ISOTOPE HYDROLOGY 1983
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PROCEEDINGS OF AN INTERNATIONAL SYMPOSIUM
ON ISOTOPE HYDROLOGY IN WATER RESOURCES DEVELOPMENT
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FOREWORD

The sixth Symposium on Isotope Hydrology, organized by the International Atomic Energy Agency in co-operation with the United Nations Educational, Scientific and Cultural Organization, was held in Vienna, Austria, from 12 to 16 September 1983. The first symposium on the same subject was held twenty years ago in Tokyo, Japan; since then, the IAEA isotope hydrology symposia have become a recurrent event, usually taking place every four years. Practically every important development and new application of isotope techniques in hydrology has been presented at these symposia. As a result of the co-operation between the IAEA and UNESCO, the use of isotope techniques in hydrology has been included among the projects of the International Hydrological Decade since the beginning and was made part of the International Hydrological Programme, both organized by UNESCO.

Isotope techniques are now in their third decade of application to hydrological investigations and have reached full maturity as scientific and practical tools. However, these Proceedings demonstrate that new ideas, such as — for example — the interpretation of stable-isotope behaviour in the unsaturated zone, continue to develop. Important technical progress can also be seen: a typical example is the use of chlorine-36 for dating groundwater, which will greatly extend the measurable age range. In other words, isotope hydrology is still a field undergoing scientific evolution and not merely a set of routine techniques for practical purposes.

After so many years of work in isotope hydrology, it is perhaps the right time to express the Agency’s gratitude to those who encouraged this activity. The following paragraph is an excerpt from the opening speech at the Symposium made by M. Zifferero, IAEA Deputy Director General, Head of the Department of Research and Isotopes.

"The application of isotope and nuclear techniques to hydrological problems is a field of activity in which the Agency entered soon after its establishment in 1957. Many of those who advised and assisted the Agency in this activity are with us today. I would like to pay a special tribute to Henry Seligman, Eric Eriksson of the Uppsala University and Bryan Payne who initiated the Agency programme in isotope hydrology more than twenty years ago. I would like also to mention, among those who actively contributed to the development of this programme since its inception, Willi Dansgaard of the University of Copenhagen, George Davis, formerly of the United States
Geological Survey in Washington, D.C., Vassili I. Ferronsky of the All-Union Institute for Water Problems in Moscow, Joel Gat of the Weizmann Institute of Science in Rehovot, Jacques Guizerix of the French Atomic Energy Commission in Grenoble, Ferdinand Neumaier and Heribert Moser of the Gesellschaft für Strahlen- und Umweltforschung in Neuherberg, Karl Otto Münnich of the University of Heidelberg, Brian Smith of the United Kingdom Natural Environment Research Council, Hans Suess of the University of California at San Diego, and Ezio Tongiorgi of the University of Pisa; and above all, we shall not forget the active support of Willard Libby, Nobel Laureate, who passed away in 1980.”

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ENVIRONMENTAL ISOTOPES IN PRECIPITATION AND SURFACE WATER STUDIES

(Session I)
Chairman

D.B. SMITH
United Kingdom
HYDROMETEOROLOGICAL FACTORS CONTROLLING THE TIME VARIATION OF D, $^1$H, AND $^2$H IN ATMOSPHERIC WATER VAPOUR AND PRECIPITATION IN THE NORTHERN WESTWIND BELT


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Abstract

HYDROMETEOROLOGICAL FACTORS CONTROLLING THE TIME VARIATION OF D, $^1$H, AND $^2$H IN ATMOSPHERIC WATER VAPOUR AND PRECIPITATION IN THE NORTHERN WESTWIND BELT.

Long-term records of D, $^1$H, and $^2$H in daily composite samples of water vapour and precipitation, together with relevant hydrometeorological parameters, are presented for Heidelberg and Cracow. Short-period isotope records of the water vapour at Paris, Hannover and Miami are also discussed. The records of $\delta D$ and $\delta ^1$H in water vapour reveal strong short-term variations comparable with the range of their seasonal variation ($\Delta \delta D \approx 80\%$ and $\Delta \delta ^1$H $\approx 10\%$).

A simple water vapour advection model simulates fairly well the seasonal variation of the monthly mean isotope data. The application of this Rayleigh condensation model to a description of the isotopic depletion along the trajectories of individual air masses yields isotope data at the observation point being in most cases inconsistent with the actual findings. This discrepancy is reflected by a poor temperature correlation for the daily isotope data, whereas monthly means are very well correlated (2.8 ky $^\circ$C for $\delta D$ and 0.3 ky $^\circ$C for $\delta ^1$H).

A power spectral analysis of the $\delta D$ records yields a prevailing group of periodicities of
50–67, 29–36, 20–22 and 10–11 days. These moving 'wave patterns' show a constant phase shift of about one day between Heidelberg and Cracow. The $^3$H data of water vapour and precipitation show that the surface atmosphere over western and central Europe is permanently contaminated by quasi-continuous discharges of tritium from nuclear energy installations; the average level of this contamination is significantly lower than that observed in the preceding decade.

1. INTRODUCTION

The increasing interest in heavy isotopes of water, deuterium and oxygen-18, as indicators of climatic changes in the past (variations of $\delta^2$D and $\delta^{18}$O in ancient groundwaters, plant material, speleothems, etc.), has recently drawn new attention to the problem of how the isotopic composition of local precipitation is linked with the local climate and the parameters of the atmospheric water vapour transport.

The IAEA/WMO Global Precipitation Network has been in operation since 1961, providing monthly mean data on $^2$H, $^{18}$O and tritium content in local precipitation [1]. Already in the early sixties, this extensive collection of data allowed a number of correlations to be established between the heavy-isotope content of local precipitation and various environmental parameters characterizing the given sampling point, like local surface air temperature, altitude above sea level or distance to the coast [2]. These purely empirical relations, so-called 'effects', proved to be a useful tool in applications of heavy isotopes in hydrology and glaciology. The first attempts to model the observed variations in heavy-isotope content of precipitation on a global scale were undertaken by Eriksson in 1965 [3]. He used a general circulation model of atmospheric water vapour to derive the isotope characteristics of the vapour and found that the $^2$H and $^{18}$O content of tropospheric moisture should decrease exponentially with height and that the isotopic composition of precipitation should be closely related to the quantity called 'precipitable water'. This quantity is defined as the amount of water vapour contained in a unit area column of air which extends from the earth's surface to the top of the atmosphere at a given instant.

Systematic measurements of deuterium content in the water vapour sampled from various levels of the troposphere [4, 5] confirmed to some extent earlier predictions of Eriksson [3] regarding the vertical distribution of the heavy isotopes in atmospheric water vapour. However, the observed vertical gradients of deuterium content appeared to be generally larger than predicted by Eriksson. This interesting point has been discussed recently by Rozanski and Sonntag [6] who tried to explain the observed gradients on the basis of numerical modelling of precipitating cloud systems, assuming complete isotope exchange between water vapour, cloud droplets and raindrops.
The heavy-isotope ratios observed in European precipitation have been simulated [7] using a one-dimensional model of advective transport of water vapour over the European continent and a Rayleigh model of the condensation process. This numerical modelling revealed that the isotopic composition of local precipitation is primarily controlled by regional scale processes, i.e. by the water vapour transport patterns into the continent and by the average precipitation/evapotranspiration history of the air masses precipitating at a given place. Recently, a more rigorous analytical approach has been proposed [8], where heavy-isotope ratios of atmospheric moisture and precipitation are derived directly from parameters of the water vapour transport.

An advanced modelling of the heavy-isotope variations observed in atmospheric water vapour and precipitation requires more detailed information about short-term variations of the isotopic composition of water vapour as well as of the relevant meteorological parameters. So far, only sporadic measurements of this type have been completed [9–13]. Systematic measurements of daily composite samples of water vapour collected at ground level were initiated in Heidelberg (Federal Republic of Germany) in June 1980. One year later, similar measurements were undertaken in Cracow (Poland). Recently, three additional stations have been included in the network: Hannover (Federal Republic of Germany), Paris (France) and Miami (USA).

The tritium content in atmospheric water vapour becomes more and more interesting, since in the last decade nuclear energy installations for both civilian and military use of nuclear energy have become an additional important source of tritium with regard to present bomb tritium levels [14]. Near-ground water vapour seems to be a far more sensitive indicator for such tritium discharges from nuclear energy installations than the precipitation which is usually formed at a certain distance from the ground level. These additional tritium releases can effectively alter the bomb tritium patterns in precipitation and thus render difficult its application to hydrology. For these reasons, besides routine D and \(^{18}\)O analyses, the tritium content in daily composite samples of water vapour collected at the stations mentioned above has also been measured.

A summary of the results obtained so far, together with a tentative interpretation of the data, is presented below.

2. SAMPLING TECHNIQUE

To trace effectively the short-term variations of isotopic content of atmospheric water vapour, a suitable sampling technique ensuring continuous 24-hour sampling is necessary. The use of conventional Horibe-type traps, cooled down to \(-78^\circ\)C in acetone/dry ice slush, is troublesome since they require continuous care to keep the temperature low enough. Another method,
based on vapour adsorption on molecular sieve beds, although being tested successfully in field measurements [15], is also unpractical in this case, since an extraction step is necessary which needs additional apparatus and time. For these reasons, we decided to develop a simple system which would secure continuous vapour collection without significant isotope effects and simultaneously would need minimum care. First attempts to develop such a system date back more than a decade [16]. Our sampling device is based on a commercially available, electrically operated one-step cooling unit producing a temperature of about -50°C. Samples are collected in specially designed glass traps (see Fig.1)
### TABLE I. CORRECTION FACTORS (ΔδD, Δδ^{18}O) RESULTING FROM NON-COMPLETE SAMPLING OF WATER VAPOUR

<table>
<thead>
<tr>
<th>Condensation temperature (°C)</th>
<th>Residual vapour content in the sampled air (g/m³)</th>
<th>Fraction of the vapour lost during sampling (%)</th>
<th>Correction factorsb</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-45</td>
<td>0.067</td>
<td>0.64</td>
<td>-7.9</td>
<td>-0.69</td>
</tr>
<tr>
<td>-46</td>
<td>0.061</td>
<td>0.58</td>
<td>-7.5</td>
<td>-0.64</td>
</tr>
<tr>
<td>-47</td>
<td>0.055</td>
<td>0.53</td>
<td>-6.9</td>
<td>-0.60</td>
</tr>
<tr>
<td>-48</td>
<td>0.049</td>
<td>0.47</td>
<td>-6.4</td>
<td>-0.55</td>
</tr>
<tr>
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a 24-hour sampling with a flow rate of 0.5 L/min is assumed. Parameters of the sampled air: temperature +10°C, rel. humidity 70%.

b A Rayleigh condensation process is assumed:

\[ \Delta\delta = \delta_{\text{measured}} - \delta_{\text{calculated}} \approx e \cdot F \cdot \ln(F) \]

where: \( e = \alpha - 1 \) = equilibrium fractionation at the given temperature, \( F \) is fraction of the vapour lost during sampling.

which operate alternately with 24-hour intervals, ensuring continuous collection of the water vapour.

At the working temperature (−47°C/−50°C) the residual saturation water vapour pressure (0.03 torr) leads to incomplete removal of the moisture from the sucked air and thus to enrichment of heavy isotopes in the sampled water. Therefore, certain correction factors are calculated for each measured sample, assuming that the vapour undergoes a Rayleigh condensation process. The actual temperature in the sampler as well as the absolute humidity of the air at the inlet have to be known. One can see from Table I that lowering the temperature to −70°C would diminish the correction factors to below the typical error values quoted for D and ^{18}O analysis by modern mass spectrometers.

Since the total error of analysis including correction (experimentally determined
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±5.9 ±0.8 ±0.8 ±3 ±7.1 ±0.9 ±1.0 ±6 ±2.1 ±0.8
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\[ d = \text{deuterium excess defined as: } d = \delta D - 8 \cdot \delta^{18}O; \ T = \text{tritium concentration.} \]

\[ a \text{ Monthly means weighted by amount of precipitation.} \]

\[ b \text{ Calculated from surface air temperature and relative humidity data.} \]

\[ c \text{ Percentage of snow precipitation is given in parentheses.} \]
to be $\pm 2.8\%$ and $\pm 1.1\%$ for $\delta D$ and $\delta^{18}O$, respectively) is still acceptable for routine isotope monitoring of atmospheric water vapour, we decided to keep the temperature at $-50^\circ C$, since its further lowering would mean a significant complication of the sampling device.

3. RESULTS AND DISCUSSION

The following discussion is based on the results obtained at the stations with the longest data records (Heidelberg and Cracow). Since a complete presentation of the daily data obtained so far would be beyond the scope of this paper, an intermediate way has been chosen. Tables II and III summarize the monthly means of the essential parameters recorded at Heidelberg and Cracow over the total observation period. Figure 2 shows daily values of a two-year record at Heidelberg, demonstrating characteristic short-time and seasonal variations. A comparison of the daily deuterium content in water vapour during January-April 1983 for all five stations is given in Fig.3.

3.1. Variations in D and $^{18}O$ content of atmospheric water vapour — links with water vapour circulation models

The fact that variations in heavy-isotope content observed on a global scale in monthly precipitation must have their origin in relevant changes of the isotopic content of atmospheric water vapour was recognized as early as the early sixties [2, 3]. However, some doubts arose as to what extent the monthly precipitation, which often is a result of a few rainy periods only, can be assumed to be a representative sample correctly reflecting the atmospheric conditions prevailing in a given month. The data presented in this paper provide a good experimental basis for a better understanding of the extent to which the time and spatial variations of D and $^{18}O$ in precipitation reflect the actual water vapour circulation patterns. This can be obtained by testing simple models of water vapour transport in the atmosphere by means of available isotope data.

The simplified advection model which links parameters of water vapour transport with changes in its D and $^{18}O$ content has been discussed in detail in Ref.[8]. Here, only some essential points will be discussed.

Assuming a time-independent water storage in the atmosphere, the continuity equations of the horizontal water vapour flux [17] and the corresponding isotope flux can be formulated:

$$\text{div } \bar{Q} = \bar{u} \cdot \text{grad } W = E - P$$

$$\text{div } (\bar{R} \cdot \bar{Q}) = \bar{u} \cdot \text{grad } (\bar{R}W) = \bar{\alpha}_c \cdot \bar{R} (E - P)$$
where
\[
\vec{Q} = \int_{0}^{\infty} q(z) \vec{u}(z) dz
\]
is the vertically integrated vapour flux (with \(\vec{u}(z)\) the horizontal wind vector and \(q(z)\) the absolute humidity in the atmosphere). \(\vec{Q}\) is expressed by the precipitable water
\[
W = \int_{0}^{\infty} q(z) dz
\]
such that \(\vec{Q} = \vec{u} \cdot W\), where the moisture advection velocity \(\vec{u}\) is the mean wind velocity weighted by the absolute humidity \(q(z)\). \(E\) and \(P\) are the local evapotranspiration and the precipitation rate, respectively. \(\bar{R}\) is the bulk isotope content of the water vapour and \(\bar{\alpha}_e\) is the mean equilibrium fractionation factor between precipitation and water vapour. Assuming further an exponential decrease of the absolute humidity \(q\) with altitude as well as of its heavy-isotope content \(R\), the precipitable water \(W\) and its bulk isotope content \(\bar{R}\) are determined exclusively by the ground-level values of the water temperature \(T_g\), relative humidity \(h\) and isotope content \(\bar{R}_g\):
\[
W = h \cdot q_s(T_g) \cdot \bar{z}; \quad \bar{R} = \bar{R}_g / \bar{\alpha}_e
\]
(3)

where \(q_s(T_g)\) is the absolute humidity for saturation conditions at the temperature \(T_g\), and \(\bar{z} = 2.5\) km is the mean scale height of the absolute humidity profile.

An elaboration of the differential equation (2) utilizing Eq.(1) and subsequent integration leads to a Rayleigh condensation formula in terms of either the horizontal vapour flux or the precipitable water:
\[
R / R_0 = (Q_n / Q_{n,0}) \bar{\alpha}_e^{-1} = (W / W_0) e = F^e
\]
(4)

where \(Q_n\) is the component of the total horizontal water vapour flux \(\vec{Q}\) in the direction of the vertical gradient \(W\). \(Q_{n,0}\), \(W_0\), \(R_0\) are the initial data for the vapour source region somewhere over the subtropical ocean. Since the initial isotope content of the water vapour over the ocean is \(R_0 = \alpha^{-1} \cdot R_{SMOW}\), Eq.(4) in \(\delta\)-notation reads:
\[
\delta_{vap} = \alpha^{-1} \cdot F^e - 1
\]
(5)
\[
\delta_{prec} = (\alpha_e / \alpha) F^e - 1
\]
(6)
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<td>T (TU)</td>
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d = deuterium excess defined as: \( d = \delta D - 8 \cdot \delta ^{18}O \); \( T \) = tritium concentration.

\( ^a \) Monthly means weighted by amount of precipitation.

\( ^b \) Calculated from surface air temperature and relative humidity data.

\( ^c \) Percentage of snow precipitation is given in parentheses.

\( ^d \) \( ^{18}O \) content has been measured only in every fifth sample.
FIG. 2. Two-year record of daily time series of δD, deuterium excess and tritium content in atmospheric water vapour as well as of selected hydrometeorological parameters from the Heidelberg station (1981 and 1982).
The model discussed above reveals acceptable predicting quality when applied to monthly means of isotope data. Attempts to use it on a smaller time scale (e.g. for weekly or daily mean values) showed that its predicting quality drops considerably [18]. This effect may have two reasons. First, it is difficult to define precisely 'source regions' for the vapour passing a given sampling point in a day-by-day sequence. Of course, the isotopic composition of the vapour in the source regions has to be known as well. Second, the assumption of constant water storage in the atmosphere, being sufficiently justified for monthly means, seems to be no longer valid when daily values are considered. In other words, the calculation of daily mean values of precipitable water on the basis of Eq.(3) with fixed relative humidity and scale height is not justified.

Equation (4) has been used to predict monthly means of deuterium content in atmospheric water vapour collected at Cracow, using Heidelberg data as input parameters in the model calculation. The precipitable water has been evaluated with the aid of Eq.(3), assuming constant relative humidity at all tropospheric levels and constant scale height \( \bar{f} \) of absolute humidity in the atmosphere throughout the year. The mean fractionation factor \( a_0 \) has been chosen assuming equilibrium between water vapour and precipitation at the ground-level temperature and is linearly interpolated between the corresponding temperatures recorded at Heidelberg and Cracow.

Figure 4 gives a comparison of the observed monthly means of deuterium content in atmospheric water vapour collected at Cracow with the predicted values of the model. The seasonal variations of deuterium content are nicely reproduced by the model, although a slight shift towards more negative \( \delta D \) values is observed for certain months (e.g. January, June, October 1982). For June 1981 and March 1983 a prediction has not been possible since the amount of precipitable water, evaluated on the basis of Eq.(3), appeared to be larger at Cracow than at Heidelberg. This discrepancy is probably caused by the fact that the water vapour transport over the European continent is not purely zonal as assumed by the model. An enhanced contribution of the vapour transported meridionally (with relatively high deuterium content) to the total vapour flux passing the area in question may be responsible for the observed difference between the predicted and measured \( \delta D \) values for certain months. A closer inspection of the meteorological charts indeed shows that for these months meridional circulation prevailed over central Europe.

The influence of circulation patterns on the short-term variations of heavy-isotope ratios observed in atmospheric water vapour is shown in Fig.3. During January 1983 the weather at all European stations was controlled by westerly circulation steered by a low-pressure area situated above Greenland. There was a decrease in deuterium content with increasing distance to the coast (about 12\% between Paris and Heidelberg and 21\% between Hannover and Cracow). This led to a continental deuterium gradient of 26–29\% per 1000 km.
FIG. 3. Daily time series of deuterium content in atmospheric water vapour collected at Miami, Hannover, Paris, Heidelberg and Cracow during the first four months of 1983.

At the beginning of February 1983 the low-pressure area moved slowly over Iceland towards central Europe, bringing at its back-side first maritime arctic and later continental polar air masses. The north-east winds transported isotopically depleted water vapour to all stations (see sketch weather maps in Fig. 3). The deuterium content of the local vapour decreased rapidly by
about 100‰, which decrease was aggravated by a widespread snowfall area. It is worth noting that owing to the easterly circulation an opposite continental gradient of deuterium content was observed, i.e. the $\delta^D$ values measured at Heidelberg were about 20‰ lower than those at Cracow and there was an additional depletion between Heidelberg and Hannover of about 10‰. Around 12 February a high-pressure area situated above the North Atlantic changed the circulation patterns over western and central Europe. Maritime polar air masses influenced the local weather and the deuterium content of atmospheric moisture increased considerably. This increasing trend was stopped for Heidelberg and Hannover by a cold front coming from the north (20–21 Feb.), whereas Paris was still under the influence of maritime air masses (local temperature 3°C higher than at Heidelberg). During the last days of February, maritime tropic air masses controlled the weather at all west European stations, whereas Cracow remained still under the influence of the cold front.

Miami (25.7°N, 80.2°W) is a typical coastal station with prevailing influence of maritime air masses. The heavy-isotope composition of the vapour collected there during periods of easterly circulation should be close to that expected for undisturbed marine vapour evaporated somewhere on the subtropical ocean. It can be seen in Fig.3 that during these periods the $\delta^D$ value was about $-75$‰. For the average surface ocean temperature and humidity prevailing during the period in question (+26°C and 80%, respectively) one can derive the average deuterium content of the ocean surface using a proper fractionation
factor $\alpha (\alpha = \alpha_e \cdot \alpha_k = 1.0811)$. This calculation yields the value of $\delta D = 0.0\%_\circ$, which indeed seems to confirm the earlier assumption that the Miami station during easterly circulation is influenced by isotopically undisturbed maritime moisture.

A more detailed insight into factors controlling the daily variation of deuterium content in atmospheric water vapour can be gained when the relation between $\delta D$ content of water vapour and surface air temperature is considered. Figure 5 shows such a relation for the Heidelberg station, for daily and monthly means. The range of $\delta D$ variations for daily composite samples collected at a given temperature reaches about 100% and seems to be larger during winter months. This spread of data is reduced to about 20% when monthly means are
considered. It is worth mentioning that a linear regression fit yields an identical relation between δD and temperature for both types of data in use. The large spread of deuterium content for daily composite samples when drawn versus daily mean temperature can be explained by the fact that the daily surface air temperature is controlled mostly by local insolation, whereas the isotopic composition of the vapour sampled on a certain day is determined by the whole rainout history of the given air mass, often extending back in time for some days or even weeks. When larger time-scales are considered (e.g. months or seasons) the effects of the prevailing atmospheric circulation over the given region become dominant. The mean (monthly or seasonal) local surface air temperature, or more precisely the difference between the temperatures of vapour source regions and those measured somewhere on the continent, becomes a good measure of the mean moisture losses, which in turn are reflected by a lowered heavy-isotope content of water vapour and precipitation.

The temperature gradient of deuterium content in water vapour observed at Heidelberg (monthly means of δD and temperature for the total observation period are considered) is (2.8 ± 0.2)%/°C, which has to be compared with (2.2 ± 0.4)%/°C observed for monthly precipitation. For Cracow the observed gradients reach (3.3 ± 0.3)%/°C and (3.0 ± 0.5)%/°C for water vapour and precipitation, respectively. These values are in agreement with gradients found by Hübler et al. [12] for the German Democratic Republic and with our earlier observation [7] that the apparent temperature gradient of deuterium content in monthly precipitation over western and central Europe increases further inland.

It is well known that the time series of various meteorological parameters reveal certain regularities. Besides the most obvious seasonal fluctuations, often shorter periodicities are observed. The quasi-stationary circulation of the free atmosphere, producing so-called Rossby waves, is believed to be a primary source for these short-term periodicities recorded at the ground level. Boogaard [19] reported a dominating role of the waves numbers 5 and 6 (corresponding to a period of about 12 days at 50°N latitude) in meridional transport of atmospheric water vapour between the equator and 40°N.

Having a complete time series of deuterium content in atmospheric water vapour as well as of selected meteorological parameters, we tried to carry out a power spectral analysis of these data. Figure 6 shows a power spectrum of δD values based on the total set of Heidelberg data. The most noticeable groups of periodicities (except for the one-year period) are: 50–67 days, 29–36 days, 20–22 days and 10–11 days. The shortest periodicity coincides with that reported by Boogaard [19]. The Cracow station data reveal groups of periodicities analogous to those observed at Heidelberg. If these periodicities are caused by different phase velocities of the Rossby waves superimposed on the western drift, a certain phase shift should be observed between the two stations. A Fourier analysis of both data sets indeed leads to a constant
phase shift of about one day between these two stations. This shift corresponds to an average water vapour transport velocity of about 9.2 m/s, which is in reasonably good agreement with the value of 8.8 m/s based on an analysis of aerological data over the western part of the European continent [20].

3.2. Relations between D and \(^{18}\)O content of atmospheric water vapour and precipitation

The \(\delta D - \delta^{18}\)O relations for precipitation and water vapour data recorded at the Heidelberg and Cracow stations are shown in Fig. 7. In both cases the data points lie close to the world meteoric water line (\(\delta D = 8 \cdot \delta^{18}\)O + 10), although small systematic deviations from this relation can be observed.

A linear regression fit yields the following relations:

Heidelberg:

\[
\begin{align*}
\delta D_{\text{prec}} & = (7.8 \pm 0.3) \delta^{18}\text{O}_{\text{prec}} + (4.5 \pm 2.5) \\
\delta D_{\text{vap}} & = (7.4 \pm 0.1) \delta^{18}\text{O}_{\text{vap}} + (2.0 \pm 2.5)
\end{align*}
\]

(monthly means) \( r = 0.98 \)

(monthly means) \( r = 0.97 \)

Cracow:

\[
\begin{align*}
\delta D_{\text{prec}} & = (7.9 \pm 0.1) \delta^{18}\text{O}_{\text{prec}} + (8.0 \pm 1.2) \\
\delta D_{\text{vap}} & = (6.8 \pm 0.2) \delta^{18}\text{O}_{\text{vap}} + (-8.7 \pm 4.9)
\end{align*}
\]

(monthly means) \( r = 0.99 \)

(single measurements) \( r = 0.96 \)
FIG. 7. $\delta D - \delta^{18}O$ relationship for atmospheric water vapour and precipitation samples collected at the Heidelberg and Cracow stations.
The data available so far for the Paris station (October 1982 — April 1983) yield similar relations:

\[ \delta D_{\text{prec}} = (7.9 \pm 0.2) \delta ^{18}O_{\text{prec}} + (9.6 \pm 1.4) \]  
(daily means)  \[ r = 0.98 \]

\[ \delta D_{\text{vap}} = (7.0 \pm 0.1) \delta ^{18}O_{\text{vap}} + (-4.1 \pm 1.8) \]  
(daily means)  \[ r = 0.99 \]

The water vapour data, especially for Cracow, show a slight shift towards higher values of deuterium excess during winter months. The reason of this shift is unclear. One possible explanation could be a significant admixture of evaporated soil moisture to the sampled vapour (note that from June 1981 to June 1982 the vapour at the Cracow station has been sampled only 2 metres above the ground). Evaporation from bare soils, contrary to evapotranspiration by plant cover, can provide a kinetically depleted water vapour characterized by larger deuterium excess compared with equilibrium vapour. Although the evaporation flux during winter months is significantly reduced, the larger vertical stability of the atmosphere and the lower total vapour content as well as the fact that the admixture of kinetically evaporated moisture is a cumulative effect moving inland make the above explanation plausible.

An opposite effect is observed for monthly means of Heidelberg precipitation. A systematic shift towards lower values of deuterium excess compared with water vapour data is observed (see Table II), which may be caused by evaporation of raindrops beneath the cloud base level. A slight evaporation of the already collected samples cannot be excluded either. Obviously, more experimental data are needed for stations to draw definite conclusions regarding the origin of both effects mentioned above.

The simplified advection model of water vapour transport discussed in the preceding section assumes isotopic equilibrium between water vapour and precipitation at all atmospheric levels. This assumption can be experimentally tested at the ground level using the available data. A linear regression fit yields the following relations between the heavy-isotope contents of precipitation and water vapour collected at the ground level:

Cracow (monthly means):

\[ \delta D_{\text{vap}} = (0.7 \pm 0.1) \delta D_{\text{prec}} - (89.9 \pm 8.9) \]  
\[ r = 0.81 \]

Heidelberg (monthly means):

\[ \delta D_{\text{vap}} = (0.8 \pm 0.1) \delta D_{\text{prec}} - (91.2 \pm 7.1) \]  
\[ r = 0.77 \]

Heidelberg (rainy periods only):

\[ \delta D_{\text{vap}} = (0.7 \pm 0.1) \delta D_{\text{prec}} - (100.4 \pm 4.4) \]  
\[ r = 0.72 \]

It is worth mentioning that, within the errors quoted, all data sets provide identical relations. However, the water vapour and precipitation data should be
FIG. 8. Difference between measured deuterium content in monthly precipitation and deuterium content calculated from monthly averages of $\delta D$ of the vapour, assuming isotope equilibrium at the ground-level temperature.

compared for rainy periods only (last equation). The relations between monthly means are of great practical importance for applications of stable isotopes to surface water hydrology, since for the isotope balance of lakes or other small water bodies a knowledge of the heavy-isotope content of vapour being in contact with the lake water is required. As a rule, the isotopic composition of this vapour is calculated from monthly precipitation data, assuming isotopic equilibrium at the ground-level temperature. It has to be noted that the relations found differ considerably from the relation reported by Zimmermann [11] ($\delta D_{\text{vap}} = \delta D_{\text{prec}} - 76\%$) which was based on a smaller data set.

The extent to which equilibrium exists between monthly precipitation and water vapour is illustrated in Fig. 8, which gives the difference between measured and calculated deuterium contents of monthly precipitation for Heidelberg and Cracow, assuming equilibrium with the vapour at the ground-level temperature. A distinct seasonal trend (especially for Cracow) is observed, with isotopically depleted precipitation during winter as compared with the equilibrium value. The isotopic composition of snow flakes is fixed somewhere at the cloud level, at temperatures significantly lower than those recorded at the ground, whereas raindrops adjust their isotopic composition relatively fast to that represented by the surrounding moisture. One could therefore expect that for months with prevailing snowfall a larger departure from equilibrium will be observed. The high percentage of snow precipitation in the total amount collected at Cracow (see Tables II and III) supports this to some extent; however, it does not
FIG. 9. Expected versus measured tritium content in monthly precipitation at Heidelberg and Cracow (the calculation is based on available water vapour data, assuming equilibrium at the ground-level temperature).

explain the large disequilibrium value observed, for example, at Heidelberg and Cracow in November 1982 when only liquid precipitation occurred. An additional effect, which could contribute to the observed disequilibrium during winter is an admixture of isotopically heavy, evaporated soil moisture to the sampled vapour (see discussion in the preceding section).
FIG. 10. (a) Temporal variations of apparent tritium excess in atmospheric water vapour at the Heidelberg station (see text for details). (b) Tritium content in monthly precipitation of the Heidelberg, Hof and Cracow stations during the period January 1981 to December 1982.

3.3. Tritium in near-ground atmospheric water vapour and in precipitation

The tritium content in monthly precipitation and in water vapour samples collected at Heidelberg and Cracow is compared in Fig. 9, which is a drawing of tritium content of monthly precipitation $C_p$ versus equilibrium concentration $\alpha \cdot C_v$ ($\alpha = \text{equilibrium fractionation factor for tritium}$, $C_v = \text{monthly mean of tritium content in water vapour}$). A constant fractionation factor, $\alpha = 1.1$, has been assumed [21]. Temporal variations of tritium excess in water vapour (defined as a difference: $\alpha \cdot C_v - C_p$) recorded at Heidelberg are shown in Fig. 10(a). Figure 10(b) summarizes tritium levels recorded in monthly
precipitation samples collected at the Heidelberg, Cracow and Hof stations during the period January 1981—December 1982.

A comparison of Figs 10(a) and 10(b) shows that enhanced tritium levels in water vapour are in most cases not accompanied by a corresponding increase in tritium content in monthly precipitation (see March and October 1981, January and September 1982). The most prominent peak of tritium excess at Heidelberg (October 1981, ~40 TU) has been caused by very high tritium concentrations (~242 TU maximum) recorded in daily composite samples on 19–22 October 1981. During this time, high tritium levels in water vapour have been observed also at Freiburg (ca. 200 km south-west) but not at Schauinsland, which station has nearly the same geographical position as Freiburg but lies about 1000 m higher. This fact strongly suggests that the tritium responsible for the peak observed in Heidelberg and Freiburg comes only from surface emission.

June 1981 was the sole month in which negative tritium excess was observed. The negative value of tritium excess means that precipitation is loaded by a surplus of tritium compared with the near-ground water vapour. Such a situation is expected when the tritium source is relatively distant (e.g. somewhere on the Atlantic coast) and vertical turbulent diffusion is able to transport this tritium excess to higher levels of the atmosphere where precipitation is formed. The temporal fluctuations of the tritium excess (Fig.10(a)) seem to be related to seasons, with minimum values recorded during summer months. This could be caused by enhanced vertical mixing of the atmosphere as well as by the fact that during the summer months precipitable water and water vapour flux are significantly higher than in winter, which makes the surface atmosphere less sensitive to tritium releases at the ground level. An alternative explanation could be a seasonal trend in the emission rates of tritium.

A quite distinct seasonal trend is also observed for tritium concentrations recorded in monthly precipitation (Fig.10(b)), confirming the still dominant role of the bomb tritium. Superimposed on this seasonal trend are short-time peaks, presumably having their origin in surface emissions of tritium. The already mentioned peak in June 1981 was observed at the Hof station but not at Cracow. In August 1981 all three stations recorded enhanced tritium activity. The peaks observed in April, May and August 1982 at both German stations were again not visible in Cracow. In July 1982 a distinct peak was observed only at the Cracow station. It is worth noting that during this month the \(^{85}\text{Kr}\) activity of the surface atmosphere in Cracow was considerably higher than that recorded at Freiburg (W. Weiss — personal communication). These examples seem to confirm the regional character of the surface emissions of tritium.

The influence of pulsed tritium releases from nuclear energy installations on the regular pattern of bomb tritium observed in monthly precipitation has
### TABLE IV. YEARLY AVERAGES OF THE RATIO OF TRITIUM CONCENTRATIONS IN MONTHLY PRECIPITATION AT THE STATIONS HOF, CRACOW AND VALENTIA TO THE TRITIUM CONCENTRATION IN MONTHLY PRECIPITATION AT THE VALENTIA STATION\textsuperscript{a,b}

<table>
<thead>
<tr>
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</thead>
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<tr>
<td>Hof (50.2°N, 11.9°E)</td>
<td>9.9</td>
<td>6.8</td>
<td>5.5</td>
<td>7.3</td>
<td>5.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Vienna (48.2°N, 16.4°E)</td>
<td>8.5</td>
<td>5.5</td>
<td>4.9</td>
<td>5.9</td>
<td>4.6</td>
<td>4.4</td>
</tr>
<tr>
<td>Cracow (50.0°N, 19.5°E)</td>
<td>8.8</td>
<td>5.6</td>
<td>5.0</td>
<td>6.4</td>
<td>4.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The data for Vienna, Cracow and Valentia were kindly provided by T. Florkowski (IAEA).

\textsuperscript{b} Yearly averages have been calculated as a geometric means:

\[ R_x = C_x / C_{Val} = \left( \frac{C_{Val} - C_0}{C_{Val} - C_0} \right)^{1/N} \]

where: \( C_x \) = tritium concentration in composite precipitation sample for month \( i \) at station \( x \), \( C_{Val} \) = the same for the reference station (Valentia) — see text for details, \( C_0 \) = North Atlantic surface water concentration (W. Roether — personal communication), and \( N \) = total number of months.

been discussed in detail by Weiss et al. [14] who concluded that most of the ground-level releases of tritium appear in nuclear fuel reprocessing plants. They also found that the ratio of tritium content observed in monthly precipitation at the Hof and Valentia stations has increased considerably after 1970, reaching a maximum value of about 13 in 1975. A roughly constant value of this ratio (2.7 ± 0.8) was observed before 1970. The Valentia station (51.9°N, 10.3°W) on the west coast of Ireland has been used as a reference station, representing undisturbed marine conditions. The above-mentioned ratio can be assumed as a rough measure of the extent to which continental European precipitation is contaminated by ground-level releases of tritium. The time trend of this ratio after 1975 is shown in Table IV, where results of analogous calculations carried out for the Cracow and Vienna stations are also presented. For all three stations reduced ratios are observed after 1975; however, the value obtained for 1981 is still distinctly higher than the 'natural' level observed before 1970. Table IV shows also that the precipitation collected at the Cracow and Vienna stations is significantly less contaminated than that collected at the Hof station. This would confirm earlier conclusions of Weiss et al. [14] that ground-level emission of tritium takes place mainly in nuclear reprocessing plants which are located in the western part of Europe.
In view of the reduced tritium levels observed in monthly precipitation at Cracow, the concentrations of tritium in water vapour recorded at this station are surprisingly high (see Table III and Fig.9). Concentrations of up to ten times higher than the equilibrium value have been observed. The reasons for this effect remain unclear. Strictly local contamination of the surface atmosphere near the sampling place, which is not completely excluded in this case, could produce such a picture. The sampling apparatus itself has been thoroughly tested and did not show any internal contamination. Further observations are needed to come to more definite conclusions.

The tritium data available so far for Miami clearly show an alternating influence of maritime and continental air masses on the local weather. The tritium concentrations recorded in atmospheric water vapour during periods of easterly circulation (around 5 T.U.) agree well with the recent tritium content of North Atlantic surface water. For continental air masses, up to five times higher tritium levels have been observed.

4. CONCLUDING REMARKS

The observed spatial and temporal variations of the heavy-isotope content of atmospheric water vapour and precipitation are tightly linked with the parameters of water vapour transport in the atmosphere. Even a highly simplified model of this transport has acceptable predicting quality for monthly and/or seasonal means of heavy-isotope ratios in water vapour or precipitation. It seems that the principal reasoning of the model is still valid for shorter timescales — weeks or even days. In this case, however, the input parameters needed for the model have to be much more carefully evaluated. The results presented in this paper confirm earlier suggestions that the heavy-isotope content of the vapour or precipitation collected at a given place is essentially controlled by the conditions prevailing at the vapour source regions and by the whole rainout history of the precipitating air masses. To a first approximation, the degree of rainout is determined by the change of the water storage in the atmosphere between the source regions and the point where precipitation is formed.

A power spectral analysis of the daily time series of deuterium content in near-ground atmospheric water vapour, available for the first time for such a long period and for different places, revealed periodicities similar to those observed earlier for other meteorological parameters. A constant phase shift of the isotope signal recorded at two different stations has been observed. This shift appeared to be in agreement with the mean transport velocity of the water vapour between these two stations.

The variations of heavy-isotope content in atmospheric water vapour appeared to be well correlated with those observed in monthly precipitation;
some caution is, however, needed when these two types of data are compared. The often quoted assumption regarding isotope equilibrium between precipitation and water vapour at the ground-level temperature seems to be only partially fulfilled; during winter, significant departure from equilibrium has been observed. This fact has to be taken into account when the heavy-isotope content of water vapour is calculated from the available monthly precipitation data, e.g. for purposes of the isotope water balance of lakes.

The excess of tritium content observed in atmospheric water vapour and in precipitation over western and central Europe proves that the contamination of the surface atmosphere by ground-level discharges of tritium from nuclear energy installations is still continuing, although the average level of this contamination seems to be smaller than observed in 1975. Atmospheric water vapour collected at the ground level appeared to be a much more sensitive indicator of such contamination compared with monthly precipitation. Contrary to the situation in 1975, the seasonal fluctuations of tritium in monthly precipitation are again easy to distinguish, thus confirming the still dominant role of bomb tritium. Small peaks reflecting ground-level releases of tritium are superimposed on this seasonal trend.

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ICE DYNAMICS AND ACCUMULATION RATES
ON CHANGME-KHANGPU GLACIER, SIKKIM,
BY RADIOISOTOPIC METHODS

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India

Abstract

ICE DYNAMICS AND ACCUMULATION RATES ON CHANGME-KHANGPU GLACIER, SIKKIM, BY RADIOISOTOPIC METHODS.

A systematic study of fresh snow, a vertical sequence in the accumulation zone and at the snout, and a longitudinal profile along the glacier Changme-Khangpu in the Sikkim valley has been made using environmental and bomb-produced radionuclides. The surface snout ice of the glacier has been dated by the radioisotopes $^{32}$Si and $^{209}$Pb, both giving a concordant age of about 100 years. This age allows the average flow rate of glacier surface ice during the past century to be calculated as 40 m/a. Silicon-32 studies indicate an increase, by at least a factor of six, in the age of ice at the bottom of the snout, yielding basal flow rates of $< 8$ m/a. The modern average surface flow rates are a factor of three lower than the radiometric estimates of past flow rates, suggesting that the glacier is not in a steady state at present. The $^{137}$Cs depth profile in the accumulation zone shows several peaks which match the Chinese nuclear explosions, assuming that the accumulation rate of ice is 0.7 m/a for the past decade.

1. INTRODUCTION

The Himalayas possess over 15 000 glaciers which hold within them huge amounts of fresh water ($10^{12}$ m$^3$) in the form of snow and glacier ice, accumulated over a period of many centuries. The solid water reservoir is comparable to the usable groundwater reservoirs and plays an important role in the country’s water management. Glaciers and overlying snow make an important contribution to north Indian rivers, particularly in the early summer months before the onset of monsoon when other sources become insignificant.

The estimation of the long-term mass balance of a glacier constitutes an important parameter in understanding glacier dynamics. Direct measurements of glacier flow rates and ablation rates have been made in the Himalayas by
<table>
<thead>
<tr>
<th>Sample code</th>
<th>Sample/collection date</th>
<th>Altitude (m)</th>
<th>Water collected (L)</th>
<th>Net $^{32}\text{P}$ (counts/h)</th>
<th>$^{32}\text{Si}$ (dis/min per tonne)</th>
<th>$^{32}\text{Si}$ apparent age (years)</th>
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<td>CK-1-81$^a$</td>
<td>Fresh snow 30.7.81 to 6.8.81</td>
<td>5200</td>
<td>800</td>
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<td>Snout ice (0–30 cm) 28.8.78 to 7.9.78</td>
<td>4850</td>
<td>2380</td>
<td>3.73</td>
<td>0.34 ± 0.03</td>
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<td>Snout ice (5 m depth) 7.8.81 to 10.8.82</td>
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<td>1035</td>
<td>2.7</td>
<td>0.38 ± 0.04</td>
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<tr>
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<td>1035</td>
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<td>&gt;650</td>
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<tr>
<td>CK-36-78, 1 m$^b$</td>
<td>Snout melt water</td>
<td>4850</td>
<td>1640</td>
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<td>CK-36-78, 2 m$^b$</td>
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<td>10.5</td>
<td>0.56 ± 0.05</td>
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</tbody>
</table>

$^a$ Nijampurkar [8].
$^b$ Nijampurkar et al. [9], 1 m = first milking of $^{32}$P, 2 m = second milking of $^{32}$P.
conventional and modern techniques [1–3]. The accumulation rates have been estimated on a seasonal or annual basis by conventional techniques since winter observations are difficult. These estimates fluctuate significantly from year to year and it has not been possible to obtain long-term average accumulation rates from such data. Deposited natural radioisotopes as well as nuclear debris from discrete events during the second half of the century have provided time-markers which can be used to study some aspects of glacier dynamics. In particular, tracer techniques on radiolabelled ice have provided dynamic parameters of glaciers, averaged for several years. Extensive radiotracer studies on the Alps and the polar ice caps are presented in Refs [4–6]. We have used the cosmogenic $^{32}$Si (half-life = 105 years) and the radiogenic $^{210}$Pb (half-life = 22.3 years) to date ice from several glaciers in the Himalayas in order to obtain estimates of glacier flow rates. Results on some glaciers have been reported earlier [1, 2]. Here we present the results on the Changme-Khangpu glacier in the Sikkim valley.

The Changme-Khangpu (CK) glacier is located in the Tista river basin, in the upper catchment of Lachung Chu, which is one of the major tributaries of Tista in north-east Sikkim. It is a transverse valley glacier trending north-south, having a length of about 5.8 km and a width varying between 600 m and 1 km. The glacier originates from the southern slope of Garudogmar peak (27°58'N, 88°42'E) and the melt water of the glacier feeds into Sebu Chu, a tributary of Lachung Chu [7].

