] but the validity of this interpretation is more doubtful as the number of paths increase and the individual tracer responses overlap.

The assessment of solute movement through rocks

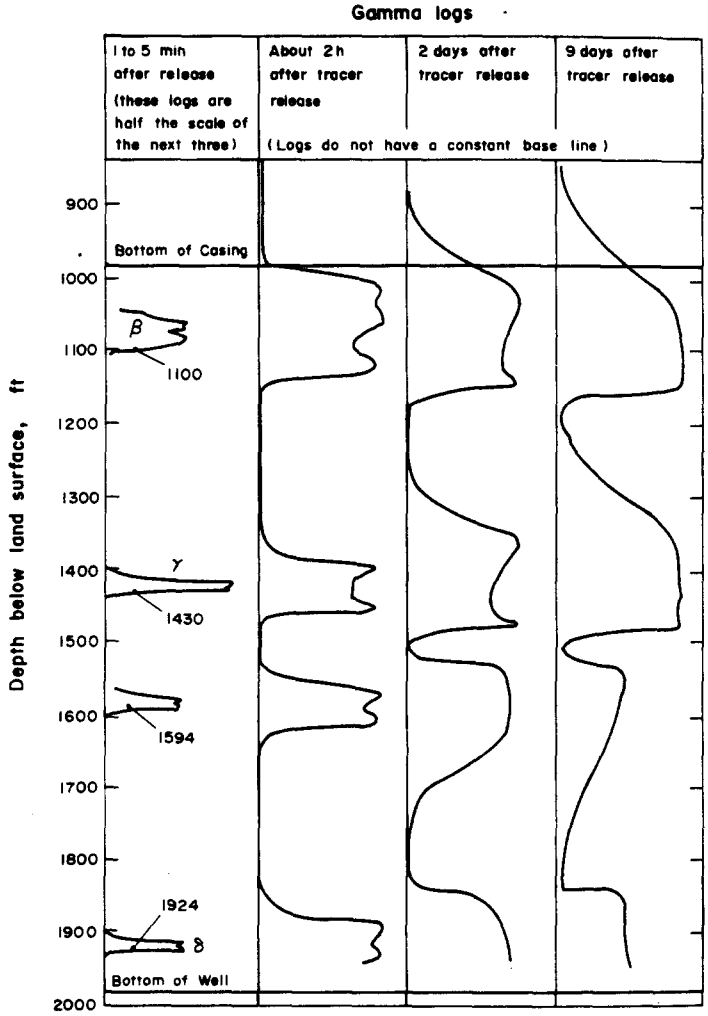

FIG. 13(a). Tracer movement in a borehole in granite.[80]

