Determination of groundwater movement by means of environmental isotopes: state of the art

H. MOSER & W. RAUERT
GSF-Institut für Radiohydrometrie,
D-8042 Neuherberg, Federal Republic of Germany

ABSTRACT The present state of analytical techniques enables measurements of the heavy isotope content of the water molecules (²H, ³H, ¹⁸O) as well as of specific isotopes (¹³C, ¹⁴C, ³⁵Cl, ³⁹Ar, ³⁷Kr) in solutes like HCO₃, CO₂, Cl⁻, and noble gases, with high detection sensitivity and low detection limit. Labelling of water with the environmental isotopes mentioned above occurs in the atmosphere and upper soil layers by isotopic fractionation effects during phase transitions or by uptake of cosmic-ray produced or manmade isotopes. Precipitation water, thus labelled, with respect to its distribution in space and time infiltrates into the aquifers. From the isotopic content of groundwater relative to the initial isotope content during infiltration and with simplifying assumptions concerning the flow, conclusions can be drawn for residence times, mixing processes and, sometimes, for the location of the recharge area of the groundwater. The time scale of groundwater movement in these studies depends on the time scale of the variations in isotope content, subject to the influence of three different factors: the half-life of the radioactive nuclides under consideration (e.g. ¹⁴C, ³⁵Cl, ³⁹Ar, ³⁷Kr), the climatic factors influencing the isotope fractionation (e.g. in the case of ²H, ¹⁸O), and the anthropogenic variations of the isotopic input (e.g. in the case of ³H, ³⁷Kr).
simplifiant les hypothèses concernant le débit, on peut, à partir de la concentration en isotopes de l'eau souterraine comparée à la concentration initiale durant l'infiltration, tirer d'une part des conclusions sur le temps de séjour, d'autre part sur les processus de mélange et parfois sur la localisation du site de recharge de l'eau souterraine. L'échelle de temps du mouvement de l'eau souterraine qui est mise en compte dans ces études dépend de l'échelle de temps des variations des concentrations d'isotopes qui est contrôlée premièrement par la demi durée des nucléides radioactifs considérés (p.e. $^{14}$C, $^{36}$Cl, $^{39}$Ar, $^{81}$Kr), en second lieu par les facteurs climatiques influencant le fractionnement d'isotopes (p.e. $^{2}$H, $^{18}$O) et enfin par l'apport d'isotopes modifiée par l'intervention de l'homme (p.e. $^{3}$H, $^{85}$Kr).

INTRODUCTION

Parameters of groundwater movement

Commonly used parameters of groundwater movement (Table 1) are the flow velocity and the flow direction as well as the filter velocity of groundwater. In many cases, the residence time and the mean residence time, or the groundwater age are used as complementary measures. However, the exact nature of the beginning point of a groundwater age and a residence time is sometimes not clearly specified (e.g. groundwater recharge time, time of infiltration of rainwater or riverwater). Often, the groundwater age is defined as the length of time the water has been isolated from the atmosphere (e.g. Davis & Bentley, 1982). The dispersion coefficient and the dispersivity serve in general as a measure for mixing processes of groundwater within the aquifer.

Mathematical description of groundwater movement

The groundwater movement is mostly described by the potential theory. Thereby the filter velocity $v_f$ follows from the permeability $K$ and the groundwater head gradient $\Delta h/\Delta l$ (Darcy's law):

$$ v_f = K \frac{\Delta h}{\Delta l} \quad (1) $$

Various hydrodynamic flow models are used for determining residence times and involve assumptions for certain mixing processes within the aquifer. Examples are the piston flow model [without mixing within groundwater flow (Fig.1(a))], the dispersion model (with hydrodynamic dispersion along the flow path), and the exponential model [with mixing of water portions of different residence times, the separate portions diminishing exponentially with increasing residence time (Fig.1(b))], e.g. Grabczak et al. (1982). In the case of the exponential model, the weighted mean of the residence times of each water portion corresponds to the mean residence time of the groundwater under consideration.
TABLE 1 Parameters of groundwater movement