The areal coverage of the glaciarized part of the basin is about 12.85 km$^2$, of which 10.35 km$^2$ is perennial ice and the rest is rock faces. The ratio between the accumulation and ablation zones is 5:7. Almost the entire ablation zone of the glacier is under a thick mantle of supraglacial morainic debris. The terminal part of the glacier is completely buried under the moraine. This morainic cover has generated an enormous amount of dust which is present everywhere. The glacier snout is located at an altitude of 4850 m a.s.l. and is about 6 m thick. The glacier has shown a negative mass balance of $\sim 2 \times 10^7$ m$^3$/a since 1978 and a receding trend for the past few years.

2. EXPERTIMENTAL TECHNIQUES

Three types of samples, i.e. fresh snow, surface ice along the glacier, and deeper ice from both accumulation zone and terminus, were collected during two expeditions to the CK glacier in 1978 and 1981. Fresh snow samples (CK-1-81, 800 L, and CK-3-81, 33 L) from 5200 m altitude, representing the average snowfall for the period November 1980 to April 1981, were collected for $^{32}$Si and $^{210}$Pb studies to obtain their fallout values. Three more large-volume samples, ranging from 1035 to 2380 L (Table I), from surface and deep ice at the glacier snout, and melt water flowing near the terminus were also analysed for $^{32}$Si and
<table>
<thead>
<tr>
<th>Sample code</th>
<th>Sample</th>
<th>Collection date</th>
<th>Altitude (m)</th>
<th>Volume processed (L)</th>
<th>Total $^{210}$Bi activity (counts/min)</th>
<th>$^{210}$Pb Activity (dis/min per L)</th>
<th>Age (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK-35-78$^a$</td>
<td>Fresh snow</td>
<td>29.8.1978</td>
<td>5450</td>
<td>0.46</td>
<td>0.48</td>
<td>8.0 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>CK-34-78$^a$</td>
<td>Fresh snow</td>
<td>29.8.1978</td>
<td>5400</td>
<td>1.68</td>
<td>1.4</td>
<td>2.9 ± 0.3</td>
<td>6.7 ± 0.5</td>
</tr>
<tr>
<td>CK-33-78$^a$</td>
<td>Fresh snow</td>
<td>29.8.1978</td>
<td>5300</td>
<td>1.32</td>
<td>1.47</td>
<td>8.5 ± 0.4</td>
<td>3.3 ± 0.2</td>
</tr>
<tr>
<td>CK-3-81$^b$</td>
<td>Fresh snow</td>
<td>6.8.1981</td>
<td>5200</td>
<td>33</td>
<td>37.95</td>
<td>5.3 ± 0.5</td>
<td>13.0 ± 0.5</td>
</tr>
<tr>
<td>CK-22-78$^a$</td>
<td>Surface ice</td>
<td>3.9.1978</td>
<td>5150</td>
<td>0.138</td>
<td>1.8</td>
<td>2.3 ± 0.2</td>
<td>40.0 ± 0.6</td>
</tr>
<tr>
<td>CK-18-78$^a$</td>
<td>Surface ice</td>
<td>3.9.1978</td>
<td>4950</td>
<td>0.214</td>
<td>0.31</td>
<td>0.58 ± 0.06</td>
<td>90.0 ± 0.6</td>
</tr>
<tr>
<td>CK-6-81$^b$</td>
<td>Surface ice (0–30 cm)</td>
<td>10.8.1981</td>
<td>4900</td>
<td>14</td>
<td>0.72</td>
<td>0.088 ± 0.03</td>
<td>135.0 ± 0.03</td>
</tr>
<tr>
<td>CK-7-81$^b$</td>
<td>Ice at 12 m depth</td>
<td>10.8.1981</td>
<td>4900</td>
<td>9.5</td>
<td>0.12</td>
<td>0.33 ± 0.02</td>
<td>100.0 ± 0.27</td>
</tr>
<tr>
<td>CK-4-81$^b$</td>
<td>Snout ice (0–30 cm)</td>
<td>9.8.1981</td>
<td>4850</td>
<td>10</td>
<td>0.38</td>
<td>0.21 ± 0.02</td>
<td>117.0 ± 0.27</td>
</tr>
<tr>
<td>CK-39-78$^a$</td>
<td>Snout ice (0–30 cm)</td>
<td>3.9.1978</td>
<td>4850</td>
<td>60</td>
<td>2.85</td>
<td>0.08 ± 0.008</td>
<td>150.0 ± 0.08</td>
</tr>
<tr>
<td>CK-5-81$^b$</td>
<td>Snout ice at 5 m depth</td>
<td>9.8.1981</td>
<td>4850</td>
<td>50</td>
<td>0.63</td>
<td>1.3 ± 0.1</td>
<td>58.0 ± 0.1</td>
</tr>
<tr>
<td>CK-37-78$^a$</td>
<td>Snout water</td>
<td>5.9.1978</td>
<td>4850</td>
<td>100</td>
<td>33.85</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Nijampurkar et al. [9]. $^b$ Nijampurkar [8].
$^{210}$Pb activities. Additionally, a few surface samples along the glacier were analysed for $^{210}$Pb to study the ice dynamics at intermediate altitudes on the glacier.

On the night of 28 August 1978 there was snowfall over the whole glacier. Samples (nominally 1 L) of this fresh snow were collected for studies of $^{210}$Pb and $\delta^{18}$O to estimate their altitudinal variation, if any, in the precipitation.

In 1981, a sequence of 32 samples (CK-91-81 to CK-122-81) in sections of 30 cm were collected from an ice face in a crevasse in the accumulation zone at an altitude of 5250 m. This profile covers 0–9.6 m, except for 420–460 cm, constituting two samples which were lost in transit. Because of the inclination of the crevasse (~ 30°), the 960 cm depth would correspond to a vertical depth of 830 cm and each sample would represent a vertical column thickness of 26 cm. These samples were measured for $^{137}$Cs and $^{210}$Pb activities, $\delta$D and $\delta^{18}$O. The sampling and radiochemical procedures and the measurement techniques have been described in detail [2–7, 10] and some results on stable isotopes have been reported [1]. For the present study, $^{32}$Si and $^{210}$Pb were extracted from a few litres to a few tonnes of melt water, using Fe(OH)$_3$ as a scavenger, and transported to the laboratory for radiochemical purification and separation. Silicon-32 was estimated by analysis of its daughter product $^{32}$P, and $^{210}$Pb by its daughter $^{210}$Bi. Both radioactive daughters were radiochemically purified. The chemical extraction efficiency was generally around 50% for phosphorus and around 80% for bismuth, with a few exceptions (low yield of around 20%). The $^{32}$P and $^{210}$Bi activities were measured on a low-background gas-flow GM counter with a NaI(Tl) active anti-coincidence shield, placed in a 10 cm thick lead housing, having a background of about 0.8 counts/h and an efficiency of about 40%. The decay was followed for several half-lives. Replicate measurements carried out for some samples gave consistent activity. The statistical errors due to counting for $^{32}$Si and $^{210}$Pb are usually less than 5% but, considering errors in chemical analysis etc., an overall error of about ± 10% is given in Tables I and II. The results of the $^{32}$Si measurements are given in Table I. Measurements of $^{32}$P in a second extraction in both snout ice and snout water samples agree within the measurement errors. In both cases the silica recovered was more than the amount of dissolved silica, possibly because of some amount of dust present. On the basis of our experience in the analysis of similar samples, the efficiency of silica extraction is assumed to be 95%.

The $^{137}$Cs activity in samples from the crevasse was measured as follows. The water samples were acidified with 1–2 ml of HCl and the dust was filtered. The $^{210}$Pb activity from the water was scavenged by adding FeCl$_3$ and co-precipitating with Fe(OH)$_3$. Caesium-137 was measured in the filtrate, which was evaporated to a small volume, together with the Fe(OH)$_3$ precipitate and dust, before the precipitate was chemically processed for bismuth. Caesium-137 was counted by its gamma radiation on a high-purity germanium detector placed in a 10 cm lead shield. The background in the peak channels was (0.11 ± 0.01) counts/min and the $^{137}$Cs counting efficiency was determined to be 3.8%.
3. RESULTS AND DISCUSSION

3.1. Fallout rates

The dating of ice with radioactive tracers such as $^{32}$Si and $^{210}$Pb requires a knowledge of their fallout values in the accumulation zone.

Lal and Peters [11] have calculated the cosmic-ray production of $^{32}$Si in the atmosphere to be $1.6 \times 10^{-4}$ atoms cm$^{-2}$ s$^{-1}$, of which 30% is assumed to be produced in the troposphere and deposited practically independently of the latitude. Most of the $^{32}$Si produced in the stratosphere is assumed to be transferred to the troposphere at mid-latitudes (30–45$^\circ$) and to be deposited mainly there. The mean annual weighted concentration of $^{32}$Si in Indian rains in the latitudinal belt of 0–30$^\circ$ is 0.3 dis/min per tonne [12]; the mean fallout value for the Alps is taken to be 0.75 dis/min per tonne [4]. Himalayan glaciers are at higher altitude but at lower latitude. Since the annual fallout value at a given location shows seasonal as well as annual variation, it is desirable to consider the mean value of several years for this latitudinal belt for dating purposes.

The $^{32}$Si and $^{210}$Pb activities measured in fresh snow samples (CK-1-81 and CK-3-81) are determined to be (0.88 ± 0.09) dis/min per tonne and (8.5 ± 0.4) dis/min per litre, respectively (Tables I and II). The $^{210}$Pb measurements of the precipitation sample analysed here (Fig. 1) also show some increase
in activity with altitude. The mean value of $^{210}\text{Pb}$ above an altitude of 5200 m is 6.5 dis/min per litre. Since these values are consistent with those adopted earlier [1], we use the same values for fallout, $F_0 = 0.7$ dis/min per tonne for $^{32}\text{Si}$ and $F_0 = 8$ dis/min per litre for $^{210}\text{Pb}$, in the present work. The half-life of 105 years for $^{32}\text{Si}$, as measured recently [13, 14], has been used for calculating the apparent ages of ice samples (T) from the observed activity A, using the decay equation $T = (1/\lambda) \ln F_0/A$. Similar calculations were also made for $^{210}\text{Pb}$.

3.2. Dating of terminus ice and flow rates of ice

The results of Table 1 clearly show that the $^{32}\text{Si}$ activity in surface snout ice samples (CK-36-78) is depleted by nearly 50% and the $^{32}\text{Si}$ activity of snout ice at 5 m depth (CK-2-81) is depleted by over 98% (Fig. 2). The deeper snout ice is estimated to be $> 650$ years old, older than the surface snout ice by at least $\sim 550$ years. Similarly, the $^{210}\text{Pb}$ data show a gradual increase in the age of ice from the accumulation zone towards the snout, and a further increase with depth near the terminus. The age of surface ice from the snout obtained by $^{32}\text{Si}$ and $^{210}\text{Pb}$ analysis is concordantly about 100 years. Of course, the high age values, as obtained by $^{32}\text{Si}$, fall outside the domain of $^{210}\text{Pb}$ dating. Also, even small contributions from in-situ decay of $^{238}\text{U}$ series nuclides present in the dust can yield erroneous younger ages. This seems to be the case for the deep snout ice: $^{32}\text{Si}$ gives an age of $> 650$ years, whereas $^{210}\text{Pb}$ — present at very low levels (0.08 dis/min per litre) — gives an age of only 150 years. It thus appears that the ages of surface ice, which are all less than 100 years, are probably realistic and the higher age values, near the limit of $^{210}\text{Pb}$ dating, may be underestimates. The snout water, representing a mixture of ablating ice from all altitudes, yields a young age of 21 years.

These ages allow us to calculate the flow rates of ice. An average surface flow rate of 40 m/a from the accumulation zone to the terminus is obtained on the basis of the radioactivity levels in surface ice. The average surface flow rates between the accumulation zone (point A, Fig. 2) and an altitude of 5150 m, between 5150 and 4950 m, and between 4950 and 4900 m are calculated to be about 81, 60 and 15 m/a, respectively, based on $^{210}\text{Pb}$ activity. The lowermost sample near the snout is not considered here since a small contribution of non-fallout $^{210}\text{Pb}$, produced by in-situ decay, can give erroneous results, as pointed out earlier. These rates should be compared with the modern flow rates obtained by the Geological Survey of India for several years, using the technique of displacement of stakes. These velocities vary between 1 m/a at an altitude of about 4850 m and 50 m/a near the equilibrium line at about 5250 m altitude, and again decrease towards the accumulation zone, being 40 m/a at an altitude of 5300 m [9]. These velocity contours give an average area-weighted flow rate of 13 m/a, which should be compared with about 40 m/a obtained by radiometric methods.
FIG. 2. Silicon-32 activity (dis/min per tonne) and lead-210 activity (dis/min per litre) in surface and deep samples of CK glacier ice [8, 9].
In spite of the errors inherent in the two methods, the discrepancy is probably significant enough to suggest that the contemporary and past flow rates are different, which indicates that the glacier is not in a steady state at present. This observation seems to support the geomorphological evidence based on moraine deposits of at least four, if not more, glacial phases and inter-phases in the past [9]. Also, it has been observed that for the past few years the CK glacier as well as other glaciers in the basin are, in general, in the process of recession.

The $^{32}$Si ages of surface and deep ice at the snout are significantly different. The basal flow rate is calculated to be $< 8 \text{ m/a}$. The vertical gradient of the flow rates calculated from these data is very high, since at about five metres depth there is a decrease in flow rate by more than a factor of five. The basal flow rates are difficult to measure, but the glacier flow models [15–17] predict that the deep ice will flow at a much slower rate than the surface ice. Our results seem to support such models qualitatively.

3.3. Accumulation rates of ice

The ice accumulation rates in the Himalayas are not accurately known because of the difficulty of making continuous observations due to severe weather conditions. We have measured the vertical profile of $^{137}$Cs and $^{210}$Pb in samples taken from a crevasse in the accumulation zone [10]. The results are shown in Fig.3.

Four major peaks in $^{137}$Cs are clearly visible in the depth profile. China and France have carried out atmospheric nuclear tests during the past few years. The French tests, however, were in the southern hemisphere and the dominant contribution to the fallout of $^{137}$Cs at the CK glacier probably comes from the Chinese tests at Lop Nor (41°N, 89°E) [18]. The timing and strength of these tests is indicated in Fig. 3. If a phase lag of a few months is allowed between injection in the atmosphere and fallout, then a good match between the Chinese nuclear tests and the fallout peaks is obtained if an accumulation rate of 0.7 m/a is assumed for the CK glacier.

4. CONCLUSIONS

We have presented results for the CK glacier which show that several dynamic parameters like accumulation rate and surface and basal flow rates can be determined using natural and artificial nuclear tracers. The surface ice flow rate of 40 m/a determined by radioactive methods is significantly higher than the contemporary flow rate of 13 m/a. This departure suggests that the glacier is not in a steady state. This conclusion is supported by field observations of geomorphology and morainic deposits, which indicate several phases of glacier advance and retreat in the past, and the current observation of retreat of the glacier terminus.
FIG. 3. Variation of $^{137}$Cs activity (dis/min per litre) in ice as a function of depth, in the accumulation zone of the CK glacier. The arrows represent atmospheric nuclear tests. The length of the arrows corresponds to the test yields, and the number of tests (more than one) is also indicated. French tests are designated by F. An accumulation rate of 0.7 m/a has been assumed to obtain the time scale [10].

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SUBSURFACE HORIZONTAL WATER TRANSPORT AND VERTICAL MIXING IN LAKE CONSTANCE TRACED BY RADON-222, TRITIUM, AND OTHER PHYSICAL AND CHEMICAL TRACERS

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Abstract

SUBSURFACE HORIZONTAL WATER TRANSPORT AND VERTICAL MIXING IN LAKE CONSTANCE TRACED BY RADON-222, TRITIUM, AND OTHER PHYSICAL AND CHEMICAL TRACERS.

From 25 profiles of the Rn excess near the bottom of Lake Constance (Obersee) the intensity of vertical and horizontal mixing is estimated. In the one-dimensional approximation, apparent vertical eddy diffusion values of between 0.02 and 0.3 cm²/s are obtained. The more realistic two-dimensional approximation yields vertical diffusion values of 0.02–0.05 cm²/s and horizontal diffusion values of 100–400 cm²/s. The absolute values of the radon exhalation rates obtained are related to the porosity of the sediments. The 'core layer' of the Alpenrhein, i.e. the depth range of 10–20 m of the lake, is characterized by very high radon excess and low tritium concentrations. A quantitative interpretation of the tritium levels observed clearly shows that the water flux in the core layer is about 2.5 times the input of the Alpenrhein to the lake. The steady decrease of the radon excess of the core layer in the direction of the mean flow is consistent with a mean transport velocity within the core layer of 3.5 km/d.

INTRODUCTION

The physical processes of subsurface horizontal water transport and of turbulent horizontal and vertical mixing play an important role in the attempt to quantitatively understand the trophic evolution of lakes. The absolute values of the parameters characterizing these processes can be derived from field data of physical and/or chemical tracers. The most important physical tracers commonly
used for this kind of work are the water temperature, tritium, and the noble gases $^3$He and $^{222}$Rn. This paper presents field data for $^{222}$Rn and tritium from Lake Constance (Obersee), which have been collected during several field programmes between 1977 and 1980.

One objective of these programmes was sediment/water exchange and the relative importance of turbulent horizontal and vertical mixing of the water near the bottom of the lake. These items are of particular importance for a quantitative understanding of, for instance, the phosphorus budget of the hypolimnion of lakes [1]. The classical tracer approach to this problem [2], which has been used throughout this work, is based on the vertical distribution of the radium/radon tracer pair near the bottom of the lake. Another objective was to understand the dynamical processes influencing the subsurface horizontal water transport in the lake. It is well known that the Alpenrhein, which provides about 70% of the water input to Lake Constance, strongly influences the horizontal transport and mixing of the lake at about 20–40 m depth. The subsurface Alpenrhein flow system has previously been studied to some extent and the mean flow pattern of the system is known [3]. Information about the dynamical processes, however, to be considered for the formation of this flow system, such as the entrainment of lake water, are poorly understood. Very little is known about the absolute value and the variability of the mean transport velocity in the ‘core layer’ of the system. Combined measurements of tritium and $^{222}$Rn have been used to answer these questions.

Detailed information about the analytical procedures used throughout this work as well as the numerical results obtained are presented in two unpublished reports [4, 5].

**METHODS**

Radon sampling, degassing and counting was done on board a ship. The analytical techniques used are described in detail by Zapf [4], Fischer [6] and Kromer [7]: Radon sampling is by a submersible pump; a typical sampling time is 20 minutes per sample. For near-bottom work the positioning of the pump is achieved by a pinger; the overall precision of positioning is better than ± 40 cm. For gas extraction, a fast vacuum extraction unit of high efficiency is used. Radon gas counting is by several sets of four-pulse ionizing chambers. The overall precision of the radon data is ± 3%.

Radium measurements are done by the radon ingrowth method. Experimental details are described by Schlosser [8]. The precision of the radium data is ± 2.5%.

The radium/radon scales have been intercalibrated by comparison of marine radon and radium samples from intermediate depths where equilibrium between radium and radon can be expected [9]. The overall agreement between the radon/radium scales according to these measurements is better than 4%.
Tritium measurements were done by gas counting without electrolytical enrichment. The overall precision of the tritium data is ± 4% [10].

BACKGROUND CONCENTRATIONS OF RADON-222 AND BOMB TRITIUM IN LAKE CONSTANCE

Radon-222 has previously been used as a tracer for vertical near-bottom eddy diffusion in the ocean [2] and in lakes [1]. With a radioactive lifetime of 5.5 days, $^{222}\text{Rn}$ is an ideal tracer for dynamical processes with time scales of days to a few weeks. The distribution of $^{222}\text{Rn}$ is determined by that of its parent nuclide $^{226}\text{Ra}$ ($T_{1/2} = 1600$ years). Radium-226 is highly concentrated in sediments as compared with water; sediments therefore provide a strong source of $^{222}\text{Rn}$. Far away from sediment surfaces, $^{222}\text{Rn}$ is in radioactive equilibrium with $^{226}\text{Ra}$ dissolved in water. In Lake Constance this equilibrium concentration, according to both $^{226}\text{Ra}$ and $^{222}\text{Rn}$ measurements, is 7.1 dis/min per 100 litres of water [5]. Mineral particles which are transported into the lake by rivers have a characteristic $^{226}\text{Ra}$ concentration of 2 dis/min per gram [5]. For typical particle concentrations of the lake water of 5 mg/L an increase relative to particle-free water of about 1 dis/min per 100 litres is expected for the $^{226}\text{Ra}$ and the background $^{222}\text{Rn}$ concentration. In the 'core layer' of the Alpenrhein in Lake Constance such a $^{226}\text{Ra}$ excess has in fact been measured. The $^{222}\text{Rn}$ concentrations measured at the same location and depth were, however, well above the expected equilibrium level. This is explained by the fact that part of the Alpenrhein water originates from groundwater in the recharge area [11]. It is well known that groundwaters are highly enriched in $^{222}\text{Rn}$, with concentrations of up to $10^5$ dis/min per 100 litres [12].

The distribution of bomb tritium in Lake Constance has previously been studied in detail [11]. For many years, tritium homogeneity has been observed in the lake. In 1980 the measured tritium concentration of Lake Constance was 110 TU. The overall variability of this value is ± 10%. The input of water [13] and of tritium [11] into the lake is mainly by the Alpenrhein. In recent years the tritium concentrations of the Alpenrhein fell below those of the lake. In 1980 the tritium concentration of the Alpenrhein was 62 ± 6 TU or 55% of the tritium concentration of the lake. The tritium deficit of the Alpenrhein exceeds the variability of the tritium background of the lake by a factor of five. Admixtures of waters originating from the Alpenrhein can thus be identified by low tritium concentrations.

NEAR-BOTTOM RADON PROFILES

25 vertical profiles of near-bottom $^{222}\text{Rn}$ of Lake Constance were analysed between 1977 and 1979. The profiles are equally distributed over the
FIG. 1. Near-bottom radon profiles from the northern part of Lake Constance (Obersee; horizontal distance between the stations = 1 km). Solid lines are best fits of the experimental data, which are based on assumed steady-state one-dimensional (two-dimensional) radon distribution. The dashed line represents the equilibrium concentration between $^{226}$Ra dissolved in the water and $^{222}$Rn.

Obersee of Lake Constance [4]. For technical reasons, no profiles are available from the centre of the lake where the water depth exceeds 150 m. One profile was taken in another part of the lake, i.e. the Überlinger See. The station positions were chosen according to the local bottom topography, preferably in areas with a flat bottom (see below). In a few cases, two or three closely spaced stations were chosen, following the mean slope of the bottom of the lake. No time series are available for selected lake sites. A typical profile consists of five to six samples from the lowermost 15 m of the lake; the vertical resolution at between 1 and 5 m above the sediment is about 1 m. For details about the station positions and the numerical results obtained, see Ref. [4].

Figure 1 gives two examples of the results obtained. Both radon profiles were taken in September 1979. The horizontal distance between the profiles is about 1 km. They show the well-known exponential decrease of the radon excess with distance from the sediment/water interface. However, closer inspection of the data exhibits distinct differences in the apparent boundary conditions of the profiles: the $^{222}$Rn concentrations observed at 5–10 m distance from the bottom at station 13 are about a factor of two higher than those observed at the same distance at the nearby station 14. At one metre distance, this systematic difference between the stations still exists but the absolute value is much smaller. A quantitative interpretation of the radon profiles is given in the next section.

It should be emphasized at this point that a little more than half of the stations occupied show well-defined exponential $^{222}$Rn profiles, e.g. stations 13
and 14. In some of the remaining stations the exponential profile is poorly defined; in some cases no or only little excess radon is found in the lowermost 10 m of the lake. From the latter results it becomes obvious that the intermediate nature of the mixing processes near the bottom of lakes may result in disturbances of the steady-state radon distribution. In these cases a quantitative interpretation of the experimental results is difficult. Although the number of profiles available so far is too small for a quantitative argument, one can conclude from the present data set that sporadic horizontal and vertical eddy mixing plays an important role in the overall mixing regime of Lake Constance.

NEAR-BOTTOM VERTICAL AND HORIZONTAL MIXING

The interpretation of the well-defined exponential radon profiles is twofold. In the simplest case, a one-dimensional steady-state radon distribution in the water above the sediment/water interface is assumed. In this approximation [2] the concentration of excess radon, C, varies with distance above the sediment/water interface x in accordance with Eq. (1)

\[ C = C_s \exp(-x \sqrt{\lambda/K_z}) \]

(1)

where \( \lambda \) is the decay constant of \(^{222}\text{Rn} \) and \( C_s \) is the radon boundary condition at the sediment/water interface. Throughout this work the coefficient of eddy diffusion, \( K_z \), is assumed to be independent of the diffusion scale. The radon excess C is estimated for each station, assuming that the radon concentrations measured at between 10 and 20 m distance from the bottom at each station represent equilibrium conditions. The radon boundary condition \( C_s \) and the coefficient of eddy diffusion \( K_z \) are calculated by fitting the experimental results according to Eq. (1). The results are that \( K_z \) varies between 0.02 and 0.3 cm\(^2\)/s and \( C_s \) varies between 50 and 170 dis/min per 100 litres of water. The e-folding lengths of the radon profiles according to the above \( K_z \) values vary between 1 and 3.5 m. The radon concentrations measured at 10–20 m distance from the sediment/water interface can therefore be expected not to be too far from equilibrium with the \(^{226}\text{Ra} \) dissolved in the water. However, if compared with the measured \(^{226}\text{Ra} \) background of 7±1 dis/min per 100 litres [5], most of these radon concentrations are found to be significantly higher, with values up to 23 dis/min per 100 litres.

Previously it has been stated that the near-bottom radon excess of lakes is not due to vertical mixing alone; with a two-dimensional treatment of the problem, however, the radon data from Lake Greifensee [1] have been found to be adequately described. This finding is supported by a reinterpretation of the same data set [14]. The mathematical treatment used for the two-dimensional interpretation of the
present data set is based on analytical solutions of the differential equation
describing the two-dimensional steady-state distribution of excess radon near the
bottom of the lake. Solutions are available for three different types of the bottom
topography:

(a) a tilted bottom of infinite extension and known slope
(b) a semi-infinite flat bottom limited on one side by a tilted (semi-infinite)
    bottom of known slope (distance between sampling station and tilted
    boundary known)
(c) like (b), but with tilted boundaries of known slopes at known distances from
    the sampling station on both sides.

In all cases, exponential-type solutions of the two-dimensional differential
equation are found [4]. The coefficients of turbulent horizontal and vertical
mixing, $K_x$ and $K_z$, are the only free parameters. The type of the bottom topo-
graphy, the absolute value of the parameters characterizing it, and the variability
of these parameters at a given sampling site are taken from topographic maps of
the lake. The coefficients of horizontal and vertical mixing are obtained
in the following way: From the one-dimensional treatment of the data a lower
limit of $K_x$ is estimated. On the basis of this value, $K_x$ is estimated by a best fit
of the experimental data [4]. The results are: $K_z = 0.02–0.15 \text{ cm}^2/\text{s}$ and
$K_x = 100–1000 \text{ cm}^2/\text{s}$; the respective mean values are 0.06 and 500 \text{ cm}^2/\text{s}.
These values are comparable to those estimated for Lake Greifensee; they are,
however, at least one order of magnitude smaller than the ones found in the
Atlantic and in the Pacific Ocean [2, 15]. The two-dimensional treatment of the
data provides estimates of the equilibrium radon concentrations of the lake which
are in agreement with the measured $^{226}\text{Ra}$ concentrations; this is not the case
for the one-dimensional treatment. This is taken as evidence that the two-
dimensional interpretation provides an appropriate description of the mixing
regime of the lake.

It is worth mentioning that the highest values of both $K_x$ and $K_z$ are found
at two stations where, according to independent evidence, enhanced mixing is
expected. If these stations are excluded, the mixing coefficients of Lake Constance
(Obersee) are found to be fairly constant: $K_x = 100–400 \text{ cm}^2/\text{s}$ and $K_z = 0.02–
0.05 \text{ cm}^2/\text{s}$. From the present data set a possible seasonal variation of these figures
cannot be excluded; this requires further investigations. On the basis of the above
mixing coefficients it is estimated that the vertical distribution of excess radon
above the sediments of Lake Constance (Obersee) is strongly influenced by the
intensity of horizontal mixing. Only in the lowermost few metres of the lake does
vertical mixing become the dominating process. It should be mentioned that this
may be different for other gases dissolved in the water. It is strictly true for $^{222}\text{Rn}$
because in this case the mixing time scales are comparable to the radioactive life-
time of the tracer. For tracers of different radioactive and/or chemical lifetimes
the relative importance of horizontal and vertical mixing for vertical tracer
distribution may be different; this difference can be estimated if the respective
lifetimes are known.

SEDIMENT/WATER EXCHANGE

The intensity of the sediment/water exchange can be estimated by comparing
the standing crop of radon in the sediments with that of the overlying water [16].
The following procedure is used: The total amount of radon lost from the sedi-
ments is calculated by vertical integration of the near-bottom radon excess. The
results are: standing crops varying between 0.07 and 0.9 dis/min per cm², with
a mean of 0.2 dis/min per cm². Qualitatively, one expects these values to depend
on the 226Ra content of the sediments and on their porosity. The absolute values
of the calculated standing crops are clearly related to the sediment type: for
sediments with a mean grain size below 5 μm the calculated standing crops are
smaller than 0.3 dis/min per cm², whereas they are greater than 0.3 dis/min per cm²
for sediments with a mean grain size greater than 5 μm.

No systematic data of the 226Ra content of the sediments are available so
far. From the existing 226Ra and 230Th data the standing crop of excess radon
in the sediment is estimated. It is found to be 50% larger than the correspon-
ding values in the water. This finding is consistent with the idea of the existence of a
stagnant water layer at the sediment/water interface through which radon
transport is by molecular transport only. As molecular transport is a slow
process, some of the radon excess of the sediment is lost by radioactive decay
before it enters the overlying water layers where turbulent mixing dominates.
From the observed difference, the thickness of this diffusion layer is estimated
to be 1–5 cm. This is consistent with literature data [16]. With the knowledge
of the thickness of this diffusion layer the transfer of other substances from the
sediment to the water and vice versa can be estimated.

DISTRIBUTION OF RADON AND TRITIUM IN THE 'CORE LAYER'
OF THE ALPENRHEIN IN LAKE CONSTANCE (OBERSEE)

The 'core layer' of the Alpenrhein in Lake Constance (Obersee), i.e. the
range of 10–20 m depth in this part of the lake, is characterized by a high radon
excess and by a tritium deficit relative to the background level of these tracers.
Other factors to be considered, such as electrical conductivity, turbidity of the
water and mass of suspended matter, show similar effects. The latter items are
less suitable for a quantitative description of water transport and mixing
processes in the lake because their values can be changed by physical, chemical
and biological processes in the water. Tritium and radon, however, truly trace the transport, mixing and dilution of the water.

In July 1980 the vertical distribution of these tracers in the uppermost 40 m of Lake Constance was measured at 28 stations [5]. The results are characteristic for a period of high water input of the Alpenrhein to the lake. Figure 2 gives a typical example of the vertical distribution of $^{222}$Rn and tritium, and of the electrical conductivity of the water in the northern and the eastern parts of Lake Constance. The sampling station is located near the town of Wasserburg, i.e. at about 6 km distance from the ‘Rheinbrech’ where the Alpenrhein enters the lake. It is obvious that the tracer distribution in the depth range of 0–24 m is influenced by admixtures of water originating from the Alpenrhein (see above). According to both the radon and conductivity data, this influence is maximal at 12 m depth, i.e. in the lower part of the epilimnion of the lake (see temperature profile). Some influence of the Alpenrhein is even found at the depth of the local thermocline. The tritium concentration of 75 TU observed in the uppermost 16 m of the lake can be explained by a mixture of about 25% of lake water (background tritium concentration: 110 TU) and 75% water originating from the Alpenrhein (tritium concentration: 62 TU). A similar mixing ratio is obtained from the distribution of the electrical conductivity [5]. The radon excess observed in the core layer cannot be interpreted in such a simple and straightforward way; because of the short radioactive lifetime of radon the effects of mixing as well as of radioactive decay have to be considered.
FIG. 3. Vertical $^{222}$Rn sections perpendicular to the mean flow of the Alpenrhein in the northern part of Lake Constance (Obersee). The dotted area indicates the slope of the near-shore sediments. The sections are located in the vicinity of the following towns [5]: section 1: Wasserburg/Nonnenhorn, section 2: Langenargen, section 3: Friedrichshafen. The direction of the mean flow is from section 1 to section 3.

In the centre of the lake and along the southern shore, virtually no admixture of Alpenrhein water is found. In the eastern part, i.e. the source area of the Alpenrhein, strong tracer signals are observed, which are, however, highly variable from station to station. No clear-cut picture of the mean horizontal flow pattern of the water in the core layer is obtained in this area. Along the northern shore of the lake, where - according to previous investigations [3] - most of the water transport within the core layer of the Alpenrhein takes place, the tracer data are very conclusive. The present article concentrates on the results obtained from this part of the lake.

Figure 3 shows the two-dimensional distribution of radon observed at three vertical sections which are perpendicular to the shoreline, i.e. to the expected direction of the water transport in the core layer. Three features are obvious: (1) The radon concentrations are maximal near the shore, indicating that the water transport in the core layer is concentrated there at a mean depth of 10–15 m. (2) The radon concentrations decrease in the direction of the mean flow, mainly as a result of radioactive decay (see below). (3) The distribution of the radon excess is similar for all sections, with characteristic vertical and horizontal scales of 15–20 m and 1–2 km, respectively. It becomes obvious from section 3 of Fig. 3 that the core layer is starting to break up into two vertically separated layers. The concentrations of tritium and of electrical conductivity for the sections on the average increase steadily in the direction of the mean flow, i.e. they approach asymptotically their background concentrations. According to these data, near Friedrichshafen (section 3) the fraction of the core layer originating from the Alpenrhein is only 30%. The tritium and conductivity data are thus indicative of the dilution of the tracer signal in the core layer by admixture of lake water. A quantitative interpretation of these observations is given in the following section.
FIG. 4. $^{222}$Rn excess, $c^*$, in the core layer of the Alpenrhein in the northern part of Lake Constance (the mean flow is from left to right). The values of $c^*$ are corrected for the dilution of the radon concentration of the core layer by admixtures of lake water. The corrections are based on measured tritium concentrations. The solid line represents the best fit of the data.

WATER BALANCE OF THE CORE LAYER AND ITS MEAN TRANSPORT VELOCITY

On the basis of the tritium concentrations observed at individual stations the fractions of water originating from the Alpenrhein are estimated. These fractions vary between 80% in the vicinity of the 'Rheinbrec' and 30% at about 35 km distance. Most of the dilution of the tracer signals originally present in the Alpenrhein takes place immediately after it enters the lake; compared with this initial 'entrainment' of lake water, the dilution of the tracer signal of the core layer by horizontal and vertical mixing is of minor importance. The mean fraction of undiluted Alpenrhein water estimated from all stations in the northern part of the lake is 40%. This means that the water flux within the core layer is more than twice the water supply rate of the Alpenrhein to the lake. Since the outflow rate of the Searhein during the period in question is only 20% higher than the inflow rate of the Alpenrhein (the surplus being of the order of the additional contributions by smaller rivers) at least half the water in the core layer does not leave the lake directly but rather recirculates in it. Some of this water supposedly enters another part of the lake, the Oberlinger See; most of the water, however, seems to be recirculated in the Obersee itself [3].

The effect of admixture of lake water to the core layer on its radon concentration can be corrected for either by its tritium content or by its conductivity levels. The tritium-corrected radon data of the core layer, $c^*$, are presented in Fig. 4 as a function of its geographical position. The total distance of the mean water flow covered by the stations is 28 km. It is obvious that the
corrected radon concentrations of the core layer on the average decrease exponentially. The decrease is interpreted as a result of radioactive decay of radon during the travel time of the water in the core layer. The mean slope of the data provides an estimate of the transport velocity of the water, v, in the core layer of 3.4 km/d. If the corrections are based on the conductivity data, a value of 3.8 km/d is obtained; because of a higher variability of the conductivity of both the Alpenrhein and the lake this value is considered to be less precise than the previous one. The weighted average of both estimates of the transport velocity is 3.5 km/d, with an uncertainty of ±25%. This value is well within the range of published transport velocities of 2.5–12 km/d. A comparison with these estimates is, however, not very meaningful unless all boundary conditions that could influence v are known.

Independent and more reliable evidence of the representativeness of the present estimate comes from the available tracer data. It has been shown above that the water mass transported in the core layer is about 2.5 times the water input of the Alpenrhein to the lake, i.e. during the time period in question 2.5 × 640 m³/s. In addition, since the vertical and horizontal scales of the core layer are known from the radon sections (Fig. 3), the mean transport velocity can be estimated from this information. The estimated mean transport velocities are 3–6 km/d, which is on the high side of the previous estimate. This is not unlikely because the latter estimates are based on the assumption that all the water transported to Lake Constance by the Alpenrhein is to be found in the main branch of the core layer along the northern shore. In reality, however, some of this water enters the eastern part of the lake and is then lost from the main branch. The branching ratio is not known; it could be of the order of 20/80 [3], which would reduce the above figures by 20% and make the two independent estimates even more comparable.

CONCLUSIONS

Measurements of near-bottom radon and combined measurements of radon and tritium in the core layer of the Alpenrhein provide a powerful tool for investigating the processes of sediment/water exchange, turbulent mixing of the near-bottom water, and the water balance and dynamics of the core layer of the Alpenrhein. The results presented are considered as a case study. More experimental data are certainly needed for the assessment of the spectra of the mixing, transport and exchange parameters in question. Time series of these measurements over a period of at least one year are needed in order to study the seasonal variation of these parameters. Work of this kind is planned for the near future. One of the aims of the forthcoming work is to achieve a deeper insight into these processes. The second equally important aim of this work is to provide basic information about the actual state of the water dynamics of the
lake which can be used for a more realistic interpretation of measurements of biological and/or chemical relevance in the lake.

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GROUNDWATER CONTRIBUTION TO STREAM FLOW IN SWEDISH FORESTED TILL SOIL AS ESTIMATED BY OXYGEN-18

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Abstract

GROUNDWATER CONTRIBUTION TO STREAM FLOW IN SWEDISH FORESTED TILL SOIL AS ESTIMATED BY OXYGEN-18.

Hydrograph separation by $^{18}$O was performed in ten basins situated in different parts of Sweden. The basins, with areas of 0.03–6.6 km², are dominated by coniferous forested till soils. For the 16 separated spring floods, the total volume fraction of groundwater ranged between 41% and 86%, with a median value of 59%. The separation of 15 rainfall-generated events gave groundwater fractions of from 68% to nearly 100%, with a median value of 85%. The groundwater table is shallow in the basins; their areas are conveniently classified as influent or effluent areas for groundwater. Assuming that all precipitation (rain water or melt water) on influent areas infiltrates, while all precipitation on effluent areas forms overland flow, the groundwater fractions of the effluent area could be estimated from the separations. A few field surveys suggested that most of the estimated groundwater fractions were reasonable. The figures on groundwater fractions refer to pre-event groundwater, since groundwater recharged during the events is included in the rain-water or melt-water component of the separations. Attempts were made to give a better estimate of the groundwater fraction by estimating the course of groundwater $^{18}$O during the events. It was thereby assumed that infiltrated water is mixed in a reservoir of constant volume.

1. INTRODUCTION

The process of stream-flow generation in natural basins is not yet known. It is now becoming generally accepted that the traditional view, as formulated by Horton [1], has little relevance to humid areas. However, many basic questions still remain to be solved before an alternative theory can be formulated, describing the dynamics and flow-paths of water, from precipitation to the draining stream.

In Swedish till soils, which are the object of the present study, the groundwater level largely follows the topography, with a depth of, say, 2–3 m in elevated areas. In lower parts of certain hill slopes and in certain low-lying areas, the groundwater table is in or above the ground level. With regard to inflow into or outflow from the groundwater zone, a basin can be divided into influent and effluent areas for groundwater [2].
The infiltration capacity of till soils generally exceeds the infiltration capacity of rainfall or snow melt. Because of the short distance between the ground surface and the groundwater, the groundwater table in certain localities can be raised rapidly by the infiltrated water. It has been found [3] that the saturated hydraulic conductivity in till soil may increase rapidly with height in the top soil layers. The raising of the groundwater table increases both the transmissivity and the hydraulic gradient, resulting in increased outflow in effluent areas. Consequently, storm flow in streams consists of two components, outflowing groundwater on the one hand and on the other hand rain water or melt water that forms overland flow in the effluent areas where no infiltration can take place.

This paper presents the results of a study on the relative contributions to stream flow of rain water or melt water and groundwater in several Swedish basins.

2. METHOD

Stream flow is assumed to originate from two reservoirs, precipitation (rain water or melt water) and groundwater, with isotope contents $\delta_p$ and $\delta_g$ respectively. A steady-state mass balance for isotope and water flow gives the groundwater fraction, $X$, in stream flow as

$$X = \frac{\delta_p - \delta_s}{\delta_p - \delta_g}$$  \hspace{1cm} (1)

where $\delta_s$ is the isotope content of stream water. This is the widely used formula for two-component hydrograph separation by water chemistry or isotopes [4].

However, as a result of the infiltration generating the outflow of groundwater, $\delta_g$ may change during the event. If the infiltrated water reaching the groundwater is assumed to mix completely in a groundwater reservoir of constant volume, $V$, the rate of isotopic change of groundwater with respect to time is given by

$$\frac{d\delta_g}{dt} = \frac{q \cdot X}{V} (\delta_p - \delta_g)$$  \hspace{1cm} (2)

where $q$ is the specific discharge (total stream flow per unit area).

The fraction of groundwater can be related to basin characteristics by Eq.(3). It is thereby assumed that all precipitation on influent areas infiltrates, while all precipitation on effluent areas reaches the stream as saturation overland flow. The basin fraction of the effluent area is then

$$Y = \frac{q}{P} (1 - X)$$  \hspace{1cm} (3)
TABLE I. DESCRIPTIONS OF THE BASINS

<table>
<thead>
<tr>
<th>Basin</th>
<th>Area (km²)</th>
<th>Altitude (m a.s.l.)</th>
<th>Fraction of Outcrop* (%)</th>
<th>Till (%)</th>
<th>Clay (%)</th>
<th>Peat (%)</th>
<th>Lake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Min.</td>
<td>Max.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>Svarberget Övre</td>
<td>0.20</td>
<td>285</td>
<td>310</td>
<td>0</td>
<td>60</td>
<td>0</td>
<td>40</td>
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<tr>
<td>Svarberget B</td>
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<td>235</td>
<td>310</td>
<td>0</td>
<td>95</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Svarberget Nedre</td>
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<td>310</td>
<td>0</td>
<td>80</td>
<td>0</td>
<td>20</td>
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<tr>
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<td>320</td>
<td>390</td>
<td>&lt;2</td>
<td>&gt;98</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>354</td>
<td>&lt;5</td>
<td>&gt;87</td>
<td>0</td>
<td>8</td>
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<tr>
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<td>55</td>
<td>25</td>
<td>55</td>
<td>16</td>
<td>4</td>
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<td>67</td>
<td>13</td>
<td>12</td>
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<td>Gårdsjön F1</td>
<td>0.04</td>
<td>116</td>
<td>135</td>
<td>47b</td>
<td>53</td>
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<td>0</td>
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<tr>
<td>Gårdsjön F2</td>
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<td>113</td>
<td>135</td>
<td>48b</td>
<td>40</td>
<td>0</td>
<td>12</td>
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<tr>
<td>Gårdsjön F3</td>
<td>0.03</td>
<td>114</td>
<td>150</td>
<td>32b</td>
<td>63</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

* Outcrops are defined as areas with a soil cover of < 0.5 m.

In the Gårdsjön basins, outcrops are defined as areas with a soil cover of <0.2–0.3 m.

where P is the precipitation rate. Because of the time delay between precipitation and runoff, which is not taken into account above, Eq. (3) cannot be used instantaneously, but only for mean values of q, P and X during runoff events.

3. SITE DESCRIPTION

The investigated basins represent examples of the most characteristic type of landscape encountered in Sweden, i.e. coniferous forested till soils on fractured gneiss or granite rock. Data on the basins, which are located between the cities of Umeå and Gothenburg, are given in Table I, where the basins are listed from north to south. Svarberget Övre and Svarberget B are sub-basins to Svarberget Nedre; the Gårdsjön basins are different basins.

4. ISOTOPE DATA AVAILABLE

Stream water was sampled for $^{18}$O at discharge stations at the basin outlets. During most spring floods, one sample was collected per day, except for a few days of intense sampling (≈4 samples per day). Denser sampling (2–4 samples
FIG. 1. Total spring flood in Svalbard. Separated hydrograph and $\delta^{18}O$ of stream water and snow pack (ranges of snow-pack $\delta^{18}O$ shown). Estimated $\delta^{18}O$ of groundwater and corresponding calculated groundwater
fractions.