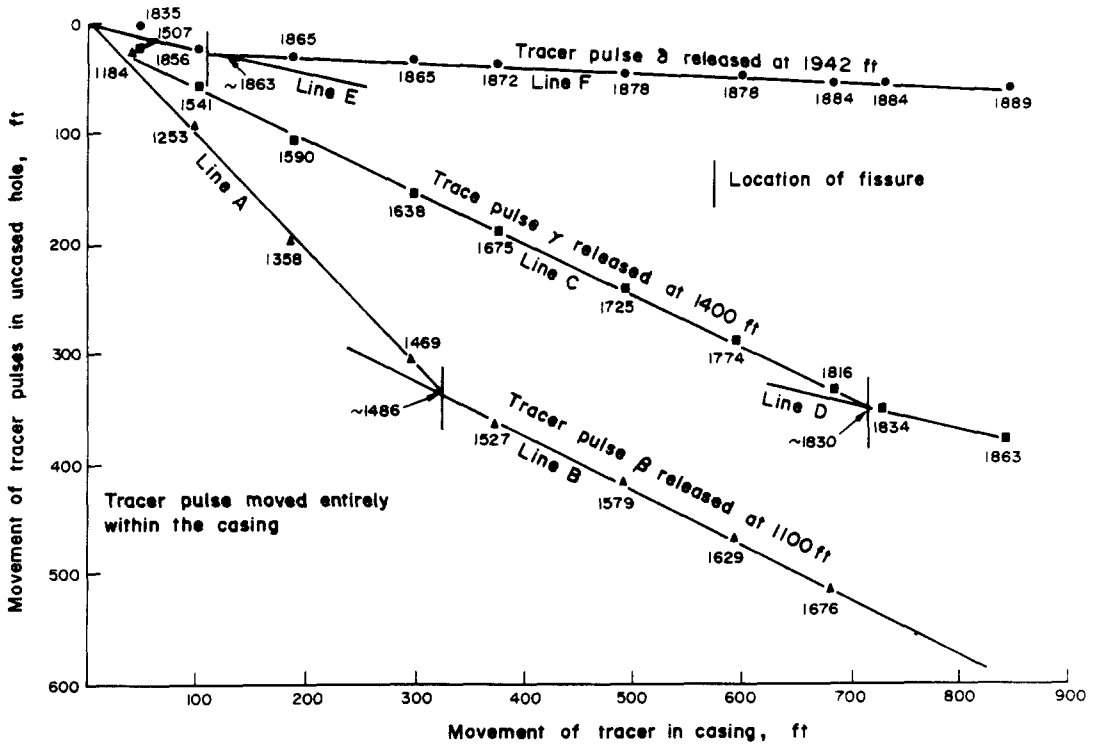

FIG. 13(b). Location of fissues from tracer movement.[80]

is under considerable review because of relevance to the possible escape paths of radioactive waste buried in geological formations. Burial of waste is being considered within a "multi-barrier" concept where the waste is incorporated in a solid glass or synthetic rock, sealed in containers and buried in geological formations such as crystalline or argillaceous rocks, or salt deposits. The most likely final path through which waste would return to the surface is via ground water movement. Consequently, hydrological investigations are increasing in this general area and tracers are seen to have a significant role to play. Similarly,

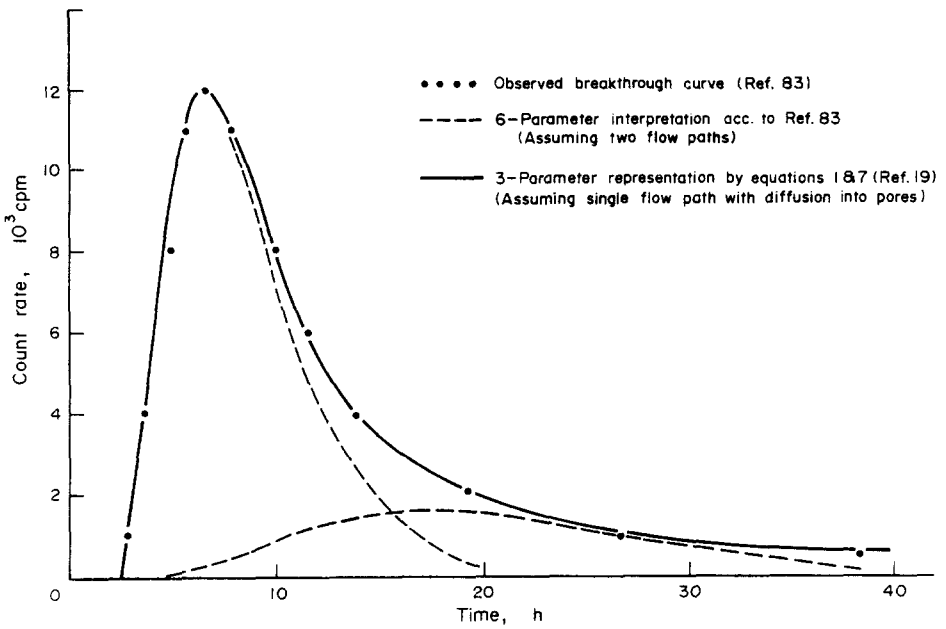

FIG. 14. Data from two-well technique interpreted according to models assuming single and multiple flow paths.[19]

an increasing awareness is developing on the relevance of ground water movement studies to efficient exploitation of oil fields such as those in the North Sea. Developments in these areas can be expected which will advance the use of tracers to hydrologists and their understanding of ground water behaviour and aquifer properties.