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Definition</th>
<th>Measuring technique</th>
<th>Problems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow velocity</td>
<td>$v_a$</td>
<td>$v_a = \frac{\Delta l}{\Delta t} = K(\Delta h/\Delta l)n = \frac{v_f}{n}$</td>
<td>Two-well labelling experiment</td>
<td>Determination of mean transit time. Setting up measuring points in flow direction</td>
</tr>
<tr>
<td>Filter velocity</td>
<td>$v_f$</td>
<td>$v_f = \frac{Q}{A_{gw}} = K(\Delta h/\Delta l)$</td>
<td>Single-well method</td>
<td>Borehole construction, inhomogeneity of aquifer</td>
</tr>
<tr>
<td>Flow direction</td>
<td>$R_i$</td>
<td></td>
<td>Single-well method, hydrological triangle</td>
<td>Borehole construction, inhomogeneity of aquifer</td>
</tr>
<tr>
<td>Average age (&quot;mass age&quot;)</td>
<td>$t_a$</td>
<td>Average age of the whole water mass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean residence time</td>
<td>$t_r$</td>
<td>(a) Mean time the water is flowing in a hydrological system</td>
<td>Isotopic age determination</td>
<td>Dependence on the applied flow model</td>
</tr>
<tr>
<td>(average turnover time)</td>
<td>$V/Q$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$A_{gw}$ = effective cross section for groundwater flow (m$^2$)

$\Delta h/\Delta l$ = groundwater head gradient

$K$ = permeability of aquifer (m s$^{-1}$)

$l$ = length of flow path, distance between two points in flow direction (m)

$n$ = effective porosity

$Q$ = groundwater discharge (m$^3$/s$^{-1}$)

$V$ = volume of reservoir (m$^3$)
Groundwater movement and groundwater quality

An exact understanding of groundwater movement provides a solution to many groundwater problems. For example, the storage volume of an aquifer, which in turn determines the usable groundwater amount, can be evaluated from the residence time and discharge. In particular, groundwater quality is often related directly to groundwater movement. As an example, the decomposition of many noxious substances in the aquifer depends to a large extent on their residence time in the aquifer, a feature which is used for determining the size of protection zones for water supply. Also, the possible spread of noxious substances can be only estimated if the groundwater movement in the area under investigation is known. In issues relevant to environmental protection such as garbage, chemical and radioactive waste disposal, this information on groundwater movement is demanded. Depending on the problem, groundwater residence times have to be determined ranging from days to tens of thousands of years, and groundwater velocities from some tens of metres per day down to the diffusion velocity (mm day$^{-1}$).

Measurement of groundwater movement

Groundwater flow velocities and groundwater flow directions can be measured by "indirect" and "direct" methods. An "indirect" method is, for example, the evaluation of the flow velocity $v_a$ (Table 1) using Darcy's law (equation (1)):

$$v_a = \frac{V_f}{n} = \frac{K}{n} \frac{\Delta h}{\Delta l}$$  \hspace{1cm} (2)

where $n = \text{effective porosity}$. With $v_a = \Delta l/\Delta t$ the flow time $t = \Sigma \Delta t$ can be calculated from equation (2):

$$\Delta t = \frac{n (\Delta l)^2}{K \Delta h}$$  \hspace{1cm} (3)

The quantities of $K$, $\Delta l/\Delta h$, and $n$ are difficult to measure especially in the unsaturated zone and if the aquifer permeability is non-homogeneous or anisotropic, such conditions lead to uncertainty in the determination of the flow velocity and residence time of groundwater.

In the case of the "direct" method ("tracer method"), the water
entering the hydrological system under investigation is labelled (input). The parameters of groundwater movement are then determined by detection of this labelling at one or several groundwater measuring points situated downstream (output). In a limited investigation area with relatively short flow paths, and in the case of the limited duration of field experiments, the groundwater can be labelled by intentional addition of a labelling substance (e.g. a fluorescent dye). This provides controlled initial and boundary conditions.

Moreover, one can take advantage of the "natural labelling" of groundwater, which arises from the temporally and/or locally changing water quality, i.e. the contents of chemical ingredients and isotope species. For such investigations no limits exist, in principle, concerning the investigation area and the duration of field experiments; however, problems arise with this method due to deficiencies in information for the input function of the labelling substance, to the small detectable concentrations of labelling substances, and to the possible interactions of the labelling substances with the solid matrix of the aquifer (e.g. sorption etc.). In spite of these problems, the natural labelling of groundwater by its quality, is in many cases, the only possibility for the determination of groundwater quantity, especially in the case of small groundwater velocities and associated long residence times. In the following sections, the subject will be limited to labelling of groundwater by different isotope species occurring in nature ("environmental isotopes"). The use of water chemistry in studies of groundwater movement is covered by Fritz in this symposium.