FIG. 2. Small winter melting in Nâstsen. Separated hydrograph and $\delta^{18}O$ of stream water, snow pack (ranges of snow-pack $\delta^{18}O$ shown) and groundwater, calculated groundwater fractions.
per day) was performed for a few spring floods. During snow-free periods, sampling was mostly undertaken at time intervals of 1 day to 1 week, with a few runoff events being intensely sampled (2–13 samples per day).

Snow sampling during snow melt was generally carried out with time intervals of about one week. Vertical snow cores through the snow pack were collected at 5–10 stations within each basin.

Precipitation was mostly sampled daily at one station, within or close to each basin.

The $^{18}$O content of the samples was measured with a Varian-mat mass spectrometer at the Division of Hydrology, University of Uppsala. The accuracy of the measurements is about ±0.10%.

5. RESULTS

The groundwater fractions at the moments of stream-water sampling were calculated by Eq.(1). The calculations were performed with constant values of $\delta_g$, i.e. $V = \infty$ in Eq.(2), or with $\delta_g$ calculated by various values of $V$. By using a constant value of $\delta_g$, a lower limit of the groundwater fraction is obtained, namely the fraction of 'pre-event' groundwater. If not otherwise stated, groundwater fractions mentioned in this text refer to such values.

The constant value of $\delta_g$, or the initial value, was assumed equal to stream-water $\delta^{18}$O before any snow melt had occurred or before the first rainfall associated with the event.

The $\delta^{18}$O of melt water was assumed equal to snow-pack $\delta^{18}$O at each moment. Daily values of snow-pack $\delta^{18}$O were estimated through interpolation between the days of snow sampling.

5.1. Snow-melt events

In total, 16 spring floods could be separated, each spring flood being composed of 1–3 melting periods. Two examples of separated snow-melt runoff events are presented in Figs 1 and 2. Table II gives some data on the hydrological situation for the spring floods and summarizes quantitative results for all the spring floods.

The course of stream-water $\delta^{18}$O during many events indicated a change in groundwater $\delta^{18}$O. After a sufficiently long time of stream-flow recession, stream water very probably originates from groundwater only. Thus the value of stream-water $\delta^{18}$O after the event suggests a new value of groundwater $\delta^{18}$O. The model reservoir volume, describing the indicated change in groundwater $\delta^{18}$O, can then be assessed by trial and error.
### Table II. Total Spring Floods

Hydrological situation and results of hydrograph separations

<table>
<thead>
<tr>
<th>Basin</th>
<th>Year</th>
<th>Snow pack</th>
<th>P</th>
<th>Peak flow</th>
<th>Fraction of groundwater, x</th>
<th>Sensitivity of x to</th>
<th>Fraction of effluent area from</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(mm)</td>
<td>(mm)</td>
<td>(L·s⁻¹·km⁻²)</td>
<td>(%)</td>
<td>Δδₑ</td>
<td>Δδₚ</td>
</tr>
<tr>
<td></td>
<td>1982</td>
<td>205</td>
<td>44</td>
<td>98</td>
<td>59</td>
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<td>±11</td>
</tr>
<tr>
<td></td>
<td>1982</td>
<td>205</td>
<td>44</td>
<td>n.d.</td>
<td>64ᵃ</td>
<td>±9</td>
<td>±16</td>
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<tr>
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<td>1981</td>
<td>200</td>
<td>11</td>
<td>144</td>
<td>47(53)</td>
<td>±9</td>
<td>±23</td>
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<tr>
<td></td>
<td>1982</td>
<td>205</td>
<td>44</td>
<td>146</td>
<td>51(55)</td>
<td>±6</td>
<td>±17</td>
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<tr>
<td>Aspåsen</td>
<td>1981</td>
<td>246</td>
<td>36</td>
<td>218</td>
<td>42(53)</td>
<td>±9</td>
<td>±30</td>
</tr>
<tr>
<td></td>
<td>1980</td>
<td>98</td>
<td>23</td>
<td>128</td>
<td>53(63)</td>
<td>±9</td>
<td>±18</td>
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<tr>
<td></td>
<td>1981</td>
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<td>47</td>
<td>227</td>
<td>59(67)</td>
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<td>±20</td>
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<tr>
<td>Buskbäcken</td>
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<td>±6</td>
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<td>108</td>
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<tr>
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<td>±4</td>
<td>±11</td>
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<td>±8</td>
<td>±13</td>
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<td>±12</td>
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<td>85</td>
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<td>209</td>
<td>56(72)</td>
<td>±15</td>
<td>±17</td>
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<td>71</td>
<td>80(85)</td>
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<td>±5</td>
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<tr>
<td>Gårdsjön F2</td>
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<td>43</td>
<td>67</td>
<td>±14</td>
<td>±12</td>
</tr>
<tr>
<td>Gårdsjön F3</td>
<td>1980</td>
<td>56</td>
<td>0</td>
<td>71</td>
<td>80(85)</td>
<td>±9</td>
<td>±5</td>
</tr>
</tbody>
</table>

ᵃ Discharge assumed equal to the discharge at Svarterget Nedre.
ᵇ The sensitivity is given for Δδₑ = ±0.5‰ and Δδₚ = ±1.0‰.

**Note:** The figures within brackets are calculated using variable δₑ with the 'best' value of Vchosen from two alternatives, 250 or 500 mm.
Assuming that stream flow at Svatberget Nedre (Fig.1) originates from groundwater only at the end of May, V values of around 250 mm are obtained. With this value of V, the total fraction of groundwater for all the spring floods is 53%, as compared with 47% for V = ∞. As is seen in Fig.1, a smaller reservoir volume would have been required to simulate the indicated change in groundwater δ¹⁸O during the first, small runoff event. Similar tendencies, but less pronounced, were found in other basins, suggesting that more realistic simulations of groundwater δ¹⁸O would be obtained if V were allowed to increase with discharge.

Changes of groundwater δ¹⁸O during the events, of similar magnitudes as those from stream-water δ¹⁸O, were observed on samples of shallow groundwater in some of the basins. In no case did the groundwater samples show changes opposite to what was expected from the δ¹⁸O of the infiltrated water, but the change rates varied largely.

The very small runoff event in Nåsten (Fig.2) was caused by a few millimetres of melt water from a snow pack of 120 mm water equivalent. No change in groundwater δ¹⁸O is indicated, since the δ¹⁸O of stream water returns to its original value. A lower limit of the reservoir volume of 100 mm is obtained.

For most ‘total’ spring floods¹ in the basins, a reservoir volume of 250 mm roughly described the indicated change in groundwater δ¹⁸O. For a few spring floods, 500 mm gave a better fitting.

The discharged volumes of groundwater (with constant δν), given as fractions of total discharged volumes, are listed in Table II. For all 24 separated melting periods, the volume fraction of groundwater ranged between 32% and 91% of total flow, with a median value of 64%. For the 16 ‘total’ spring floods, the fraction ranged between 41% and 86%, with a median value of 59%. For the ‘total’ spring floods, the calculated basin fractions of effluent area (with constant δν) ranged between 9% and 49%, with a median value of 26% (Table II).

Even if the estimates by Eq.(3) are rough, they provide a mean for field checks of the results of stream-flow separation by δ¹⁸O. The results of a few field surveys of saturated areas, interpreted as effluent areas, are listed in Table II. The surveys were carried out either statistically or by mapping, for the days close to spring-flood culmination. For some spring floods (Aspåsen, 1981; Stormyra, 1982), Eq.(3) gives too large fractions. Apart from methodological errors the discrepancy may be due to the existence of unsaturation overland flow. For other spring floods, the surveys show that the results of the hydrograph separations and their interpretation by Eq.(3) are not unrealistic.

¹ Total spring floods are the floods resulting from melting of the entire snow pack.
FIG. 3. Large summer event in Gårdsjön, stream F1. Separated hydrograph and δ¹⁸O of stream water and rain water; rainfall intensity.

FIG. 4. Medium-size summer event in Stormyra. Separated hydrograph and δ¹⁸O of stream water and rain water; rainfall intensity.
5.2. Rainfall-generated events

Two examples of separate rainfall-generated events are shown in Figs 3, 4. In the Gårdsjön event, rainfall was sampled several times per day. In the Stormyra event, as in all others, daily rainfall sampling was performed.

The detailed sampling of the prolonged rainfall at Gårdsjön stream F1 (total rainfall 56 mm) shows very large variations of rainfall $\delta^{18}O$ with time. Because of the time lag between rainfall input and stream-water output, it was not considered possible to utilize the varying $\delta^{18}O$ of rainfall for the separation, which was performed using the weighted mean ($-13.5\%o$) as a constant value. In this manner, little information was obtained on the variation in groundwater fraction with time during this large summer runoff event. The estimated total volume fraction of 81% was, however, comparatively safe. The basin fraction of the effluent area obtained by Eq. (3) was 4%.

Except for the first few millimetres, the rainfall $\delta^{18}O$ deviated progressively more from the groundwater $\delta^{18}O$. Since the disposition of the ground to generate overland flow (saturation as well as unsaturation) can be expected to increase as the rainfall proceeds, the use of the weighted mean of rainfall $\delta^{18}O$ tends to underestimate the groundwater fraction in this particular case.

For the Stormyra event, the variation in rainfall $\delta^{18}O$ prevents a very safe separation by $\delta^{18}O$. Since, however, the two first rainfall samples, accounting for 42 mm of the 47 mm of rainfall associated with the main discharge peak, were isotopically not too different from each other and on the same side of the line for groundwater $\delta^{18}O$ (Fig.4), a rough separation could be performed. As daily values of $\delta_p$, accumulated daily means were used, calculated separately for the two discharge peaks. For this summer runoff event of medium size, the total groundwater fraction was about 80%, corresponding to a basin fraction of the effluent area of 2%.

Even if the exact shapes of the rain-water and groundwater hydrographs are uncertain, their internal relationship is reasonable, with the groundwater hydrograph being delayed in time and having the smoothest peak. It should be noted that the smallest instantaneous groundwater fraction appeared when the discharge was still low – only a few litres per second.

The variation of the groundwater fraction, as suggested by the Stormyra event, was supported by other, less densely sampled events in this and other basins. The lowest groundwater fractions were found during the hydrograph rise or at peak flow. In no case did the groundwater fraction decrease significantly after peak flow. This finding enabled estimates of groundwater fractions to be made for comparatively sparsely sampled events, provided that one sample was taken close to the moment of peak flow.

Total-volume fractions of groundwater could be estimated for 15 events. The fractions ranged between 68 and 100% of the total flow, with a median value
of 85%. The fractions of the effluent area, as calculated by Eq. (3), ranged between 0 and 17%, with a median value of around 2%. No field surveys were carried out in connection with the rainfall events, but basin physiography and experience from the spring floods suggest that the obtained values may be realistic.

5.3. Errors — some comments

The assumption of equal δ18O of melt water and snow pack at each moment tends to overestimate δp and thus to underestimate the groundwater fraction during the spring floods. Instantaneous differences between the δ-values of snow pack and melt water may reach 1–2‰ at the early stages of snow melt [5]. Thereafter, the values gradually decrease. The differences have to be treated as errors, together with the effect of the areal variability in snow-pack δ18O (see the ranges marked in Figs 1 and 2). Included in these errors are also those effects caused by molecular exchange with the atmosphere and drainage of isotopically different melt water.

Rainfall during melting complicates the separations by 18O. If the δ18O values of the rain water and snow pack are equal, no error is introduced. If they differ, however, the resulting composition of the drained water is not known and the influence of rainfall on δp has to be treated as an error. The amounts and δ-values of rainfalls at Nästen (1982) and Stormyra (1979 and 1982) suggest that the groundwater fractions may have been overestimated for these spring floods. For the other spring floods, the influence of rain water is small. (Note that the precipitation amounts given in Table II include both snowfall and rainfall. Snowfalls and small rainfalls are taken into account by repeated snow-pack sampling.)

The sensitivities of the calculated groundwater fractions to an error of ±0.5‰ in δp and ±1.0‰ in δp are given in Table II.

One factor which has not been regarded above is systematical errors caused by a possible enrichment of δ18O during surface-water flow through the basins. A rough idea of the magnitude of such an enrichment during an event, Δδp, is given from the following equation

$$\Delta \delta_p = \frac{E Y'}{q} \left( \delta_p - \delta_e \right)$$

(4)

where E is mean rate of evaporation from wet surfaces (mm·d⁻¹), q is mean specific discharge (mm·d⁻¹), Y' is the basin fraction of wet areas exposed to the atmosphere (Y' < Y), and δp and δe are the isotope contents of stream-water inflow and net evaporate, respectively.

Using the model of Craig and Gordon [6], reasonable values of δp can be estimated. With δe = -15‰ (assumed to be due to melt water only), δ18O of the atmospheric water vapour = -20‰ and a relative humidity of 0.7, δp - δe is
around 30%. Estimates for the investigated spring floods show that values of $\Delta \delta$ of 0.5% are readily obtained. This is the case particularly for basins of little slope and large effluent areas, such as Nästen.

At the present stage, the estimates of $\Delta \delta$ by Eq. (4) are regarded as mere speculations, since there are no field data available. Reports on enrichment during surface-water flow in humid areas have not been found in the literature. The existence of such an enrichment could be detected by studies of the D/$^18$O relationship, but deuterium analyses were not possible in the present study.

At the rainfall-generated events, the rain water was either higher or lower in $^18$O than the groundwater (see Figs 3 and 4), making the isotopic conditions for separation fundamentally different. The results of the separations were similar for the two groups of events, which supports the method used, since systematical errors due to enrichment would act on the groundwater fraction $X$ in opposite directions.

6. CONCLUSIONS

During all separated rainfall-generated runoff events and during most of the separated snow-melt events, the total discharged volumes were dominated by groundwater. The results agree with the findings of several environmental isotope studies performed in central Europe and Canada (see, for instance, Refs [7–9]).

The results of a few field surveys of saturated areas during snow melt showed that the extensions of such areas were of similar magnitude as the areas required to generate the overland runoff component of stream flow.

Since the study is based on the interpretation of stream-water $\delta^18$O at the basin outlets, it gives little information on the various processes involved in stream-flow generation within the basins. However, integrated results of these processes are obtained. They support the important role of the groundwater in stream-flow generation in the investigated basins, as pointed out in Section 1. This influence is partly direct, by the contribution of groundwater to storm flow, and partly indirect, by the regulating effect of the groundwater level on the extent of saturated areas — areas which generate direct rain-water or melt-water runoff.

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STUDY OF THE INTERRELATIONSHIPS BETWEEN GROUNDWATER AND LAKE WATER AT NEUSIEDLERSEE, AUSTRIA

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Abstract

STUDY OF THE INTERRELATIONSHIPS BETWEEN GROUNDWATER AND LAKE WATER AT NEUSIEDLERSEE, AUSTRIA.

Neusiedlersee (area 300 km², average depth 1 m) is a steppe lake situated in the Pannonian plain at the eastern border of the Alps. The lake has only little surface inflow and no natural surface outflow, and its water balance is mainly determined by precipitation and evaporation. The subterranean inflow, of which little is known because of the complicated hydrogeological conditions, is an important factor in this water balance. The current activities represent an attempt to learn more about the subterranean inflow by means of investigations concerning the groundwater conditions in the lake-side area and the inter-relationships of groundwater and lake water applying environmental isotope methods. The paper deals with the eastern lake side and the seepage springs in the western reed belt. The results of the isotope investigations indicate that there is no continuous and homogeneous shallow aquifer at the eastern lake side of Neusiedlersee and therefore inflow to the lake is very small. Seepage spring water in the western reed belt is assumed to come from a widely ramified karst- and/or crack-water system with its catchment area situated in the highest ranges of the Leithagebirge.

1. INTRODUCTION

Neusiedlersee is a steppe lake situated near Vienna at the Austrian/Hungarian border (latitude 16°45', longitude 47°50') where the outlying hills of the eastern Alps slope into the Pannonian plain (Fig.1). The water surface is at 115.5 m above sea level and the total area is almost 300 km², of which about 180 km² are covered by reeds. The mean water depth is about one
metre. Originally, the steppe lake was without discharge. However, today the water level is regulated by a channel (Einserkanal) constructed years ago in order to drain the lake and to use its area for agricultural purposes. In 1965, Austria and Hungary agreed upon a minimum discharge in order to stabilize the water level. Assuming a more or less reliable figure of 650 mm for mean precipitation, a mean evaporation of 900 mm per year, and a mean water level of 115.45 m, the lake’s hydrology may be characterized by the following parameters (in million cubic metres per year) [2]:

FIG. 1. Site plan of Neusiedlersee area at the Austrian/Hungarian border (according to Ref. [1]).
Inflow by surface waters 65
Subterranean inflow estimated at 10–70
Outflow at the sluice 0–60
Subterranean outflow unknown but small
Precipitation over the lake 160
Evaporation 200

This applies to a water surface area of 250 km² and a water volume of
223 million m³. The water balance of the lake therefore is preferably determined
by precipitation and evaporation, including the indeterminate subterranean
inflow which probably depends on the varying amounts of precipitation. The
lake has disappeared more than once in its history, the last time 100 years ago.

**FIG. 2. Model of subterranean inflow to Neusiedlersee (according to Ref.[3]).**

Little is known of the subterranean inflow to Neusiedlersee. A conceptual
model of the very complicated hydrogeological conditions, partly determined by
Quaternary tectonics (Fig.2), does exist, but in the past it has only been taken
as a remainder in the water balance equation. Accordingly the estimated values
vary. The present activities — a co-operative project of Austrian and Hungarian
institutes — represent an attempt to learn more about the subterranean inflow
by more accurate investigation of the lake-side areas and the interrelationships
of groundwater and lake water, and subsequently to arrive at a quantitative
estimation. Moreover, it is of interest to what extent nutrients and noxious
substances flow into the lake with the groundwater on account of the intense
agricultural utilization of the surroundings (vineyards) and tourism. The
results of the analyses are also important with regard to considerations of how
to prevent the lake from eventually drying up again, which may be caused by a
series of very dry years. The paper deals with groundwater conditions and
interrelationships of groundwater and lake water at the eastern lake side of
Neusiedlersee, and with an investigation of groundwater seepage in the western
reed zone.
FIG. 3. Hydro Iso-hypographs and main groundwater flow directions in Seewinkel (1975-06-20). Location of sampling points. The water ages are indicated for some boreholes at the lake side (estimated from $^3$H and $^{14}$C values assuming an initial $^{14}$C content of 85% modern [4]).
FIG. 4. Survey sampling in spring 1980: \( ^3H \) and \( \delta^{18}O \) values of precipitation, groundwater and surface water in Seewinkel.

2. INVESTIGATION AT THE EASTERN LAKE SIDE OF NEUSIEDLERSEE

According to the regional hydro/iso-hypsographic map (Fig. 3), one has to reckon with an inflow from the Quaternary gravels and sands of plain Seewinkel and the Parndorfer Platte to Neusiedlersee. The intention of the investigation was to obtain a mathematical model of the flow velocity and the amount of groundwater inflow to the lake by an environmental isotope study. However, the first survey sampling from about 80 wells and shallow boreholes at Seewinkel in 1980 yielded a distribution of environmental isotopes which showed no analogies to the flow pattern according to hydro/iso-hypsographs. The measured \( ^3H \) values of groundwater varied from 0 TU (boreholes near the lake...
FIG. 5. Content of ³H versus height of water column at sampling points (hinting at stratification of shallow groundwater at Neustedersee's eastern lake side). Insert: Temporal changes of conductivity, ³H and δ¹⁸O values in well 103 during one pumping period.

side) to 170 TU (Fig.4) and thus certify completely different water ages for different sampling points. The actual precipitation ³H value in comparison amounts to 40 TU (mean of 1980). The relationship between ³H content and height of the sampling points' water column (Fig.5) indicates stratification of groundwater at least in some areas of the eastern lake side. This becomes especially clear at the adjacent sampling points P 3, 124 and I 3, 14 (Figs 4, 5). This is also proved by different δ¹⁸O values and by mineralization, although sometimes the younger water and sometimes the older water is more mineralized. Another hint at such a stratification is a change of the isotope values in well 103 (8.3 m water column) during one pumping period (Fig.5). Consequently, with increasing water removal, more and more younger water from near the surface is delivered whilst older water decreases. This indicates little transmissivity of the lower aquifer. After water removal, the original isotopic composition is slowly restored. The δ¹⁸O values of the investigated
groundwater vary from −5 to −12‰, with a precipitation mean of −9.7‰ (Fig.4) which, because of the small differences in level, may be taken as a basic value for the whole of Seevelinkel. Some sampling points clearly show an enrichment of $^{18}$O which is traceable to water infiltration from small shallow lakes ('Lacken'), e.g. Kühbrunnlacke with a $\delta^{18}$O value of +1.8‰. In the eastern lake side's southern area, small quantities of lake water pass over to the groundwater (1 10, Figs 4, 8).

Of special interest are the low-$^3$H groundwaters at the eastern lake side of Neusiedlersee which show an exceptionally low content of $^{18}$O compared with precipitation (Fig.4). Barring the possibility of an infiltration area on a higher level, waters developed from precipitations of a glacial period must be involved. The measurement of $^{14}$C certified this assumption (Fig.3). According to our expectations, the highest ages of up to 28,000 years were shown by the deeper artesian waters included in the investigation.

Altogether, the measured isotope values indicate a stratification of shallow groundwater at the eastern lake side of Neusiedlersee. There are two main aquifers which in themselves are again non-uniform. This was confirmed by the different reactions of the groundwater level of individual observation points to precipitation events. It follows from the evaluation of hydrological observation data that the upper aquifer's groundwater level is distinctly influenced only by intensive precipitation and that generally the groundwater level is noticeably influenced by evaporation in the warm season, especially in areas with a very shallow groundwater level. A hint at the evaporation ratio was given by a hand drilling in the area of Podersdorf where the first groundwater found showed a very low $^3$H content. This allows the conclusion that practically no infiltration leading to groundwater recharge takes place in this area. The deeper aquifer's groundwater level does not react significantly to meteorological influences. In all, the findings of these investigations contradict a considerable groundwater inflow in the middle and southern areas of the eastern lake side (high age of water or small groundwater level gradient). Most likely there is a subterranean inflow which is important to the water balance in the northern area. On one hand, the hydro/iso-hypsographs certify the largest groundwater level gradient towards the lake; on the other hand, groundwater of relatively short residence time was found at borehole N 1 (Fig.3). Therefore, in 1982 stress was put on the investigation of this area.

In September 1982, five 20 m deep exploration drillings at about 1 km distance from each other were made (Fig.3). In each of the drillings similar geological conditions were found, although the thicknesses of the individual strata change remarkably (Fig.6). The Quaternary overburden (humus, loam, sands, gravel) is not very thick in the drilling area (3.5 m at B 821, 1.3 m at B 825, less than 1 m at others). During the drilling period these layers contained no water. As drillings further east show, the thickness of the
Quaternary strata increases rapidly towards the east. The Tertiary series (Upper Pannonian) consists of clayey marls with groundwater-bearing layers of silty/clayey sands in between, and of clean gravel-bearing medium sands. Often, silty/clayey layers of thicknesses of millimetres to centimetres are enclosed in the sands, so that the permeability of this series is higher parallel to layers than normal to them. By means of geoelectric measurements it was proved that the underground conditions do not change considerably between drilling points, so that aquifers of little permeability have to be reckoned with in all of the lake-side area.

The results of isotope measurements of water samples taken during drilling (Fig.6) certify an average residence time of at least 30 years for almost all groundwater found in the boreholes. Only in B 824 and 825 younger water (about ten years old) could be traced in thin layers near the surface. In the uppermost part of B 821, 822 and 823 a small percentage of young water was found. However, the average residence time of this uppermost non-artesian water was more than 30 years. The appertaining layers are not very thick. Apart from the near-surface layer, the artesian waters of B 821, 822 and 823 as well as the water from B 825 show ages of about 100 to some thousand years. Their origin is different because the waters vary significantly in their $^{18}$O content.

Supplementary to these exploration boreholes, some hand drillings were done to investigate the uppermost aquifer (Fig.3). The ascertained thickness of this aquifer — fine and medium sands — varied from 0 to more than 2 m; the groundwater level lay between 0.25 and 1.34 m below ground surface. The level gradient towards the lake varied from 1‰ to several per milles. The isotope values of the water samples taken differ widely (Figs 7, 8). They show partly evaporation effects and do not indicate a continuous and homogeneous groundwater body.

Taking into account all hydrogeological and isotope-hydrological data leads to a tentative conceptual model of hydrogeological conditions and inter-relationships of groundwater and lake water at the eastern lake side of Neusiedlersee (Fig.9). According to this, shallow groundwater is to be found in Quaternary layers, obviously influenced by precipitation and evaporation. A continuous aquifer cannot be certified. Where the aquifer does exist in the lake-side area, it is thin. At the eastern lake side, in the assumed recharge zone, horizontal permeability, water-table gradient and aquifer thickness — relevant parameters for a subterranean inflow to the lake — are very small. From this it follows that precipitation water in the Seewinkel area mainly evaporates after a certain residence time in the ground and that inflow to Neusiedlersee from shallow groundwater can be estimated to be very low. At various depths in Tertiary layers another, again non-homogeneous, aquifer is to be found. The water of this aquifer has long residence times and hardly moves. Therefore, one may assume that from the second aquifer no considerable recharge takes place. Distinct connections between the upper and lower aquifer may be excluded.
FIG. 7. $^3$H and $\delta^{18}$O values of shallow groundwater in the investigation area Neusiedl-Podersdorf.

FIG. 8. Stable-isotope composition of shallow groundwater from the investigation area Neusiedl-Podersdorf, of lake water and of groundwater from borehole 110 where lake water enters the aquifer.
FIG. 9. Generalized conceptual model of hydrogeological conditions at the eastern lake side of Neusiedlersee.

FIG. 10. $^3$H and $\delta^{18}O$ values of seepage springs in the western reed belt, water supply station Purbach, of two karst springs and some groundwaters in the Wulka valley. Precipitation values for Neusiedlersee and Wulka are also specified.
3. SEEPAGE SPRINGS IN THE WESTERN REED BELT

The southern flank of the crystalline anticline of Leithagebirge is overlain by Leitha limestones and conglomerates generally dipping southwards under marls and clays of the Upper Tertiary. The water coming from the upper regions of Leithagebirge is assumed to reach the subsoil of the lake (reed belt) through karst aquifers and to ascend to the surface water through clefts and cracks of tectonic fracture zones (Figs 1, 2).

During winter, when the lake was covered by ice and snow, some places free of ice were found in the reed belt near Purbach (Fig. 10), indicating the existence of seepage springs. The diameter of these seepage springs is 1–1.5 m and the depth is approximately 1 m (Fig. 11). The water temperature lies between 7°C in winter and 11°C in summer. The water chemistry indicates karst or crack water. The isotope values are quite different from those of the lake water and the groundwaters from the Wulka basin (Fig. 10). The δ¹⁸O value (−11.2‰) shows no temporal changes and therefore no short-term influences of precipitation, and points to a higher catchment area (Fig. 12). The same δ¹⁸O value and therefore the same catchment area height apply to the water supply station of Purbach (collector well with 20 m depth, water probably of karst origin) at 1 km distance, and to the Hackelsberg spring. Differences were found in the δ³H concentration (Fig. 10), indicating different mean water residence times. The Hackelsberg spring has the oldest water (6 TU). The karst spring of Winden obtains its water from another lower catchment area and also shows a different temporal behaviour; for instance, the δ³H values increased after the high water of August 1982.

The catchment area of the seepage springs in the reed zone seems to be in the upper regions of Leithagebirge (level difference about 350 m). This assumption is confirmed by the fact that some springs in higher regions in the area of Eisenstadt also show a δ¹⁸O value of −11.2‰. The relatively large altitude effect of more than 0.4‰ per 100 m resulting from this is somewhat surprising. The reasons for this (different infiltration rates during the year?) have to be investigated.

An estimate of the mean water residence time of the seepage springs by application of an exponential model (Fig. 13) and a Gaussian distribution model gives values of about 100 years. Since the δ³H values of the individual seepage springs differ slightly, the mean residence times also differ.

A summary of the outcome of these investigations reveals that seepage springs in the reed area are supplied by a karst- and/or crack-water system from the highest ranges of Leithagebirge. This system is widely ramified because obviously even the distant Hackelsberg spring receives water from it. The mean residence time is about 100 years. On the basis of this outcome it will be possible to trace subaquatic springs in the open lake by environmental isotope investigations.
4. CONCLUSIONS

In the Neusiedlersee area with its complicated hydrogeological conditions the measurement of environmental isotopes has proved to be a useful instrument in the investigation of interrelationships of groundwater and surface water. The use of this method is aided by the great differences of the surface water and groundwater isotopic composition which is due to a high evaporation rate over the shallow Neusiedlersee. Thus, more information on the mechanism of the so far rather speculatively estimated subterranean inflow to Neusiedlersee is obtained.

At Neusiedlersee’s eastern lake side there is no continuous and homogeneous shallow aquifer. The horizontal groundwater transport and the subterranean inflow to the lake are very small. Therefore, the input of nutrients by groundwater is also negligible.
STUDIES IN THE
UNSATURATED ZONE

(Session II)
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Federal Republic of Germany
ISOTOPIC EVIDENCE OF THE ORIGIN OF GROUNDWATER IN ARID ZONES

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Abstract

ISOTOPIC EVIDENCE OF THE ORIGIN OF GROUNDWATER IN ARID ZONES.

The contribution of different pathways of recharge to the groundwater in the Negev desert, the southern arid part of Israel, is examined by means of isotope and chemical signatures which are imprinted on the waters. In regions covered by sand dunes, with no perennial vegetation cover, it was found that evaporation amounts to about 30%, while 70% of the rainwater infiltrates into the subsurface. In dune areas covered by deep-rooted vegetation, all water flowing into the subsurface may be transpired by the vegetation. In limestone areas, recharge to groundwater is of the order of 2% and is mainly through gravel-filled river beds by flood water. The water from springs and wells in the Eocene limestone terrain conserves the mean isotopic composition of rainfall, with a tendency for enrichment in the heavy isotopes. The salinity of the groundwater is a function of rock dissolution rather than of evaporation. In chalk-built terrains the water flows in solution channels developed along joints in the vicinity of river beds. The tritium content of the water points towards a 'piston-action' model of recharge by floods. A preliminary study of the isotope salinity relations in the runoff from a small watershed has shown that rains which do not pass a certain threshold (2 mm) evaporate totally. Evaporation from surface flows produced by stronger rains is small. Salinity is increased by a factor of two as a result of flushing of salts left behind by previous, totally evaporated rains. All data lead to the conclusion that in arid regions the total quantity of water in local basins is limited. However, base-level basins, such as inter-mountain basins, rift valleys, etc., form a sink into which relatively small quantities from local watersheds flow which may accumulate to substantial quantities that could be used for regional development projects. The Arava rift valley is discussed as a case study.

INTRODUCTION

The study area is part of the Negev region, the arid southern half of Israel (Fig. 1). Elevations range from sea level to 600 m. The average annual precipitation is from 100 to 210 mm, while average temperatures fluctuate between 10 and 26°C
FIG. 1. Landsat images to be used as reference and location maps (processed by Telespazio).
for December and July, respectively. The diurnal temperature variation is about 10–13°C. Class-A pan evaporation is about 2.5 mm/a. Thus, the climate of this area is that of a typical continental desert.

The region consists of carbonate rocks (limestones, dolomites, chalks and marls), partly covered with loess soil and sand dunes.

Hydrogeologically, the region can be described as a system of aquifers, in the following order from top to bottom:

1. Perched water-tables in the alluvium and sands underlain by an impermeable layer consisting of marls, clays or silts;
2. Water-table in the chalky limestones and chalks of Eocene age perched on the marls of Palaeocene age;
3. Regional water-table in the limestones and dolomites of Cenomanian Turonian age;
4. Regional water-table in the alluvial fill of the Arava rift valley;
5. Palaeowater in the Nubian sandstones of Lower Cretaceous age.

This area is sparsely populated, with widely scattered settlements. Since this part is arid, hydrological information is scarce. Thus, in order to acquire a better knowledge of the hydrological regime of this region, without the need of investing large sums in a hydrological data collection network, it was decided in the first research stages to put special emphasis on the hydrochemical aspects of the hydrological cycle and especially on the environmental isotopes, with a view of using them as tracers and indicators for the processes and systems within the hydrological cycle. Preliminary results were reported by Levin et al. [1]. These and subsequent studies [2, 3] have shown that different recharge pathways engender characteristic isotopic compositions which then can be traced into the aquifer systems, thus giving information on the relative importance of different recharge mechanisms. Waters retained in open-pore soils and sands are enriched in heavy isotopes relative to the composition of rain, whereas large regional floods flowing towards the Arava water course and the Mediterranean Sea have depleted isotopic values.

ISOTOPIC COMPOSITION OF PRECIPITATION

Thanks to the use of the self-sealing water sampler [4] the isotopic composition of the rain water of this region is rather well known. Recently, the relationship between the \( ^{18} \text{O} \) and deuterium contents of the rain water brought in by different air mass trajectories has been established [5]. These results show that the span of the isotopic composition data is rather wide and ranges from about \(-8\%\) to \(-1\%\) for \( ^{18} \text{O} \) and from \(-75\%\) to \(-10\%\) for \( ^{2} \text{H} \). The majority of the samples have a deuterium excess of between 10 and 22\%. These samples
have different meteorological histories. Two extreme groups stand out: One group has deuterium excess values of more than 22‰ and is connected with air masses coming mainly from Europe and approaching the region from west to north-west. The other group has deuterium excess values of less than 10‰ and is associated with air masses approaching the region from the south-west. In this group, rather depleted isotopic values are common.

RATE OF INfiltrATION INTO A SAND-Dune Aquifer

The problem of recharge to a sand-dune aquifer in an arid zone has been treated mainly by two approaches. One approach puts emphasis on empirical methods, e.g. measurement of the moisture and isotope ratios in the dunes. The other approach is based on theoretical aspects of the hydrometeorological balance.

The two approaches try, each in its own way, to overcome the problem of scarcity of data on precipitation, evaporation and soil moisture before a rainstorm, and the randomness in space and time. The spatial variation is caused by the spottiness of rainstorms as well as by the highly complicated morphology of the dunes and the varying directions of the slopes. In addition, there is the influence of scattered vegetation which has a profound effect on the overall water balance of the unsaturated zone.

In order to overcome these random factors, a ‘black box’ approach is used, e.g. direct measurement of the outflow (output) in the subsurface of dune-covered areas and its correlation with the average precipitation (input). It is argued that a groundwater system is a well-defined flow measure as it integrates in space and time the random effects of space and time.
One region studied is that of the sand dunes in the Mediterranean coastal plain of the Sinai peninsula, which are about 10–15 m high, covering a layer of sandy loam of about 2–5 m, which in turn overlies a sand and sandstone layer about 20 m thick. These layers overlie a thick clay layer of about 10 m which separates the sand-dune aquifer from a lower sandstone aquifer in which saline water is found (Figs 1, 2).

The flow in the sand-dune aquifer was calculated by applying Darcy’s law, using hydrological parameters obtained from specially drilled observation wells and transmissivity coefficients determined by pumping tests, for which Jacob’s method of interpretation was used. The calculated flow is between 330,000 and 400,000 m³/a for a 1 km wide section of the sea shore. For a dune area of 3 km length an average annual recharge of 110–170 mm has been calculated.

The average multi-annual precipitation in these areas can be obtained by interpolation between the stations of Khan-Yunis and Rafiah (for which long-term observations exist) and was found to be about 200 mm. Thus the multi-annual recharge to a dune aquifer is estimated from hydrological balance considerations to be between 55 and 65% of the precipitation.

Another area studied is that of the sand dunes extending into the north-western Negev, forming the eastern extension of the dunes of Sinai. These dunes overlie palaeosols of the loess type. These soils are semi-permeable and have an infiltration coefficient (f) of 35 mm/h [6, 7]. The loess layer overlies chalks of Eocene age. The dunes are covered by sparse forest vegetation which was planted to stop dune migration.

The dunes are traversed by the wadis of Besor and Nahal Lavan which cut through the sands and loess and expose the chalk layers. No seepage was observed at the sand/chalk boundary during the rainy seasons in any part of the area.

A balance approach cannot be used in this area, so an indirect method of following the displacement rate of a wetting front was applied. The measurement of the humidity in these sand dunes after rainstorms [2] reveals that the wetting front in the sands can be observed quite clearly by using a neutron logger as well as by measuring the stable-isotope content of the humidity in the sand.

After a rainstorm in January 1979 with a precipitation of 30 mm the percentage of the recharge to a depth of about 100 cm was calculated and it was found that a 30 cm thick sand layer was saturated by the rain water [2]. Assuming an increase of 6% in the water content of the sand, which is the effective porosity, about 60% water inflow is obtained.

An alternative approach, giving a lower-limit estimate of the evaporative water loss, uses the enrichment of heavy isotopes in the residue of an evaporating water body by comparing the deuterium and ¹⁸O content of groundwaters with that of the precipitation. Gat and Levy supplied data [8] for waters which drain the sand dunes surrounding the Bardwil coastal ponds. The groundwater outflow from the base of the dunes shows values of δ¹⁸O ~ +0.5‰, to be compared with the
mean input which is estimated at between $\delta^{18}O = -2.5\%$ and $-4.5\%$ (based on spot sampling). Applying a simple Raleigh formula, $\delta = \delta_0 - \epsilon \ln f$ (which is an acceptable approximation for the case of surface waters evaporating into rather dry air), yields an estimate of $f = 0.72 - 0.52$ for the fraction of water left behind. Obviously, some more water could be lost by diffusive or transpiratory mechanisms in which isotopic fractionation does not occur to a significant degree. Thus, a water loss in the range of 25–50% must be considered to be a lower limit for water loss into the ambient atmosphere.

A similar estimate is obtained from a test on irrigation of tomatoes on the sand dunes of Rafiah (Ben-Asher, personal communication) in which 1350 mm of irrigation water was applied by a drip-system. From this, about 70% was 'lost' below the vegetation root zone, since it turned out that only about 30% of this amount was effectively transpired by the plants or evaporated from the sand.

More general estimates of the water balance of the sand dunes in central Israel (average annual precipitation is about 500 mm), needed for planning intensive groundwater exploitation, have given a general relation of $R = 0.81 \times (P - 94)$ [9], where $R$ is recharge (mm) and $P$ is precipitation (mm).

The following is a model which incorporates all the observations and data presented above for the case of sand dunes.

(a) Direct evaporation and transpiration by annual vegetation amounts to 30% of the precipitation; thus, about 70% of the annual precipitation may infiltrate below the root zone of this vegetation.

(b) Rainstorms supplying less than a 'minimum amount' — which is used up by the vegetation and direct evaporation — will not be available for groundwater replenishment. This 'minimum amount' will depend on the type of dune vegetation and on the storability coefficient of the sand. In general, it can be estimated that isolated rainstorms of less than 5 mm, namely those which saturate the sand (storage coefficient = 10%) to less than 50 mm depth, may be lost for groundwater replenishment in a region where annual vegetation exists. As such storms account for about 40% of the precipitation in the central Negev area, one can estimate a priori that groundwater replenishment will not be more than about 60% of the precipitation.

(c) In regions with deep-rooted perennial vegetation, groundwater replenishment will be a function of the amount transpired by this vegetation. If one compares the inland sand dunes with the coastal dunes on the satellite picture, one can see quite clearly the difference in the vegetation cover, which also explains the difference in their replenishment coefficient (Fig. 1). It can be estimated that in areas with perennial vegetation, with a root-zone depth of 1.5 m, a minimum accumulation of 150 mm of rain water is needed for a certain percentage to permeate through the root area and to be able
to replenish the groundwater. In such areas the replenishment may be more or less according to the equation derived by Chana and Zelinger [9],
\[ R = 0.81 \times (P - 94) \]

(d) The general equation for infiltration, suggested for an area like the coastal dunes, is as follows:
\[ R = 0.7 \times P - (\Sigma \tilde{P} + \Sigma \tilde{P}) \]

where \( R \) is replenishment to groundwater (mm), \( P \) is precipitation, \( \tilde{P} \) is precipitation of rainstorms failing to saturate the perennial vegetation root zone, and \( \tilde{P} \) is precipitation of rainstorms failing to saturate the layer below the perennial vegetation root zone.

From work carried out in Saudi Arabia, one estimate by Caro and Eagelson [10] points to an area with an average annual precipitation of 129.8 mm and a recharge of about 14 mm, i.e. about 10%, while an area with an average precipitation of 79.5 mm showed a recharge of about 6 mm, which is approximately 7.6%.

The estimate derived by Dinçer et al. [11], based on tritium profiles in sand dunes, showed an annual precipitation of 89.7 mm and a recharge of 23 mm, i.e. about 25%.

INfiltration Into GROUNDWATER FROM RIVER BEDS

River beds can be divided into three types, which are discussed below.

**Type 1.** River beds with or without gravel overlying a thick loess layer
Because of the low infiltration rate of the loess in these wadis (20–30 mm/h), no deep percolation takes place [6, 7], except in some areas where an artificial dam or natural bottleneck causes the formation of temporal pools. In these places a high water head exists for several hours or days, which may cause a higher infiltration rate, driving the wetted front below the root zone (usually, rain-water penetration does not exceed 0.5 m [12]). Some water can thus reach the underlying highly permeable gravels of an ancient river bed [7]. In cases where this gravel bed overlies the impermeable marls and chalks of Palaeocene or Senonian age, a shallow, thin, perched water-table may exist, such as that found in gravel overlying Palaeocene chalk marls in the Mashash Farm (Fig. 1).

A well (Mashash-2) was sampled on a weekly basis, from June 1980 to May 1981, i.e. throughout the dry summer and into the rainy season of 1980/81. Mashash-2 is located in the gravel fill of the talweg of Wadi Mashash. The evolution of the isotopic composition of the well is shown in Fig. 3. The samples show a steady, relatively depleted isotopic content with just a hint of a positive deviation during the rainy season.
Type 2. River beds containing coarse gravels overlying permeable limestone layers

High infiltration rates (final average infiltration capacity: 300 mm/h [6]) in this area enable deep water percolation (up to 5 m [13]), the major portion (albeit rather small) contributing to the deeper aquifers which are mainly found beneath this flow section. Observations of a well at Nahal Haroa revealed groundwater at a depth in the limestones underneath the alluvium [14].

According to Evenari et al. [15], only about 5% of the precipitation in the upstream area reaches the section of the wadi filled with gravel. Thus, any amount infiltrating into the groundwater will be less than this order of magnitude.

It was shown by Levin et al. [1] that the huge typical desert floods have the same isotope ratios as the surface flow from small catchment areas, indicating that they are activated selectively by the high-intensity rains which overpass a minimum threshold. The salinity of the water of the first flood wave is about a factor of 5 to 10 – higher than the salinity of the rain. The relatively low salinity of the flood water at later stages of the event shows that salt flushing from the surface is not continuous. More data are needed before the values of the flood hydrograph, salinity, precipitation and isotopic graphs can be correlated. Such a correlation might be possible when the planned observation field in the Makhtesh Ramon is operating. Flushing of salts left behind by previous evaporated rain water does not remove all the airborne salts from the surface, as was shown by Nativ et al. [16]. The salt balance is positive, i.e. more salt is brought in by the rains than transported away by the floods.
Thus, it can be concluded that in limestone-built areas in arid regions infiltration into groundwater does not exceed 2% and is probably much less. A general order of magnitude of this value can be deduced from the observation that the springs draining the Eocene limestone plateau of Avdat issue about 500 000 m³/a; when the issue from the rivers is added, a figure of 900 000 m³/a is reached, which for an area of 900 km² with 100 mm average annual precipitation constitutes about 1% of the total precipitation.

The other aquifer in this region, namely that of the Judea limestone of Cenomanian-Turonian age, contains water with 1500 ppm Cl. This seems to be mostly recent water, as it differs markedly from the palaeowater in the Nubian sandstone aquifer of Lower Cretaceous age underlying the Judea limestone aquifer. This water resembles more closely the water in the limestone aquifers on the foothills of the Judean mountains, although a general trend to lower ¹⁸O content, indicating some mixture with palaeowater, can be observed.

Thus is can be concluded that in regional limestone aquifers in arid zones some recharge takes place. Relative to the total amount of precipitation this recharge seems negligible (between 1 and 2%). However, its total volume may be rather high, depending on the drainage network which runs either directly on exposed bedrock or on gravel overlying the bedrock. These findings are quite different from those for the Sinai region built of crystalline rocks where groundwater infiltration was found to reach about 15% [17]. The reasons for this may be due partly to the fact that some of the precipitation in the Sinai highlands is snow, which has a higher infiltration potential, and partly to the nature of rock jointing and fissuring, which allows faster and deeper water percolation to the subsurface.