4.2.4 *Sediment movement.* The behaviour of sediments in the environment is of interest to the hydrologist where pollution of water bodies may occur or where obstructions to drainage paths may develop. Recreational use of streams and reservoirs may be affected by the presence of excess sediments or, more importantly, perhaps, the movement of any particulate pollutants such as heavy metals may be dictated by the general behaviour of sediments in the receiving waters. Sewage effluent dispersion may result in bacterial contamination of estuarine regions by the upstream movement of "saline wedges" in river courses.

Most tracing of sediments is carried out using radioactive tracers, the merits of which are discussed in Section 3. The methods employed for measurement of sediment flow are similar to those used for water flow measurement but with the extra constraints that mixing is more difficult to achieve, the high "longitudinal dispersion" and variable depth of mixing make impossible accurate determination of the concentration integral, and steady state conditions do not generally exist over the measurement period.

A further method, termed the spatial integration method, used for bed-load movement studies, consists of determining separately the mean transport velocity, width and depth to obtain the discharge. The mean velocity is derived by determining the distance moved by the centre of gravity of the tracer pulse between the two successive surveys and the depth profile is determined from core sampling. In this method, it is not necessary to have steady state conditions between the surveys.[86]

The water borne movement of sediments such as the dispersion of sewage is measured dynamically by measurement of the tracer plume from boats traversing the area. Usually surface labelling with ^{198}Au or ^{110m}Ag, depending on the duration of the test, is used although, for fine sediments, the use of tracers such as ^{82}Br to label the water is more common.

5. Conclusions

Environmental and artificial tracers play an important role in understanding aspects of the water cycle. Correlation of the variation of stable isotopes in ground waters with paleoclimatic information, and the exploitation of radioactive decay of naturally occurring isotopes, now allow timescales to be placed on hydrological processes such as recharge or mixing in water bodies. As a result, strategies of water extraction or artificial recharge can be planned with some understanding of their consequences.

The early work with tracers was associated with artificial tracers but with improvements in instrumentation, environmental tracers have been increasingly used over the past two decades. Their use has also been encouraged by the release into the atmosphere of the products of nuclear weapons trials, such as tritium and ^{85}Kr, which have become incorporated into the water cycle. Environmental tracers are, because of their ubiquitous nature, usually associated with regional studies or the identification of isolated water bodies. Artificial tracers, on the other hand, are site specific—they are introduced only in the region of interest. Advances in this field have been mainly related to increased availability of radioactive isotopes, and improvements in detection methods, such as high resolution solid-state detectors for radioactive tracers, robust optical field equipment for dyes or portable XRF techniques. Another important area of advance is in the development of mathematical models to describe the behaviour of the tracers in the environment. These developments and the availability of electronic data recording and computation equipment have increased the contribution of the tracer methods to a broader understanding of hydrology.

A major step forward in the use of environmental isotopes can be expected as a result of the development of particle accelerators for mass spectrometer measurements of cosmic-ray produced isotopes such as ^{14}C, ^{10}Be and ^{36}Cl. Timescales can be extended and, as very small samples are required, the areas of application will broaden. How costly these measurements are remain to be seen. The development of small proportional counters provides another, less expensive, way of measuring the concentration of certain radioactive isotopes in small samples. These techniques are seen to be particularly appropriate to studies of deep ground water movement related to radioactive waste disposal options or to water movements in the unsaturated zone.

As stated in the Introduction, the discipline of hydrology is wide-ranging and embraces all aspects of the water cycle. Applications of tracers in this field have made significant contributions to current understanding and it seems likely that this state of affairs will continue in the forseeable future.

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