ENVIRONMENTAL ISOTOPES AS HYDROLOGICAL TRACERS

Table 2 indicates those environmental isotopes in common usage together with those with potential as hydrological tracers. Their most important properties for practical applications are included in the table. The environmental isotopes can be classified, according to their half-life, as either stable or radioactive isotopes. They can also be classified, on the basis of possible interaction with the solid matrix of the aquifer, as isotope species of water molecules, or of noble gases and other water ingredients (gases, ions). Moreover, considerable differences between environmental isotopes exist with regard to their present detection limits, together with the requisite volume of water samples and to the sample throughput, important aspects for geo-statistical interpretation.

Deuterium (2H) and oxygen-18 (18O)

The concentration differences listed in Table 2 for water molecules labelled with 2H and 18O, are essentially caused by temperature dependent isotope fractionation within the water cycle (e.g. Gat & Gonfiantini, 1981). In this way, 2H and 18O contents of precipitation result with characteristic differences in time and space. These differences label the infiltrated groundwater, according to its origin and residence time. Figure 2 (upper part)
<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (years)</th>
<th>Chem. composition in natural water</th>
<th>Production</th>
<th>Isotope ratio abundance in recent groundwater</th>
<th>Max. decay rate (dpm per m³ water in natural water)</th>
<th>Detection limit (µl H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>²H</td>
<td>stable</td>
<td>²H₂O</td>
<td>N</td>
<td>(90-170)·10⁻⁶ ²H/¹H</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>³H</td>
<td>12.43</td>
<td>³H₂O</td>
<td>N,A</td>
<td>≈ 10⁻¹⁷ ³H/²H</td>
<td>10⁶ b)</td>
<td>2</td>
</tr>
<tr>
<td>¹⁴C</td>
<td>5730</td>
<td>¹⁴CO₂, ¹⁴CO₃⁻</td>
<td>N,A</td>
<td>1.2·10⁻¹² ¹⁴C/¹²C</td>
<td>≈ 10³ b)</td>
<td>0.5</td>
</tr>
<tr>
<td>¹⁸O</td>
<td>stable</td>
<td>H₂¹⁸O</td>
<td>N</td>
<td>(1880-2018)·10⁻⁶ ¹⁸O/¹⁶O</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>³²Si</td>
<td>108</td>
<td>³²SiO₂</td>
<td>N</td>
<td>≈ 2·10⁻¹⁶ ³²Si/Si</td>
<td>[≤ 0.2·0.6 b)</td>
<td>1</td>
</tr>
<tr>
<td>³⁹Ar</td>
<td>269</td>
<td>dissolved gas</td>
<td>N</td>
<td>≈ 10⁻¹⁵ ³⁹Ar/Ar</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>⁸¹Kr</td>
<td>2.1·10⁻⁵</td>
<td>dissolved gas</td>
<td>N</td>
<td>6·10⁻¹³ ⁸¹Kr/Kr</td>
<td>8·10⁻⁶</td>
<td>7</td>
</tr>
<tr>
<td>⁸⁵Kr</td>
<td>10.76</td>
<td>dissolved gas</td>
<td>A</td>
<td>6·10⁻¹² ⁸⁵Kr/Kr</td>
<td>2.8</td>
<td>3</td>
</tr>
<tr>
<td>³⁶Cl</td>
<td>3·10⁻⁵</td>
<td>³⁶Cl⁻</td>
<td>N,A</td>
<td>2·10⁻¹² ³⁶Cl/Cl</td>
<td>0.2 b)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Notes:**

- a) 2σ criterion for the measured isotope ratio in a water sample
- b) influenced by nuclear weapon tests
- c) published values vary between 101 and 701 years
- d) using accelerator measurement: ≈ 10 mg C
- e) using resonance ionisation spectroscopy: 10⁻⁵ m³ Kr (≈ 1 l H₂O)