**Type 3. River beds cutting into chalks**

Although chalks are classified as impermeable, wells were excavated by the ancients into the chalks (mainly of Middle and Lower Eocene age). A detailed survey has shown that permeable conditions may develop in the vicinity of ancient drainage systems. This permeability develops mainly along joints and fissures in the chalks (Fig.4).

Isotopic data — in this case tritium data — have confirmed this general system. The average tritium content of the various water resources in the limestone and chalk aquifers of the region is a function of the depth of the water-table, which is also a measure of the storage capacity of the aquifer. Thus, the average tritium content of Ein Kudeirat, which is the largest spring with a rather stable discharge, is about 5 TU, while that of Ein Avdat is 5 TU. Ein Aeqv, which emerges a little higher from the same layer and which is of a more sporadic nature, has an average tritium content of about 13.5 TU. The same pattern applies to the well of Nizzana, which is located in the chalks near the river bed of Wadi Nizzana. The depth of the water table is about 20 m and its tritium content is
about 12 TU. At the well of Beerotaim, upstream on the same river bed, the
depth of the water table is about 5 m and the tritium content is higher, namely
about 22 TU.

The variations in the tritium content of the various water sources as a
function of time may seem rather chaotic at first (Fig. 5), but a closer examination
and averaging of the periodical tritium content show a general trend which may
help to better understand the hydrogeological regime (Fig. 6).

The time variations are such that the tritium content generally decays during
the months September to December and increases in the spring and summer
months, April to August. After the flood events of December 1979, February/
March 1980 and December 1980, a decrease in tritium content was observed.
This is especially remarkable in the measurement of February 1981 (Fig. 6) where
the water-table in the Nizzana observation well is at a maximum, while the tritium
content, although rising, is still low. In April of the same year the tritium content
is at its maximum, while the water-table starts to decay. The following hydro-
geological model explains these phenomena.

The groundwater in this region flows in solution channels developed along
joints and fissures in the rocks. These solution channels are mostly developed in
the vicinity of rivers and stream channels. The larger and the more ancient a
FIG. 5. Tritium content of water in observation wells.

FIG. 6. Average tritium content of water in observation wells.
system (two features which, in most cases, go together), the more developed are the solution phenomena. It can be assumed that the flow rate in the zone of solution channels is higher than in a region without such channels. This can be confirmed by measuring the salinity of the water found in these rocks which increases with distance from and depth below river channels. It can be assumed that the water in the vicinity of river beds (horizontally and vertically) is younger than the water in areas which are not flushed. Thus, when a rainstorm occurs and the stream channels are flooded, the process of recharge to groundwater starts. This is first a piston-like action on the more ancient water, resulting in a rise in the water-table of the wells. Only in spring (and sometimes only in summer) does the newly recharged water arrive in the groundwater to affect its tritium content.

This hydrogeological model explains some observations made in this region.

(a) The gravel layers in river beds overlying chalk layers were found to be dry, while wells excavated in chalks, which are ordinarily impermeable, were found to contain water. It is interesting to note that the wells of Byzantine times, near the ancient Nabatean-Byzantine towns of Rehovot, Nizzana and Avdat, were excavated in chalks and not in gravel.

(b) In the same area and the same chalk layers, one exploration well (Nizzana) had abundant water (about 20 m³/h), while another well nearby failed. The small quantity of water found in this well was more saline.

(c) Salinity also increases with well depth.

(d) In an experimental spreading of flood water on fields near Kibbutz Revivim during the 1940s, a rise in the water-table in a shallow well drilled into the chalks was observed simultaneously with a rise in salinity (from about 1000 to 2000 ppm Cl).

INfiltration INTO GROUNDWATER DIRECTly FROM OUTCROPS OF LIMESTONE Terrain

Limestone outcrops from small watersheds in the investigated area produced 10–20% of the total rain as runoff [13, 18]. This value is strongly dependent on the nature of the slope and soil, and on rainfall intensity. The threshold amount of rainfall required to initiate runoff is 1.5–3.5 mm [19]. All observations made along road cuts, in caves, etc. show that water infiltration into deep layers and interstitial storage is negligible as the depth of rain-water penetration seems to be only 50–70 cm. However, water penetration is possible mainly through joint systems in the bedrock which develop between stratification planes of rocks. Here the soil moisture content can be more than 30% [20]. The question is whether this water is significant for groundwater recharge or not.
Three factors influence the runoff regime over arid hill slopes [19, 21]:

(a) The structure of the hill-slope surface (the upper part of the slope consists of massive limestone and the lower part of colluvium). The bare bedrock provides high runoff yields while the colluvium has a relatively high water absorption capacity.

(b) The extremely low flow velocity of water sheets (1–3 m/min), which causes a high degree of roughness of the stony environment.

(c) The short duration of the rain events (even rainstorms with more than 20 mm consist of several individual short showers with a few millimetres of rain in each shower). This duration is often shorter than the threshold for runoff generation.

Therefore, runoff generated upslope generally does not reach the surface drainage channel but infiltrates into the upper part of the colluvium. Only the lower part of the slope can contribute to this channel flow. This area consists of 0.5–1.0 m thick loessial sediments covered by a thin layer of gravel. From moisture analysis of soil samples taken from excavations in the bedrock and in the colluvium [20] it seems that the contribution of water to the bedrock is significantly reduced toward the bottom of the slope. The only exception may be in the northern expanses of the slopes where a higher percentage of soil moisture (16%) was found near the bedrock.

The aim of the present investigation was to relate the geochemical and isotope parameters to the flow pattern, and in particular to compare short showers, which engender discontinuous runoff flow, with the more continuous flows which follow from intensive rainstorms.
<table>
<thead>
<tr>
<th>Date</th>
<th>Description</th>
<th>$\delta^{18}O$ (%)</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Cl</th>
<th>SO$_4$</th>
<th>HCO$_3$</th>
<th>T.D.S.</th>
<th>E.F.$^a$</th>
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</thead>
<tbody>
<tr>
<td>28.01.82</td>
<td>Rain (1.9 mm)</td>
<td>-4.12</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
<td>0.02</td>
<td>0.75</td>
<td>0.5</td>
<td>0.4</td>
<td>2.87</td>
<td>–</td>
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<tr>
<td>28.01.82</td>
<td>Runoff from plot A</td>
<td>-4.52</td>
<td>1.7</td>
<td>0.1</td>
<td>0.6</td>
<td>0.10</td>
<td>0.8</td>
<td>0.6</td>
<td>1.2</td>
<td>5.10</td>
<td>1.78</td>
</tr>
<tr>
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<td>Runoff from plot B</td>
<td>-4.31</td>
<td>1.8</td>
<td>0.1</td>
<td>0.6</td>
<td>0.11</td>
<td>0.7</td>
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<td>-4.34</td>
<td>1.9</td>
<td>0.3</td>
<td>0.7</td>
<td>0.08</td>
<td>1.2</td>
<td>0.7</td>
<td>1.3</td>
<td>6.18</td>
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<tr>
<td>05.02.82</td>
<td>Rain (first, 2 mm)</td>
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<td>1.0</td>
<td>0.3</td>
<td>0.3</td>
<td>0.02</td>
<td>1.0(?)</td>
<td>0.5</td>
<td>0.5</td>
<td>3.62</td>
<td>–</td>
</tr>
<tr>
<td>05.02.82</td>
<td>Rain (second, 2 mm)</td>
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<td>0.2</td>
<td>0.2</td>
<td>0.01</td>
<td>0.5</td>
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<td>0.4</td>
<td>2.41</td>
<td>–</td>
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<tr>
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<td>0.8</td>
<td>0.6</td>
<td>1.1</td>
<td>5.08</td>
<td>1.68</td>
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</table>

$^a$ Enrichment factor relative to salinity of rain water.
FIG. 8. Cumulative chemical and $\delta^{18}O$ diagram of rains and runoff from experimental plot (1982-01-28).

FIG. 9. Cumulative chemical and $\delta^{18}O$ diagram of rains and runoff from experimental plot (1982-02-05).
For this purpose, the study plot [19, 21] (Fig. 7), with a total area of 842 m², was subdivided into three sections: A, B and C, with an area of 407, 295 and 140 m², respectively. Section A drains the entire length of the slope, while a retaining wall, which separates sections B and C, enables separate sampling of the runoff from the exposed rock in the upper part of the slope and the colluvial section in the lower part. In the present set of experiments the total runoff from a particular rain event in each section was channelled into a collecting tank and sampled as soon as possible after the storm. Also, rain water was sampled on the hill crest, using a fractional collector which separately samples consecutive portions of 2 mm of rain.

During the 1981/82 season the annual rainfall was 71 mm, with most rainstorms yielding less than 3 mm of precipitation. In spite of the relatively modest total amount of rainfall, nine runoff events were recorded which were activated by rain events ranging from 1.5 to 10 mm/day.

Detailed analyses for two extreme cases were presented, namely the event of 28 January 1982, with 1.9 mm rain, and the major storm of 5 February 1982, with 9 mm rain. The chemical and isotopic data are given in Table I and also plotted on a cumulative combined chemical isotope diagram [22] (Figs 8, 9).

On 28 January 1982 the flow along the slope was not continuous and the runoff from the hill crest was evidently retained in the upper section of the colluvium. This is expressed by the similarity of the chemical data in sections A and B. The salt concentration in section C was higher by a factor of almost two (where the flow continues from crest to bottom, one would expect the water to pick up salinity continually, so that the highest salinity would be expected to be at the very bottom). It is interesting to note from the detailed ionic ratios (Table I) that in section C the chemical composition of rain water is conserved, except for the addition of Ca(HCO₃)₂. The water which drains from the colluvium (sections B and A), on the other hand, shows more significant geochemical changes. Most noticeable is the loss of magnesium, leading to a relative enrichment of sodium. The Ca(HCO₃)₂ is equally enriched in all parts of the hill side.

The runoff event of 5 February 1982 was triggered by a much stronger rainstorm, the evidence for flow continuity being along the entire hill side. This is expressed by the chemical data for the runoff from section A (draining the entire hill side) which is the most saline (Fig. 9). From a comparison of data for section A with those for the divided slopes B and C it is obvious that much of the salinity at the bottom of the hill is contributed from the upper, rocky section of the slope rather than from the lower half. The absolute salinity levels are, however, not very high compared with the rain, indicating the effect of flushing.

Isotopically, the runoff follows the rain composition rather closely; this is in accord with previously reported data for this runoff plot.
The general information to be derived from these data is as follows:

(a) Runoff from small catchments begins after a certain threshold has been passed. (This can also be concluded from the fact that flood samples are of a lighter isotopic composition than the first rain samples (for the first two millimetres).)

(b) Evaporation from rain above the threshold at which runoff from small catchments forms is negligible. Salinity is thus derived from the total evaporation of the first rains below this threshold. Thus, in small catchment basins there is no partial evaporation. However, all the water below the threshold at which runoff forms is lost, either by evaporation (or transpiration, which a priori can be estimated as negligible on the rocky terrain) or by infiltration.

In order to better correlate the evaporation rate and the flushing of salts, more data need to be processed. This is currently being carried out in collaboration with Professor A. Yair, who has been collecting hydrological data on the small experimental catchment basin discussed above [23].

ALLUVIAL BASE-LEVEL BASINS

The main conclusion from the preceding chapters is that in arid regions the water infiltration into aquifers in a carbonate-built province is of the order of a few per cent. In sand-built provinces the infiltration rate may be rather high in cases where there is no vegetation cover. In both provinces the total quantity of water which can be tapped is a function of the spatial spread of the outcrops and the subsurface geological structure. When aquifers are perched on an impermeable layer, there is a thin saturated zone and the extraction possibilities are rather limited. On the other hand, one can see from the isotopic data that surface water flows over carbonate-built provinces are rather high, and the evaporation rates from the flood water are rather small [1]. Thus, it may be concluded that these flood waters should be stored. In most cases this approach is not economical because of the stochastic nature of the flood regime as well as the high evaporation rates from water bodies in arid regions. The optimal solution will thus be to search for subsurface reservoirs into which flood water infiltrates rather quickly. Such conditions may be found in alluvial basins at or near the base-level of the surface drainage systems.

In the Negev, the Arava rift valley forms such a base-level basin (Fig. 1) which collects the floods as well as the groundwater flows from the highlands bordering it. In the valley the subsurface flow is split; part of it flows towards the Dead Sea and part of it towards the Red Sea [3].
The floods emerging from the highlands are spread over alluvial fans built of cobbles and gravel, and infiltrate rather quickly into the subsurface reservoirs built of gravel and sands. These reservoirs receive also the flow from the palaeo-water aquifers of the Nubian Sandstones emerging along the fault faces bordering the rift valley.

In order to be able to discriminate between the different contributors to the rift valley reservoir, cumulative chemical curves containing the isotope ratios have been constructed.

Figure 10 shows that three types of water exist which may be defined as the primary contributors. One is flood water, found in the alluvium of the main wadi draining into the Arava valley (Paran 629). This water contains a lower quantity of salts and is less depleted in isotopic content.
The second water source is from the Upper Nubian sandstone flowing towards this region from the direction of Sinai (Yaalon 3). This water is also of low salinity and depleted in its $^{18}$O and deuterium content (paleowater).

The third water source is that found in sandstones of Palaeozoic age (Timna FB 178). This water is rather saline, but is also depleted in its isotopic content.

Taking these three types as the basic components, an area of triangular shape can be drawn for which the ratio of mixture of these three components can be roughly estimated. Such an estimate gives an additional parameter for the calculation of the hydrological balance of the alluvial aquifer of the Arava rift valley.

REFERENCES


EFFECT OF CLIMATE AND VEGETATION ON OXYGEN-18 AND DEUTERIUM PROFILES IN SOILS

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Abstract

EFFECT OF CLIMATE AND VEGETATION ON OXYGEN-18 AND DEUTERIUM PROFILES IN SOILS.

The processes by which isotope fractionation occurs within the unsaturated zone are reviewed. Fractionation of soil water by vegetation transpiring under semi-arid conditions is investigated and it is shown that when the soil becomes very dry, enrichment of $^{18}$O occurs, but deuterium in the soil water is depleted. This effect can be explained on the basis of the decomposition of root material. Little evidence for a genuine fractionation effect occasioned by vapour transport to roots is seen. Laboratory experiments in which water loss was either by evapotranspiration or by evaporation alone show that the depth $\delta$-value profiles have a shape similar to that observed in steady-state experiments, but the part of the profile beneath the maximum is described by a complementary error function rather than an exponential function. At the present level of development of theory, only the depth of the maximum is useful for determining the evaporation rate from the $\delta$-value profiles. When vegetation is present, the zone of enrichment extends deeper, owing to the lower rate of evaporation from the soil surface. However, the mean $\delta$-value for soil water is more positive when no vegetation is present, since, in this case, more water is held in the zone subject to enrichment. In studying isotope profiles over a climatic transect where mean annual rainfall varies between 100 and 710 mm (and recharge between ~1 and 150 mm yr$^{-1}$), an approximately linear relationship is found between the delta-value displacement of soil water at depth from the meteoric line and the inverse of the square root of recharge. Such a relationship is predicted by a simple model.

1. INTRODUCTION

Many workers have studied the relationship between the isotopic composition of groundwater and that of rainfall. This has been used to obtain information on both the source of water and its mode of recharge.

However, studies of groundwater bodies underlying areas where local recharge is known to occur have shown that,
depending on circumstances, groundwater can be enriched [1], unmodified [2] or depleted [3] with respect to rainfall. Selection of rainfall events as well as various evaporative mechanisms have been used to explain these effects.

Although much of the modification of the isotopic composition of rainfall is likely to take place in the unsaturated zone, relatively few studies have been made of the changes in isotopic composition which occur as rainfall percolates through this zone. The topic was first discussed in detail by Gat and Tzur [4], who reviewed the processes which might take place.

Many previous studies of groundwater bodies have shown that the wide fluctuations in the δ-values of rainfall are considerably smoothed by the time the water reaches the water table. This is well demonstrated by studies of water draining from lysimeters [5]. However, in areas of relatively high recharge and where the materials have low water-holding capacity (e.g. sand), the effects of diffusion and mixing are minimised and the seasonal variations in the isotopic composition of precipitation can still be identified [6]. For decreased recharge flux or for materials in the unsaturated zone which hold more water per unit depth, diffusion will be more important and seasonal fluctuations will be diminished.

In one of the early studies of the isotopic behaviour of water in the unsaturated zone, Zimmermann et al. [2] found that soil water beneath a bare soil plot had a δD value about 10‰ higher than that beneath an adjacent grassed plot. They attributed this enrichment to direct evaporation being more important for the bare soil. Their work suggested that transpiration was non-fractionating and this hypothesis was supported by a laboratory experiment where plants were grown in (presumably) aqua-culture. After 50% of the water had been transpired, no fractionation was observed in the water which remained.

In line with Zimmermann et al.’s [2] observations, lysimeter experiments in areas with non-arid climates [5] showed that the isotopic composition of the percolate was influenced by land use, but the effect was small. This suggests that in such climates selective infiltration of rainfall is as important as any fractionation effects. However, while this holds for non-arid areas, in more arid climates the generally drier soils and less frequent rainfall may make fractionation processes more important. Also, when plants are under water stress, in contrast to the conditions used by Zimmermann et al. [2], there is a possibility that fractionation might occur at the root/soil interface.

Dincer et al. [7] and Barnes and Allison [8] showed that strong fractionation can occur near the surface in the unsaturated zone of arid areas. Much smaller fractionation has
been observed for isotope profiles measured in the United Kingdom [9].

Zimmermann et al. [2] developed a model to describe isotope profiles which develop under steady-state conditions in a saturated soil subject to evaporation. Münich et al. [10] and CSIRO studies [11-13] have extended their approach to the unsaturated zone. The effects of both temperature gradients and vapour movement have now been incorporated in these models, and good agreement between theory and experiment for evaporation under steady-state conditions has been obtained [10,12]. Problems concerned with the effect on isotope profiles of removal of water by plant roots have been discussed briefly [11], but no detailed studies were performed. Gat and Tzur [4] observed a small enrichment in lysimeter percolate and, as this appeared to occur along a $\delta_{18}^D$-$\delta_{18}^O$ line of slope 8, they postulated that vapour movement may have been responsible.

In this paper we discuss fractionation processes which occur in the root zone of vegetation grown under conditions simulating those of the arid zone. Secondly, we use laboratory data to show how evaporation and transpiration can be partitioned using isotope profiles. Thirdly, as real soils are subject to both diurnal and annual temperature cycles, the possible effect of such temperature fluctuations on isotope profiles is discussed. Fourthly, stable-isotope data from field samples taken over a wide climatic transect are given and the possibility of using isotope profiles for recharge estimation is discussed.

2. ANALYTICAL TECHNIQUES

Soil water was removed from soil samples (from which visible root materials had been removed) by azeotropic distillation with toluene. Traces of toluene (which interfere with oxygen-18 analysis) were removed by warming the samples in sealed containers with low-melting-point hydrocarbon wax (R.M. Brown, unpublished work). Oxygen-18 was analysed as CO$_2$ using the Epstein-Mayeda technique [14] and deuterium by reduction of 15 mg of water by uranium metal at 800°C. The mass spectrometer used was a VG Micromass 602D. Results are reported as $\delta$-values in parts per million relative to V-SMOW.

3. FRACTIONATION DURING TRANSPERSION

In the experiment carried out by Zimmermann et al. [2] to test for fractionation during root uptake of water, only 50% of the available water was used. However, in many field situations a much greater fraction of the water present may be used and the water may be removed from the soil under much higher suctions. For example, for sandy materials, the gravimetric water content
(θ) at field capacity may be ~0.1 while that at wilting point may be as low as 0.01, representing a ten-fold depletion of the soil water store. The relative loss from a clay soil is not as great, for instance from 0.35 at field capacity to 0.20 at wilting point.

3.1. Experimental

Wheat and sunflower were grown in naturally occurring sand, low in organic matter. For wheat, 4-6 plants were grown in 500 ml heavy-walled plastic containers filled with sand. The plants were allowed to germinate and grow under optimum water content for plant growth. When the plants were about 200 mm high, the pots were flushed with nutrient solution of known isotopic composition and allowed to drain for a short time. The drainage holes at the bottom of the pots were then sealed and the soil surface covered with 5-10 mm of a soft hydrocarbon wax which also sealed around the stems. Controls showed that this seal prevented any evaporation. The plants were allowed to grow until the available soil water was used and the plants died, usually about 4 weeks after sealing. To ensure that the root zone did not become anoxic, oxygen was injected into the pots twice weekly. In the period between sealing the pots and for about 6 weeks after death of the plants, pots were taken at random, the sand removed from the roots and the soil water extracted and analysed for $^{18}$O and D. Two separate experiments were run using sunflowers growing in the same soil type as the wheat but using glass pots with one sunflower per pot. The sunflower stem was sealed in the metal lid with a pliable epoxy. The soil was sampled in the same way as for the wheat pots. To check that there were no experimental artifacts which might modify the isotopic composition of the soil, controls having a low gravimetric water content of ~0.03 were sampled throughout the experiments. No change in isotopic composition was observed.

3.2. Results and Discussion

For the three experiments described here, the initial values of $θ$ were between 0.2 and 0.3. Final water contents were 0.005-$θ_0$, thus the volume reduction of soil water was greater than 10-fold. For the three experiments, $δ^0$ and $δ^{18}$ values are shown plotted against $θ$ in Fig.1. All experiments show similar features, namely, as the soil dries, the $δ^0$ values decrease and the $δ^{18}$ values increase. The most likely explanation for this unexpected phenomenon is that it results from breakdown of the roots and exudates by bacteria to water and CO$_2$. Ferhi and Letolle [15] showed that $δ^{18}$ values for plant material for C3 plants ranged between +25 and +30$%_o$, and
FIG. 1. Relationship between $\delta_{D}$ and $\delta_{18}$ and gravimetric water content, showing the presumed effect of decomposition of root material. The solid lines show the time course of $\delta$-values during the experiment.

Ziegler et al. [16] showed that $\delta_{D}$ values for C3 plants ranged between -120 and -140°/oo. Climate and isotopic composition of feed water appeared to have little effect on these values. The isotopic composition of the oxygen injected into the pots was not measured, but is expected to be the same as that in air (+23.5°/oo), which is about the same as that in plant material. These values are consistent with the hypothesis that the change in $\delta$-values of the soil water is due to breakdown of the organic material in the soil. Assuming that the $\Theta_g$ of the soil is known and that the isotopic composition of water produced from plant material is -120°/oo and +25°/oo for $\delta_{D}$ and $\delta_{18}$, respectively, the approximate amount of water produced by decomposition can be calculated. In making such a calculation, it must be assumed that the breakdown of the organic matter is non-fractionating.
For the experiment, the results of which are given in Fig. 1b, the initial $\delta_D$ and $\delta_{18}$ values for the soil water were $-32^\circ$ and $-5.1^\circ$ respectively. At the end of the experiment, these changed by $8^\circ$ and $1^\circ$ respectively. At this time, $\theta_g$ was $\sim 0.005$, which is equivalent to 3 g of soil water in the pot. Using these data, it can be calculated that the amount of water produced by the decomposition is $\sim$0.3 g per pot (9% of the soil water) using deuterium or $\sim$0.1 g (3% of the soil water) using oxygen-18. The total amount of organic material present in the root zone on death of the plants is likely to be about equal to that in the top, i.e. $\sim$2 g (K. Martin, priv. comm.). Thus the change in $\delta_D$ values suggests that about 25% of the organic material in the root zone had broken down to water and CO$_2$ following death of the plants. The discrepancy between estimates made using $\delta_D$ and $\delta_{18}$ may be, in part, explained by equilibration between the CO$_2$ produced by decomposition and the soil water.

The original aim of these experiments was to test for the presence or otherwise of fractionation during transpiration at low water contents. In the experiments performed, only one (b) showed any evidence of fractionation due to transpiration. As Figure 1 shows, there is a slight tendency for the $\delta_D$ values to increase just below a gravimetric water content of $\sim$0.1. If real, this is likely to be a result of vapour-phase movement to the roots. However, this effect is little greater than experimental error and is dominated by breakdown of root material as the water content decreases.

Neither the effect of breakdown of organic material in the root zone nor possible enrichment during transpiration described here are likely to be of real importance in hydrologic studies as it is likely that rainfall variability, selection of rainfall events, and enrichment due to evaporation will dominate. Also, these effects will only be observable in soils with very low water contents at wilting point. However, both effects are worthy of further study. The rate of breakdown of organic materials in soil is of considerable interest [17] and the rate of change of $\delta_D$ or $\delta_{18}$ may give an indication of this. The presence or otherwise of vapour-phase movement to roots has been the subject of considerable debate [18]. It has been suggested that isotope profiles can be interpreted to suggest the presence of vapour movement to roots [19] and studies such as these, especially on the relationship between $\delta_D$ and $\delta_{18}$, may give some insight into the processes occurring.

4. EFFECT OF VEGETATION ON ISOTOPE PROFILES

Early work by Zimmermann et al. [2] and Sauzay [5] has shown that in areas where local recharge occurs the isotope composition of soil water at depth can be dependent on the
presence or otherwise of vegetation as well as vegetation type. This work was carried out in areas which were non-arid, and to test for the effect of vegetation on isotope profiles in arid areas the following laboratory experiment was carried out.

4.1. Experimental

Twelve pots, 1.8-2 m in length and 150 mm in diameter, were packed to a bulk density of 1.05 with a 70:30 mixture of sand and particles of expanded shale, 1-3 mm in diameter, the latter being added to allow deep root penetration. The volumetric water content was approximately 0.12 when the pots were freely drained and <0.005 when they were air-dry.

Four wheat plants were grown in each of eight of the twelve pots, the other four being left unplanted, and when the plants were established, water having an isotopic composition of δD=-22°/oo and δ18O=-4.2°/oo was flushed through all 12 pots. They were then allowed to drain for 48 hours before being sealed at the bottom. The pots were then sampled at four intervals, three pots at each time (2 wheat and 1 unplanted), over a period of about 6 months. Over this period, temperatures were always approximately uniform with depth, although temperatures increased from 16°C to 22°C during the growing period. Soil samples were taken at 50 mm depth intervals and θe, δD, and δ18O estimated as before. The pots were weighed intermittently to estimate the loss of water by evaporation, although with the large weight of the pots there are problems of sensitivity for small water losses.

4.2. Results and Discussion

The isotope and water content profiles at the four sampling times are shown in Fig. 2. Both δD and δ18O were measured and, as the profiles were similar for both isotopes, only δD profiles are reported here. As expected, the position of the maximum in the isotope profile, zef, moves to greater depths as evaporation proceeds. The depth zef corresponds approximately to the position in the profile above which vapour movement dominates and below which liquid movement dominates [11]. From zef it is possible to calculate the instantaneous evaporation rates, E, using the following equation derived from eqs (10), (12) and (13) of ref. [11].

\[ E = \left(1-h_a\right) \frac{N_{sat} \times \tau \times B^v (p - \theta_v)}{(p_{sat} \times \tau \times B^v)} \]  

where \( h_a \) is the relative humidity of the free air, \( N_{sat} \) is the saturated vapour pressure of air, \( B^v \) the diffusivity \( \tau \), the tortuosity, assumed to be 0.67 [20], \( p - \theta_v \) the difference between total porosity and volumetric water content estimated at 0.59 for this study, and \( p \) the density of
FIG. 2. Depth profiles of $S_0$ and volumetric water content $\theta$, for laboratory pots, both bare and planted with wheat.
<table>
<thead>
<tr>
<th>Time (days)</th>
<th>z_{ef} from δ_{18}O profile (mm)</th>
<th>Column temp. (°C)</th>
<th>( E ) (mm·day^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>By fitting an exponential isotope profile beneath ( z_{ef} ) From ( z_{ef} ) From weights</td>
</tr>
<tr>
<td>49</td>
<td>50</td>
<td>16</td>
<td>0.35</td>
</tr>
<tr>
<td>73</td>
<td>80</td>
<td>16</td>
<td>0.22</td>
</tr>
<tr>
<td>128</td>
<td>110</td>
<td>18</td>
<td>0.17</td>
</tr>
<tr>
<td>182</td>
<td>150</td>
<td>22</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>For pots with wheat</td>
</tr>
<tr>
<td>49</td>
<td>75</td>
<td>16</td>
<td>0.23</td>
</tr>
<tr>
<td>73</td>
<td>200</td>
<td>16</td>
<td>0.08</td>
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<tr>
<td>128</td>
<td>200</td>
<td>16</td>
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<td>*</td>
<td>150</td>
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<td></td>
<td>275</td>
<td>22</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>22</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* Plants died between 128 and 182 days.

liquid water. The estimates of \( E \) for the 12 pots are given in Table I.

These estimates are necessarily approximate, as sampling intensity around the maximum in the isotope profile was insufficient to estimate \( z_{ef} \) with precision. However, there is good agreement between measured and observed evaporation rates for the bare soils, especially when the difficulty of weighing a 100 kg soil pot to within a few grams is considered.

For the pots with wheat, most of the water is removed by transpiration, but the isotope profiles are developed because of evaporation through the soil surface. The evaporation rate can then be estimated from \( z_{ef} \) as for bare soil. Hence it is possible to separate evaporation rate from the soil surface from the total evapotranspiration flux.
Methods which rely on change of water content with time or change in weight (lysimeter studies) can only estimate total evapotranspiration flux.

Water-content profiles have sometimes been used to estimate the thickness (z_{et}) of the layer through which vapour transport occurs. However, comparison of the water content and isotope profiles shows that this technique is unsatisfactory, at least for the examples given here. The position of the maximum in the isotope profile (δ_{i}^{max}) may be marginally affected by the isotopic composition of the atmosphere; but in most cases this will be a second-order effect and can be corrected for if necessary.

The broadening of the isotope peak occurs over a zone in which both liquid and vapour movement occur [13]. It increases in width as the average water content decreases and movement in the vapour phase becomes more significant. Thus, in the pots with wheat where the water contents are generally lower, the peaks are much broader than in the pots without plants (Fig. 2).

It can also be shown theoretically that the effect of a combined liquid and vapour movement region is to lower the peak maximum. Hence, the wheat pots with lower water contents also have lower peaks, i.e. the broader the peak the lower the maximum.

Under steady-state conditions, ignoring regions of simultaneous liquid and vapour flow, eqns (13) and (18) of ref. [11] can be combined as eq(2) to give the maximum δ value,

$$\delta_{i}^{\text{max}} = a_{i}^{*} \delta_{i}^{a} + \varepsilon_{i}^{*} + \left\{ \eta_{i} (1+\delta_{i}^{\text{res}}) + (\delta_{i}^{\text{res}} - \delta_{i}^{a}) \right\} (1-h_{a})$$

(2)

which is independent of depth. In this equation, $\alpha_{i}^{*}$ is the equilibrium fractionation factor (=$1-\varepsilon_{i}^{*}$), $\delta_{i}^{a}$ is the isotope composition of water vapour in the free atmosphere, $\eta_{i}$ is the diffusion ratio excess [11] and $\delta_{i}^{\text{res}}$ is the isotopic composition of soil water at depth. Substituting the values $\delta_{i}^{a}=-100^\circ/\text{o}_o$, $\delta_{i}^{\text{res}}=-22^\circ/\text{o}_o$, $\eta_{i}=24.9^\circ/\text{o}_o$, $\varepsilon_{i}=70.0^\circ/\text{o}_o$ and $h_{a}=0.5$, appropriate to the conditions of the experiment, a value $\delta_{i}^{\text{max}}=23^\circ/\text{o}_o$ is obtained for $\delta_{i}^{\text{max}}$. This compares well with values of 15-20^\circ/\text{o}_o observed for the bare pots, where the isotope peaks are not severely broadened by vapour movement. These results, however, should be interpreted with care, as the pots cannot be regarded as having been under steady-state conditions.

Münich et al. [10] suggested that in the non-steady state, the downward movement of the drying front as evaporation proceeded was equivalent to a stationary evaporating front with water moving at the velocity of the drying front. However, in their model, as there is no upward flux of water, there is no longer a balance between the upward evaporative flux and the
downward diffusive flux. In this case, it can be shown that the distribution of isotopes in the zone where liquid-water movement dominates is no longer exponential but has a complementary error function form. Initial work suggests that a procedure for estimating evaporation rate, analogous to that for steady evaporation from a water table [2,21], will be difficult for non-steady-state conditions as the upward flux of water varies with depth. As a result, even though the isotope profiles can be forced to give a reasonable fit to the exponential form of Eq. (21) of [11] (see also [13] if redistribution of isotopes in the vapour phase is important), the estimates of $E$ given in Table 1 do not agree with those made using $z_{eq}$. Because of the large change in volume of a given quantity of water in going from the liquid to the vapour phase (cf. [22]), the depth of the evaporating front will reflect accurately the instantaneous rate of evaporation. An alternative approach which shows some promise is based on the observation that the total amount of isotope enrichment for a drying profile increases approximately proportionally with the square root of time and with cumulative evaporation (see Section 6).

4.3. Deuterium - Oxygen-18 Slopes

As the thickness of the dry layer increases with time, so does the path length for diffusion of water vapour generated at the evaporating front. As shown previously [10,11], this leads to an increase in the importance of kinetic fractionation. Because no separation of isotopes is expected during diffusion in the liquid phase [11], a $\delta_D - \delta_{18}$ slope characteristic of the conditions of evaporation at the evaporating front should be observed in soil water beneath the evaporating front. As the slope of the $\delta_D - \delta_{18}$ line is dominated by the isotopic composition near the evaporating front, the fact that the columns were not evaporating under steady-state conditions should not have a very great effect on the slope of the line. For both the bare and the planted pots the slope of the $\delta_D - \delta_{18}$ relationship decreases with time. For the bare pots the slopes at the four sampling times were 3.5, 3.1, 3.0 and 2.7. There was little difference between the bare and planted pots.

The conditions under which these isotope profiles developed were chosen to be representative of an arid environment. The amount of isotopic enrichment occurring in such an environment will be reflected in the isotope concentrations of water which percolates deep into the soil profile, as discussed in Section 6.

5. THE EFFECT OF TEMPERATURE FLUCTUATIONS ON ISOTOPE PROFILES

Although there were small long-term temperature changes in the laboratory pots described in the previous section, no
temperature gradients were observed. In field soils, both diurnal and seasonal changes occur with depth. Diurnal temperature changes almost disappear at a depth of 300 mm and seasonal ones at about 6 m [23]. Under steady-state conditions the time constant for establishment of isotope profiles for all but the most rapid rates of evaporation is several days or longer, and the shape of the isotope profile will be a function of the mean daily temperature. The main effect of changing temperature is on the magnitude of the isotope peak [13].

For lower evaporation rates, where the characteristic time for development of the isotope profile (diffusivity/δ²) is of the order of one year, there will be interaction between the isotope and temperature profiles, causing δ¹⁸ to change with temperature owing to the temperature dependence of ε¹⁸. Kinetic fractionation (determined by η) is insensitive to temperature and because of its relatively greater importance for oxygen-18, it is expected that the δ¹⁸ profile will be less sensitive to temperature fluctuations than the δ¹⁰ profile. For profiles having a very low rate of evaporation and a characteristic time of several years, the isotope profile will again be controlled by some average temperature.

6. INTERPRETATION OF ISOPOTE PROFILES IN THE FIELD

In this section we give examples of δ¹⁰-δ¹⁸ relationships for soil water collected from the unsaturated zone at four sites having similar soil types in southern Australia. The mean annual rainfall at these sites varies between 100 and 710 mm. The isotope profiles observed all show features similar to those seen in the experiments described in Section 4. However, if sampling takes place a short period after rain, the top part of the profile will be considerably distorted by the rainfall [19]. If sampling takes place towards the end of the dry period (i.e. summer in southern Australia), no such problem exists. Profiles in field soils often show a slight minimum some distance beneath the maximum [19,24] and some variations in the δ-values beneath the minimum (although much damped compared with the variations in isotopic composition of the rainfall). The surface minimum is not present when the water content is sufficiently high near the surface.

The minimum at depth in the isotope profile can be explained by assuming that evaporation proceeds under non-isothermal conditions where the soil temperature at depth is lower than at the evaporating surface [13]. This is the condition prevailing during summer when most evaporation takes place.

Fig. 3 shows δ¹⁸ and δ¹⁰ depth profiles at one of the four sites, a deep sand profile at Gawler, 25 km north of Adelaide, having a mean rainfall of 480 mm·a⁻¹. The general shape is
FIG. 3. Depth profiles of $\delta_{18}$ and $\delta_D$ for a deep sand at Gawler, 25 km north of Adelaide.

typical for a summer profile (i.e. not influenced by recent rainfall) for all sites which we have sampled (about 20 in all, of which four are reported here). We find that for sites with differing rainfall and lithology, the general shape of the profile remains the same. This constancy may result from the fact that the relevant diffusivities which control the shape of the profile only vary slowly with changes in water content and soil parameters. This suggests that the parameters which determine the movement of isotopes may be more robust than those used for determining water movement directly; hydraulic conductivity typically varies over orders of magnitude for the changes in water content observed in the field.

In Fig. 4, $\delta_{18}$ and $\delta_D$ data for the four representative sites are plotted in $^{18}O$-$D$ space. These data are only for that portion of the profiles in which liquid movement dominates (i.e. beneath the near-surface maximum). At all sites the data fall into two classes. Firstly, the near-surface data - i.e. those in the approximately exponential part of the profile - fall on a line of low slope. As discussed in Section 4, this low slope is consistent with soil water having been evaporated through a static boundary layer [10,11]. Secondly, the data from greater depths in the profile all fall to the right of the local meteoric line, but on a line which is approximately parallel to it. This phenomenon has been observed by us before [8].
FIG. 4. \( \delta_D - \delta_{18} \) relationships for four sites in southern Australia having varying rainfall and recharge.
The explanation we offer is as follows. The composition of the source rainfall for the near-surface enrichment, the $\Delta_D$ and $\Delta_{18}O$ values for which fall on AB in Fig. 4b, is represented by A. If this enriched water is displaced downwards by a subsequent rainfall event of sufficient magnitude to remove it from the influence of evaporation, the composition of this parcel of water will now be represented by C. Because water content is usually higher at depth than near the surface, it will be concentrated into a smaller depth interval. For a subsequent rainfall event with an isotopic composition different from A, enrichment would proceed along a line almost parallel to AB. A following recharge event would then displace this enriched water, and the composition of this displaced water will fall on a line through C and parallel to the meteoric water line. In this way we expect that the soil water at depth (the recharge water) will fall on a line of a slope equal to the meteoric line, but displaced from it.

The amount of this displacement is determined by a balance between the isotopic enrichment attained in the upper layers of the soil and the dilution of this by rainfall. At sites where the rainfall (and hence recharge) is low, dilution will be minimised and the change in isotopic composition of soil water at depth (which becomes local recharge) will be maximised.

An attempt to quantify this effect is given by the following very simplified conceptual model.

For a uniform soil exposed to constant evaporative demand, cumulative evaporation will increase linearly with \( \sqrt{\text{time}} \) from the last rainfall event [25]. The enrichment of isotopes ($\Delta_D$ or $\Delta_{18}O$) can also be shown to be proportional to $\sqrt{\text{time}}$ from the last rainfall event. If there are $n$ rainfall events per annum, each having a constant amount of rainfall per event, the time between each event will be $1/n$ year. The total production of isotope excess is then proportional to $n \times \Delta$ isotope enrichment at the end of each period, i.e. total production is proportional to $n \times 1/\sqrt{n} = \sqrt{n}$. The shift of isotope delta value is proportional to total isotope production divided by total recharge (which is proportional to the number of rainfall events), i.e. the $\Delta$-value shift $\propto \sqrt{n}/n = 1/\sqrt{n} \propto 1/\sqrt{\text{recharge}}$.

Although obviously extremely crude, this simple model provides a conceptual framework for investigating the relationship between isotopic enrichment and recharge. Estimates of recharge, obtained using either natural chloride or tritium, for the 4 sites for which isotope data are displayed in Fig.4 are given in that figure. For the conceptual model developed here to be valid, there should be a linear relationship between the $\Delta_D$ shift between rainfall and soil water at depth and the inverse of the square root of mean annual recharge. Fig. 5 suggests that this is so, although it must be stressed that this is for one soil type only (deep sand) and the slope of the
relationship may be expected to vary for different types of soils.

If this technique does have general validity, it appears to be insensitive to changes in mean annual recharge rate greater than about 10 mm per year. However, if validated, it may be useful to estimate recharge at arid sites with recharge rates lower than this.

The extent of the δ-values along the line parallel to the meteoric line (Fig. 4) gives an indication of the isotopic composition of rainfall events which bring about recharge. As expected, the range of δ-values increases as the climate becomes more arid.

The precipitation-weighted mean isotopic composition for the nearest available rainfall collection station is shown as a circle on the meteoric lines in Fig. 4 [26]. For sites (a) and (b), the two least arid sites, the source waters for events giving rise to recharge are scattered around the mean value. However, for the two more arid sites, all of the recharge events are more depleted than the mean rainfall, indicating a strong bias towards rainfall events very depleted in $^{18}O$ and D, in agreement with the observation that the most intense rainfall events are the most depleted [27]. Recharge at site (c) is higher than expected for this arid site because it is situated in a depression and runoff is known to occur from the surrounding area.
7. CONCLUSIONS

(i) For the soils and plant species used here, we have shown that little, if any, fractionation of soil water occurs during water uptake by roots. However, decomposition of organic material under very dry conditions may modify the isotopic composition of soil water. We have not excluded the possibility that plant species adapted to survival in arid zones may, because of their ability to extract water from the soil under very high suctions, be able to induce vapour movement to roots and hence bring about fractionation of soil water.

(ii) Laboratory data for wheat growing in pots show that it is possible to partition evaporation from the total evapotranspiration flux in the laboratory by determining the thickness of the dry surface layer using isotope profiles. This method is applicable in the field for estimating actual evaporation rates from the soil.

(iii) Periodically varying temperatures will not affect the form of the isotope profiles greatly, except when the period is similar to the characteristic time for establishing the profile. The major effect is on the maximum δ-value.

(iv) Isotope profiles which develop in soils over a wide range of climatic regimes show close similarities. We have developed a simple conceptual model which enables interpretation of the δD-δ18O relationships for such profiles in terms of the rate of local recharge. The model predicts that the isotopic composition of soil water at depth is shifted from the meteoric line by an amount proportional to the inverse of the square root of the recharge rate. With further development and testing, this model may be useful for estimation of low rates of local recharge.

ACKNOWLEDGEMENTS

Mr. J.C. Dighton of CSIRO assisted throughout this work, providing invaluable assistance with sampling and analysis.

REFERENCES


[27] DANSGAARD, W., Stable isotopes in precipitation, Tellus 16 (1964) 436.
ESTIMATION OF WATER TRANSIT TIME IN SOILS UNDER AMAZON FOREST COVER USING VARIATIONS IN $\delta^{18}O$ VALUES

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Abstract

ESTIMATION OF WATER TRANSIT TIME IN SOILS UNDER AMAZON FOREST COVER USING VARIATIONS IN $\delta^{18}O$ VALUES.

The work was carried out at the forest reserve of the Instituto Nacional de Pesquisas da Amazônia, located at km 45 of Manaus, in an area characterized by Amazon vegetation of the 'terra-firme' type. To extract the soil water, four soil-water collecting stations were installed, and in each the porous cups were placed at 15, 25, 50, 80 and 120 cm depth from the soil surface. The rain-water and soil-water samples were collected only weekly for analysis of the $^{18}O$ content. In an attempt to estimate the soil-water transit time using the variation in $^{18}O$ values, a statistical model was used. This model is based on linear regression analysis applied to the values observed for soil water and rain water. From this analysis, regression coefficients are obtained which vary according to time. The values of the coefficients obtained can be adjusted generally, according to a quadratic regression, with the maximum value of the function representing the time in which the best statistical correlation between the observed $^{18}O$ values occurs. The time obtained from these correlations represents the mean time necessary for the water to run from one collecting point to the next.

1. INTRODUCTION

Because of their characteristics, the stable isotopes $^2H$ and $^{18}O$ have been used by several investigators in behaviour studies of the hydrological cycle of the Amazon region. Matsui et al. [1] determined the relative outflow of the rivers Negro and Solimões, forming the Amazon river, using the variation in $^{18}O$ values; Reis et al. [2] used $^2H$ and $^{18}O$ contents in a characterization of waters surrounding the Marajó island.
Salati et al. [3] and Dall'Ollio et al. [4], using $\delta^{18}O$ data, noted that there is important water recycling within the Amazon basin, which confirms the importance of the re-evaporated humidity for the water balance throughout the basin. A comparison of $^{18}O$ data for advective humidity with data for river water disproved the concept of complete condensation of all water vapour entering the basin, as pointed out by Salati et al. [3].

According to calculations, 44% of the advective humidity leaves the basin as water vapour, with an average isotopic composition of $\delta^{18}O = -19.3\%$, depleted by about 7.8% in relation to Atlantic Ocean advective humidity.

Gonçalves [5] studied the transit time of surface waters from rainfall in some hydrographic basins of the Amazon region by observing $\delta^{18}O$ values of river water and rain water. Dall'Ollio [6], Salati et al. [7] and Matsui et al. [8] also used isotope techniques in studies of the hydrological cycle of the Amazon region.

The present work was done on the basis of the research work by Gonçalves [5], to estimate the transit time of water in soils under Amazon forest cover of the 'terra-firme' type, using the variation in $^{18}O$ data for rain water and soil water. This variation is significant for the region, as the water transit time is related with the underground flow rate and, once this is altered, either by deforestation or some other factor, it will interact with the dynamics of the environment.

2. METHODOLOGY

The work was carried out at the forest reserve of the Instituto Nacional de Pesquisas da Amazônia, located at km 45 of the Manaus-Caracaraí road, in an area of the Model Basin near km 14 of ZF-2. The area is characterized by Amazon vegetation of the 'terra-firme' type.

To obtain rain-water samples of the portion reaching the soil (throughfall), either through leaf-dripping or internal precipitation, 30 pluviometers were installed in the forest. Owing to local difficulties, the samples were collected only weekly; about 20% of the total volume in each pluviometer was separated and a sufficient amount of sample taken from the resulting mixture for $^{18}O$ analysis.

To extract the soil water, a method similar to that described by Reichardt et al. [9] was used. Four soil-water collecting stations were installed in the forest, and in each the porous cups were placed at 15, 25, 50, 80 and 120 cm depth from the soil surface. Stations 1 and 2 were installed on relatively even ground, in a soil whose texture was classified as clay, while stations 3 and 4 were placed in the lower part of the area on sandy-clay soil. The difference in level between the higher and lower parts where the stations were installed was about 28 m, the horizontal distance was about 80 m.
Figure 1 is a sketch of the soil-water extraction system. Soil-water samples were collected weekly and a sufficient quantity was taken from each depth for the respective isotope analysis.

The $^{18}$O content of the samples was analysed in accordance with the method of Matsui [10]. The values were expressed as deviations, defined by

$$\delta^{18}O(\%o) = \left( \frac{a - ap}{ap} \right) \times 10^3$$

where $a$ is the $^{18}$O content of the sample and $ap$ is the $^{18}$O content of the international standard sample, SMOW.

3. STATISTICAL MODEL USED TO ESTIMATE THE TRANSIT TIME IN SOIL WATER USING THE VARIATION IN $^{18}$O DATA

In an attempt to estimate the soil-water transit time, using the variation in $^{18}$O values, a table was prepared for each station and each sampling point. This table contained the following information: Column 1 gave a series of $\delta^{18}$O values observed for rain water during the experiments, for layers from 0 to 15 cm depth.
TABLE I. EXAMPLE OF A HYPOTHETIC SITUATION

<table>
<thead>
<tr>
<th>$\delta^{18}O$ (%) of rain water</th>
<th>Transit time (weeks)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>$X_1$</td>
<td>$Y_1$</td>
</tr>
<tr>
<td>$X_2$</td>
<td>$Y_2$</td>
</tr>
<tr>
<td>$X_3$</td>
<td>$Y_3$</td>
</tr>
<tr>
<td>$\ldots$</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>$\ldots$</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>$\ldots$</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>$\ldots$</td>
<td>$Y_{n-1}$</td>
</tr>
<tr>
<td>$X_{n-1}$</td>
<td>$Y_{n-1}$</td>
</tr>
<tr>
<td>$X_n$</td>
<td>$Y_n$</td>
</tr>
</tbody>
</table>

For the next layers, from 15 to 25 cm depth, column 1 showed the respective $\delta^{18}O$ values observed at a collecting point located at 15 cm depth, and similarly for the other layers. Column 2 gave $\delta^{18}O$ values for the first layers (0–15 cm) obtained at a collecting point located at 15 cm depth at time $t = 0$; for the next layers (15–25 cm) the values recorded were those obtained at the collecting point located at 25 cm depth. For the other layers, a similar procedure was applied. Columns 3–6 showed the $\delta^{18}O$ values obtained at the various collecting points at times $t = 1$, $t = 2$, $t = 3$, etc., which are the values for the layers of column 2 obtained at 1, 2, 3, etc. weeks after the first sampling. In this way, a hypothetical situation is generated where the water from one collecting point, characterized by a certain $\delta^{18}O$ value, reaches the next point after 1, 2, 3 or $n$ weeks.

Table I is a schematic listing of $\delta^{18}O$ values and transit times for the first layers (0–15 cm). $X_1$, $X_2$, ..., $X_n$ are $\delta^{18}O$ values obtained for rain water on the 1st, 2nd, ..., nth sampling week. For the next layers (15–25 cm) the values are those noted at sampling points located at 15 cm depth; for the 25–50 cm layers the values are those obtained at 25 cm depth, and so on. $Y_1$, $Y_2$, ..., $Y_n$ are soil-water values for the first layers (0–15 cm) obtained at 15 cm depth on the 1st, 2nd, ..., nth week. For the next layers (15–25 cm) the values are those obtained at 25 cm depth, and similarly for the other layers.
### TABLE II. REGRESSION COEFFICIENTS CORRELATED WITH TRANSIT TIME

<table>
<thead>
<tr>
<th>Time</th>
<th>Regression coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$r_0$</td>
</tr>
<tr>
<td>1</td>
<td>$r_1$</td>
</tr>
<tr>
<td>2</td>
<td>$r_2$</td>
</tr>
<tr>
<td>3</td>
<td>$r_3$</td>
</tr>
<tr>
<td>4</td>
<td>$r_4$</td>
</tr>
</tbody>
</table>

### TABLE III. VARIATION IN $\delta^{18}O$ VALUES ($\%$) OF SOIL WATER OBSERVED FOR STATION 01, AS A FUNCTION OF DEPTH

<table>
<thead>
<tr>
<th>Sampling number</th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$-5.7$</td>
</tr>
<tr>
<td>3</td>
<td>$-4.0$</td>
</tr>
<tr>
<td>4</td>
<td>$-2.5$</td>
</tr>
<tr>
<td>5</td>
<td>$-1.7$</td>
</tr>
<tr>
<td>6</td>
<td>$-2.1$</td>
</tr>
<tr>
<td>7</td>
<td>$-2.2$</td>
</tr>
<tr>
<td>8</td>
<td>$-2.3$</td>
</tr>
<tr>
<td>9</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$-1.7$</td>
</tr>
<tr>
<td>11</td>
<td>$-1.5$</td>
</tr>
<tr>
<td>12</td>
<td>$-1.6$</td>
</tr>
<tr>
<td>13</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>
TABLE IV. VARIATION IN $\delta^{18}$O VALUES (‰) OF SOIL WATER OBSERVED FOR STATION 02, AS A FUNCTION OF DEPTH

<table>
<thead>
<tr>
<th>Sampling number</th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>-6.9</td>
</tr>
<tr>
<td>2</td>
<td>-4.8</td>
</tr>
<tr>
<td>3</td>
<td>-3.8</td>
</tr>
<tr>
<td>4</td>
<td>-2.9</td>
</tr>
<tr>
<td>5</td>
<td>-3.2</td>
</tr>
<tr>
<td>6</td>
<td>-2.5</td>
</tr>
<tr>
<td>7</td>
<td>-1.5</td>
</tr>
<tr>
<td>8</td>
<td>-2.1</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-1.5</td>
</tr>
<tr>
<td>11</td>
<td>-1.6</td>
</tr>
<tr>
<td>12</td>
<td>-1.5</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
</tr>
</tbody>
</table>

Through linear regression analysis applied for the values of the first and other columns, regression coefficients are obtained which vary according to time. These coefficients are correlated with the respective times, and a table can be prepared recording the values for time on the first column and the values for regression coefficients on the second (see Table II). The values of this table can be adjusted generally according to a quadratic regression, with the maximum value of the function (determined through its derivative) representing the time in which the best statistical correlation between the observed $\delta^{18}$O values occurs. The time found represents, therefore, the mean time necessary for the water to run from one collecting point to the next and it can be considered as the mean transit time.

4. RESULTS

The variation in $\delta^{18}$O values observed for the soil water during the sampling period, as a function of different depths and stations, is shown in Tables III—VI.
<table>
<thead>
<tr>
<th>Sampling number</th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>-7.1</td>
</tr>
<tr>
<td>2</td>
<td>-4.8</td>
</tr>
<tr>
<td>3</td>
<td>-3.0</td>
</tr>
<tr>
<td>4</td>
<td>-2.1</td>
</tr>
<tr>
<td>5</td>
<td>-1.8</td>
</tr>
<tr>
<td>6</td>
<td>-1.5</td>
</tr>
<tr>
<td>7</td>
<td>-1.2</td>
</tr>
<tr>
<td>8</td>
<td>-1.9</td>
</tr>
<tr>
<td>9</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-1.1</td>
</tr>
<tr>
<td>11</td>
<td>-1.0</td>
</tr>
<tr>
<td>12</td>
<td>-1.4</td>
</tr>
<tr>
<td>13</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

Table VII gives $\delta^{18}O$ values of rain water and the respective quantities in millimetres. These quantities refer to internal precipitation, i.e. the rain water that actually reaches the forest soil.

As an example of the application of the method of estimating the mean transit time of the soil water, Table VIII gives $\delta^{18}O$ data relating to the soil layers at 15–25 cm depth, observed at sampling station 04.

Through a linear correlation between the $\delta^{18}O$ values of soil water at 15 cm depth and the respective $\delta^{18}O$ values at 25 cm depth at times 0, 1, 2, 3 and 4 weeks, correlation coefficients are obtained which vary according to time. Table IX shows the correlation coefficients as a function of time, obtained for the data of Table VIII.

As can be seen in Fig. 2, the data of Table IX can be adjusted according to a second-degree equation. Figure 2 gives the respective second-degree equation
TABLE VI. VARIATION IN δ¹⁸O VALUES (%o) OF SOIL WATER OBSERVED FOR STATION 04, AS A FUNCTION OF DEPTH

<table>
<thead>
<tr>
<th>Sampling number</th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>-8.3</td>
</tr>
<tr>
<td>2</td>
<td>-4.0</td>
</tr>
<tr>
<td>3</td>
<td>-3.2</td>
</tr>
<tr>
<td>4</td>
<td>-1.9</td>
</tr>
<tr>
<td>5</td>
<td>-1.0</td>
</tr>
<tr>
<td>6</td>
<td>-1.0</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>-2.1</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-1.4</td>
</tr>
<tr>
<td>11</td>
<td>-0.9</td>
</tr>
<tr>
<td>12</td>
<td>-1.7</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
</tr>
</tbody>
</table>

obtained for the 15—25 cm depth layers at station 04 as well as correlation coefficients and mean transit times obtained by this equation.

In accordance with the proposed method, the mean residence time was calculated for the other layers; the results obtained, as a function of depth and sampling station, are shown in Table X. These results, given in days, are cumulative data, representing the mean time the water needs to run from the surface to the respective collecting points.

5. DISCUSSION AND CONCLUSIONS

Comparing the values of Tables III—VI with those of Table X, it can be noted that, within the expected accuracy, the model adopted showed satisfactory results.
TABLE VII. VARIATION IN $\delta^{18}$O VALUES
(%) OF RAIN WATER AND THE
RESPECTIVE QUANTITIES IN MILLIMETRES

<table>
<thead>
<tr>
<th>Sampling number</th>
<th>$\delta^{18}$O</th>
<th>mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-7.9</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>-2.6</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>-3.0</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>-1.7</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>-2.0</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>-1.7</td>
<td>17</td>
</tr>
<tr>
<td>7</td>
<td>-2.5</td>
<td>38</td>
</tr>
<tr>
<td>8</td>
<td>-1.9</td>
<td>17</td>
</tr>
<tr>
<td>9</td>
<td>-0.4</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>-1.2</td>
<td>48</td>
</tr>
<tr>
<td>11</td>
<td>-1.8</td>
<td>41</td>
</tr>
<tr>
<td>12</td>
<td>-1.3</td>
<td>31</td>
</tr>
<tr>
<td>13</td>
<td>-0.7</td>
<td>14</td>
</tr>
</tbody>
</table>

Tables V and VI show that, for stations 03 and 04, and for a $\delta^{18}$O value of $-7.9\%$ (Table VII) for rain water observed in the first week, the soil water showed a relatively immediate response measured at sampling points located at 15 and 25 cm depth, indicating a mean transit time of less than, or of the order of, one week.

As can be seen in Table X, the model applied was effective in estimating for the given stations and depths a mean transit time within a certain range of variability, i.e. less than one week for the layers at 0–15 cm and of the order of one week for the layers at 15–25 cm depth. In accordance with the tables, it can be concluded that the water mass characterized by the $\delta^{18}$O value of $-7.9\%$ (Table VII) in general needed 2 weeks to reach the 50 cm depth, 3–4 weeks to reach the 80 cm depth, and about 5–8 weeks to reach the points located at 120 cm depth. The values of $\delta^{18}$O for the last depth remained at between $-6.4\%$ and $-6.0\%$ at station 03. These results are of the same order of magnitude as those shown in Table X, indicating a reasonable time estimate obtained by the proposed model.
TABLE VIII. $\delta^{18}$O VALUES (%) OF SOIL WATER OBTAINED AT A POINT LOCATED AT 15 cm DEPTH, AT STATION 04, COMPARED WITH VALUES OBTAINED AT 25 cm DEPTH AT ONE-WEEK INTERVALS

<table>
<thead>
<tr>
<th>$\delta^{18}$O of soil water at 15 cm depth</th>
<th>$\delta^{18}$O of soil water at 25 cm depth (one-week intervals)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t=0</td>
</tr>
<tr>
<td>-8.3</td>
<td>-7.7</td>
</tr>
<tr>
<td>-4.0</td>
<td>-5.4</td>
</tr>
<tr>
<td>-3.2</td>
<td>-3.1</td>
</tr>
<tr>
<td>-1.9</td>
<td>-2.3</td>
</tr>
<tr>
<td>-1.0</td>
<td>-1.5</td>
</tr>
<tr>
<td>-1.0</td>
<td>-1.5</td>
</tr>
<tr>
<td>-2.1</td>
<td>-2.1</td>
</tr>
<tr>
<td>-1.4</td>
<td>-1.7</td>
</tr>
<tr>
<td>-0.9</td>
<td>-1.4</td>
</tr>
</tbody>
</table>

FIG. 2. Variation in correlation coefficient as a function of time, in accordance with data for the 15–25 cm depth layers at sampling station 04.
TABLE IX. VARIATION IN CORRELATION COEFFICIENTS AS A FUNCTION OF TIME, OBTAINED FOR THE DATA OF TABLE VIII

<table>
<thead>
<tr>
<th>Time (weeks)</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9727</td>
</tr>
<tr>
<td>1</td>
<td>0.9868</td>
</tr>
<tr>
<td>2</td>
<td>0.8095</td>
</tr>
<tr>
<td>3</td>
<td>0.4377</td>
</tr>
<tr>
<td>4</td>
<td>-0.2985</td>
</tr>
</tbody>
</table>

TABLE X. MEAN CUMULATIVE TRANSIT TIME IN DAYS, AS A FUNCTION OF DEPTH AND SAMPLING STATION

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Sampling station</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>01</td>
</tr>
<tr>
<td>15</td>
<td>9.6</td>
</tr>
<tr>
<td>25</td>
<td>11.9</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>-</td>
</tr>
</tbody>
</table>

Also, comparing the values of Table X with those of Tables III and IV, it is noted that the results for the first layers of fine-textured soil are coherent.

It is believed, however, that the proposed method has been hampered by the sampling interval which, as already mentioned, was of the order of one week. In view of the results obtained, it should be stated that more accurate values could be obtained if the sampling intervals were of the order of days since, as can be seen in Table X, intervals of less than one week have been obtained in general for the first layers.

Another aspect to be considered is the type of soil. The results given in Tables III–VI indicate that the most impressive variations in $\delta^{18}O$ values occurred
in soil of a rough texture; in the soil classified as clay, a mixture of pre-existing waters was found, increasingly deeper down. These differences are mainly due to the different retention capacities shown by the two soils studied. Similar observations for soil water have been made by Brinkmann et al. [11], Vandor et al. [12] and Zimmermann et al. [13].

As a consequence of the mixture of pre-existing waters, no significant correlation between the $\delta^{18}O$ values of soil water at certain depths at stations 01 and 02 has been obtained, as shown in Table X where the mean transit time was estimated for the first layers of the respective stations. For station 04 at 120 cm depth, no result was obtained for the referred time, because of lack of sufficient $\delta^{18}O$ data, as can be seen in Table VI.

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ESTIMATION OF GROUNDWATER RECHARGE AND MOISTURE MOVEMENT IN SANDY FORMATIONS BY TRACING NATURAL OXYGEN-18 AND INJECTED TRITIUM PROFILES IN THE UNSATURATED ZONE

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Abstract

ESTIMATION OF GROUNDWATER RECHARGE AND MOISTURE MOVEMENT IN SANDY FORMATIONS BY TRACING NATURAL OXYGEN-18 AND INJECTED TRITIUM PROFILES IN THE UNSATURATED ZONE.

In the unsaturated zone, $^{18}$O of soil moisture has been found to reflect the seasonal variations of this isotope in precipitation. It has been possible to trace the vertical displacement of $^{18}$O-depleted soil moisture derived from winter precipitation. The temporal shift of the $^{18}$O-depleted moisture has been verified by tracing injected tritium. Tritium and $^{18}$O profiles of soil moisture were obtained from soil coring; tritium profiles were also monitored by the soil-air suction method using molecular sieves. The methods of soil-air suction and laboratory extraction of moisture from the soil cores and the molecular sieves are explained. Rates of soil moisture movement and recharge estimates by these two independent tracers have been compared and the agreement is found to be quite good. It is also shown that $^{18}$O-depleted soil moisture derived from two years' successive snow-melt periods can be used to estimate yearly recharge.

INTRODUCTION

In cold climates the seasonal variations of $^{18}$O in precipitation are expected to be preserved in soil moisture in the unsaturated zone. In Uppsala, Sweden, the summer and winter precipitations differ in their $\delta^{18}$O values by about 6–8‰ (Fig.1), which makes it possible to trace the seasonal $^{18}$O variations in the soil moisture. When snow cover is considerable and snow melt is quick, the infiltrating melt water labels the horizon with isotopically light water and pushes down heavier old moisture derived from the preceding summer precipitation, giving the soil moisture a distinct isotopic profile. Deuterium profiles, probably due to seasonal variations of deuterium in precipitation, have been reported in sand dunes [1].
In the present study, it has been possible to trace the vertical displacements of $^{18}$O-depleted soil moisture derived from winter precipitation. These temporal displacements have been verified by tracing injected tritium, assuming that the movement of soil moisture is layered [2]. Oxygen-18 profiles of soil moisture were obtained from soil cores only, while profiles of tritium were monitored by soil coring and soil-air suction [3]. The use of tritium as an independent tracer of water is already established and has been widely reported [4–6].

Rates of soil-moisture movement and recharge estimates by the tracers $^3$H and $^{18}$O have been compared and found to be in good agreement.

GEOLGY OF THE SITES

Uppsala

This site is situated on the western flank of the Uppsala esker. The area is covered by a shallow deposit of post-glacial sand and fine sand. Underlying the post-glacial deposit is an old Archaean formation of granite. Occasional outcrops of the bedrock occur in the area. The homogeneity of the soil profile in the vertical is disturbed by the occurrence of thin clay lenses at certain depths. The water table at the site is below 3.5 m.
Skediga

The Uppsala esker's north-westerly stretch along a fault line is disturbed by the occurrence of a discontinuous and spread esker portion, north-west of the fault line. The Skediga site is situated on one such formation about 10 km north of Uppsala town. The material in Skediga consists of coarse sand and gravel. The soil profile is layered, coarse sand up to 150 cm depth, followed by a thick clay lens up to 190 cm and fine sand below. The water table in the area varies from 9 to 11 m.

EXPERIMENTAL METHODOLOGY

Tritium injections

Tritium as HTO is injected in 2 m × 2 m plots. For a uniform labelling of soil moisture, HTO is injected in a square grid, the injection points being at 10 cm intervals. A stainless-steel tube (dia. 10 mm) is driven down to 30 cm below the soil surface and then a brass tube (dia. 6 mm) is lowered into the hole and 10 mL HTO (0.5 μCi/mL) is injected by a constant-volume pipetting device attached to the brass tube. The injections were done before the beginning of snow melt.

FIELD SAMPLING OF SOIL MOISTURE

Soil coring

Soil cores, 10 cm long, are taken by a Veihmeyer tube from up to 2–3 m depths. For 18O analysis, corings are done about 5 m away from the edges of the tritium-tagged plots. Soil cores are stored in stainless-steel cans fitted with airtight plastic caps. These samples are stored later in the laboratory in a frozen state before moisture extraction.

Soil-air suction

A probe (Fig.2), consisting of an inner tube with a perforated lower section terminating in a pointed end and an outer tube with a mechanism for covering and uncovering (see inset in Fig.2) the perforated section, is driven into the tritium-tagged plots. The inner and outer tubes are isolated from each other by a rubber O-ring. Once the probe is driven into the soil down to the right depth, the outer tube is lifted by rotating the handle to open the inner perforations.
The inner tube is then connected to a Pyrex glass cylinder containing a 150 g, 4 Å molecular sieve, and soil air is sucked through the sieve by vacuum pumping for about 10 minutes. The vacuum meter is used to check for leakage in the system, and the flow can be regulated by a valve and a flow meter. The moisture-laden molecular sieve-bed is transferred to bottles for later moisture extraction in the laboratory. Before proceeding to the next level, the outer tube is lowered to cover the perforations and the whole tube is again hammered down. This device is well suited for relatively dry soil conditions.

LABORATORY EXTRACTION OF MOISTURE FROM SOIL CORES

For tritium and $^{18}$O analysis, moisture extraction from soil cores is done by vacuum distillation at 50–60°C (Fig.3). Cans containing the soil cores are weighed and placed in desiccation chambers fitted with 55 W disc-shaped
heating elements which are temperature-regulated by a relay. Each desiccation chamber is connected to two glass vapour traps put in series to ensure complete moisture recovery. The glass traps are evacuated before their placement in a cooling chamber containing alcohol and kept at −60°C by a compressor. During evacuation of the traps, the desiccation chambers are kept closed by a valve. About 20 minutes are needed to cool down the traps, and at this stage the chambers are slowly opened and heating is started. About 5 hours are required to remove all moisture from the soil cores. In this set-up, six soil cores can be distilled simultaneously. The weight loss of the cans is checked against the weight gain of the traps. During standardization of the technique, oven-dried soil was mixed with a certain amount of water of known $^{18}$O content. It was observed that the recovery of moisture is almost 100% and practically no fractionation in $^{18}$O occurs during storage and extraction. The same procedure was repeated with oven-dried soil mixed with a certain amount of tritium. No loss of tritium during extraction was observed. It may be mentioned that tritium does not suffer from fractionation effects at the activity level used in the injections. This technique can also be used for extraction of natural tritium from soil cores.

The error in $^{18}$O measurements is ±0.1‰ and the results are expressed as $\delta^{18}$O (SMOW), whereas tritium activity is given in counts/min per millilitre.
MOISTURE EXTRACTION FROM MOLECULAR SIEVES

The moisture-laden molecular sieve-bed is transferred again to Pyrex glass cylinders, five of which can be placed in a specially designed oven maintained at 450°C. The released vapours are collected in traps cooled to −60°C in the same way as for vacuum distillation of soil cores. In this case, the oven replaces the desiccation chambers. It takes about 3 hours to extract all moisture. The last remnants of moisture from the system are driven out by flushing dry nitrogen for about 15 minutes. The theory of molecular sieves and related information has been reported earlier in detail [1, 3]. The present system is an improved version of the previous one [3], as it allows extraction from five samples simultaneously and does away with metal cylinders (as sieve containers) which had a cumbersome system of heating and cooling.

MOISTURE MOVEMENT AND RECHARGE ESTIMATES

The downward movement of soil moisture is determined from the shift of the peak tritium concentration (or its centre of gravity) and, in the case of 18O, from the shift of the mean depth of the isotopically light moisture layer (henceforth called 18O-depleted layer).

If the tritium-tagged layer or the 18O-depleted layer moves from depth \(z_1\) to \(z_2\) in time \(t_1\) to \(t_2\), then

\[
v = \frac{z_2 - z_1}{t_2 - t_1}
\]

where \(v\) is the rate of soil-moisture movement (average particle velocity of water molecules) during the period \(t_1\) to \(t_2\). If \(\theta\) is the average soil moisture (volume fraction) between \(z_1\) and \(z_2\), and \(z_2 - z_1 = \Delta z\) is the corresponding displacement, then recharge during the period is expressed as

\[
R = \theta \cdot \Delta z
\]

RESULTS OF FIELD STUDIES

Uppsala

At the beginning of snow melt, soil moisture in the uppermost layers has a low \(\delta^{18}O\) value, but later the isotopically heavy water from summer rains pushes the lighter moisture deeper down (Fig.4). In July 1982, sampling
FIG. 4. Tritium, $\delta^{18}O$ and soil moisture profiles in Uppsala.

FIG. 5. $\delta^{18}O$ and tritium profiles in Uppsala.
### Table I. Rate of Moisture Movement and Recharge Estimates by Oxygen-18 and Tritium Tagging Methods

<table>
<thead>
<tr>
<th>Location</th>
<th>Time period</th>
<th>Displacement of $^2$H-tagged and $^{18}$O-depleted layers</th>
<th>Average moisture content (vol.%</th>
<th>Rate of moisture movement (particle velocity) (mm/d)</th>
<th>Recharge (mm)</th>
<th>Precipitation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average peak positions (cm)</td>
<td>Shifts (cm)</td>
<td>$^{18}$O $^{2}$H</td>
<td>$^{18}$O $^{2}$H</td>
<td>$^{18}$O $^{2}$H</td>
</tr>
<tr>
<td>U₁</td>
<td>1982-03-12 to 05-04</td>
<td>40–65 35–65</td>
<td>25 30</td>
<td>16.8 17.4</td>
<td>4.7 5.7</td>
<td>42 51</td>
</tr>
<tr>
<td>U₁</td>
<td>1982-05-04 to 07-22</td>
<td>65–110 65–95</td>
<td>45 30</td>
<td>17.3 17.3</td>
<td>5.8 3.9</td>
<td>77 51</td>
</tr>
<tr>
<td>U₁</td>
<td>1982-07-22 to 09-24</td>
<td>110–125 95–115</td>
<td>15 20</td>
<td>10.8 11.5</td>
<td>2.4 3.2</td>
<td>16 23</td>
</tr>
<tr>
<td>U₁</td>
<td>1982-05-04 to 09-24</td>
<td>65–125 65–115</td>
<td>60 55</td>
<td>14.1 15.9</td>
<td>4.3 3.9</td>
<td>85 88</td>
</tr>
<tr>
<td>U₂</td>
<td>1982-07-22 to 09-24</td>
<td>115–155</td>
<td>40</td>
<td>11.2</td>
<td>6.5</td>
<td>45</td>
</tr>
<tr>
<td>U₂</td>
<td>1982-09-24 to 12-12</td>
<td>155–170</td>
<td>15</td>
<td>22.2</td>
<td>1.9</td>
<td>33</td>
</tr>
<tr>
<td>U₂</td>
<td>1982-07-22 to 12-12</td>
<td>115–170</td>
<td>55</td>
<td>23.6</td>
<td>3.8</td>
<td>130</td>
</tr>
<tr>
<td>Skediga</td>
<td>1982-03-28 to 07-23</td>
<td>40–120</td>
<td>80</td>
<td>11.0</td>
<td>6.9</td>
<td>88</td>
</tr>
<tr>
<td>U₁</td>
<td>May 1981 to May 1982</td>
<td>70–235</td>
<td>165</td>
<td>17.0</td>
<td>280</td>
<td>691</td>
</tr>
<tr>
<td>U₂</td>
<td>May 1982 to June 1983</td>
<td>65–190</td>
<td>125</td>
<td>18.5</td>
<td>231</td>
<td>520</td>
</tr>
<tr>
<td>U₂</td>
<td>Summer 1981 to Summer 1982</td>
<td>82–240</td>
<td>160</td>
<td>21.0</td>
<td>336</td>
<td>600</td>
</tr>
</tbody>
</table>
was extended to another plot, U₂, 10 m away from U₁. It is observed that in U₂ (Fig.5(a)) the \(^{18}\)O profiles are well defined and the temporal displacements of the depleted layer could be determined accurately as compared with U₁. The shifts or displacements of tritium-tagged and \(^{18}\)O-depleted layers observed during 1982 (Fig.4) are in good agreement. Tritium profiles are well developed and have a Gaussian distribution pattern. The rates of soil moisture movement are higher just after snow melt, but later on decrease considerably (Table I). Some field variability in moisture content and moisture movement is observed between plots U₁ and U₂.

Skediga

The \(^{18}\)O-depleted layer moved from 40 to 120 cm depth between March and July 1982 (Fig.6(a)), but tritium-tagged moisture found at 80 cm depth in March could not be traced in July (Fig.6(b)). Further, the \(^{18}\)O-depleted layer hardly moved between July and September. It appears that the thick clay lens (note the high moisture content) between 150 and 190 cm depth impedes the vertical flow of moisture and a lateral flow develops. This lateral
flow accounts for the disappearance of the tritium front which was ahead of the $^{18}$O-depleted layer earlier and was probably washed out laterally by the incoming snow melt. Previous studies in this area have also shown a fast movement of tritium in the upper layers, but subsequently the peaks are sustained at about the same level and ultimately disappear.

Soil-air suction and coring — a comparison

A comparison of the tritium concentration distribution obtained by soil-air suction and coring methods is shown in Fig.5(c). The centres of gravity of the distributions are in close agreement, but the total tritium concentration observed by the suction method is lower than that obtained by coring. This may be due to field variability, dilution of tritium activity by atmospheric moisture leaking in during suction in the field, or both.

Estimation of recharge

The estimated recharge values from May to September 1982 (Table I) as obtained from $^{18}$O and tritium tracing are 85 mm and 88 mm, respectively, in Uppsala, $U_1$. Between July and September the recharge at $U_1$ was less than that at $U_2$. In Skedga the recharge during July–September was also small, but just after snow melt, i.e. from March to July, the recharge was about 88 mm.

The active root zone in these areas extends to about 60 cm. Since the tritium peaks and the $^{18}$O-depleted layer had crossed the root zone in May, the yearly recharge was calculated from May onward. A cyclic distribution of $^{18}$O in soil moisture emerges during May 1982 (Fig.4(b)). The first; $^{18}$O-depleted layer (average depth 65 cm) represents the snow melt 1982; the second layer, with high $^{18}$O, is derived from the summer rains 1981. The third layer, which is again depleted in $^{18}$O (average depth 235 cm), is contributed by the snow melt 1981. The total soil water present in between the two $^{18}$O-depleted layers is that which entered the soil after the snow melt 1981 and is the storage or recharge from snow melt 1981 to snow melt 1982. The recharge for this period is 280 mm and precipitation is 691 mm (Table I). Thus, loss by evapotranspiration is 411 mm/a.

The $^{18}$O-depleted layer which was at 65 cm depth in May 1982 was found at 190 cm in June 1983 (Fig.5(b)), showing a 125 cm displacement in one year. Thus, the recharge during 1982–1983 is 231 mm. The precipitation is 520 mm and the loss by evapotranspiration is 299 mm.

One can also trace heavy isotopic inputs from summer rains. For example, the average depth of moisture derived from 1982 summer rains is 80 cm in December 1982 (Fig.5(a)) and the input from summer 1981 is at an average depth of 240 cm (soil moisture has a higher $^{18}$O at this level); then, the recharge from summer 1981 to summer 1982 is 336 mm.
The yearly loss by evapotranspiration estimated from regional water balance studies [7] is about 400–450 mm for this area; the corresponding values obtained by $^{18}$O studies are about 300–400 mm.

CONCLUSIONS

The simultaneous use of tritium labelling and $^{18}$O tracing shows that the seasonal variations of $^{18}$O in precipitation can be exploited to study soil-moisture movement and recharge. An accurate estimation of recharge is possible when $^{18}$O-depleted moisture, contributed by successive snow-melt periods, is found in the unsaturated zone. The choice of tritium (which does not suffer from isotopic fractionation effects) as a tracer not only provides a check on the validity of the results obtained by the $^{18}$O method but also gives independent information about moisture movement and recharge. Oxygen-18 profiles of soil moisture observed at various times of the year indicate that besides dispersion and molecular diffusion, exchange between soil carbon dioxide and soil moisture tends to damp the amplitude of $^{18}$O variations in the unsaturated zone.

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ISOTOPIC AND CHEMICAL INVESTIGATIONS OF SPRINGS FROM DIFFERENT KARST ZONES IN THE SWISS JURA

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Abstract

ISOTOPIC AND CHEMICAL INVESTIGATIONS OF SPRINGS FROM DIFFERENT KARST ZONES IN THE SWISS JURA.

The karst hydrology of a region in the Jura of Neuchâtel has been studied by means of a large number of isotopic, chemical and bacteriological analyses. Three springs are considered which represent different karst zones: saturated phreatic karst, confined karst and unsaturated karst. Runoff component analysis by means of tritium and oxygen-18 reveals that in all three springs aged reservoir water contributes the major part to discharge peaks, quick runoff of precipitation water being less important. The discharge of fresh water, as identified by isotopic composition and also by dilution of ionic concentrations and increased bacteria content, reaches its maximum for some springs considerably after the hydrograph peak. Under favourable conditions, a component separation is also possible using chemical analyses. The result that pre-event reservoir water is so important for peak discharge points to the existence of water reserves situated in large-volume, highly permeable karst channels. The mean age and volume of this reservoir water have been estimated. Discharge as well as isotopic composition of springs draining unsaturated karst exhibit regular oscillations. Four different characteristic times can be defined for karst springs: the hydraulic response time, the flow time of fast fresh water, the recession time constant and the mean age of reservoir water.

1. INTRODUCTION

In limestone aquifers of the Jura mountains, western Switzerland, there are problems of water supply typical for karst regions. For this reason the area considered here, situated in the canton of Neuchâtel, has been studied with respect to its hydrogeology and water chemistry for several decades [1–3]. Since 1977 a multidisciplinary investigation has been carried out there by the Centre d’hydrogéologie (University of Neuchâtel) and the Physikalischntes Institut
(University of Bern) in the frame of the national programme "Water Balance of Switzerland" of the Swiss National Science Foundation. The main goal was to localize water reserves and to study volume, renewal and quality of karst water. For this purpose, natural tracers were analysed in connection with hydrographs of springs, including isotopes (²H, ¹⁸O/¹⁶O), chemistry and bacteriology.

Figure 1 shows the observational network. The numbers 1, 2, 3 indicate the karst springs of Areuse, Ubena and Fontainemelon which are discussed below. From the end of 1977 to summer 1979 these springs were equipped with automatic samplers (1 sample every 4 hours) and continuous recorders for temperature, electrical conductivity and sodium ion activity. The network further included a federal meteorological station (La Brévine) and three recording rain gauge stations.

In May 1979, an artificial tracer experiment with ten different tracers (dyes, salt solutions, suspensions of spores and bacteria) was carried out by the International Working Group for the Application of Tracer Techniques in Hydrology, consisting of scientists from Austria, the Federal Republic of Germany, Switzerland and Yugoslavia. The results of this experiment were discussed and compared with natural tracer studies in Ref.[4], and a summary is given in Ref.[5].

Furthermore, geophysical techniques were adapted to the hydrogeological exploration of fractured and permeable zones, including geoelectric, seismic and electromagnetic, very-low-frequency techniques [6, 7].
FIG. 2. Continuous records of discharge, temperature, electrical conductivity and sodium ion activity in Areuse spring in 1979.
2. HYDROGEOLOGICAL SITUATION

The region studied is composed of sedimentary rocks: mesozoic limestones and marls. The marls are considered to have a low permeability, in contrast to the well-consolidated fractured limestones which act as karst water reservoirs. The sedimentary rocks are folded and form anticlins and synclines which define the hydrogeological basins. Here we consider three springs that emerge from different karst zones. The springs of Fontainemelon, emerging in a railway tunnel, represent water from the unsaturated zone in Kimmeridgian limestone; Areuse spring is the outflow of a recharge basin formed by two synclines in compact Malm limestone; and Ubena spring emerges near a fault affecting Argovian marls of low permeability, which probably provides a connection from deeper aquifers in Dogger limestone.

An important characteristic of these aquifers is the intrinsic heterogeneity of infiltration and the distribution of permeability. A network of highly permeable karst channels provides a drainage system for a quick flow component. Diffusely infiltrated precipitation percolating through blocks of low permeability forms a slow flow component. These different flow mechanisms are reflected in the hydrographs of springs as well as in fluctuations of chemical and physical properties of the water. This is illustrated by Fig.2. During discharge peaks, the quick flow component causes a chemical dilution and a bad bacteriological water quality within a short time, while in periods of prolonged base-flow the older slow flow component leads to higher concentrations of dissolved solids and better bacteriological quality. Since the slow and fast flow components have different physical and chemical properties, it is possible to use isotopic and chemical analyses as indirect tools for exploring reservoir characteristics.

3. LONG-TERM ISOTOPIC VARIATIONS AND WATER AGE

When analysing the data from karst springs, one has to take into account the heterogeneity of the aquifer which results in a strongly variable composition of the spring water.

In periods of base-flow, sufficiently long after flood events, it is essentially aged water from the karst reservoir which runs off, while after rainstorm or snow-melt events, rapid runoff of fresh water also plays a role. Consequently, it would not make sense to talk of one mean age of the spring water. Rather, we wish to determine the mean age of the aged reservoir water. In order to accomplish this, we compare the isotopic composition of precipitation (Fig.3) with that of spring water during periods of low discharge (Fig.4), using the exponential model (or one-box model; see Ref.[8]).
There are two possible methods to estimate a mean age. The first one is based on the long-term trends of tritium in the input (precipitation) and output (spring). As input values we use mean values for the hydrological year (October to September) weighted by precipitation, giving weights of 0.5 to the summer half year and 1 to the winter half year, thus taking into account higher evaporation losses in summer. By comparing model-calculated values with observed data, a mean age of the reservoir water of $(2.0 \pm 0.5)$ years is obtained for Areuse spring.

The second method is based on the attenuation of the quasi-periodic seasonal variations of $\delta^{18}O$ and $^3H$ in precipitation. Under the simplifying assumption of constant infiltration and discharge, these variations (approximated by a sine function with a 1 year period) appear in a spring attenuated by a factor

$$a = [1 + (2\pi T)^2]^{-0.5}$$

where $T$ is the mean age in years [9].

For Areuse spring the observed attenuation of seasonal isotopic variation differs significantly between different years, reflecting the interannual variability.
FIG. 4. $\delta^{18}O$ and tritium in Areuse spring (a) and Ubena spring (b). In general, the data are from times of low to moderate discharge. Analytical errors (1σ): 4 TU/0.07‰.
of recharge and runoff conditions. The range of a is about 0.1 to 0.3, corresponding to a mean age of between 0.5 and 1.5 years. Thus the two methods do not yield quite the same results. This probably indicates that the actual age distribution is not quite exponential. Young water (up to a few months old) may be more strongly represented, leading to larger seasonal amplitudes than expected from the exponential model. However, one should not take the results of the exponential model literally, since the model is based on the assumption of stationary conditions (reservoir volume, discharge and infiltration rate), which is obviously far from reality. We conclude that presumably the mean age of karst groundwater of the Areuse spring is in the range of 1 to 2 years.

This permits the volume of karst groundwater to be estimated, since this volume is given by the product of the mean age and the mean groundwater discharge rate. We estimate that ~80% of the total annual runoff of the Areuse spring is reservoir water [4]. Therefore, the volume of the karst water reserves can be given as \((1.2 - 2.4) \times 10^8\) m³.

Ubena spring (Fig.4(b)) has similar tritium concentrations as Areuse, which indicates that its water age must be comparable to that of Areuse. On the other hand, the seasonal amplitudes are smaller in Ubena for both isotopes. The combined evidence suggests that reservoir water in Ubena has a mean age similar to or slightly higher than that of Areuse, but that there is less young water (up to a few months old) in the reservoir of Ubena. This is in agreement with the relatively good bacteriological quality of Ubena water, in contrast to Areuse water. It is generally accepted that groundwater is bacteriologically pure after a subsurface residence time of 50 days, which implies that during base-flow conditions Ubena has nearly no contribution of water younger than about 50 days, while this is not the case for Areuse.

4. HYDROGRAPH SEPARATION OF HIGH-DISCHARGE EVENTS

4.1. Areuse spring

If spring water and precipitation are clearly different in their isotopic composition, isotope analyses permit the determination of the contribution of precipitation to the total discharge. Isotopic hydrograph separation has been performed by a number of authors (e.g. Refs [10, 11]). Thanks to the automatic sampler devices it was possible to analyse in detail several peak discharge events from the three Jura springs. In the following discussion we define reservoir water as water which was in the aquifer already before the event, and fresh water as precipitation (rain or snow melt) that infiltrated during the event.

On 24 December 1977, there was a rainstorm (24 mm at La Brévine) after 13 days of dry weather. At the same time it became warmer so that the snow
cover of about 40 cm, accumulated since mid-November, melted within two days. This resulted in an areally homogeneous infiltration with a tritium level of (43 ± 8) TU. Figure 5 shows that the tritium concentration in Areuse and Ubena did decrease, but by no means came near to the input levels. From mean base-flow values of 122 TU for Areuse and 126 TU for Ubena and an input value of 43 TU, the contribution of fresh water to the peak discharge can be estimated. For Areuse, the mean value of 96 TU for the period 25–27 December corresponds to a mean fresh-water contribution of 32%, while for Ubena, with
FIG. 6. Correlation of different water properties during the event in December 1977 in Areuse spring: (a) tritium/sodium, (b) conductivity/sodium. 20 = 20 Dec. 1977; 24/11 h = 24 Dec. 1977, 11 a.m.

114 TU during 24–26 December, the contribution is as low as 14%; the calculated maximum contributions are 42 and 27%, respectively. This can be compared with an increase of the discharge by factors of about 14 (Areuse) and 45 (Ubena). The conclusion is that a major fraction of the high discharge consists of reservoir water. This water must obviously have been stored in wide karst channels, otherwise it could not respond so quickly to the increased hydrostatic pressure. Thus, aged reservoir water is not restricted to low-permeability blocks.