A = man made
dpm = disintegrations per minute
N = natural
FIG. 2 Seasonal trends of the deuterium content of precipitation (upper) and runoff (lower) in a mountainous basin of area 19 km$^2$ (Upper Bavaria, FRG). Values shown are event averages (points) and weighted monthly means (histogram) and are expressed as $\delta$ values being the deviation from standard (SMOW) (Herrmann & Stichler, 1982).

shows as an example the $^2$H contents of single precipitation events in a small basin in Upper Bavaria (Federal Republic of Germany). Accordingly, the $^2$H contents of subsequent precipitation events can differ considerably under the given climatic conditions; however the monthly means of $^2$H contents result in an annual variation following the course of the mean monthly temperature in its pattern. The concentration-time distribution of $^2$H contents (input function) and especially the differences between single precipitation events
or between the seasons can be used as time markers for groundwater movement, if no extensive mixing has taken place in the aquifer. Figure 2 (lower part) shows, for the same basin the $^2$H contents measured in the discharge (output function). By comparing with the $^2$H contents of precipitation, one can see that some of the changes due to single precipitation events can be recognized in the discharge a short time later. The seasonal variations, however, are smoothed together. One can thus conclude, that a remarkable groundwater discharge exists in addition to the direct surface runoff. Its mean residence time has been estimated, using the above-mentioned exponential model, to be about two years (Herrmann & Stichler, 1982). The determination of groundwater dynamics, using $^2$H and $^{18}$O, depends essentially on the input function. Under humid climatic conditions existing at medium latitudes, mean residence times from days up to a few years can be evaluated from $^2$H and $^{18}$O contents, depending on hydraulic conditions and the applied model assumptions.

Due to the dependence of isotope fractionation on temperature and air humidity, climatic changes are also reflected in $^2$H and $^{18}$O contents of precipitation. An impressive example of this application with $^{18}$O is demonstrated with ice-core samples from Greenland, which show a significant increase of $\delta^{18}$O values during the transition from Pleistocene to Holocene, about 12 000 years ago (e.g. Dansgaard et al., 1974). Similar observations have been made on old groundwaters recharged in the same time period. For this an example is shown in Fig. 3 with $^{18}$O contents of groundwater from eastern England in relation to their "age"; groundwater ages of more than 10 000 years are significantly correlated with lowered $^{18}$O contents. Thus, there is the potential for differentiating between groundwater of the Pleistocene and Holocene periods (for further examples see e.g. Moser & Rauert, 1980).

Tritium ($^3$H) and krypton-85 ($^{85}$Kr)

Current levels of radioactive isotopes $^3$H and $^{85}$Kr in the hydrological cycle are largely of anthropogenic origin. Nuclear testing between 1952 and 1963 produced increased $^3$H in the

---

**FIG. 3** $^{18}$O contents of groundwater from the unconfined and confined area of a Triassic non-marine sandstone aquifer in eastern England, in relation to the geochemically corrected $^{14}$C age (after Bath et al., 1979).
stratosphere. Since then, it has been transported to the atmosphere with a seasonal periodicity, oxidized to \(^3\)H\(_2\)O and rained out since 1963 with a progressive decline in annual mean concentration towards the current state (Fig. 4). Definition of this input function has been based on the IAEA/WMO sampling network at the global scale and has been supplemented by many national programmes.

Krypton-85 is released from nuclear plants into the air and becomes distributed uniformly in the atmosphere. In contrast to \(^3\)H, the \(^{85}\)Kr concentration in the air and therefore also in the precipitation, has increased monotonically without seasonal variation (Fig. 5).

Tritium and \(^{85}\)Kr contents of groundwaters are, therefore, suitable for the resolution of residence times up to about 100 years, depending on the hydrological model used for interpretation. Fig. 6 shows, in the case of the exponential model, the \(^3\)H and \(^{85}\)Kr contents of groundwaters with different mean residence times.

![Graph showing monthly means of \(^3\)H contents of precipitation in the catchment area of River Rhine (after Weiss & Roether, 1975) completed by data since 1974 from Upper Bavaria.](image)

![Graph showing annual means of atmospheric \(^{85}\)Kr concentrations between 40° and 60°N latitude (Salvamoser, 1982); mMol and ml refer to krypton (STP); dpm = disintegrations per minute.](image)
calculated from known $^3$H and $^{85}$Kr input functions (Figs 4 and 5). The measurement of $^{85}$Kr contents is much more expensive than that of $^3$H. However, single $^{85}$Kr analyses can be used successfully in overcoming those uncertainties associated with the dynamics of $^3$H input for determining residence time (e.g. Salvamoser, 1982). On the other hand a sufficiently long time series of $^3$H data (and/or $^{85}$Kr) from a single groundwater sampling point can be instructive for insights into flow mechanisms and choice of model together with an assessment of errors in calculated residence times. Figure 7 shows the measured and calculated (by means of the exponential model) time series of $^3$H contents in the Funtenen spring near Meiringen (Switzerland). It is apparent from the general

FIG. 6 $^3$H and $^{85}$Kr contents of groundwater for different mean residence times $t_t$ calculated from $^3$H and $^{85}$Kr input functions (Figs 4 and 5) by means of the exponential model for groundwater samples taken in 1979 (Salvamoser, 1982).

FIG. 7 $^3$H content of Funtenen spring near Meiringen (Switzerland) with mean residence times $t_t$ calculated on the basis of the hydrological exponential model (after Siegenthaler & Schotterer (1977) and personal communication).
correspondence of the plotted points with $t_t = 13$ years, that the model form and residence time are realistic.

Carbon-14 ($^{14}$C)

Radiocarbon is steadily produced in the atmosphere by cosmic-ray interaction and is oxidized to CO$_2$. According to the model of Münich (e.g. 1968), it enters the soil zone mainly by the decomposition of plants and forms calcium bicarbonate and CO$_2$ in the groundwater. Using the law of radioactive decay, the $^{14}$C model age of a sample from (deep) groundwater is calculated from the ratio of the initial $^{14}$C content ($c_0$) of the groundwater at the time of recharge and the $^{14}$C content of the groundwater under investigation. The value of $c_0$ often lies between about 60 and 100% modern, the latter being the approximate $^{14}$C content of recent plants if (among other things) the influence of $^{14}$C produced by nuclear weapon tests can be neglected or accounted for. Changes in cosmic ray production of $^{14}$C in the past might not considerably increase the uncertainty of $^{14}$C model ages. The uncertainty of $c_0$ is due to, among other effects, the geochemistry of the recharge area (e.g. karst, crystalline rock), the possible $^{14}$C content of soil carbonates, the dissolution of limestone by humic acids, and carbon isotope exchange between the soil gas and water. Furthermore, $^{14}$C can be lost from the groundwater through isotope exchange with the carbonate in the aquifer, or the $^{14}$C content can be diminished by admixture of CO$_2$ of fossil biogenic or magmatic (volcanic) origin. The various methods for isotopic and geochemical corrections of $^{14}$C dates have been reviewed, for example, by Fontes & Garnier (1979) and by Eichinger (1981). Major parameters of these models are the concentrations of the dissolved inorganic carbon (HCO$_3^-$, CO$_2$) and the ratios of the stable carbon isotopes, $^{13}$C/$^{12}$C, in the soil gas, carbonate rocks and groundwater. These isotope ratios (expressed as $^{13}$C/12C values) point to the biological or carbonate origin of the carbon. Despite its many uncertainties, the $^{14}$C method appears at present to be the only means for providing hydrogeologists with order-of-magnitude estimates of groundwater ages between about one thousand years and a few tens of thousands of years.

Carbon-14 dating of groundwater can be complicated by possible diffusion and/or convective transport of $^{14}$C across low permeable layers which separate horizons of groundwater with strongly distinct contents of $^{14}$C and/or hydraulic heads (Klitzch et al., 1976; Geyh & Backhaus, 1979). This is a general problem with the use of cosmogenic radionuclides in dating groundwater. A further general complication is that wells from which samples are drawn are often screened at various depths thus producing water of mixed ages.