It is interesting to consider, besides isotopes, also chemical parameters. Conductivity and dissolved ion concentrations decreased owing to dilution by precipitation water. In Fig.6(b) the concentration of Na⁺ is plotted versus electrical conductivity at 20°C for Areuse. Conductivity is approximately proportional to total dissolved solid concentration, since the latter is dominated by Ca²⁺ and HCO₃⁻ ions. From 20 to 23 December, Na⁺ increased while the conductivity stayed about constant; then, from 23 December, 19 h, to 24 December, 11 h, the reverse trend was observed, in parallel to increasing discharge. From then on, a dilution in both parameters was observed, and conductivity and Na⁺ concentration were linearly correlated, which might suggest a two-component mixture. For the values of 24 December, 11 h, the maximum dilution calculated on the basis of Na⁺ is 38% (comparable with the result from tritium); it is somewhat lower (25%) when calculated on the basis of conductivity. Extrapolation of the linear correlation to Na⁺ = 0 yields a conductivity value of 120 µS/cm, which might be regarded as the conductivity of a (hypothetical) fresh-water component. However, Fig.6(a) indicates that there must be more than two water components, since the correlation between sodium concentration and tritium is not very good. This can be explained by the
FIG. 7. Rainstorm event in Areuse spring, June 1979. 73 mm of rain fell at La Brèvine on 12 June, with $\delta^{18}O = -7.8\%_o$. From top to bottom: discharge, with decomposition into reservoir water ($Q_{res}$) and direct runoff of fresh water ($Q_{dir}$); $\delta^{18}O$; Na$^+$ concentration.
TABLE I. RUNOFF COMPONENT ANALYSES BASED ON ISOTOPIC AND CHEMICAL DATA

<table>
<thead>
<tr>
<th>Date</th>
<th>$Q_{\max}$</th>
<th>$f_{\max}$</th>
<th>$\bar{f}$</th>
<th>Isootope used</th>
<th>$f_{\max}$ (based on $\kappa$)</th>
<th>Ion used</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Areuse</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24–27 Dec. 1977</td>
<td>36</td>
<td>0.42</td>
<td>0.32</td>
<td>$^3$H</td>
<td>0.25</td>
<td>0.38 Na</td>
</tr>
<tr>
<td>7–10 Aug. 1978</td>
<td>38</td>
<td>$\sim$0.53</td>
<td>$\sim$0.4</td>
<td>$^{18}$O</td>
<td>0.10</td>
<td>0.44 Mg</td>
</tr>
<tr>
<td>2 June 1979</td>
<td>11</td>
<td>$\leq$0.15</td>
<td>$\leq$0.1</td>
<td>$^3$H</td>
<td>0.09</td>
<td>$\sim$0.16 Mg</td>
</tr>
<tr>
<td>12–15 June 1979</td>
<td>17</td>
<td>0.42</td>
<td>0.24</td>
<td>$^{18}$O</td>
<td>0.17</td>
<td>0.33–0.45 Na</td>
</tr>
<tr>
<td>7–9 Oct. 1980</td>
<td>16</td>
<td>0.10</td>
<td>0.04</td>
<td>$^3$H</td>
<td>0.08</td>
<td>0.22 Mg</td>
</tr>
<tr>
<td><strong>Ubena</strong></td>
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<td></td>
<td></td>
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<tr>
<td>24–27 Dec. 1977</td>
<td>1.2</td>
<td>0.27</td>
<td>0.14</td>
<td>$^3$H</td>
<td>0.17</td>
<td>0.16 Na</td>
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<tr>
<td>11–12 July 1978</td>
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<td>0.14</td>
<td>$^{18}$O</td>
<td>0.06</td>
<td>0.13 Na</td>
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<tr>
<td><strong>Fontainemelon</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8–11 Dec. 1978</td>
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<td>0.3–0.5</td>
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<tr>
<td>12–15 Dec. 1978</td>
<td>0.012</td>
<td>$\leq$0.15</td>
<td>$^3$H</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

$Q_{\max}$ is the maximum discharge during the event (m$^3$/s)

$f_{\max}$ is the maximum fraction of fresh water

$\bar{f}$ is the mean fraction of fresh water during discharge peak

$\kappa$ is conductivity.

The assumption that the reservoir water of Areuse did not consist of one homogeneous water type. This does, however, not mean that the component analysis based on tritium is not valid: the tritium level of the input is so much below that of spring water that some uncertainty in the latter does not affect the qualitative results. The good correlation between Na$^+$ and conductivity could, for instance, be explained by assuming, besides fresh water, two reservoir water components with different tritium concentration but similar Na$^+$ contents and conductivities.

On 12 June 1979, a heavy local storm brought 73 mm of rain within 2 hours to the region of La Brévine. The $6^{18}$O of the rain was $-7.8\%$ (average of two samples), significantly above the value of the spring reservoir water ($-10.8\%$). Subsequently, the discharge of Areuse spring rose to a maximum
of 17 m$^3$/s and δ$^{18}$O increased. The maximum value of δ$^{18}$O and the minima of conductivity and ion concentrations were reached about 24 hours after peak discharge and 32 hours after the end of the rainstorm (see Fig.7). This information directly indicates the flow time of fresh water from the surface to the spring. Based on δ$^{18}$O, the maximum fraction of fresh water in the spring is 42% (see Table I), again much less than would be obtained from a classical separation of runoff components based on hydrograph analysis.

The correlation between δ$^{18}$O and Na$^+$ concentration and between conductivity and Na$^+$ is relatively good, even if not perfect (Fig.8). As indicated in Table I, dilution calculations based on conductivity and magnesium underestimate the fraction of fresh water. Sodium yields a value similar to that obtained from isotopic component separation, but there is some uncertainty as to the base-flow Na$^+$ concentration (1.03–1.15 mg/L, see Fig.8).

On 7/8 October 1980, there was a rainstorm event which could be studied in detail, using besides isotopic and chemical analyses also bacteriological analyses [12]. The arrival of fresh water in the spring, as determined from isotopes and chemical dilution, was manifested also by a strong increase in faecal bacteria and the appearance of chlorophyll algae, i.e. algae which originate from the surface. The increase of bacteria must be due to sewage water rapidly transported through karst channels together with fresh water.

Table I lists the results from further events at Areuse spring; details are given in Ref.[4]. The maximum fractions of precipitation water during an event are in the range of from ~10% to 50%; averaged over the whole discharge peak, this fraction is at most 40%. These values seem to increase with the peak
discharge value, but apparently they also depend on the previous condition of the aquifer. We estimate that, on a yearly mean, rapid runoff of discharge (within a few days) makes up about 20% of the mean total discharge of 4.7 m³/s [4]. The reservoir volume of Areuse spring can be estimated as the product of mean reservoir discharge (0.8 × 4.7 m³/s) and mean subsurface residence time (1–2 years), which yields a value of (1.2–2.4) × 10⁶ m³.

This volume of water, distributed over the recharge area of about 130 km², corresponds to a saturated karst volume of between 90 and 360 m thickness, if typical porosity values of 0.5–1% are assumed. This clearly shows that the major part of the reservoir is situated below the level of the spring, i.e. in the two synclines underlying the recharge area. It also explains an apparent discrepancy: The mean water age of Areuse spring as determined from isotope data is considerably larger than the recession time constant, defined as the reciprocal of the recession coefficient for base-flow. This flow-out time is about 38 days [2]. However, the two characteristic times refer to different volumes. While the mean water age (or residence time) is equal to the ratio of total water volume to mean discharge, the recession time constant is related only to the water volume above the level of the spring, which determines the hydrostatic pressure. The ratio of the two characteristic times (1:8 to 1:15) gives an estimate of the ratio of volume above spring level to total volume.

If the fraction of fresh water in periods of high discharge is estimated on the basis of conductivity and under the assumption that the conductivity of fresh water is near zero, too low values are often obtained (see Table I). Using the concentration of Mg²⁺ or Na⁺, often, but not always, leads to values that agree with those obtained by means of ¹H or δ¹⁸O data. This can be interpreted in two ways: First, the fresh-water component rapidly dissolves CaCO₃ to reach a conductivity of 100–300 μS/cm (compared with 10–40 μS/cm for rain water). Although it is generally observed that the concentrations of Ca⁺⁺ and HCO₃⁻ ions increase more quickly than those of Na⁺ and Mg⁺⁺, it is not clear if fresh water can take up soil CO₂ and dissolve CaCO₃ so rapidly [13].

A second possibility is that the water driven out of the reservoir by hydrostatic pressure during an event has a different chemical composition (higher concentrations of Ca⁺⁺ and HCO₃⁻ but not of Na⁺ and Mg⁺⁺) than the pre-event base-flow. This may well be the case in principle. However, the reasonably good linear correlation between the different tracers, as shown in Figs 6 and 8 and observed also during other events, would then have to be fortuitous. It is at this stage not possible to decide which of the two interpretations is correct.

For Areuse spring, a hydrograph separation using Na⁺ or Mg⁺⁺ yields more or less correct results. Conductivity variations during individual events cannot easily be interpreted, but an analysis of the long-term trends yields reasonable results if the water is considered to be a mixture of fresh water (conductivity ~40 μS/cm) and chemically saturated aged water (~450 μS/cm) [13]. These
FIG. 9. Rainstorm event in Ubena spring, 11–12 June 1978. Precipitation on 11 June had $\delta^{18}O = -4.1\%_o$. $Q_{dr}$: direct runoff of rain water, determined on the basis of $\delta^{18}O$.

observations indicate that, if calibrated by means of isotope data, chemical analyses or simple conductivity measurements may be used for component separation with good results, which may considerably facilitate such studies. It must, however, be emphasized that this chemical method works under favourable conditions only and is not generally applicable. Thus, it has been observed that chemical concentrations increased, instead of decreased, during discharge peaks in the French Pyrenees [14].

4.2. Ubena spring

Ubena spring has characteristics different from those of Areuse. Its reservoir has not been identified with certainty; it is presumably situated in Dogger limestone overlain by a low-permeability marl layer, i.e. in a confined
aquifer. Ubena has a peculiar hydrograph (Figs 5 and 9): base-flow discharge is nearly constant; during floods, the discharge rises and falls rapidly and soon reaches, with a distinct break in the hydrograph, nearly the same value as before the event.

Component separation for December 1977 has been discussed above, together with the Areuse results. On 11/12 July 1978, there were about 20 mm of rain with an average $\delta^{18}$O of $-4.1\%$. The discharge of Ubena spring increased from 38 L/s to nearly 800 L/s, but the direct runoff of precipitation, as estimated from $\delta^{18}$O, made up 16% at most (see Fig. 9 and Table I). Conductivity and Na$^+$ concentration decreased nearly parallel to the increase of $\delta^{18}$O, and, like $\delta^{18}$O, came back almost to their pre-storm values even before the discharge reached its base-flow value. Dilution, as calculated from conductivity, Na$^+$ or Mg$^{2+}$, was not different, within error limits, from the freshwater fraction obtained from $\delta^{18}$O (Table I).

Thus, direct runoff of precipitation water contributed a rather small fraction to the total discharge in both events studied for Ubena, although discharge increased strongly. In Section 3 we concluded that Ubena spring has probably about the same mean water age as Areuse spring, but — in view of the smaller seasonal amplitudes — less water that is only a few weeks or months old. This explanation is in line with the observation that there is only very little rapid runoff of fresh water. Probably the aquifer is confined, as mentioned above, and therefore the spring mainly reacts in a piston-type way to increased hydrostatic pressure. This concept is supported by the result of the large-scale artificial tracer experiment in May 1979 when no tracer could be observed in Ubena spring; not even active charcoal adsorbers yielded unequivocally positive results [4]. The fresh-water contribution reaches the spring through a separate system of karst channels, as is suggested by field observation.

4.3. Fontainemelon springs

The Fontainemelon springs emerge in a railway tunnel. They drain an unsaturated karst zone bordered by impermeable marls. The karst is partly covered by thin Quaternary deposits where some water may be stored for a prolonged time. Not enough samples have been measured for $^3$H and $\delta^{18}$O to establish long-term trends. At the end of November 1978, after a long dry period, the springs had a value of 110 TU, ~15 TU higher than Areuse and Ubena springs. This may be due to the influence of summer precipitation high in tritium (see Fig. 3), but $\delta^{18}$O does not support this. Instead, the relatively high tritium levels may indicate that at this time, base-flow water at Fontainemelon was older than that of Areuse and Ubena.

On 8 December 1978, 27 mm of rain fell at La Brévine, with a tritium concentration of 25 TU. At the same time a snow cover of ~14 mm water
FIG. 10  Discharge events in Fontainemelon springs, December 1978. From top to bottom: amount of precipitation per 12 h; $\delta^{18}O$ and tritium in the springs; discharge Q; conductivity $\kappa$; Na$^+$ concentration.
equivalent melted; its tritium content was not directly measured but was certainly below 80 TU. Correspondingly, the average input concentration was in the range of 25–45 TU. The discharge of the Fontainemelon springs increased from \( \sim 1 \) to 12 L/s (Fig.10), and tritium decreased from 110–120 TU to about 80 TU, which corresponds to a maximum fresh-water contribution of 30–50\%.

On 11–14 December, a total of 56 mm of rain fell, causing a second rise of discharge in the springs. The tritium level of this rain was even below 20 TU, but the spring reacted by a decrease of 10 TU at most. Thus, rain water contributed 15\% or less during the second period. This result is rather unexpected for springs draining an unsaturated zone. It indicates that, possibly, there is some reservoir in the aquifer, in contrast to hydrogeological assumptions.

Conductivity and concentration of sodium (and all other ions) strongly increased during the event (see Fig.10). This must be attributed to the salt which had been sprayed on the roads in the catchment basin for de-icing and which was washed into the underground with the rain and melt water. This salt can be considered as an artificial tracer and its rapid appearance in the springs shows that fresh water reached them without delay. Also during the second discharge peak, on 12/13 December, the chemical concentrations first rose, although not as much as during 8/9 December.

During the high discharge period, tritium and \( \delta ^{18}O \) exhibited significant oscillations which are partly parallel with variations of conductivity and \( \text{Na}^+ \) (Fig.10). This indicates a fluctuating percentage of fresh water. The discharge of Fontainemelon spring exhibits rather regular oscillations, with a period of about two days. They could not be observed in the flood period illustrated in Fig.10, but were most clearly expressed in a recession period one month earlier (Fig.11). We do not have an exact hydrogeological explanation, but a mechanism suggests itself whereby a karst siphon is filled to a certain level and then emptied, etc. Possibly the isotopic fluctuations in December 1978 were caused by the same mechanism.

5. CONCLUSIONS

We have studied three karst springs from the same region, representing three different types of karst aquifers: phreatic saturated karst, confined karst and unsaturated karst. We found that aged reservoir water (or 'pre-event water') made the major contribution to high discharge peaks, while rapid runoff of fresh water was always of minor importance.

Since the springs' discharge reacts immediately and strongly to rainfall and snow melt, this finding is contrary to what could be expected; it is especially astonishing for the group of springs draining unsaturated karst. This result shows that in the saturated karst large-volume storage reservoirs exist which are rapidly
drained by wide flow channels. The case of the unsaturated zone is not yet completely understood.

Chemical analyses permit in the region studied a qualitative and partly a quantitative separation of runoff components. The time of fresh-water flow is directly indicated by the maximum chemical dilution (minimum of conductivity and ion concentrations), so that chemical or simply conductivity measurements, instead of expensive dye tracer experiments, yield the required information. These measurements can be performed at relatively low costs by means of a continuously recording apparatus at the site of the spring. A quantitative separation of runoff components based on chemical analyses involves uncertainties but can yield quite reliable results if calibrated first by means of isotope data.

In connection with runoff component analysis it is important to clearly distinguish between hydraulic response and compositional changes of springs. Data on isotopic and chemical composition give information on the identity of the water or its components. While a discharge peak is obviously caused by, for instance, a rainstorm, our results as well as those of many other authors (e.g. Refs [10, 11]) clearly indicate that very often the water during a flood of a spring or a stream is pre-event water, pressed out of the aquifer by hydrostatic pressure, rather than rain water. The conventional hydrograph separation techniques thus generally tend to overestimate grossly the contribution of rapid runoff of fresh water.
In general, there is, of course, a contribution of quickly flowing fresh water in karst springs, as is demonstrated by artificial tracer experiments [4]. Artificial tracers are, however, mostly injected into large sinkholes which directly lead into large karst channels, so that these results concern only a small part of the whole karst system. On the other hand, isotopes do trace the whole infiltration, including large and small sinkholes as well as diffuse infiltration.

We can define four different characteristic times for karst springs:

- The *hydraulic response time* of the spring discharge is generally short, e.g. a few hours for Areuse.
- The *flow time of the fast fresh-water component* can be identified by changes of isotopic and chemical composition or by artificial tracers; it is typically one day to a few days (Areuse).
- The *recession time constant*, the inverse of the recession coefficient for base-flow, is determined by the geometry and the hydrodynamic properties of the aquifer; for Areuse it is about 40 days.
- The *mean age of reservoir water*: The product of mean age and mean base-flow discharge yields the volume of stored reservoir water.

ACKNOWLEDGEMENTS

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REFERENCES


ENVIRONMENTAL ISOTOPE STUDIES OF LIMESTONE AQUIFERS IN CENTRAL ITALY

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Abstract

ENVIRONMENTAL ISOTOPE STUDIES OF LIMESTONE AQUIFERS IN CENTRAL ITALY.

Environmental isotopes (oxygen-18, deuterium, tritium) have been used to investigate two hydrogeological problems relating to Mesozoic limestone aquifers, which constitute the major source of good-quality groundwater in central Italy. On the basis of the hydrological budget, the hypothesis was put forward that the two karst systems of Monti Simbruini-Emic- Cairo and of Monti Lepini in southern Latium were hydraulically interconnected and groundwater was flowing from the first into the second system. There is no evidence of such flow in the isotopic composition of groundwater, and therefore it is concluded that the supposed interconnection between the two systems, which is geologically problematic, actually does not exist. It was feared that the discharge of some large springs exploited for water supply might decline as a consequence of the water-table lowering due to groundwater drainage by a motorway tunnel recently excavated in the Gran Sasso ridge in Abruzzo. The springs in the northern part of the ridge, where the tunnel is located, have the same isotopic composition as the water seeping into the tunnel and therefore could in principle be affected. Other springs in the southern part of the ridge have a quite different isotopic composition and therefore will not be affected significantly.

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1. INTRODUCTION

The Cassa per il Mezzogiorno — the Italian state authority for the development of the south of the country — is currently engaged in a large project aimed at the evaluation and optimal management of water resources in the regions of Latium (area south of Rome), Abruzzo, Molise and Campania. In this area of about 33 000 km², groundwater is one of the most important water resources and therefore a large part of the project is dealing with hydrogeological investigations. These include a complete inventory of the existing springs and wells and related data, followed by detailed studies performed with geophysical and geochemical techniques, exploratory drillings, infra-red prospecting, etc. [1].

Among the geochemical studies, environmental isotope techniques have been used to investigate the groundwater flow patterns in the limestone systems of Monti Simbruini-Ernici-Cairo and of Monti Lepini-Ausoni-Aurunci in southern Latium, and of Gran Sasso/Monte Sirente in Abruzzo. The reason why such special attention has been devoted to the study of limestone aquifers is the importance of their water potential production, which has been evaluated at $9.2 \times 10^8$ m³/a [1] and represents 88% of the renewable groundwater resources in the area.

This paper presents the results and the relevant hydrogeological information obtained with environmental isotope techniques in southern Latium and in Abruzzo. The isotopic analyses have been carried out at the Isotope Hydrology Laboratory of the International Atomic Energy Agency, with the exception of part of the tritiom determinations, which have been performed at the Centre de Recherches Géodynamiques, Thonon-les-Bains, France, under the supervision of Dr. Ph. Olive.

2. STUDY OF THE SYSTEMS OF MONTI SIMBRUINI-ERNICI-CAIRO AND OF MONTI LEPINI-AUSONI-AURUNCI IN SOUTHERN LATIUM

2.1. Hydrogeological background

The ridge of Monti Simbruini-Ernici-Cairo, oriented from north-west to south-east, is a single hydrogeological system [1], mainly consisting of limestone of Cretaceous age with rare strips of Miocene limestone. In the central part of the ridge, small outcrops of Triassic dolomite occur, which is the basis of the carbonate deposit series. The Cretaceous limestone, fractured and karstified, is the major water-bearing formation [2, 3].

The north-eastern flank of the hydrogeological unit coincides with the front of the limestone deposits overlapping the flysch formation of Valle Roveto. In
the south-western flank a system of faults has brought the limestone aquifer in contact with the clay-marl-sand deposits of Valle Latina (also called Valle Sacco).

Hydrogeologically, the Monti Simbruini-Ernici-Cairo ridge can be subdivided into three main subsystems. In the northern part the groundwater flow is mainly directed to the north, to feed some large springs exploited since Roman times to supply the city of Rome with water through the 91 km long Aqua Marcia aqueduct, built in the years 140–130 B.C. In the south-eastern part the groundwater feeds mainly the Cassino springs, which have a mean discharge of 23 m³/s. In the central part the groundwater patterns are rather complicated owing to the occurrence of a complex network of fissures and fractures of tectonic origin. The aquifer transmissivity ranges from $10^{-1}$ to $10^{-3}$ m²/s, and its total water production is estimated at $1.3 \times 10^9$ m³/a.

The Monti Lepini-Ausoni-Aurunci ridge is located south of the Monti Simbruini-Ernici-Cairo and is oriented parallel to this, from which it is separated by the Valle Latina. On its north-eastern flank it overlaps the clay-marl-sand deposits of the Valle Latina, partially covered by Quaternary deposits. The groundwater flow patterns in the limestone aquifer are partially influenced by the volcanic deposits of the Colli Albani in the north and by the overlying lacustrine, marshy and marine deposits in the coastal plain of Piana Pontina (Figs 1,2).

The Monti Lepini-Ausoni-Aurunci ridge is separated by tectonics into four main subunits, which are most probably fully independent from a hydrogeological point of view: the Monti Lepini, the Monti Ausoni, the Western Monti Aurunci and the Eastern Monti Aurunci. The transmissivity ranges from $10^{-1}$ to $10^{-5}$ m²/s and the total water production is estimated at $1.1 \times 10^9$ m³/a. Most of this water is discharged by a number of basal springs issuing from the contact of the limestone aquifer with the Piana Pontina deposits. In the Monti Lepini subunit the mean storage coefficient has been evaluated at 4% [4, 5].

On the basis of this structural set-up the Monti Simbruini should not be hydraulically connected with the Monti Lepini system [2, 3]. However, considering the hydrological budget, the hypothesis has been set up that the limestone outcrops in the Valle Latina flysch may represent the top of horst structures of a deep limestone formation. The latter would hydraulically interconnect the Monti Simbruini aquifer with that of Monti Lepini, allowing groundwater to flow from the first into the second [6]. The main objective of the isotope investigation has been to study the groundwater patterns in order to throw some light especially on the problem of the possible interconnection between the Monti Simbruini and the Monti Lepini systems.

2.2. Isotopic results and interpretation

Most of the sites the location of which is shown in Fig.1 have been sampled repeatedly during the years 1979–81. They did not show any significant temporal

Text continued on page 182.
FIG. 1. Hydrogeological map of southern Latium. 1 – alluvial and lacustrine deposits and travertines; 2 – pyroclastic rocks and lavas; 3 – sandstone, clay and marl; 4 – limestone and dolomitic limestone; 5 – main groundwater flow directions; 6 – sampled spring; 7 – sampled well. (The numbers of the sampling sites correspond to those of Table 1.)
FIG. 2. Geological cross-section SW-NE in southern Latium (position indicated in Fig. 1). 1 – alluvial and lacustrine deposits and travertines; 2 – sandstone, clay and marl; 3 – limestone and dolomitic limestone; 4 – fault; 5 – overlap.

FIG. 3. Deuterium versus oxygen-18 plot. 1 – wells tapping the Quaternary of Piana Pontina; 2 – wells and springs tapping the limestone in the Piana Pontina, in the Monti Lepini-Ausoni-Aurunci ridge, in the Amaseno valley and in the Valle Latina; 3 – wells and springs tapping the limestone aquifer of Monti Simbruini-Ernici-Cairo; 4 – springs issuing from the Gran Sasso/Monte Sirente system; 5 – water from the Gran Sasso tunnel (mean values).
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<td>DW</td>
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<td>-5.52</td>
<td>-5.52</td>
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</tbody>
</table>

* S = spring; DW = drilled well; SW = shallow well.
* L = Cretaceous limestone; V = volcanic deposits; Q = Quaternary deposits of Piana Pontina.
* Only one tritium measurement available.

Note. Sites 1–34 are located in the Piana Pontina and on the south-western flank of Monti Lepini-Ausoni-Aurunci. Sites 35–44 are located in the Amaseno Valley, between Monti Lepini and Monti Ausoni. Sites 68–76 are located on the south-western flank of Monti Simbruini-Ernici-Cairo. The locations are indicated in Fig.1.
<p>| | | | | | |</p>
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<td>Altitude (m a.s.l.)</td>
<td>Depth (m)</td>
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<td>L</td>
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<td>L</td>
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<td>L</td>
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<td>L</td>
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<td>L</td>
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<td>L</td>
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<td>68</td>
<td>Tufano</td>
<td>S</td>
<td>L</td>
<td>280</td>
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<tr>
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<td>Monte Radicino</td>
<td>S</td>
<td>L</td>
<td>220</td>
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</table>

* Type: S = Spring, DW = Drilled Well
  * Aquifer: L = Lower
variation in stable isotope composition nor, in most cases, in tritium content. Therefore, in Table I, only the average isotopic values are reported, and the range of the tritium variation is indicated only if significant. This lack of isotopic seasonal variations of springs, in spite of their often considerable discharge variations (the maximum winter discharge is 2–4 times greater and the minimum summer discharge is 3–10 times smaller than the mean discharge reported in Table I), confirms that precipitation mixes with and mobilizes older groundwater, rather than directly contributing to the spring discharge. This fact has already been shown many times by using environmental isotopes.

The tritium content of springs is always high (above 20 TU), indicating that these are supplied mainly by relatively shallow groundwater horizons of the limestone aquifer, with fast circulation and short residence time. Only sulphurous springs, such as No. 7 (Acquapuzza, literally Stinking Water) and No. 73 (Bucone), and most of the drilled wells have relatively low tritium (below 10 TU) because their water derives from a deeper circulation system.

Figure 3 shows the usual δD-δ18O plot for all the sites in southern Latium and Abruzzo (the results of the latter area are discussed in Section 3). The slope of the overall δD-δ18O correlation is close to 8 and the mean deuterium excess is 15.6‰ — considerably higher than the mean global value of 10‰, as it generally occurs in the Mediterranean basin.

The mean δ18O values of groundwater for the various hydrogeological sub-units are reported in Table II. The altitude effect on the isotopic composition of precipitation on the Thyrrenian slope of Monti Lepini can be obtained by using the mean δ18O values of the Quaternary aquifer in the Piano Pontina (−6.03‰, mean altitude ≈10 m), of the Mesozoic limestone aquifer recharged in the Monti Lepini (−6.69‰, mean altitude of the recharge basin ≈500 m, maximum height 1536 m), and of spring No. 5 (Sambuco, −7.7‰, at 1310 m a.s.l.). We obtain a gradient of −0.13‰ per 100 m, which is somewhat lower than that reported for central Italy by Zuippi et al. [7] who measured a δ18O mean gradient of −0.34‰ per 100 m on precipitation samples.

The Monti Lepini-Ausoni-Aurunci and the Valle Latina subunits all have a very similar stable isotope composition, which in turn is significantly different from that of northern Monti Simbruini (−8.55‰ in δ18O) and also from that of the south-western flank of Monti Simbruini-Emici-Cairo (−7.48‰; mean altitude of the recharge basin ≈800 m, maximum height 2014 m). These differences are probably due to a combination of both altitude and continental effects, the first one alone not being sufficient to produce them, especially for northern Simbruini. Incidentally, the influence of the continental effect would also explain the larger gradient of δ18O with altitude found by Zuippi et al. [7].

Let us now discuss the problem of the possible groundwater flow from the Monti Simbruini to the Monti Lepini system, which in principle may contribute substantially to the discharge of the Lepini basal springs. The observed facts are as follows:
TABLE II. MEAN δ¹⁸O VALUES OF GROUNDWATER IN THE
HYDROGEOLOGICAL SUBUNITS OF SOUTHERN LATIUM

<table>
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<tr>
<th></th>
<th>Mean δ¹⁸O</th>
<th>σ1</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Quaternary of Piana Pontina</td>
<td>−6.03</td>
<td>0.40</td>
<td>6</td>
</tr>
<tr>
<td>(b) Monti Lepini</td>
<td>−6.69</td>
<td>0.28</td>
<td>21</td>
</tr>
<tr>
<td>(c) Monti Ausoni</td>
<td>−6.71</td>
<td>0.30</td>
<td>11</td>
</tr>
<tr>
<td>(d) Monti Aurunci</td>
<td>−6.81</td>
<td>0.29</td>
<td>8</td>
</tr>
<tr>
<td>(e) Valle Latina</td>
<td>−6.38</td>
<td>0.17</td>
<td>12</td>
</tr>
<tr>
<td>(f) Monti Simbruini, north</td>
<td>−8.55</td>
<td>0.18</td>
<td>6</td>
</tr>
<tr>
<td>(g) Monti Simbruini-Ernici-Cairo, south-western flank</td>
<td>−7.48</td>
<td>0.15</td>
<td>10</td>
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</tbody>
</table>

Note. Group (a) includes sites 9, 12, 14, 15, 24, 26
Group (b) includes sites 2–4, 6–8, 10, 11, 13, 16–19, 35–38, 40, 43, 44, 46
Group (c) includes sites 20–23, 26–28, 39, 41, 42, 56
Group (d) includes sites 29–34, 59, 60
Group (e) includes sites 45, 47–55, 57, 58
Group (f) includes sites 61–66
Group (g) includes sites 67–76 of Table I.

Site No. 5 has been excluded from group (b) because of altitude. Groups (b) and (c) include also wells in the Piana Pontina which exploit the limestone aquifer.

(a) The three subunits, Monti Lepini, Monti Ausoni and Monti Aurunci, have a very similar mean stable isotope composition of groundwater. On the other hand, for Monti Ausoni and Monti Aurunci a groundwater contribution deriving from Monti Simbruini is considered impossible on a hydrogeological basis. It therefore seems reasonable to conclude from the isotopic data that a similar contribution can also be excluded for the Monti Lepini system.

(b) The more mineralized and sulphurous basal springs issuing from the Lepini system are believed to be those which contain a higher fraction of groundwater deriving from a deep circulation system and possibly from a distant origin. Springs of this type are No. 7 (Acquapuzza) and No. 17 (Laghi del Vescovo). The stable isotope composition of these springs is very similar to that of other springs and wells in the same subunit, and there is no evidence at all of any significant contribution from the Simbruini system.
(c) The $\delta^{18}O$ values observed in the Valle Latina groundwater do not show any evidence of a groundwater component flowing from the Monti Simbruini system which later would eventually reach the Lepini system. This would also indicate that the limestone blocks of Valle Latina are not the outcrops of horst structures of a supposed deeper limestone formation, and therefore there is no hydraulic continuity between Monti Simbruini and Monti Lepini. The Valle Latina groundwater is believed to be recharged by local precipitation and by infiltration from rivers. (For comparison, one measurement of the isotopic composition of the main river of the Valle Latina, Sacco River, in May 1979 has given $\delta^{18}O = -6.44\%$.)

(d) Among the basal springs of Monti Lepini, only Ninfa (No. 2) could contain, in principle, a considerable fraction ($\approx 50\%$) of water which, on the basis of stable isotopes, may derive from the Monti Simbruini system. However, the high tritium content indicates that also in this case the recharge area of the Ninfa spring is in the Monti Lepini.

On the basis of the above isotopic data and observations, we conclude that the two hydrogeological systems of Monti Simbruini and Monti Lepini are independent of each other, and there is no significant groundwater flow from the first into the second.

3. STUDY OF THE GRAN SASSO/MONTE SIRENTE SYSTEM IN ABRUZZO

3.1. Hydrogeological background

The bulk of the hydrogeological system of Gran Sasso/Monte Sirente (Fig. 4) consists of highly permeable limestone and dolomitic limestone of Mesozoic age. Transition lithotypes (dolomite, limestone, marly limestone, marl) appear on the northern, eastern and southern edges.

The structural set-up is characterized by a large fold-fault in the north and by a series of successive monoclines in the south. This peculiar structure determines the behaviour of the aquifer, which acts as a series of interconnected 'reservoirs', with elevation gradually decreasing from north-west to south-east. The main tectonic discontinuities are characterized by wide cataclastic and mylonitic bands, rather poorly permeable, which reduce but do not fully hinder the hydraulic interconnections between 'reservoirs'.

In the northern zone of the Gran Sasso ridge the groundwater flow is in part directed to the north, to supply various springs (Chiarino, Rio Arno, Vacelliera, etc.), and in part to the south, to supply springs at decreasing elevation, including the large springs of Capo Tirino, Bussi and Capo Pescara (Fig. 4). The altitude of the basal springs ranges from 1600 to 250 m a.s.l. and
FIG. 4. Hydrogeological map of the Gran Sasso/Monte Sibente system. 1 - alluvial and lacustrine deposits; 2 - sandstone, clay and marl; 3 - limestone and dolomitic limestone; 4 - main groundwater flow directions; 5 - sampled spring. (The spring numbers correspond to those of Table III.)

their total discharge is about $1.1 \times 10^9$ m$^3$/a. On its long flow pattern southwards, the groundwater is mixing continuously with that locally recharged by precipitation at an altitude which gradually becomes lower and lower. The main groundwater flow directions are indicated in Fig. 4.

Recently, a 10 km long double motorway tunnel has been bored at an elevation of 900 m a.s.l. in the northern, highest zone of the Gran Sasso ridge (Figs 4, 5). The tunnel drains a considerable amount of groundwater, which in the years 1978–81 totalled a volume of $4.4 \times 10^9$ m$^3$, corresponding to a mean
FIG. 5. Geological cross-section across the Gran Sasso tunnel. 1 — alluvial deposits; 2 — sandstone, clay and marl; 3 — limestone with interbedded marl; 4 — dolomitic limestone; 5 — fault; 6 — overlap; 7 — water-table or piezometric surface; 8 — borehole; 9 — spring. (Arrows below the tunnel indicate the sampling points listed in Table IV.)
TABLE III. MEAN ISOTOPIC COMPOSITION OF SPRINGS IN THE GRAN SASSO/MONTE SIRENTE SYSTEM IN THE YEARS 1979–1982

<table>
<thead>
<tr>
<th>No.</th>
<th>Location and/or name</th>
<th>Altitude (m a.s.l.)</th>
<th>Mean discharge (m³/s)</th>
<th>δ¹⁸O (%)</th>
<th>δD (%)</th>
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<td>2</td>
<td>Rio Arno</td>
<td>1520</td>
<td>0.1</td>
<td>-10.76</td>
<td>-68.4</td>
<td>62-39</td>
</tr>
<tr>
<td>3</td>
<td>Vacelliera Alta</td>
<td>1020</td>
<td>0.10</td>
<td>-10.40</td>
<td>-65.4</td>
<td>61-53</td>
</tr>
<tr>
<td>4</td>
<td>Vacelliera Bassa</td>
<td>940</td>
<td>0.12</td>
<td>-10.39</td>
<td>-66.0</td>
<td>55-45</td>
</tr>
<tr>
<td>5</td>
<td>Mescatore</td>
<td>620</td>
<td>0.01</td>
<td>-10.23</td>
<td>-64.7</td>
<td>59-54</td>
</tr>
<tr>
<td>6</td>
<td>Fossacieca</td>
<td>1350</td>
<td>0.03</td>
<td>-10.92</td>
<td>-69.2</td>
<td>65-48</td>
</tr>
<tr>
<td>7</td>
<td>L'Acqua – 99 Cannelle</td>
<td>620</td>
<td>0.02</td>
<td>-8.89</td>
<td>-56.8</td>
<td>45-27</td>
</tr>
<tr>
<td>8</td>
<td>Tempera</td>
<td>650</td>
<td>1.7</td>
<td>-10.50</td>
<td>-67.8</td>
<td>50</td>
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<tr>
<td>9</td>
<td>Vitella d'Oro</td>
<td>680</td>
<td>0.4</td>
<td>-10.19</td>
<td>-64.0</td>
<td>57</td>
</tr>
<tr>
<td>10</td>
<td>Mortaio d'Angri</td>
<td>690</td>
<td>0.3</td>
<td>-10.32</td>
<td>-65.1</td>
<td>40</td>
</tr>
<tr>
<td>11</td>
<td>Stiffe</td>
<td>680</td>
<td>0.2</td>
<td>-9.58</td>
<td>-62.0</td>
<td>39-27</td>
</tr>
<tr>
<td>12</td>
<td>Lago di Capestrano</td>
<td>340</td>
<td>1.0</td>
<td>-9.48</td>
<td>-60.0</td>
<td>6</td>
</tr>
<tr>
<td>13</td>
<td>Capo d'Acqua Tirino</td>
<td>340</td>
<td>4.7</td>
<td>-9.84</td>
<td>-63.5</td>
<td>12</td>
</tr>
<tr>
<td>14</td>
<td>Busi</td>
<td>300</td>
<td>5.4</td>
<td>-9.59</td>
<td>-62.0</td>
<td>10-6</td>
</tr>
<tr>
<td>15</td>
<td>Popoli-San Callisto</td>
<td>280</td>
<td>2.2</td>
<td>-9.44</td>
<td>-61.4</td>
<td>14-7</td>
</tr>
<tr>
<td>16</td>
<td>Popoli-Capo Pescara</td>
<td>250</td>
<td>7.5</td>
<td>-9.68</td>
<td>-63.5</td>
<td>17-9</td>
</tr>
<tr>
<td>17</td>
<td>Molina Aterno-Lago Barone</td>
<td>440</td>
<td>2.2</td>
<td>-9.52</td>
<td>-59.6</td>
<td>2</td>
</tr>
<tr>
<td>18</td>
<td>Raiano</td>
<td>290</td>
<td>2.1</td>
<td>-9.91</td>
<td>-63.2</td>
<td>19-8</td>
</tr>
<tr>
<td>19</td>
<td>Raiano (sulphureous)</td>
<td>290</td>
<td>2.1</td>
<td>-9.75</td>
<td>-63.5</td>
<td>12</td>
</tr>
<tr>
<td>20</td>
<td>Celano-Fontana Grande</td>
<td>790</td>
<td>0.4</td>
<td>-9.77</td>
<td>-61.9</td>
<td>41-33</td>
</tr>
</tbody>
</table>

² The tritium content decrease during the sampling period is indicated, or the mean value if no significant variations occur.
discharge of 3.5 m³/s. This flow is slowly declining, and it should reach a predicted stationary value of 1.5 m³/s when the new hydrogeological equilibrium is reached [1].

The discharge of some of the northern springs significantly decreased after the excavation of the tunnel; this happened, for instance, to the springs of the Ruzzo group (Nos. 3 – 6 in Fig. 4 and in Table III), which are exploited to supply the city of Pescara with water, and probably also to the spring of Chiarino. Also, springs at lower altitude in the southern part of the system may in principle be affected by the tunnel.

Environmental isotopes have been used to investigate the origin and dynamics of groundwater, in order to better predict the future behaviour of the limestone aquifer and the consequences of tunnel water drainage. This may also have a bearing on the exploitation of the tunnel and on the works which will be undertaken.

3.2. Isotopic results and interpretation

All sites shown in Fig. 4 have been sampled four to eight times in the period 1979–82; they did not show any significant stable isotope variation. The tritium content, on the contrary, showed a rather evident decrease in most of the springs, which was obviously a consequence of the tritium decrease in precipitation. The mean δ-values and the tritium content range are shown in Table III for the springs and in Table IV for the water seeping into the Gran Sasso tunnel.

The heavy-isotope content is lower in the tunnel water and in the northern springs, i.e. in the area with the highest altitudes (up to 2912 m a.s.l. at the Corno Grande, the highest summit in the Apennines). In the south of the Gran Sasso/ Monte Sirente ridge the altitude decreases and, as a consequence, the heavy-isotope content of the springs increases.

The less negative δ-values (δ¹⁸O = −8.89‰ and δD = −56.8‰) are observed, however, at the spring '99 Cannelle' ('99 Taps') which feeds a monumental fountain at l'Aquila. This spring is known to exploit an alluvial formation of Quaternary age, locally recharged and not connected with the limestone aquifer, and it has been sampled for comparison; it provides, in fact, the stable isotope composition of the groundwater recharged at an altitude of about 700 m.

The tunnel seepage (mean values: δ¹⁸O = −10.67‰ and δD = −68.8‰) provides the isotopic composition of groundwater recharged at about 2000 m, which is the mean altitude above the central part of the tunnel (Fig. 5). The isotopic gradients with altitude which can be computed are: −0.14 and −0.9‰ per 100 m, respectively, for δ¹⁸O and δD. These gradients are similar to those found in Monti Lepini, as discussed in Section 2.2, although the delta values are shifted towards more negative values (2‰ for oxygen-18) because of the continental effect.
TABLE IV. ISOTOPIC COMPOSITION OF GROUNDWATER IN THE GRAN SASSO TUNNEL IN THE YEARS 1979–1982

<table>
<thead>
<tr>
<th>No.</th>
<th>Distance from the Assergi (SW) or Teramo (NE) entrance</th>
<th>$\delta^{18}$O (%)</th>
<th>$\delta^{2}D$ (%)</th>
<th>TU$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>2005 m from Assergi</td>
<td>-10.40</td>
<td>-67.0</td>
<td>73–83–79</td>
</tr>
<tr>
<td>22</td>
<td>2773 m from Assergi</td>
<td>-10.89</td>
<td>-69.8</td>
<td>73–62</td>
</tr>
<tr>
<td>23</td>
<td>3590 m from Assergi</td>
<td>-10.84</td>
<td>-71.2</td>
<td>51–61–61</td>
</tr>
<tr>
<td>24</td>
<td>4043 m from Assergi</td>
<td>-10.68</td>
<td>-68.9</td>
<td>60–64–59</td>
</tr>
<tr>
<td>25</td>
<td>4270 m from Assergi</td>
<td>-10.58</td>
<td>-67.1</td>
<td>64–81–74</td>
</tr>
<tr>
<td>26</td>
<td>4580 m from Assergi</td>
<td>-10.74</td>
<td>-69.5</td>
<td>8–10–10</td>
</tr>
<tr>
<td>27</td>
<td>Total discharge at Assergi entrance</td>
<td>-10.69</td>
<td>-69.0</td>
<td>39–39</td>
</tr>
<tr>
<td>28</td>
<td>3116 m from Teramo</td>
<td>-10.66</td>
<td>-69.4</td>
<td>43–75–68</td>
</tr>
<tr>
<td>29</td>
<td>3272 m from Teramo</td>
<td>-10.60</td>
<td>-66.8</td>
<td>83–73</td>
</tr>
<tr>
<td>30</td>
<td>3355 m from Teramo</td>
<td>-10.50</td>
<td>-68.8</td>
<td>83</td>
</tr>
<tr>
<td>31</td>
<td>3690 m from Teramo</td>
<td>-10.69</td>
<td>-69.4</td>
<td>62–76–79</td>
</tr>
<tr>
<td>32</td>
<td>4180 m from Teramo</td>
<td>-10.78</td>
<td>-69.2</td>
<td>51–78–83</td>
</tr>
<tr>
<td>33</td>
<td>Total discharge at Teramo entrance</td>
<td>-10.60</td>
<td>-68.2</td>
<td>67–62</td>
</tr>
<tr>
<td></td>
<td>Average of all values</td>
<td>-10.67</td>
<td>-68.8</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The first tritium value refers to November 1979, the second to August 1981 and the third to May 1982.

With the isotopic gradients indicated above, the mean altitude of the recharge area ranges for northern springs from more than 2000 m (Rio Arno, Fossaieca) to 1600 m a.s.l. (Mescatore, Vitella d’Oro), and for southern springs from 1400 m (Capo d’Acqua Tirino, Raiano) to 1100 m a.s.l. (Lago di Capestrano, San Callisto, Lago Barone). Although these figures have a wide margin of uncertainty and should be used with caution, they do not seem unreasonable.

Even more instructive, however, is the tritium content. A first group of springs, namely Nos. 1–11 and 20, and all the sites but one in the tunnel, have a high tritium content, always above 30 TU and very often above 50 TU. In some cases the tritium content is markedly higher than that of modern precipitation, which at Genoa ranged from 40 to 30 TU in the years 1976–82. Therefore, a tritium content of up to 70 TU as observed in many tunnel sites is an indication of groundwater largely recharged in the 1960s when the tritium concentration...
of precipitation was always well above 100 TU. The fact that the highest tritium value is found in the tunnel is not surprising, and it shows that the groundwater age stratification is at least in part preserved. The only site in the tunnel with low tritium — No.26 of Table IV — exploits a pocket of even older groundwater; its tritium content should increase in the future as the fraction of old, pre-thermonuclear water will decrease and will be replaced by young water.

All the springs of the first group contain young water and therefore they should have a recharge area located close by and should exploit a system with fast groundwater circulation. These springs also include Stiffe and Fontana Grande di Celano, on the south-western flank of the Gran Sasso/Monte Sirente ridge, which are believed, on hydrogeological grounds, to be fed by small subsystems recharged locally.

In the second group of springs — Nos. 12–19, south-easterly located — the tritium content drops in general below 15 TU and very often below 10 TU. This is an indication of the relatively long mean residence time of groundwater (above 100 years assuming a simple exponential age distribution) and/or mixing with a tritium-free old groundwater component, possibly of distant origin. The older age of groundwater of the south-eastern springs with respect to that of the northern and south-western springs is also confirmed by the correlation existing between salinity and tritium shown in Fig.6: the salt content increases with age, i.e. as tritium decreases.

It is also worth noticing that some tritium measurements were already performed in the years 1971–72 on the Gran Sasso/Monte Sirente groundwater.
The measurements were carried out at the Laboratorio di Geologia Nucleare in Pisa, under the supervision of Prof. Tongiorgi, and the results were reported by Monjoie [8]. Tongiorgi's and our results are very similar and show that the tritium concentration of groundwater practically did not change during the last decade. For instance, the spring Capo d'Acqua Tirino had 6 TU in 1971 and 10 TU in 1972, and the spring Capo Pescara had 11 TU in 1971, showing no significant differences with respect to the values obtained by us ten years later. Other measurements performed by Tongiorgi in some exploration wells drilled before the tunnel excavation showed a tritium content ranging from 50 to 100 TU, also comparable with our tunnel values. In the latter case it is particularly surprising that no major change in tritium content has taken place, in spite of the time which has elapsed, being close to a half-life of tritium, and of the tritium decrease in precipitation which occurred meanwhile.