The role of $^{14}$C in dating groundwater is exemplified in the case of hydrological studies with environmental isotopes in the Younger Tertiary aquifer of the Bavarian Molasse basin (Egger et al., 1983). This aquifer tapped by wells to a maximum depth of 288 m is formed of gravel and sand with intermediate lenses of clay and silt. Man-made tritium had been detected down to depths between about 20 and 60 m, thus indicating the zone with mean groundwater residence times of up to a few decades. Based on $^3$H depth of penetration a rough estimate was made of the recharge rate in the area under
> FIG. 8 Relationship between the $^{14}$C content and the $^{18}$O content (δ values) of groundwater samples taken from the Younger Tertiary aquifer of the Bavarian Molasse basin (after Egger et al., 1983). Results of repeated sampling and analysis are indicated by arrows.

investigation (Andres, 1983). The deep groundwater showed $^{14}$C model ages up to at least 35,000 years, consistent with approximate hydraulic estimates of flow times. Groundwater with $^{14}$C contents of less than 25% modern, corresponding to ages of $10^6$ years or greater, displayed $\delta^2$H and $\delta^{18}$O values which were clearly lower than the δ values of recent groundwater (Fig. 8). The decrease in δ values is ascribed to colder climates during glaciation, consistent with determinations of groundwater formation temperature, as assessed by noble gas measurements (Rudolf & Sonntag, personal communication).

Flow velocity of groundwater can be deduced from $^{14}$C model ages increasing in flow direction if the isopiezometric contours are known, or if the aquifer permeability can be assumed to be isotropic (Vogel, 1970; Bergmann, 1971). Thus, flow velocities between about 0.7 and 7 m year$^{-1}$ were determined in aquifers in Europe, USA, and South Africa, belonging to different geological formations. Under certain conditions, flow velocities which are derived from differences in $^{14}$C model ages at different measuring points along the flowline, are largely independent of the specific procedure used for model age determination (Münnich, 1968). For example, considerable differences were exhibited by the $^{14}$C model ages of groundwater in a limestone aquifer in West Flandern, which were calculated by Fontes & Garnier (1979) from chemical and isotopic data using different models. Nevertheless, the flow velocities derived from the age differences agree fairly well for each of the flow sections.

Silicon-32 and argon-39

Silicon-32 and $^{39}$Ar having half-lives intermediate between those of $^3$H and $^{14}$C, appear to be suitable for dating groundwater within the range between 100 and 1000 years. In the case of $^{32}$Si, uncertainties exist as to its half-life, the contributions of $^{32}$Si produced by cosmic radiation in the soil and by nuclear bomb tests, and the complex silica geochemistry. As a consequence, dating with $^{32}$Si is, currently, only useful for establishing relative ages of water in a single aquifer (cf. Davis & Bentley, 1982).

Though the rare gas argon in solution does not react with the solid aquifer matrix, groundwater ages determined by $^{39}$Ar have so far
Groundwater movement and environmental isotopes

proved to be often much less than those by the $^{14}$C model. This
discrepancy could be due, in part, to subsurface production of $^{39}$Ar
according to the reaction $^{39}$K(n,p)$^{39}$Ar (Loosli & Oeschger, 1979), in
producing neutrons from the capture of alpha particles originating
mostly from the decay of U and Th in the rock. A further source of
discrepancy may be attributed to an inappropriate form of the $^{14}$C
model. Figure 9 shows $^{14}$C and $^{39}$Ar model ages of groundwaters from the
Franconian Alb-foreland (FRG), based on an initial $^{14}$C content of
85% modern. The combined $^{14}$C and $^{39}$Ar age values of the samples
no.7, 21a, and 22 cannot be explained by a mixture of groundwaters
with different ages. However, the consideration of the chemical
and isotopic composition of these groundwaters and of a possible
isotopic exchange, lead to lower $^{14}$C model ages in all three cases,
as can also be seen in Fig.9 (after Eichinger, 1981). The major
uncertainty in the $^{14}$C model age of no.21a is due to the error
range in the determination of the initial $^{14}$C content. The
reduction of the $^{14}$C model ages brings the pairs of $^{14}$C and $^{39}$Ar
ages in the range of possible mixture models and could remove the
discrepancy stated by Loosli & Oeschger (1979).

Further field and laboratory experiments as well as theoretical
considerations are underway to investigate the conditions under
which $^{39}$Ar dating of groundwater is possible (e.g. Loosli & Forster,
1982).