Concerning the specific problem of the possible influence of the tunnel drainage on the discharge of the various springs, the environmental isotope findings can be summarized as follows:

(a) The northern springs — Nos.1–6 and 8 of Table III — contain water with essentially the same isotopic composition (tritium and stable isotopes) as the tunnel water. Therefore, these springs are those which risk being more affected by the lowering of the water-table due to the tunnel drainage.

(b) The probability of an important decrease of discharge due to the tunnel drainage is lower for springs 9 and 10, which have a stable isotope composition slightly but significantly different from that of the tunnel water.

(c) Finally, the probability of being affected by the tunnel is practically negligible for the south-eastern springs (Nos.12–19) on isotopic grounds. These have a stable isotope composition much different from that of the tunnel water, which indicates a different recharge area and largely independent groundwater origin and dynamics. A minor groundwater component deriving from the northern part of the system is most probably present in these springs, where it is largely diluted by water of different, closer origin. Therefore, the low tritium content indicates that the springs are supplied by a large groundwater system with long residence time rather than by groundwater of distant origin.

REFERENCES


ISOTOPE HYDROLOGY STUDY
OF KATO NEVROKOPI OF DRAMAS

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Abstract
ISOTOPE HYDROLOGY STUDY OF KATO NEVROKOPI OF DRAMAS.
The isotopic composition of the water was used in order to define the mechanism of recharge of the high plateau of Kato Nevrokoopi of Dramas. The results of this study indicate that there are two main sources of recharge to groundwater. One is infiltration of water from the network of irrigation canals which carry water from the Vathitopos stream. The other source of recharge originates in the mountains to the east of the plain. Infiltration from the Nevrokoopi stream does occur, but is believed to be minor in this part of the plain. Recharge by infiltration of local precipitation is considered to be minor in comparison with the two main sources of recharge. An underground barrier prevents draining of the groundwater through the sinkhole, resulting in a very big reservoir under the whole central and southern parts of the high plateau. The exploitation of the groundwater of this reservoir very probably offers a low-cost solution to satisfy all needs of the area for irrigation water.

INTRODUCTION
Kato Nevrokoopi of Dramas lies near the border with Bulgaria and is one of the coldest regions of Greece. It is a high plateau, having a sinkhole in its southern part as the only outlet for surface waters.
During the winter months, all the plateau is covered by snow. Also during most of spring, a part of the plateau is covered by water. On the other hand, during the summer the available quantity of surface water is very small. So, in spite of the efforts of the public services, as well as of the local inhabitants, the exploitation of the land cannot be characterised as satisfactory.

In order to satisfy the needs of the area for water, several possible solutions are under consideration. Among these we note the use of groundwater and the much more expensive solution of the construction of an artificial reservoir.

The present study was conducted by the NRC Democritos, in collaboration with the IAEA and the Ministry of Agriculture. Its main objectives were the investigation of the recharge mechanism of the groundwater and the estimation of the volume of the groundwater reservoir.

HYDROGEOLOGICAL CONDITIONS

Fig. 1 is a simple geological map of the area under investigation. Fig. 2 is a geologic section along the axis A-B of Fig. 1.

The altitude of the high plateau is between 540 and 560 m. The mountain to the north is of schist, with some local appearances of limestone. The mountains to the west and to part of the south are of granite, with also some local appearances of limestone. To the east and to the rest of the south, the Falacro mountain is of limestone with local appearances of granite. Its maximum elevation is 1629 m. To the northwest, behind the granite mountains, is the limestone mountain Orvilos, its maximum altitude being 2172 m.

The high plateau is crossed by the streams Vrondou, Vathitopos and Nevrokopi. All these streams have a lot of water during the wet season and are connected with the sinkhole in the southern part of the high plateau.

Possible sources of recharge to the groundwater of the high plateau are local precipitation, the streams and the mountain Falacro. Also recharge from the mountain Orvilos, through possible cracks in the granite and the neogene deposits, cannot be excluded. In fact, the isoplethometric contours indicate a gradient, during the whole year, from the northwest to the southeast.
Environmental isotope techniques are based upon measurements of the variations in the environmental composition of natural waters [1, 2, 3]. Environmental isotope hydrology is most useful in problems related to the origin of water (measurements of the stable isotopes, deuterium and oxygen-18) and the dynamics of water systems (measurements of the radioactive isotopes, tritium and carbon-14).

Depending upon the altitude effect on the isotopic composition of precipitation, the isotopic composition may be used for the identification of waters coming from each of the potential sources of recharge to the groundwater of the high plateau.
The sampling of the present isotope programme covers precipitation, some springs outside the high plateau at different elevations, the water of the streams and the groundwater of the high plateau at different locations and depths. Fortunately a large number of boreholes of different depths already existed in the high plateau.

The springs outside the high plateau at different elevations were sampled in order to establish the altitude effect on the isotopic composition of the meteoric water. The precipitation in the area was sampled in order to facilitate the establishment of the tritium input function needed for the dating of the groundwater.

The sampling locations are shown in Figs 3 and 4. The results of analyses performed in Democritos are presented in Table 1.
DISCUSSION AND INTERPRETATION OF ISOTOPE DATA

a) Origin of the groundwater in the Kato Nevrokoipi plain

The frequency distribution of the $\delta^{18}O$ values of groundwater samples between the Vathitopos and Nevrokoipi streams is given in Fig. 5. The shape of this distribution is indicative of a mixing process with two sources of water, each having a different stable isotopic composition. Samples located on the western and south-western sections of the plain of Kato Nevrokoipi have more depleted $\delta^{18}O$ values, while samples from the eastern and north-eastern locations have more enriched values. The peak frequency at -8.9‰ is the same as that of the mean of the samples from the Vathitopos river (-8.96‰) over the period July 1976 to September 1982, during which no large variations in isotopic
composition were observed. The isopiezometric groundwater contours are not indicative of direct infiltration from the river itself, so it is concluded that infiltration occurs from the network of irrigation canals which carry water from the river.

With regard to the other source of recharge, the peak frequency at -8.35‰ is somewhat more depleted than the mean values of samples from the Nevrokopi stream over the period July 1976 to September 1982 (-7.93‰). However, the δ18O values of groundwater samples from locations 44, 45 and 141 to the east of the Nevrokopi stream (overall mean -8.26‰) are more depleted than the stream values. It is therefore concluded that water recharged at higher elevations (Falacro mountain) to the east contributes to the recharge of the plain in addition to possible minor infiltration losses from the Nevrokopi stream. Samples at locations 131 and 132 close to the stream vary with time and are indicative of such infiltration. With regard to infiltration of local precipitation falling on the plain as a possible source of recharge, this seems rather unimportant. The stable isotopic composition of such a source of recharge should be more
positive than that of the sources of recharge discussed above. In fact, the water sampled at location 14 (-7.8%) is believed to represent recharge by locally infiltrated precipitation. No such values are observed for any of the groundwater samples in the plain. If this recharge mechanism does occur, it must be minor in comparison to the two main sources of recharge identified in the above interpretation.

TABLE I. ANALYTICAL DATA

<table>
<thead>
<tr>
<th>Sample location and type</th>
<th>Elev. (m)</th>
<th>Depth/mean recharge elevation</th>
<th>$\delta^{18}O$ (%)</th>
<th>$\delta^{2}H$ (%)</th>
<th>Tritium* (TU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 spring</td>
<td>1040</td>
<td>1300</td>
<td>-64.8±0.7</td>
<td>-10.4±0.21</td>
<td>5.8±3.6</td>
</tr>
<tr>
<td>3 spring</td>
<td>840</td>
<td>1000</td>
<td>-60.3±0.3</td>
<td>-9.35±0.17</td>
<td>77.5±9.8</td>
</tr>
<tr>
<td>4 spring</td>
<td>880</td>
<td>880</td>
<td>-54.3±2.0</td>
<td>-8.38±0.17</td>
<td>96.0±10.4</td>
</tr>
<tr>
<td>5 spring</td>
<td>660</td>
<td></td>
<td>-53.2±0.4</td>
<td>-8.29±0.22</td>
<td>82.6±11.8</td>
</tr>
<tr>
<td>6 spring</td>
<td>650</td>
<td></td>
<td>-57.4±0.1</td>
<td>-8.84±0.20</td>
<td>72.2±12.1</td>
</tr>
<tr>
<td>7 stream (Kromer)</td>
<td>610</td>
<td></td>
<td>-58.2±1.3</td>
<td>-9.23±0.35</td>
<td>45.5±8.6</td>
</tr>
<tr>
<td>8 stream (Seremtita)</td>
<td>610</td>
<td></td>
<td>-60.1±0.9</td>
<td>-9.47±0.22</td>
<td>30.2±6.9</td>
</tr>
<tr>
<td>9 stream (Kadiar)</td>
<td>610</td>
<td></td>
<td>-56.2±0.9</td>
<td>-8.66±0.13</td>
<td>62.8±5.5</td>
</tr>
<tr>
<td>10 stream (Vathiopos)</td>
<td>590</td>
<td></td>
<td>-57.3±1.4</td>
<td>-8.96±0.22</td>
<td>53.3±5.5</td>
</tr>
<tr>
<td>11 stream (Vrondos)</td>
<td>550</td>
<td></td>
<td>-53.9±1.5</td>
<td>-8.69±0.25</td>
<td>54.2±7.7</td>
</tr>
<tr>
<td>12 borehole</td>
<td>555</td>
<td>173/</td>
<td>-56.0±0.7</td>
<td>-8.64±0.14</td>
<td>76.0±9.8</td>
</tr>
<tr>
<td>13 borehole</td>
<td>545</td>
<td>30/</td>
<td></td>
<td>-8.95±0.07</td>
<td>1.0±1.4</td>
</tr>
<tr>
<td>14 borehole</td>
<td>550</td>
<td>133/ (20m)</td>
<td>-50.5±0.5</td>
<td>-7.80±0.12</td>
<td>45.7±5.3</td>
</tr>
<tr>
<td>15 borehole</td>
<td>550</td>
<td>133/ (60m)</td>
<td>-49.6±1.1</td>
<td>-7.77±0.10</td>
<td>47.0±6.4</td>
</tr>
<tr>
<td>15 spring</td>
<td>812</td>
<td>/900</td>
<td>-56.1±1.6</td>
<td>-8.84±0.05</td>
<td>82.5±12.7</td>
</tr>
<tr>
<td>16 spring</td>
<td>800</td>
<td>/880</td>
<td>-52.3±1.2</td>
<td>-8.60±0.28</td>
<td>60.4±12.9</td>
</tr>
<tr>
<td>17 stream (Neurokopi)</td>
<td>560</td>
<td></td>
<td>-52.3±1.8</td>
<td>-7.92±0.38</td>
<td>53.0±13.9</td>
</tr>
<tr>
<td>18 stream (Lefkogon)</td>
<td>570</td>
<td></td>
<td>-53.7</td>
<td>-7.8±0.28</td>
<td>51.4±12.2</td>
</tr>
<tr>
<td>19 stream (Eoschil)</td>
<td>570</td>
<td></td>
<td>-50.9±2.6</td>
<td>-8.19±0.30</td>
<td>50.2±12.9</td>
</tr>
<tr>
<td>20 spring</td>
<td>560</td>
<td></td>
<td>-56.4±1.4</td>
<td>-8.73±0.14</td>
<td>70.2±7.2</td>
</tr>
<tr>
<td>21 borehole</td>
<td>545</td>
<td>186/ (13.5m)</td>
<td>-56.0±1.1</td>
<td>-8.42±0.23</td>
<td>1.2±2.2</td>
</tr>
<tr>
<td>22 borehole</td>
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<td>186/ (60m)</td>
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</tr>
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<td>135/</td>
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<td>Sample location and type</td>
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<td>δ18O (‰)</td>
<td>Tritium* (TU)</td>
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<tr>
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<td>57.7±11.9 (3)</td>
</tr>
<tr>
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<td>570</td>
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<td>6.0 (1)</td>
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<td>0.5±0.7 (2)</td>
</tr>
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<td>-10.8 (1)</td>
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<td>57.0 (1)</td>
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<td>65.5±19 (2)</td>
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<td>63.0±23 (2)</td>
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<td>-8.4±0.21 (3)</td>
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</tr>
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</tr>
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<td>-8.6±0.12 (3)</td>
<td>0 (2)</td>
</tr>
<tr>
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<td>-8.5±0.15 (3)</td>
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</tr>
<tr>
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<td>-8.9±0.15 (3)</td>
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<tr>
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<td>-8.7±0.17 (2)</td>
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</tr>
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<td>46 (1)</td>
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<td>-8.8±0.31 (3)</td>
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<td>-9.0±0.10 (3)</td>
<td>56±8.5 (2)</td>
</tr>
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<td>-8.9±0 (3)</td>
<td>61±5.7 (2)</td>
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<td>-9.0±0.06 (3)</td>
<td>61±24 (2)</td>
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<tr>
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<td>-8.8±0.25 (3)</td>
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<td>-8.9±0.07 (2)</td>
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<td>21±4.2 (2)</td>
</tr>
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<td>10-30*/</td>
<td>-9.2 (1)</td>
<td>17 (1)</td>
<td></td>
</tr>
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<td>-8.7±0.06 (3)</td>
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<tr>
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<td>-8.8±0.15 (3)</td>
<td>0 (2)</td>
</tr>
<tr>
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<td>544</td>
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<td>-9.0±0.21 (3)</td>
<td>0 (2)</td>
</tr>
<tr>
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<td>543</td>
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<td>-8.8±0.06 (3)</td>
<td>0.5±0.7 (2)</td>
</tr>
<tr>
<td>121 borehole</td>
<td>544</td>
<td>10-30*/</td>
<td>-57.7±0.4 (2)</td>
<td>-9.1±0.14 (2)</td>
<td>0.5±0.7 (2)</td>
</tr>
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<td>545</td>
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<td>-58.2±0.6 (2)</td>
<td>-8.9±0.28 (2)</td>
<td>3 (1)</td>
</tr>
<tr>
<td>130 borehole</td>
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<td>-54.4±1.2 (2)</td>
<td>-8.3±0.14 (2)</td>
<td>72 (1)</td>
</tr>
<tr>
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<td>548</td>
<td>10-30*/</td>
<td>-48.5±4.2 (2)</td>
<td>-8.1±0.28 (2)</td>
<td>60 (1)</td>
</tr>
<tr>
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<td>-8.0±0.31 (3)</td>
<td>48 (1)</td>
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<td>133 borehole</td>
<td>547</td>
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<td>-56.0±0.9 (2)</td>
<td>-8.5±0.07 (2)</td>
<td>55 (1)</td>
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<tr>
<td>134 borehole</td>
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<td>-51.2±0.7 (2)</td>
<td>-8.3±0.15 (3)</td>
<td>16±7.1 (2)</td>
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<tr>
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<td>10-30*/</td>
<td>-54.8±4.0 (2)</td>
<td>-8.4±0.0 (3)</td>
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### TABLE I (cont.)

<table>
<thead>
<tr>
<th>Sample location and type</th>
<th>Sample</th>
<th>Elev. (m)</th>
<th>Depth/mean recharge elevation</th>
<th>δ18O (‰)</th>
<th>δD (‰)</th>
<th>Tritium (TU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>136 borehole</td>
<td>547</td>
<td>10-30/1</td>
<td>-56.7 (1)</td>
<td>-8.50±0.14 (2)</td>
<td>5.5±5</td>
<td>(2)</td>
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<tr>
<td>137 borehole</td>
<td>547</td>
<td>10-30/1</td>
<td>-56.4±0.4 (2)</td>
<td>-8.47±0.06 (2)</td>
<td>73</td>
<td>(1)</td>
</tr>
<tr>
<td>138 borehole</td>
<td>548</td>
<td>10-30/1</td>
<td>-51.6±0.6 (2)</td>
<td>-8.13±0.12 (3)</td>
<td>59±16</td>
<td>(2)</td>
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<tr>
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<td>548</td>
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<td>-8.80±0.14 (2)</td>
<td>22±2.8</td>
<td>(2)</td>
</tr>
</tbody>
</table>

* a Standard deviation and number of values in brackets are quoted.
* b Information on exact depth of borehole is not available.

---

**FIG. 5.** Frequency distribution of the δ18O values of groundwater samples between the Vathitopos and Nevrokopi streams.

b) Origin of recharge of groundwater outside the Kato Nevrokopi plain

The plot δ18O vs mean recharge altitude of springs with well-defined recharge areas is presented in Fig. 6. In this plot the point corresponding to the water of the borehole sampled at location 14, which is believed to be fed by the water of a nearby limestone formation of 680 m mean altitude, is also included. The slope of the respective best fitting line suggests a change of 0.44‰ in the δ18O value per
100 m change in the mean recharge altitude. The value of the correlation coefficient is 0.984.

According to Fig. 6, the mean recharge altitude of Kainar spring (sample no. 6) is 900 m, as expected by the hydrogeologists. On the contrary, in spite of the belief that the spring no. 5 was fed by the limestones of Orvilos, from Fig. 6 it is concluded that the local alluvial formation is only responsible for the recharge of this spring. Also, although the spring no. 20 was considered to be recharged locally, it is concluded from Fig. 6 that more distant higher regions also contribute to its recharge.

c) Age of the groundwater

The tritium input function is of primary importance in applying the tritium method to groundwater, as the method draws conclusions from a comparison of the tritium input concentration to tritium output. Unfortunately, the required measurements usually do not cover the proper time period.
TABLE II. LEONTIADIS COEFFICIENTS

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<td>49.7</td>
<td>60.0</td>
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<td>60.0</td>
<td>44.6</td>
<td>33.9</td>
<td>20.7</td>
<td>17.6</td>
<td>14.6</td>
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</table>

The deficiencies in data may be filled by correlation with a similar area.

In the present case, the tritium concentrations of precipitation are estimated from the data available for Athens, a WMO/IAEA network station, in combination with an Ottawa-Athens correlation.

A simple way of estimating the amount of precipitation recharging the aquifer is by the use of Kessler coefficients [4]. However, these coefficients apply to the amount of water recharging the aquifer regardless of the time of the rainfall occurrence, while the tritium concentration of the precipitation is time dependent. This might affect the evaluation of the tritium input function, especially for the months January, February and March. To overcome this disadvantage, Leontiadis [5, 6, 7] arbitrarily modified the values proposed by Kessler, in order to provide a smoother distribution while keeping the total sum stable. The tritium input function (WM) is finally calculated by the use of the following mathematical formula:

\[
WM = \frac{\sum_{i=1}^{n} T_i P_i L_i}{\sum_{i=1}^{n} P_i L_i}
\]

where \( T_i \) is the tritium concentration of the precipitation, \( P_i \) is the precipitation and \( L_i \) is the value of Leontiadis' coefficient referring to the month \( i \) (Table II). As rainfall data for this calculation, those of the Exochi station are used. The resulting tritium input function is shown in Fig. 7.
The following models were tried: the exponential or mixing reservoir [8], the models employing a cascade of linear (mixing) reservoirs (from 2 to 100) [9, 10] as well as a model employing a binominal distribution. The computations were carried out on a CDC 330 computer. In each case the transit time as well as the model that gave the best fitting output to that actually observed were selected. Zero tritium content is interpreted as indicating mean transit times greater than 100 years. The respective results are given in Table III.

The age of the groundwater in the different sampling points of the high plateau supports the conclusions based on the stable isotope data. In the central and southern areas of the high plateau the groundwater is very old, indicating that an impermeable barrier probably exists, preventing the draining of groundwater through the sinkhole.

CONCLUSION

The groundwater of the plain of Kato Nevrokopi of Dramas originates mainly from two sources - infiltration from the irrigation canals of water from the Vathitopos stream and water which has infiltrated at higher elevations to the east
TABLE III. MEAN TRANSIT TIME OF GROUNDWATERS

<table>
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<tr>
<th>Sampling site</th>
<th>Mean transit time (a)</th>
<th>Sampling site</th>
<th>Mean transit time (a)</th>
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<td>53</td>
<td>&gt; 100</td>
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<td>18</td>
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</tr>
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of the plain (Falacro mountain). There is evidence of infiltration from the Nevrokopi stream. Recharge by infiltration of local precipitation does not appear to be an important source of recharge.

ACKNOWLEDGEMENTS

The authors express their gratitude to Mrs. S. Sassolos, Miss A. Lacten and Messrs. D. Assimakopoulos, P. Vasilakos, Ch. Doukas and C. Tournavitis for their assistance referring to the analytical work of this study, as well as to Mr. Vassiliadis for his appreciable help during the sampling.
REFERENCES


PROGRESS IN ENVIRONMENTAL ISOTOPE STUDIES (\(^{36}\)Cl, \(^{34}\)S, \(^{18}\)O) AT THE STRIPA SITE

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Abstract

PROGRESS IN ENVIRONMENTAL ISOTOPE STUDIES (\(^{36}\)Cl, \(^{34}\)S, \(^{18}\)O) AT THE STRIPA SITE.

Chlorine-36 analyses performed at four levels of deep groundwaters from the Stripa granite in Central Sweden show \(^{36}\)Cl/Cl\(_{\text{tot}}\) ratios much higher than 'modern' (pre-bomb) values. This is attributed to hypogene production of \(^{36}\)Cl through neutron activation of \(^{35}\)Cl. A preliminary interpretation suggests that mixing occurs within the deep groundwater. The mixing components would be (i) in the upper part of the system a water which has dissolved rock chloride in secular equilibrium with the matrix, and (ii) in the lower part of the system a water the chloride of which is not in secular equilibrium with the rock but has been in contact with it for a long time (of the order of \(10^5\) years). An alternative could be a unique source of chloride from a deep circulating brine with upward diffusion of Cl ions. The \(^{34}\)S and \(^{18}\)O contents of aqueous sulphates are interpreted as indicators of a sedimentary origin.

1. INTRODUCTION

The Stripa Project, managed by the OECD, investigates the suitability of granite as a nuclear waste repository. This project is the continuation of investigations in the Stripa mine, jointly initiated by the United States Department of
Energy (through the Lawrence Berkeley Laboratory of the University of California) and the Swedish Nuclear Fuel Supply (SKBF) (1977–1980).

The Stripa granite is a rather small intrusion of medium-grained granite or monzogranite of Precambrian age in Central Sweden (Fig.1). This batholith is in contact with the northern limb of a plunging syncline of metasedimentary rocks, rich in iron ores which were exploited until 1977.

The investigated boreholes were drilled from extensions of mine galleries:

- 345 m level: M3, a 14 m deep vertical borehole
- 360 m level: N1, a 300 m long subhorizontal borehole
  V1, a 505 m deep vertical borehole
- 410 m level: V2, a 822 m deep vertical borehole.

Water flows out from all the boreholes at rates ranging from less than 0.1 L·min⁻¹ (M3) to about 0.4 L·min⁻¹ (VI). In addition, private shallow wells (PW1 and PW4) were also sampled.

2. PROBLEMS

Several problems arose in Stripa groundwater systems, regarding

- the origin of shallow and deep groundwaters and their relationships
- the ‘age’ of groundwater, i.e. some time function of underground residence
- the origin of aqueous components.

3. PREVIOUS DATA

Many conclusive results were obtained in the pioneering work of Fritz et al. [1, 2]. This study includes groundwater chemistry (major elements), dissolved gases, stable and radioactive isotopes (²H, ¹⁸O, ³H in waters, ¹³C, ¹⁴C of total dissolved carbon, ¹³C and ¹⁸O of calcites) and elements of the uranium decay series.

An increase in salinity was observed with increasing depths. This is mainly due to gains in Cl⁻ and Na⁺. Other differences between shallow and deep groundwaters, namely lower Mg²⁺, K⁺, Ca²⁺ and HCO₃ values with increasing depths, were also reported. To account for these variations, several processes were invoked, assuming hydraulic continuity:

- calcite precipitation
- incongruent dissolution of silicates and subsequent precipitation of clay minerals
- cation exchange
FIG.1. Location map and cross-section of the Stripa site.
- mixing with residual sea water
- release of brines from fluid inclusions.

The presence of methane and the excess of nitrogen dissolved in groundwaters were attributed to bacterial reactions, which also account for the low oxygen content. The very high excess in $^4$He and $^{40}$Ar, as compared with air saturation, is due to the decay of the uranium and thorium series and of $^{40}$K. Although the calculations include hypotheses on the production diffusion rate, the excess in noble gases suggests a very long groundwater residence time. Noble-gas concentrations also allowed an estimate of recharge temperatures, ranging from 0 to 5°C for deep groundwaters in V2 and from 4 to 9°C in the flowing well M3.

Stable-isotope contents (deuterium and oxygen-18), which are lower for deep groundwaters ($\delta^{18}$O ≈ −11 to −13‰), clearly indicated a difference in groundwater origin. The distribution of points along the meteoric water line (MWL) showed that no evaporation occurred during recharge processes. The difference in heavy-isotope content was attributed to a recharge under cooler conditions for deep groundwaters compared with those for shallow groundwaters. This would imply also that deep groundwaters are significantly 'older' than present-day recharge. However, one may note that the intercepts of both groups of data (+11 for shallow waters and +8 for deep waters) are not of statistical value.

A plot of $^{18}$O versus Cl content showed a linear correlation between the upper and lower parts of the water column (M3 and V2). This indicates that a process of mixing occurs within deep groundwater. Surface waters are not on the mixing line and their contribution to the deepest parts of the system is ruled out.

The carbon-13 content of fracture calcite is highly variable (−4.5 to −15.2‰) and not in equilibrium with present-day dissolved inorganic carbon (DIC) ($\delta^{13}$C ≈ −13.2 to −23.2‰). Furthermore, two very high $\delta^{13}$C values (+13 and +15.2‰) were interpreted as indicators of methanogenesis. Fracture calcites show a very large range of $^{18}$O content, the lowest values of which (−23.7 and −21.7‰) were attributed to crystallization in waters very depleted in heavy isotopes (subglacial type palaeowaters).

Tritium analyses showed, as expected, high activities in shallow waters, but the very low $^3$H content of deep groundwater (<1 TU) was attributed to some pollution (drilling waters). However, further high-accuracy measurements [3] indicated that tritium is present in deep waters at the level of a fraction of a tritium unit.

Analyses of DIC in shallow groundwaters gave rather high activities (54−89 pmc). Deep water showed very low $^{14}$C activities (6−2 pmc) and would thus be old.

No significant differences appeared in the $^{13}$C content of DIC between shallow and deep waters and a rather large range of values (−23.2 to −13.2‰) was reported, indicating a biogenic origin. Since the organic matter available in situ for oxidation must be low, Fritz et al. [1] attributed these values to infiltration
through an active soil cover. Enrichments in $^{13}$C (up to $-15\%$) of DIC as compared with initial soil CO$_2$ (assumed to have a $^{13}$C content close to $-23\%$) were attributed to fractionation processes during carbon dissolution and mineralization. Further enrichments were taken as indications of mixing with a source of $^{13}$C-rich carbon (carbonate). In the case of deep waters, the hypothesis was that this second source of carbon may have been a sedimentary carbonate dissolved in subglacial waters. At recharge time, before glacial erosion, carbonates of sedimentary origin would have covered a larger area than at present when they occur near Stripa with a $\delta^{13}$C of $-1.4\%$.

The chemical-isotope approach of Reardon and Fritz [4] has been used to evaluate the recharge conditions in shallow waters. This treatment includes the mixing model of Tamers [5] (all the H$_2$CO$_3$ and one half of the bicarbonates are of biogenic origin, the other half of the bicarbonates is of mineral origin) and takes into account the appropriate fractionation factors between isotopic species assumed to be in equilibrium. Calculations indicated a recent recharge (carbon-14 activities, A $^{14}$C soil CO$_2$ $\approx$ 130% in PW5 (located in granite) and 100% in PW2) diluted with ‘dead’ carbonate (A $^{14}$C $\approx$ 0 and $\delta^{13}$C ranging from $-6.5$ to $-3.5\%$).

In both cases, the chemistry of the carbon species required low pH values and high CO$_2$ partial pressures ($>10^2$ torr). Solid carbonate dissolution would have occurred in a closed system along fractures, since no sedimentary carbonate occurs in the recharge area of these wells. A correction based on Pearson’s approach [6] (isotope balance of carbon of biogenic and mineral origin) was then attempted. However, the variations of the input parameters, especially $\delta^{13}$C of solid carbonates, appear too wide to give a real significance to the results.

Deep groundwaters are very depleted in DIC, probably by precipitation of calcite, as documented by their supersaturation with respect to this mineral. Thus, no modification of the $^{14}$C activity of the DIC would have occurred through calcite dissolution. Assuming that the initial supply of dead carbon is at least one half of the total DIC, ‘ages’ of 23 000 and 25 000 years are suggested for groundwaters from the 330 m level in borehole V2.

Some critical points on $^{14}$C interpretation should be stressed:

(a) The total DIC in Stripa deep groundwaters is very low (alkalinity $\approx$ 10 ppm [1]). Thus the risk of contamination with recent carbon is relatively much higher than for common waters. This may be due to exchange between aqueous and gas phases, chiefly through handling of the sodium hydroxide solution ($\approx$ 2 mL·L$^{-1}$) which is used to raise the pH above 12 during DIC sampling operations.

(b) The evaluation of the initial activity of the DIC was only possible for shallow waters (private wells) which are hydraulically independent from deep waters.

(c) Deep groundwaters are very likely a mixture of two water bodies and the significance (if any) of the concept of groundwater ‘age’ is still reduced in case of mixing.
(d) As pointed out by Andrews et al. [7], a hypogene production of $^{14}$C through neutrons induced from alpha decay has to be evaluated in a granite rich in uranium/thorium like the Stripa batholith.

(e) Carbon-14 ‘age’ estimates are in poor agreement with the high contents of noble gases from radioactive decay products (about 380 000 years, according to a model of $^4$He accumulation [7]).

(f) The presence of organic matter (methanogenesis and sulphate reduction evidenced by $\text{H}_2\text{S}$ occurrence, for instance in borehole N1) may give rise to an increase in $\text{HCO}_3^-$ through oxidation.

Taking these points into consideration, $^{14}$C concentrations in DIC cannot be interpreted in terms of time elapsed within the system.

Studies on the uranium decay series, interpreted in the most simple way (closed system), lead to differences in ages of the order of $5 \times 10^5$ years between the upper and lower parts (6.3 – 50 m and 376.5 – 471 m in V2) of the deep groundwaters. However, the decrease in uranium content suggested a deposition on fractures and thus an increase in activity ratio due to the recoil effect. The time elapsed in the system would still be greater than that calculated in a closed system.

A more detailed study on the uranium decay series for the same site, including determinations of U and Th in the rock, is presented in Ref.[7]. The leaching of uranium in the shallow (oxidized) levels gives rise to a high uranium concentration in the water, while the rock appears depleted. An overconcentration of uranium within fracture minerals ($10 000 – 25 000 \mu g \cdot g^{-1}$) or along grain boundaries in cracks ($4000 – 6000 \mu g \cdot g^{-1}$) is reported. Andrews and Kay [8] used models which take into account the various phenomena (recoil range of $^{234}$Th within the rock matrix, etch rate of uranium isotope species $^{234}$U and $^{238}$U). They calculated the various curves describing the evolution of the activity ratio $^{234}$U/$^{238}$U versus the respective etch rates for different residence times. They also considered the time variations in activity ratios with respect to the fracture width. From field data it appeared that $^{234}$Th recoil is an important process in the groundwater system. The decrease of this process at depth is probably linked to reducing conditions and the relevant precipitation of $^{234}$U.

Isotopic and chemical data were recently presented by Fritz et al. [9] who discuss the origin of deep-water salinity. The accent is on the possible effect of palaeogeographical changes on groundwater salinity. Deglaciation made the sea level rise faster than isostatic rebound. Marine water invaded the Fenno-Scanian peninsula, bringing brackish waters into, or close to, the Stripa area (Yoldia Sea between 10 000 and 9000 B.P. and Littorina Sea between 7000 and 3000 B.P.). The sea-shore contours during Holocene coincide with areas of anomalously saline groundwater [10]. Because of drastic variations, especially in earth alkaline cations, as compared with a simple process of Holocene dilution of sea water by fresh waters, Fritz et al. [9] invoke an interaction with the matrix.
New $^{18}$O and $^2$H data [9] reinforce the clear-cut distinction between deep water highly depleted in heavy isotopes ($-14 < \delta^{18}$O $< 13\%$) and water at the $-330$ m level (upper part of the deep-water body) which is richer in $^{18}$O by about $1\%$. The low $^{14}$C content of the DIC of deep waters could be the result of mixing, including several per cent of Holocene sea water in a much older groundwater. However, for the hypothesis of sea-water intrusion it would be interesting to determine whether the chloride balance is in agreement with the $^{14}$C balance. The hypothesis of a Holocene marine supply on the basis of the sulphur isotope composition of aqueous sulphates is also discussed in Ref.[9].

Low $^{34}$S contents of shallow waters reflect atmospheric fallout and rainout, including sulphur from fossil fuels. Deep aqueous sulphates exhibit high $^{34}$S contents (+16 to +21\% versus Canyon Diablo) which are attributed to marine origin. Some values of the $^{18}$O content of these deep sulphates are also available. They are close to +8.5\% versus SMOW and are attributed to a marine origin with some possible contributions of biogenic (light) sulphates.

As established by numerous measurements by Claypool et al. [11], it appears that the problem of the origin of sulphates requires a simultaneous examination of $^{34}$S and $^{18}$O contents for each sample. In the same study, attention is paid to the large isotopic disequilibrium between waters and sulphate ions. From data by Lloyd [12], the half-reaction time for reaching equilibrium would be about 150,000 years at deep-water pH values ($\geq 10$). If the environmental conditions remained the same over the whole residence time of $\text{SO}_4^{2-}$ ions within the groundwater, an 'age' of at most a few thousand years would be indicated. However, as discussed by Fontes and Michelot [13], the use of oxygen isotope disequilibrium between sulphate and water as a chronometer is rather conjectural, for the following reasons:

(a) The experiments were performed over several months at very low pH, and extrapolation to field environmental conditions (especially high pH) over a long period may be risky since no error estimate is available.

(b) The dependence has not been discussed in terms of activity ratios of $\text{H}_2\text{SO}_3$ to $\text{SO}_4^{2-}$, which are respectively easy and difficult to exchange with $\text{H}_2\text{O}$.

(c) The possible influence of microenvironmental conditions (catalytic or inhibiting effects) on the reaction has not been investigated.

(d) Reactions much faster than equilibration may interfere with the $\text{H}_2\text{O} - \text{SO}_4^{2-}$ system, especially biochemical reduction or oxidation.

(e) Values of equilibrium fractionation factors for the reaction between sulphate ion and water are still to be confirmed at 'normal' pH ranges.

Thus, until these points are elucidated, it will be difficult to obtain real-time estimates from the $\text{SO}_4^{2-} - \text{H}_2\text{O}$ oxygen isotope disequilibrium.
Further information on the origin of dissolved salts in Stripa groundwaters was recently published by Nordstrom [14]. This study is based upon a very detailed chemical investigation (43 major and trace constituents). It was concluded that deep waters could be a mixing of a low-salinity source (of meteoric origin) with a bedrock-originating Na-Ca-Cl brine. The sulphate content increases at depth more than chloride, suggesting an extra source of $\text{SO}_4^{2-}$ ion (anhydrite dissolution?). Among the ‘conservative’ tracers, $\text{Br}^-$ and $\text{Cl}^-$ are of special interest. The mass ratio $\text{Br}^-/\text{Cl}^-$ (0.0104) is much higher than in sea water (0.0034). For this reason and also because of the very high $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio (more than 100 times the marine value), marine origin of the salinity, even after a long interaction with the rock matrix, does not seem possible. However, the $\text{Br}^-/\text{Cl}^-$ ratio is probably a much better indicator of marine contribution than the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio which can increase through feldspar hydrolysis and crystallization of clay minerals.

Because of the local geothermal gradient ($15^\circ \cdot \text{km}^{-1}$), a geothermal origin of the salinity is also ruled out. Therefore, the leaching of fluid inclusions, also listed by Fritz et al. [1], is considered as a possible source of deep-water salinity.

In leaching experiments of fluid inclusions, Nordstrom [14] measured an average value of 0.0101 for the $\text{Br}^-/\text{Cl}^-$ ratio and supported the concept of a rock source for the deep-water salinity. It is obviously difficult to match this hypothesis with mass-balance considerations since natural flow patterns are not known.

From these earlier studies, it appears that several types of conclusions, corresponding to different degrees of certainty, may be drawn.

(a) Facts
- Different origins for subsurface and deep groundwaters
- Shallow groundwaters were mainly recharged locally and recently (after 1952)
- Deep groundwaters were recharged before 1952.

(b) Hypotheses (but rather probable)
- Deep groundwaters are the result of mixing between two water masses (one mass chloride-rich, $^{18}\text{O}$-depleted at the bottom of the system, and another mass with a slightly higher $^{18}\text{O}$ content and a much lower chloride content)
- Deep-groundwater recharge reflects cooler climatic conditions than at present.

(c) Points still to be proved
- Deep groundwaters are older than 20,000 years and could be 23,000 to 25,000 years
- Deep groundwaters are periglacial waters
- Chloride and sulphate contents from deep groundwaters may be due to leaching of rocks and fluid inclusions and/or to mixing with some sea-water supply.
4. OBJECTIVES AND METHODS

The main scope of this work is to contribute to the ongoing discussion on the origin of deep waters and their aqueous compounds, namely chlorides and sulphates, and their residence times. For this purpose, we have applied essentially two techniques, using (i) chlorine-36 and (ii) sulphur-34 and oxygen-18 in aqueous sulphates.

The results are discussed together with some other chemical data and are still preliminary. They will be completed and compared with other geochemical and isotopic results obtained within the framework of the working group on the hydrogeochemistry of the Stripa Project.

4.1. Chlorine-36

Chlorine-36 ($T_{1/2} = 301,000$ a), as most radionuclides, may have several origins: cosmic rays, thermonuclear tests and underground production. It is produced in the high atmosphere by spallation and activation by neutrons induced from cosmic protons on air components. The most frequent reaction is spallation of argon-40 [15].

The equilibrium between natural production and rainout gives rise to a steady-state activity close to $10^{-5} \text{ dis} \cdot \text{min}^{-1} \cdot \text{L}^{-1}$ or close to $4 \times 10^6$ atoms per litre of rain water. Thermonuclear tests raised this activity by a factor of five hundred in the late 1950s, but concentrations have now returned to pre-1950 levels.

Chlorine-36 is introduced in the water cycle as the Cl$^-$ ion. Theoretically, it thus presents the advantages of a conservative tracer: no chemical interactions with the matrix, no retardation and no precipitation.

Concentrations, expressed in atomic ratio, $({}^{36}\text{Cl}/{}^{35}\text{Cl} +{}^{37}\text{Cl}) \times 10^{15}$, range between $2 \pm 2$ for sea water and about 2000 for post-bomb water. From the observed variations in confined groundwaters [15], a radiometric span of about $10^6$ years could be explored with this radiochronometer. Most of the recharge episodes from the Quaternary could be identified and correlated with palaeoclimatic or palaeometeorological events as evidenced by stable-isotope, chloride or noble-gas contents.

However, although interest has been expressed in $^{36}\text{Cl}$ as early as the 1950s, there are several technical and theoretical limitations on the use of this nuclide for practical investigations:

- Evaluation of the cosmic-ray production rate and its possible time fluctuations (this can be documented through polar ice profiles)
- Evaluation of the crustal production, either shallow (mainly spallation of potassium and calcium and activation of $^{36}\text{Cl}$ by cosmic neutrons) or deep (neutrons induced from decay of the uranium and thorium series)
- Estimation of the distribution patterns in rainout (and possibly dry fallout), together with meteoric chloride of marine origin (sea spray).
<table>
<thead>
<tr>
<th>Well</th>
<th>Date</th>
<th>Depth interval</th>
<th>δCl/Clo, × 10^{-6}</th>
<th>CF (ppb)</th>
<th>atoms °C/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>Sep. 1982</td>
<td>203 - 205 m</td>
<td>203 ± 14</td>
<td>67</td>
<td>(2.3 ± 0.4) × 10^8</td>
</tr>
<tr>
<td>V2</td>
<td>Sep. 1982</td>
<td>0 - 82 m</td>
<td>80 ± 8</td>
<td>300</td>
<td>(4.1 ± 0.3) × 10^8</td>
</tr>
<tr>
<td>V1</td>
<td>July 1981</td>
<td>409 - 506 m</td>
<td>63 ± 11</td>
<td>580</td>
<td>(6.2 ± 0.7) × 10^8</td>
</tr>
<tr>
<td>V2</td>
<td>Nov. 1982</td>
<td>406 - 410 m</td>
<td>66 ± 14</td>
<td>620</td>
<td>(7.0 ± 1.0) × 10^8</td>
</tr>
</tbody>
</table>
The chloride content of precipitation varies according to various factors (origin of air masses, distance to the coast line, amount and height of condensation stages, type of precipitation, humidity profile of the atmosphere [16]). All these factors also vary with general and local climatic patterns. The dilution of $^{36}\text{Cl}$ by marine chlorine is of local value at a given time. It is possible to refer the $^{36}\text{Cl}$ content to a given amount of water, but in this case it is difficult to evaluate the evapotranspiration which concentrates the radionuclide.

4.1.1. Measurements

Measurements were performed using the tandem accelerator (10 MV) of the University of Rochester. Four samples were prepared by precipitation of AgCl from 1 to 2 litres of water (minimum sample size 10 mg of Cl) according to the technique described in Refs [17, 18].

Concentrations of $^{36}\text{Cl}$, expressed as atomic ratios and absolute contents, are given in Table I and Fig. 2.

4.1.2. Discussion

All samples are from the so-called ‘intermediate-deep’ waters [1] and no measurement is available on shallow recent (tritium-bearing) groundwaters. The relatively few values are reasonably distributed on a mixing curve (Fig. 2) of $^{36}\text{Cl}/\text{Cl}_{\text{tot}}$ versus $\text{Cl}_{\text{tot}}$. The conclusions of previous isotopic and hydrochemical studies are thus confirmed: mixing occurs between two sources of chloride in the deep aquifer system. However, except in the sample which integrates the whole water column (V2, 0 – 822 m), complete mixing is not achieved. Thus it is slow compared with the causes of variations in $^{36}\text{Cl}$ concentrations between the two water bodies. In other words, if the system is in a steady state (input or buildup of $^{36}\text{Cl}$ equilibrated by decay) in both mixing components, the mixing rate of $^{36}\text{Cl}$ is lower than the decay rate. This could be related to the extremely low diffusion rate determined for iodide in porous spaces of Utri granite (effective diffusivity $D_p \varepsilon_p \approx 1.3 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ ($D_p$ is pore diffusivity, $\varepsilon_p$ is porosity)) [19].

The highest $^{36}\text{Cl}/\text{Cl}_{\text{tot}}$ ratio is found in the upper part of the system, but the $^{36}\text{Cl}$ content per mass unit of water is higher in deep waters. This trend is due to the dilution of $^{36}\text{Cl}$ by common chloride at the bottom of the system. However, all the samples contain much more $^{36}\text{Cl}$ than ‘modern’ (pre-bomb) precipitation (about two orders of magnitude). Obviously, this cannot be due to any environmental concentration process (e.g. evapotranspiration). The extremely low $^3\text{H}$ content (1 – 3 TU) demonstrates the absence of recent waters in the system. The excess of $^{36}\text{Cl}$ is thus due to subsurface production. Thus, in such an environment the cosmogenic contribution is undetectable below underground-produced $^{36}\text{Cl}$ whose buildup can be used as a normal radiocchronometer in a closed system.
\[ dN = (\psi + \phi_n f) \, dt - \lambda \, N \, dt \]  

(1)

where \( N \) is the number of atoms within a given reservoir, \( \psi \) is the production rate through spallation processes, \( \phi_n \) is the neutron flux, \( f \) is the fraction of the neutron flux which is absorbed by \( ^{35}\text{Cl} \) atoms (the product \( \phi_n f \) accounts for the buildup rate of \( ^{36}\text{Cl} \) through activation), \( t \) is the time and \( \lambda \) is the decay constant of \( ^{36}\text{Cl} \) (\( 2.3 \times 10^{-6} \) a\(^{-1} \)).