Krypton-81 and chlorine-36

For dating of very old groundwaters within a time scale of $10^5$ to $10^6$
years, $^{81}$Kr and $^{36}$Cl are of particular interest. Krypton-81 has the
advantage of being inert and of originating probably only by cosmic

![FIG.9 $^{39}$Ar and $^{14}$C model ages of groundwaters from the
Franconian Alb-foreland (FRG). The $^{14}$C and $^{39}$Ar
concentrations are referred to recent concentrations
("100% modern")]. $^{39}$Ar model ages calculated with an
initial $^{14}$C content $c_0 = 85\%$ modern (Loosli & Oeschger, 1979);
$^{14}$C model ages (with error) calculated by
irradiation in the atmosphere and at shallow soil depth. As natural
$^{81}$Kr concentrations in groundwater are very small, water sample
volumes of $10^3$ m$^3$ were considered to be required for radioactivity
gas counting (Oeschger, 1978). More recently a new detection
technique, the resonance ionization spectroscopy, combining laser
technique and mass spectroscopy, seems to offer the possibility of
reducing sample size to a few litres of water, with the first data
set soon to be available (Loosli, personal communication).

Mass spectroscopy involving accelerators for nuclide
identification provides an excellent means for the measurement of
natural $^{36}$Cl concentrations in a few litres of water. Problems of
geochemical interpretation are considered to be less than with $^{14}$C,
because chloride in groundwater is neither derived normally from,
nor reacts with, the solid matrix of the aquifer (Davis & Bentley,
1982). Thus far, about 40 groundwater related samples have been
analysed using the University of Rochester tandem Van de Graaf
accelerator. A reasonable correlation was found between
hydrodynamic ages and $^{36}$Cl ages in the Fox Hills Sandstone aquifer
of North Dakota. However, the data obtained so far from
groundwater samples from the Carizzo Sandstone, Texas, cannot be as
easily interpreted. Chlorine-36 is produced in the atmosphere and
at the earth's surface. The initial $^{36}$Cl concentration of
groundwater depends, among other factors, on latitude and proximity
to the coast, since the $^{36}$Cl/Cl ratio is very low in ocean water.
Extensive studies combined with measurements of other radionuclides
are necessary to prove the $^{36}$Cl dating method as a useful tool in
hydrological investigations.

FINAL REMARKS

Figure 10 summarizes the time ranges and nuclides, the measurements
of which form the basis for dating groundwater as have been
described here. It is obvious from this review that
further development of dating techniques is necessary for
groundwaters of medium and very great age. Additional information
could be provided by other methods, but the results are likely to be
even more difficult to interpret for residence time. For example,
the accumulation of radioactive-decay products in water may be a
measure of the transit time, and measurement is progressively
simplified with increasing age. There have been attempts to use

![FIG.10 Dating ranges of environmental isotope techniques already in use (---) and under development (----), the exact range depending on the interpretation model used.](image-url)
the accumulation of $^{4}\text{He}$, originating from the decay of $\text{U}$ and $\text{Th}$ in the rock, for groundwater dating. Almost all determinations by $^{4}\text{He}$ model ages have overestimated age relative to that based on $^{14}\text{C}$ (e.g. Bath et al., 1979). This might be due, in part, to the admixture of helium which seeps upwards from deep geological sources. It should also be noted that the alternative He isotope, $^{3}\text{He}$, the decay product of $^{3}\text{H}$, might be useful for dating young groundwater. A qualitative dating of old groundwater up to $1.5 \times 10^{5}$ years appears to be possible by measuring the $^{23}\text{U}/^{238}\text{U}$ activity ratio and by following the disequilibrium of these radionuclides in circulating groundwater. For details of this method as well as for the potential utilization of chemical disequilibria (e.g. amino acid racemization) and of anthropogenic chemicals like halocarbons (e.g. freon) in groundwater dating, reference to relevant literature has to be made (for example, Davis & Bentley, 1982).

Our overview of dating methods stresses a need for further development in techniques, an improved specification of the initial input concentration and, in the case of radionuclides, a better understanding of underground production of the environmental tracers used. A major problem still to be solved, is the development of comprehensive models for data interpretation. These models should account for the geochemistry of tracer behaviour and water-rock interactions, for diffusion and dispersion processes, for the hydrodynamics of groundwater flow and for mixing processes in natural flow systems.

REFERENCES