After integration between zero and \( t \),

\[ N = \frac{\psi + \phi_n f}{\lambda} \left(1 - e^{-\lambda t}\right) \]  

(2)

At depth, within the rock matrix, \( \psi \) may be neglected.
The fraction of neutron flux used for activation is given by

\[
\frac{m_{35}^{\text{act}}}{\Sigma_i m_i \sigma_i^{\text{abs}}} \tag{3}
\]

where \( m \) is the concentration in millimoles per kilogram, \( \sigma_i^{\text{act}} \) is the neutron production (activation) cross-section for the reaction \(^{35}\text{Cl} \rightarrow ^{36}\text{Cl}(44 \text{ b})\) and \( \sigma_i^{\text{abs}} \) is the neutron absorption cross-section for isotope \( i \).

The neutron flux \( \phi_n \) is difficult to evaluate since it depends upon the content of alpha emitters and also upon the content of atoms which produce neutrons through \( \alpha, n \) reactions (Li, Be, Cd, Gd, Eu, Sm, etc.). For the Stripa granite, the latter information is not yet available. However, the rock content in uranium and thorium is extremely high (average 43.6 and 56.5 \( \mu g \cdot g^{-1} \), respectively, for borehole V2) [21]. The neutron flux is then assumed to be simply proportional to the values given by Feige et al. [22], for average granites, corrected for excess Th and U, which gives the values listed below:

<table>
<thead>
<tr>
<th></th>
<th>U (( \mu g \cdot g^{-1} ))</th>
<th>Th (( \mu g \cdot g^{-1} ))</th>
<th>Natural fission (( n \cdot kg^{-1} \cdot a^{-1} ))</th>
<th>U derived (( n \cdot kg^{-1} \cdot a^{-1} ))</th>
<th>Th derived (( n \cdot kg^{-1} \cdot a^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average granite</td>
<td>2.8</td>
<td>11.0</td>
<td>1300</td>
<td>6800</td>
<td>7800</td>
</tr>
<tr>
<td>Stripa granite</td>
<td>43.6</td>
<td>56.5</td>
<td>20000</td>
<td>106000</td>
<td>40000</td>
</tr>
</tbody>
</table>

It then follows that the neutron production (\( \approx 165 \times 10^3 n \cdot kg^{-1} \cdot a^{-1} \)) in the Stripa granite is more than ten times higher than in a standard granite.

One may assume that the chemical composition of Stripa granite (except for U and Th contents) is close to that of the average granite and thus

\[ \Sigma_i m_i \sigma_i^{\text{abs}} \approx 12500 \] [20].

The calculated steady-state (buildup equals decay) ratio \( ^{36}\text{Cl}/\text{Cl}_{\text{tot}} \) of the rock chlorine and of the dissolved chlorine is of the order of \( 300 \times 10^{-15} \) atoms per atom. In practice, this value does not depend on the chloride content of the rock; it is about 1.5 the highest \( ^{36}\text{Cl}/\text{Cl}_{\text{tot}} \) ratio measured on the Stripa system (in N1). It is thus proposed that the \(^{36}\text{Cl} \) content from N1 could represent a long-time equilibrium between buildup and decay. This hypothesis implies that chloride has been in contact with the granite for much longer (\( \gg 10^6 \) years) than could reasonably be assumed for a groundwater residence time in the upper part of the deep system. Therefore, the chloride content from N1 (67 ppm) could mainly come from the rock itself and could be attributed to fluid inclusions. The hypothesis of Nordstrom [14] on the origin of salinity could be in agreement with \(^{36}\text{Cl} \) data in the upper part of the deep system.
However, \(^{36}\text{Cl}/\text{Cl}_{\text{tot}}\) values in stagnant brines [23] suggest that the above estimated neutron production may be too low by perhaps a factor of two or more. In this case, the \(^{36}\text{Cl}\) content in the upper part of the deep groundwater system would not be in secular equilibrium with the rock. The buildup time given by Eq. (2) would range between 500 000 and 180 000 years for equilibrium ratio values of \(300 \times 10^{15}\) and \(600 \times 10^{15}\), respectively. In this case, the chloride in N1 would have been in contact with the rock for a longer time than at the bottom of the system (see below, time calculations for the deepest groundwaters). This would suggest that chloride ions diffuse upward from a circulating brine which reaches the deepest part of the system.

In fact, deep groundwaters from the bottom of the system show a much lower isotope ratio than those in the upper part. Following our hypothesis of long-time equilibrium of chloride content at the top of the system, there would be no reason for the lower part to be in disequilibrium if \(\text{Cl}^-\) was supplied by the same source (provided the granite has the same chemical composition and the same uranium and thorium contents). It is proposed that the high chloride content of the deepest groundwaters does not come from the rock itself and is not in secular equilibrium with it.

The time for deep \(\text{Cl}^-\) being in close contact with the rocks may be evaluated using Eq. (2). \(\text{Cl}^-\) ions are assumed to be well distributed in fractures and in grain porosity. Calculations are made: (i) using the values found for \(\phi_n\) and \(f\) on the basis of the U and Th content measured by Andrews [21] and assuming an average standard chemical composition of the granite; and (ii) assuming that the Cl isotope ratio in borehole N1 represents a long-time equilibrium and recalculating the corresponding neutron flux. The corresponding times of contact between chlorine and rock are 100 000 years and 160 000 years, respectively, for hypotheses (i) and (ii). The shortest residence time for chlorine of concentrated solutions from the deepest parts of the system is 50 000 years. This value is obtained for an equilibrium atomic ratio of \(600 \times 10^{15}\).

Obviously, these figures are highly hypothetical and provisional since direct experimental data are still needed on the granite chemistry, the spatial representativeness of average chemical contents, and the distribution of elements along fractures. Furthermore, a direct measurement of \(^{36}\text{Cl}\) from rock chloride is also needed in order to evaluate long-time equilibrium values of the isotope ratio and to check the calculations on hypogene neutron production. Another important investigation is the evaluation of neutron flux through production in deep groundwaters of other nuclides in secular equilibrium with the rock (e.g. \(^{39}\text{Ar}\), as suggested by H.H. Loosli). These studies are planned or in progress, together with attempts for direct measurements of the in situ neutron flux.

Whatever the results of future investigations, it may be advanced at this stage that deep groundwaters are probably significantly older than suggested by \(^{14}\text{C}\) analyses. Time indications by noble gases and uranium studies [7, 21] are thus supported.
4.2. Sulphur-34 and oxygen-18 in aqueous sulphates

Variations in the heavy-isotope content of aqueous sulphates were extensively reviewed in Refs [13, 24]. Equilibrium (thermodynamic) isotope effects in sulphur compounds are generally very high, especially at low temperatures [25]. However, since sulphur enters into metabolic cycles, isotope effects may also occur under biological (kinetic) conditions. As a rule, biocatalysts use preferentially light (i.e., common) isotopes. A concentration in heavy isotopes is thus observed in the unmetabolized fraction. These processes generally involve closed-system reactions, Rayleigh processes and reservoir effects. Since reduced sulphur species are frequently formed through bacterial reductions, their $^{34}S$ content is generally low as compared with coexisting or original sulphates. Sedimentary pyrites may show $^{34}S$ contents as low as $-70\%$ [26].

Sulphate ions represent the most frequent form of dissolved sulphur. Because of their steady-state concentration the isotopic content of oceanic sulphates is very constant ($\delta^{18}O = (+9.45 \pm 0.15)\%$ versus SMOW and $\delta^{34}S = (+20.0 \pm 0.25)\%$ versus Canyon Diablo [27]. Meteoric sulphates of oceanic origin (unpolluted by industrial dust and smoke) have similar values [28, 29].

Processes which may affect the stable-isotope content of aqueous sulphate are precipitation, partial reduction and oxidation of sulphide. Precipitation of solid sulphate occurs with a heavy-isotope enrichment in the solid phase: $3 < \delta^{18}O < 4\%$ (Ref. [12] and Fontes and Schwarz, unpublished data), and $1.4 < \delta^{34}S < 3.4\%$ [30, 31]. Further precipitation stages lead to aqueous sulphate more and more depleted in heavy isotopes. For instance, marine Mg-K sulphates have $^{34}S$ below average ocean values [32].

Kinetic effects due to bacterial reduction of sulphate give rise to linear correlations in the $\delta^{34}S$ – $\delta^{18}O$ diagram. The heavy-isotope content of the remaining fraction of aqueous $SO_4^{2-}$ increases along slopes generally ranging from 4 to 1.5 [33, 34].

The chemical oxidation of reduced species into $S^0$, $SO_3^{2-}$ and $SO_4^{2-}$ is probably not fractionating [24, 26]. Bacterial oxidation leads to a slight depletion in $^{34}S$ [35]. The formation of $SO_4^{2-}$ ions involves at least two sources of oxygen; one of these is water, another one would be dissolved oxygen [12, 36–38]. The respective contributions of these sources are still under discussion: 1/4 (according to the stoichiometry), 1/3 [12] or 1/2 [39] of the oxygen of $SO_4^{2-}$ is contributed by water. This admixture is not isotope fractionating. Although more experimental data on this process are needed, it appears that the $^{18}O$ content of a sulphate formed through oxidation of reduced species will depend upon the $^{18}O$ content of the water where the process occurs. Whatever the other source(s) of oxygen, one would expect such a $SO_4^{2-}$ to be depleted in $^{18}O$ with respect to sedimentary sulphate of marine origin.

Furthermore, oxygen isotope equilibrium between $H_2O$ and $SO_4^{2-}$ is very far from being reached in low-temperature environments, for instance in the marine
<table>
<thead>
<tr>
<th>Borehole</th>
<th>Date</th>
<th>Depth (m)</th>
<th>Cl⁻ (mg · L⁻¹)</th>
<th>SO₄²⁻ (mg · L⁻¹)</th>
<th>□H (H₂O) SMOW</th>
<th>□O (SO₄²⁻) SMOW</th>
<th>□O (SO₄²⁻) SMOW</th>
<th>□S (SO₄²⁻) C.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW4</td>
<td>June 1982</td>
<td>shallow</td>
<td>2</td>
<td>13</td>
<td>−12.91</td>
<td>−93.4</td>
<td>+1.02</td>
<td>+ 3.60</td>
</tr>
<tr>
<td>PW1</td>
<td>June 1982</td>
<td>shallow</td>
<td>15</td>
<td>10.5</td>
<td>−11.56</td>
<td>−82.5</td>
<td>+4.28</td>
<td>+ 5.13</td>
</tr>
<tr>
<td>M3</td>
<td>June 1982</td>
<td>36</td>
<td>7</td>
<td>−12.32</td>
<td>−87.7</td>
<td>+0.78</td>
<td>+11.28</td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>June 1982</td>
<td>3 – 300</td>
<td>40</td>
<td>0.6</td>
<td>−12.97</td>
<td>−93.6</td>
<td>+5.27</td>
<td>+27.92</td>
</tr>
<tr>
<td>V2</td>
<td>June 1981</td>
<td>356 – 470</td>
<td>410ᵃ</td>
<td>44.5ᵇ</td>
<td>−13.6ᵇ</td>
<td>−97ᵇ</td>
<td>+7.95</td>
<td>+15.04</td>
</tr>
<tr>
<td>V1</td>
<td>June 1982</td>
<td>5 – 506</td>
<td>64</td>
<td>−13.10</td>
<td>−93.0</td>
<td>+7.81</td>
<td>+13.79</td>
<td></td>
</tr>
<tr>
<td>V1</td>
<td>Nov. 1981</td>
<td>5 – 506</td>
<td>540</td>
<td>50</td>
<td>−13.08</td>
<td>−91.9</td>
<td>+8.10</td>
<td>+13.96</td>
</tr>
<tr>
<td>V1</td>
<td>July 1981</td>
<td>409 – 506</td>
<td>570</td>
<td>110</td>
<td>−13.25</td>
<td>−91.5</td>
<td>+7.30</td>
<td>+12.85</td>
</tr>
<tr>
<td>V2</td>
<td>Nov. 1982</td>
<td>406 – 410</td>
<td>620</td>
<td>−92.4</td>
<td>+7.54</td>
<td>+15.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V1</td>
<td>June 1981</td>
<td>409 – 506</td>
<td>630ᵇ</td>
<td>102ᵇ</td>
<td>−12.8ᵇ</td>
<td>−93ᵇ</td>
<td>+7.80</td>
<td>+12.84</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Nov. 1982</td>
<td>– 50</td>
<td>4200</td>
<td>560</td>
<td>−6.97</td>
<td>−57.7</td>
<td>+6.93</td>
<td>+19.22</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Nov. 1982</td>
<td>– 200</td>
<td>7800</td>
<td>870</td>
<td>−5.64</td>
<td>+8.83</td>
<td>+19.40</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Data from K. Nordstrom [14].
ᵇ Data from P. Fritz (unpublished).
reservoir [35, 40]. This is probably due to the extremely low reaction rate of the S-O bond at neutral pH. Experimental values for reaction rates were determined by Lloyd [12] within the temperature range 198 – 721 K. From these data, Pearson and Rightmire [24] derived the following relationship between reaction rate (expressed as half-reaction time, \( t_{1/2} \)), temperature \( T \) and pH:

\[
\log t_{1/2} \text{ (hours)} = 2.15 \times 10^3 \cdot T^{-1} + 0.44 \cdot \text{pH} - 3.09
\]

This equation could provide a geochronometer since the distance to equilibrium is time dependent. However, as stated before, there are several limitations to the use of this formula.

### 4.2.1. Sampling and analyses

Because of the very variable \( \text{SO}_4^{2-} \) contents (from less than 1 ppm to more than 100 ppm) the sample sizes varied from 2 to 60 litres. When necessary (H\(_2\)S smell), the water was treated with HCl to remove reduced sulphur species. Sulphate is precipitated as barium sulphate by adding barium chloride. The final barium sulphate, rinsed and dried, is then treated to quantitatively prepare \( \text{SO}_4 \) and \( \text{CO}_2 \) for \( ^{34}\text{S} \) and \( ^{18}\text{O} \) determinations [13].

### 4.2.2. Results and discussion

The heavy-isotope contents of aqueous sulphates from shallow and deep groundwater systems at Stripa are reported in Table II and Figs 3 and 4.

*Subsurface waters* contain aqueous sulphate with \( ^{34}\text{S} \) and \( ^{18}\text{O} \) contents intermediate between those of marine sulphate and those resulting from oxidation of reduced species. As noted by Fritz et al. [9], these sulphates can be attributed to a mixture of sea spray with sulphates produced through oxidation of fuel sulphur. Sample PW1 is probably affected by a secondary enrichment in heavy isotopes due to partial reduction of the initial \( \text{SO}_4^{2-} \) bulk. Bacterial effects would be enhanced there by water stagnation (the same well shows a low deuterium excess, which denotes evaporation). As already stated, considering \( ^{18}\text{O} \) and \( \text{Cl}^- \) data [1], shallow sulphates and thus shallow waters do not seem to have any connection with deep sulphates.

*Deep waters* from V1 and V2 have sulphates with heavy-isotope contents (+12.8 to +15.4‰ in \( ^{34}\text{S} \); +7.3 to +8.1‰ in \( ^{18}\text{O} \) which belong to the range of sea-water-derived sulphates. This may be due to (i) a true marine origin, recent or past, through leaching of evaporite deposits, or a mobilization of brines; or (ii) a succession of geochemical processes. Hypothesis (ii) implies too complicated reaction pathways (e.g. successively: dissolution of ancient evaporites, complete reduction, oxidation in the presence of a source of oxygen highly enriched in \( ^{18}\text{O} \); see Ref.[13] for a detailed discussion) and is discarded. We thus favour the hypothesis of originally marine sulphate.
Thus, the question is the mechanism of admixture of this sulphate to deep groundwater. In the $^{34}$S–$^{18}$O diagram (Fig. 3) the representative points for deep aqueous sulphates fall rather far from present-day marine values. It is well established that the heavy-isotope content of oceanic sulphate is very homogeneous and has remained quite constant over the Upper Tertiary and Quaternary [11]. Furthermore, analyses of Baltic Sea sulphates (sampling 1982-11-17, N 57°20', E 20°03', −50 m and −200 m) give values which appear quite different from open-sea averages. Whatever the reason for these differences (recent pollution?) the values are not close to those of Stripa deep sulphate. Therefore, simple marine intrusion cannot account for the $^{34}$S and $^{18}$O contents found at Stripa without substantial modifications. Changes would have consisted in a significant decrease in $^{34}$S without major variations in $^{18}$O with respect to initial sea water. Such an effect can hardly be attributed to an extra supply of sulphates through oxidation of reduced sulphur. This would have led to a decrease in $^{18}$O of the resulting sulphate.

Furthermore, there is no relationship between the $^{34}$S and SO$_2^-$ contents in boreholes V1 and V2, as would be expected in the case of mixing with a source of light sulphur. Thus, at least for boreholes V1 and V2, which show the highest sulphate contents of the system, we estimate that there was no significant mixing
with sulphate generated through oxidation. The observed values are believed to be representative of sedimentary sulphates different from Quaternary (and Upper Tertiary) marine ones. This observation is in agreement with the very high Br/Cl ratios which are probably conservative in the system and not compatible with simple marine origin [14].

The heavy-isotope content of the aqueous sulphate could also be attributed to sedimentary sulphate entrapped in the granite or in its surrounding metamorphosed layers. However, no information is available on the stable-isotope contents of Precambrian sulphates and their further possible changes during metamorphism. Furthermore, such a long underground residence time would have

FIG. 4. Sulphur-34 versus sulphate content in Strips deep groundwaters (well number, sampling depths and date; PW = shallow wells).
led to an equilibrium between chloride and rocks (assuming for both SO$_4^{2-}$ and Cl$^-$ a common origin from fluid inclusions), which does not exist. This would imply different origins for Cl$^-$ and SO$_4^{2-}$ ions, but there are no arguments for this. It can be seen in Fig.3 that the $^{34}$S contents of Stripa deep aqueous sulphates are within the range known for Permian gypsum and anhydrite, whereas the $^{18}$O contents are somewhat lower [11]. The sulphate involved would have been generated by the leaching of complex salts depleted in $^{18}$O by previous calcium sulphate precipitation. The salinity could also originate from a contribution of a heavy (post-halite) brine. No Permian deposits are recorded from these regions of Sweden. Local leaching of ancient evaporites is thus excluded. An alternative source of Permian sulphate could be the basin of the pre-Baltic Sea when it was cut off from the oceanic reservoir, as has probably been the case several times since the last interglacial period (~ 130 000 years B.P., as suggested by $^{18}$O analyses of Foraminifera from deep-sea cores). During these periods, the pre-Baltic basin was supplied by water courses from the northern parts of the Federal Republic of Germany, the German Democratic Republic and Poland. In these areas, Permian evaporites (Zechstein deposits) are present and may have supplied SO$_4^{2-}$ and Cl$^-$ from salt-dome leaching or from associated brines. It may be noted that the Br$^-$/Cl$^-$ weight ratio determined in deep waters, 0.0104 [14], is rather similar to the values measured in highly soluble chlorides from Hartsalz Flöz, Thüringen: 0.0166 for carnallite (KCl, MgCl$_2$, 6H$_2$O) and 0.00485 for sylvite (KCl) according to data by Kühn [41]. A remote origin of the salinity, through leaching of (post-halite) Permian K-Mg complex salts, or from a minor supply of residual brine, via the pre-Baltic Sea would reconcile the Permian-like isotopic signature of deep groundwater sulphates with the local absence of Zechstein deposits. However, in this case, one would still have to make a mass balance of the geochemical processes which would have eliminated K$^+$ and Mg$^{2+}$ from deep groundwaters through reactions involving fracture minerals: cation exchange and crystallization of Mg-K secondary minerals (chlorite and sericite are among the most common minerals in fracture coatings [42]). Furthermore, halite, the most common Permian evaporite (and whose Br$^-$/Cl$^-$ ratio is depleted with regard to sea-water values) would not be involved in the leaching process.

Waters from N1 and M3 have a very low sulphate content. In terms of isotope mass balance, their heavy-isotope content may thus have been modified easily by secondary processes. Bacterial reduction, evidenced by H$_2$S occurrence, is probably the cause of the high $^{34}$S content of N1. A re-oxidation of products from a previous reduction could account for the low heavy-isotope content in M3.

5. CONCLUSIONS

A review of previous data illustrates the kind of information which can be gained through geochemical and environmental isotope studies of low flow systems
in fractured rocks. Also, points and concepts are indicated which need further support from new data and investigations (significance of $^{14}$C data, periglacial origin of deep waters, origin of deep salinity).

The present work gives further confirmation of the independence of shallow and deep groundwater systems and the incomplete mixing in the deep system. Through preliminary $^{36}$Cl data, arguments are given for the following conclusions:

- Different origin of the chloride contents in the upper and lower parts of the deep groundwater system (leaching of rock chloride and secondary enrichment in saline solution, respectively); or the same origin of the chloride contents for the whole system, but with a longer residence time of Cl$^-$ in the upper part due to upward diffusion.
- Secondary origin of deep chloride, which is not in equilibrium with the rock.
- Residence times of saline waters which are probably much longer than suggested by $^{14}$C, in agreement with the high contents of noble gases.

The stable-isotope content of deep SO$_4^{2-}$ suggests a sedimentary origin for the aqueous sulphate and not simple sea-water intrusion.

More efforts are needed to investigate the chemical composition of granite and to estimate the deep neutron flux and the underground production of $^{36}$Cl. These estimates must be compared with a direct evaluation of neutron flux through other in situ nuclide production ($^{39}$Ar, $^{32}$Si, etc.). Further investigations are also required in order to determine the origin of aqueous sulphur compounds, including analyses of more samples from the Baltic Sea, from northern Europe rivers and from regional shallow and subsurface groundwaters.

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GROUNDWATER FLOW PROFILE
AND RESIDENCE TIMES
IN CRYSTALLINE ROCKS
AT ALTNABREAC, CAITHNESS, UK

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Abstract

GROUNDWATER FLOW PROFILE AND RESIDENCE TIMES IN CRYSTALLINE ROCKS
AT ALTNABREAC, CAITHNESS, UK.

Chemical, radiochemical and isotopic data have been obtained for groundwater in
 crystalline rocks at the Altnabreac research site, Caithness, UK. Oxygen and hydrogen isotope
 ratios indicate all components of all waters to be of meteoric origin. Borehole samples are the
 product of several years of precipitation mixing effectively in the surface peat/soil zone. Acidic
 infiltrating water, with $\delta^{18}O$ of about $-30\%$, is rapidly neutralized by reaction with carbonate
 in fracture infills whose $\delta^{13}C$ is $-5$ to $-8\%$. Recharging waters are thus produced having total
 dissolved solids (TDS) directly proportional to the bicarbonate content and always below
 500 mg L$^{-1}$, with $\delta^{13}C$ below about $-14\%$. There is a general decrease of pH and TDS with

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higher altitudes where short flow paths allow insufficient time for complete reaction of dissolved CO₂. Apart from a slight increase in sodium content, interaction with the rock matrix is minimal and there is no saline storage, at least in the top 300 m. Chloride and δ¹⁸O are determined by the relative importance of evaporation and transpiration. In areas of gentle slopes, δ²H contents of shallow borehole samples between 0 and 20 TU indicate a general discharge of a proportion of older water but mostly mixed with tritiated shallow groundwater flow systems probably induced by abstraction. Under hills, recent water penetrates rapidly to at least 160 m. The deepest borehole zone sampled yielded water unaffected by mixing with recent recharge, with an age of the order of 10⁶ years based on ¹⁴C and ³H contents. This is supported by geochemical pointers to different climatic and surface conditions at recharge which have been retained by the sample since it entered its discrete fracture system.

1. INTRODUCTION

A groundwater geochemical study has been carried out on the research site in the Altnabreac area of Caithness, UK, as part of the UK research programme (funded by the Department of the Environment and the Commission of the European Communities) to investigate the feasibility of disposal of high-level radioactive wastes into geological formations [1,2].

Three research boreholes approaching 300 m in depth and eighteen shallow boreholes (~40 m) provided access to the crystalline rock groundwaters in an area of subdued topography where the groundwater system has not been disturbed by any mining activity. Numerous springs, lochs, streams and rivers were available for investigation of surface waters, and the 1981-82 rainfall chemical input levels were also monitored.

This paper summarises the results obtained from the hydrochemical studies [3,4,5]. Emphasis is placed on the contribution of isotopic determinations to an understanding of the groundwater flow system.

2. GEOLOGY, GEOCHEMISTRY AND HYDROGEOLOGY

Topographically the area can be divided into two regions along the east-west trending valleys of the Rumsdale and Thurso rivers (Fig. 1). To the north, the ground is gently undulating, mostly below 200 m a.s.l., with broad flat valleys. To the south, relief differences are greater, the ground rising to over 300 m, and rivers are more deeply incised with steeper slopes [6]. The western limit of the study area (Fig. 1) coincides with the major watershed defining the Thurso river system. Three main river catchments, Sleach Water, Rumsdale Water and Glutt Water, dendritically drain the area and combine into the River Thurso. All water courses in the study area therefore ultimately drain eastwards. The sources of many tributary
FIG. 1. Map of the Altnabreac area, showing major geological features and location of borehole and other sample sites.

Streams are in small shallow (<4 m deep) lochs, generally lying below 250 m a.s.l. and varying in area up to 0.4 km². Other streams have sources in discrete perennial springs. Where the high ground is level, small peat-bounded ponds, called dubh lochs, form in very boggy terrain. The amount of immediate run-off has been enhanced by a network of drainage ditches.

The geology of the research site has been described by Lintern and Storey [7]. Peat cover in the area is almost
ubiquitous and is 0.1 - 4.0 m thick. This overlies some 0.5 - 40 m of glacial/fluvio-glacial/fluvial deposits which rest on variably weathered bedrock.

The bedrock is mostly of Strath Halladale Granite, which is dominantly a medium- to coarse-grained granodiorite, together with associated basic and amphibolitic members. The granite, in the form of a large, easterly dipping sheet, was emplaced within variably migmatized Moine metasediments, comprising quartzites, psammites and pelites with minor calc-silicates and amphibolites. Concordant granite sheets occur within the metasediments bordering the granite whose outcrop is indicated in Fig. 1. A wide variety of aplite, microgranite and pegmatite veins cut both granite and metasedimentary rocks.

Quartz, plagioclase feldspar and alkali feldspar together dominate the bulk of the rock matrix, both igneous and metamorphic. Biotite is the most important mafic mineral although it may be chloritised. Hornblende, biotite and plagioclase dominate in more mafic rock types wherein pyroxene sometimes remains. Mafic rocks, however, represent only a small fraction of the total volume of rock with which groundwater might interact. Apatite, sphene and opaque minerals (principally ilmenite) and, particularly in metasediments, zircon, are common accessories. Rock geochemistries have been reported by Storey and Lintern [8]. Petrography has shown sericitization of sodic feldspar and chloritisation of biotite to be common. Brittle fractures often contain intergrowths of calcite, siderite, iron sulphides and oxides, smectites and quartz. The presence of montmorillonite and interpretation of oxygen and carbon isotopic ratios in calcite suggest that hydrothermal processes mostly occurred when temperatures exceeded 100°C [9]. Other fractures are shear zones and contain granulated quartz, feldspars and mica.

The Moine bedrock shows a well-developed foliation dipping eastwards at 25-30°. This foliation is also present in some parts of the granite. Many crystals have extensive microcrack systems, which are probably end-connected to the primary flow systems of joints and fractures. These are well developed in all rocks. The frequency of fractures is very variable and may change rapidly over short distances [10].

All rocks tend to be weathered to considerable depths. The major effects of weathering are seen as hydration of micas, formation of solution cavities and the oxidation of iron minerals leading to iron-staining on many fracture surfaces. Decomposition and expansion of the biotite lattices has resulted in a tendency for the rock to disaggregate to depths sometimes exceeding 40 m. Weathering features are observed to the full depth of the deep boreholes. Their frequency,
however, tends to diminish with depth. Hydraulic conductivities are less variable and generally lower than $10^{-9}$ m$^{-1}$ s$^{-1}$ below about 150 m [11].

Glendinning [6] showed that local features, such as topography, faults and fracture orientations, are more important than geology in determining water transport. The fact that the average rest-water level in some boreholes does not coincide with the depth to the base of saturated peat suggests that the water table in peat is often perched. Nevertheless, the generally rapid response in borehole water level to changing weather conditions shows that hydraulic communication through the peat is quite efficient.

A flow-net approach to identifying areas of higher transmissivity within the top 40 m yielded reasonable results [6]. Maximum estimates for transit times within this zone occur in areas having low hydraulic gradient and are of the order of 10$^3$ years. When the system to 300 m is considered, generally decreasing hydraulic conductivities and necessarily longer flow paths suggest transit times could easily exceed this estimate by an order of magnitude or more.

3. SAMPLING FROM BOREHOLES

3.1. Deep Boreholes

Deep boreholes were sampled using double-packer, wireline hydraulic testing equipment [11] which was modified slightly to facilitate larger volume abstraction than is normally necessary for hydraulic testing of a low-permeability packer-isolated zone. Essentially, the system comprises a gas pump. A pump-line from the test zone bifurcates immediately above a pneumatically actuated shut-in valve (SIV), usually situated about 10 m below the borehole water level. With the valve closed, water can be flushed from the near-surface tubes using nitrogen gas pressure. Once empty, the SIV is opened, leading to an instantaneous change of head in the test zone. As water is derived from the test zone, a slug-test is performed which can be analysed to give the hydraulic conductivity and storativity. The equilibrium pressure measured in the packer-isolated zone is compared with that resulting from the borehole water column. A profile of the pressure differences ($\Delta$H) with depth identifies where groundwater is entering or leaving the open borehole and, taking into account the other hydraulic properties, the most suitable zones for sampling. A large positive $\Delta$H was found between 129-133 m depth in borehole B, of which the casing top is higher than a nearby stream. It was thus possible to operate a continuous siphon and compare such sampling with abstraction by SIV in order to demonstrate the feasibility of sampling for a full range of dissolved gases[12].
3.2. Shallow Boreholes

The very narrow completion diameter of the shallow boreholes (50 mm) presented considerable problems for chemical sampling. Early sampling programmes after completion of the boreholes (AC/1 and AC/3 series) relied on a plunger-cylinder type of depth sampler to abstract samples of small volume. These were of unsatisfactory quality. A manually operated and portable double-action lift pump was assembled in July 1981 which made it possible to abstract larger volumes of water (of the order of 2-3 borehole volumes). This accelerated the process of replacing waters of surface origin (drilling and flushing waters) with waters more representative of the borehole environments (AC/4 series). One borehole, 18, where the rest-water level is about 18 m below casing top, could not be sampled by this method.

In July 1982 a final shallow borehole sampling operation (AC/5 series) was mounted as a result of in-house development of an electric submersible pump [3]. A further three borehole volumes of water were abstracted from each of the shallow boreholes, including 18 but not 8. This hole has a hydraulic conductivity so low that it has not been possible to remove the effects of cement contamination (pH > 11). In contrast, borehole 4 also had high cement-related pH initially, which fell to normal groundwater levels after large volume abstraction.

4. RESULTS AND DISCUSSION

4.1. Origin of Altnabreac Groundwaters

All groundwaters at Altnabreac, including those from deep boreholes, have stable-isotope ratios which plot close to the Meteoric Water Line [13], with $\delta^{18}O$ ranging from -8.5 to -4.0%. Thus all components of all groundwaters sampled in this study must be of meteoric origin and will be discussed below in the context of the chemistry of precipitation input.

4.2. Precipitation Input

The results of stable-isotope ratio and chloride determinations on samples of monthly aggregated Altnabreac rainfall are plotted against the month of collection in Fig. 2. A variable chloride content of 2 - 29 mg·L⁻¹ accompanied a range in stable-isotope ratios of $\delta^{18}O$ -12.6 to -4.2% and $\delta^2H$ -89 to -33%. The stable-isotope ratios correlate well on a curve $\delta^2H = 7.9 \delta^{18}O + 9.7$ ($r^2 = 0.94$), not significantly different from the global curve. Weighted mean annual input levels are: 13.2 mg·L⁻¹ Cl⁻, -8.6% $\delta^{18}O$ and -50% $\delta^2H$. Cl⁻/Na⁺ ratios varied unsystematically between 1.0 and 2.2.
FIG. 2. Variation of monthly precipitation, chloride content, $\delta^{18}$O and $\delta^2$H in Almabreen rainfall, August 1981–August 1982. R represents the weighted mean input level.
FIG. 3. Plot of $\delta^{13}C$ against $\text{HCO}_3^-$ content for waters from Altnabreac boreholes. All samples plotted were determined after field precipitation of BaCO$_3$. The remaining samples, precipitated using SrCl$_2$, are now believed to be relatively imprecise and have been omitted from the diagram.

One rainfall sample (August 1982) was analysed for $^{3}H$ content. This sample had stable-isotope ratios close to the mean values and, at 29 ± 2 T.U., its $^{3}H$ content compares closely with the present mean monthly $^{3}H$ input.

4.3. Hydrochemical Evolution of Groundwaters

All groundwaters in the study were cold. Even at the bottom of deep boreholes, the temperature did not exceed 12.1°C. Springs and surface waters were warmer than 6°C only when the air temperature exceeded this value. For both these and deeper groundwaters, pH varied between 4.0 and 7.8 and Eh was always higher than +100 mV.

All waters had relatively low total dissolved solids (TDS), < 500 mg.$\cdot$$\text{l}^{-1}$, and bicarbonate was the dominant anion except in very dilute waters. Groundwater $\delta^{13}C$ values increased from below −30% to about −14% with increasing bicarbonate content (Fig. 3) and higher pH. Spring and surface waters with $\delta^{13}C$ values over the whole of this range all had $^{3}H$ contents greater than 16 T.U. (Fig. 4). Calcium and magnesium generally become the dominant cations with increasing TDS, although very high iron contents (up to 34 mg.$\cdot$$\text{l}^{-1}$) have been observed. Saturation levels for the principal carbon and sulphate minerals are nowhere achieved. These data collectively suggest that neutralisation of the high dissolved CO$_2$ levels in the soil/peat zone occurs by rapid dissolution of equivalent amounts of carbonate from fracture infills whose $\delta^{13}C$ is between −5 and −8% [9]. There is a general decrease
FIG. 4. Histograms of $^3$H, $^{18}$O, sodium and chloride contents for Alnabreac groundwaters.
FIG. 5. Variation of total dissolved solids with altitude for Altibrea spring/surface waters and waters from shallow boreholes.

FIG. 6. Plot of chloride content against δ18O for borehole- and surface-sampled waters. Point A is located at the intersection of the enrichment trend in more mature borehole waters with the mean δ18O of precipitation. This is the estimated composition that precipitation would achieve solely by transpiration, a process not causing isotopic fractionation [14]. Transpiration thus accounts for about half the total concentration to the average groundwater chloride content of 23 mg L⁻¹.
FIG. 7. $\delta^2$H, $\delta^{18}$O and $^3$H contents of shallow borehole samples. Note that the dates at the top of the figure refer to the date of drilling. Sampling was done in four programmes during each of which all boreholes were visited within a few days.
in TDS with higher altitudes (Fig. 5) where the short flowpaths allow insufficient time for complete reaction of dissolved CO₂.

The clustering of most borehole waters near the centres of normal distributions of chloride content and δ¹⁸O (Fig. 4) illustrates that the seasonal variation of the precipitation input is effectively smoothed. There is little evidence of interaction with minerals of the rock matrix, apart from the slight increase in sodium content (Fig. 4) for samples abstracted from deep boreholes. Since chloride does not increase in deeper groundwaters, it appears that there is no saline storage in this granite at least in the uppermost 300 m. Furthermore, the shifts in mean groundwater compositions for Cl⁻ and δ¹⁸O from the precipitation input levels can be qualitatively explained by a combination of evaporation and transpiration (Fig. 6).

²²⁴Rn contents lie on a single log-normal distribution [4], which suggests that the distribution of radionuclides and the nature of fractures are essentially similar at all sample locations. Indeed, no groundwater geochemical parameter has been recognised as an indicator sufficiently sensitive to discriminate between any or all of the host rock matrices. It is concluded that the dominant control on the groundwater chemistry is the fracture infilling material and not the rock matrices themselves.

4.4. Shallow Groundwaters

The sequence of shallow borehole sampling programmes outlined in section 3.2 above yielded the isotopic data of Fig. 7. The variation of stable-isotope ratios of oxygen and hydrogen in shallow boreholes was initially thought to reflect the weather conditions at the time of drilling, transmitted into the borehole waters with the flushing waters taken from local streams or lochs. Hence, in Fig. 7 isotopic parameters are plotted against the dates of drilling, together with notes on the weather conditions at the time. (Snow is characterised by lower δ-values than the average for a given location.) However, the various series of measurements show that the stable isotopic composition of water has remained essentially constant over the period of observation and is characteristic for each borehole. No relationship with altitude or major chemistry can be defined. Boreholes 4 and 9 still produced samples with relatively low δ²H and δ¹⁸O, even after an accumulated total of eight or more borehole volumes of water had been removed by periodic abstraction. This is believed to be a consequence of the deeper water table and thinner peat cover (found on the steep slopes where these boreholes are
located) which allowed groundwater to be less affected by surface processes.

$^3$H in UK rainfall peaked at about 2000 T.U. in 1963 [15]. It has been declining since to about 30 T.U. at the present time (Otlet, pers. comm.); however, no post-1974 statistical evaluation is available. Any source with $^3$H content below about 20 T.U. can be expected to contain a proportion of an 'old' groundwater component. By the same token, any source with $^3$H content greater than about 30 T.U. cannot have an age greater than 20 years. More than half of the shallow boreholes at some time yielded a sample indicating a proportion of pre-1953 recharge, although springs and surface waters, with one exception (Fig. 4), are dominated by recent waters.

Sequential sampling during protracted abstraction from two holes, 11 and 20, during the AC/5 series, and borehole 21, during the AC/4 series, showed that $^3$H contents often declined between sampling operations and increased markedly during pumping. For example, samples taken after 1, 3, 5 and 10 borehole volumes of water had been abstracted from borehole 12 during 2 days of pumping had $^3$H contents of 0, 3, 2 and 15 T.U., respectively. This is presumably a result of increasing hydraulic connection to the surface. Such an observation is hardly surprising since 10 borehole volumes for this borehole are approximately 1500 l. This represents the total storage of 150 m$^3$ of rock having a porosity of 1%, a reasonable estimate of the average value in the rock matrix near the surface. Superimposition of local, active shallow groundwater systems and/or rapid connection to storage at surface (mostly peat water) when the hole was pumped meant that $^3$H-free samples were not, and probably could not be, obtained.

Boreholes characterised by low $^3$H contents are situated near the base of long gentle inclines with pronounced breaks of slope down-gradient from them. Intermediate $^3$H contents are found in boreholes higher up such slopes. This is thus a geochemical confirmation of the hydraulic modelling.
Compression of essentially horizontal groundwater flow lines near the break of slope results in a borehole of a given depth intersecting a larger number of lines and thus a greater proportion of deeper flow than a borehole of equal depth further upslope [16].

The $^4$He contents of many of the shallow boreholes are above the atmospheric equilibrium levels, albeit only slightly in most cases (Fig. 8). This contribution of radiogenic $^4$He, together with generally low $^3$H contents, is believed to reflect slight upwelling of pre-1953 recharge.

### 4.5. Deeper Groundwaters

Borehole C was drilled from the top of an isolated hillock within the research area (219 m a.s.l.) and the casing top is about 70 m above those of boreholes A and B. Neither zone which was sampled in borehole C contained any excess $^4$He, and the $^3$H contents were 48 T.U. at 92-96 m and 20 T.U. at 162-166 m. Results of hydraulic testing [11] indicate a downward groundwater movement even below this level, although the effects are almost certainly exaggerated by a zone of major vertical faulting at this location.

Of the six zones selected for chemical sampling in the other two deep boreholes, only two from borehole B yielded samples of very low $^3$H content (Fig. 4). This restricted the number of samples for which it was possible to interpret isotopic data in terms of groundwater residence time. The deepest sample abstracted, from the bottom zone, 259-281 m in borehole B, was one of these. Here a $^{14}$C content of 13.6 ppm with $^{6}{^{13}}$C of -14% gives an age of 10000 to 14000 years when adjusted according to conventional models [17]. Only one other zone, in borehole A at 219-223 m, had a $^{14}$C content below 50 ppm but this was accompanied by a $^3$H content of 15 T.U.

The helium content of water from the bottom zone in borehole B was the highest observed at about $3.3 \times 10^{-5}$ cm$^3$ STP/cm$^3$ H$_2$O, although significant $^4$He excesses were observed in all deep samples from boreholes A and B (Fig. 8). Assuming that there is no significant crustal diffusion of helium and if all the $^4$He generated dissolved in the fracture fluids, the residence time of the fluid can be calculated from the helium production rate and the radioelement content of the host rock if the rock density and porosity are known [18]. For average U and Th contents of local Moine metasediments of 4 and 7 ppm, respectively [8], and a matrix porosity of 12%, a $^4$He age for the deepest sample in borehole B approaches $2 \times 10^5$ years. If, however, this sample had spent most of its history in a rock matrix with the highest determined radioelement contents (13 ppm U and 32 ppm Th), and the average porosity of unaltered
rock were as low as the minimum observed, 0.5% [19], a minimum age of 2.5 x 10^4 years would be indicated. Deep borehole B actually bottoms in granitic sheets [7] which have radioactive contents similar to these maximum values [8]. Thus, the ^14C age and ^4He residence time agree quite well and three other lines of evidence add additional weight. Firstly, dissolved inert gas contents for this sample indicate recharge temperatures slightly displaced to the low-temperature side of the mean annual air temperature, which is about 5.6°C, based on the winter temperatures commonly observed for perennial springs [4]. Secondly, it is interesting to note that at -8.4%, δ^18O (and δ^2H) for this water is quite distinctly lower than that for all other borehole samples low in δH (Fig. 4) and this also suggests a lower recharge temperature. Thirdly, its bicarbonate content, and thus TDS, is only about half the level of shallower samples having 'mature' δ^13C values (Fig. 3) which also carry excess ^4He. If this deep water recharged under colder climatic conditions than for the shallower waters, the peat/soil zone was perhaps then less well developed. This would have produced lower levels of dissolved CO₂ at recharge and consequently would explain the lower bicarbonate content. The fact that characteristic isotopic ratios can be preserved locally in the groundwater system suggests that mixing does not occur to any great extent once a groundwater enters a given fracture system.

4.6. Uranium contents and isotopic activity ratios

Uranium contents and ^234U/^238U isotopic activity ratios reflect the scheme of water maturation already described. Contents are generally below 2 µg·kg⁻¹. According to the Eh-pH stability field diagrams for uranium species in bicarbonate waters [20,21], uranium should always be mobile in the oxidising regime of the top 300 m at Altnabreac (Fig.9). The highest activity ratio of 10, found in the bottom zone of borehole B, could have been generated by preferential dissolution of the ^234U isotope in less than 1000 years, or if dissolution were only active near the ground surface, by α-recoil processes [22] in about 64000 years [5]. The much lower residence times derived by other methods suggest that these two processes have both been active.

5. SUMMARY AND CONCLUSIONS

The results of this study indicate that there is an active groundwater flow system at least within the uppermost 300 m of crystalline rocks at Altnabreac. All components of all waters are of meteoric origin. There is no saline storage, at least to 300 m depth, and reactions of high soil/peat-zone-derived
CO$_2$ levels with carbonate minerals in fracture infills result in bicarbonate-dominated waters. There is little evidence of reaction with minerals of the rock matrix. Recharging water rapidly percolates deeply below hill top areas. Many shallow boreholes have yielded samples having $^3$H contents below the mean precipitation input level, which indicates a proportion of pre-1953 recharge. This suggests that there is slight upwelling away from the hills and that most groundwater flow must be essentially horizontal. This observation makes it probable that the tritium found in most packer samples from deep boreholes resulted from mixing of modern water contained in the borehole with deep groundwater during abstraction rather than from rapid flowpaths from surface. The paucity of uncontaminated samples illustrates that abstraction of wholly representative deep groundwater from boreholes in low-permeability crystalline rock is difficult to achieve.

Nevertheless, the data from one deep zone indicate that stable-isotope ratios and major-element chemistry at Altnabreac are controlled by near-surface processes and these are apparently preserved once a groundwater enters a given fracture system. The $^{14}$C age (10000 to 14000 years), $^4$He data, lower than average $\delta^{18}O$ and $\delta^2$H, a cooler inert-gas–derived recharge temperature and lower TDS than other mature waters suggest that this water, which was sampled nearly 300 m below surface and 1 km from the nearest hill, entered the groundwater system near the end of the last ice age when the peat/soil zone was perhaps less well developed.

The dynamics of the system examined at Altnabreac are summarised in the schematic flow profile shown in Figure 9.
With hydraulic conductivities lower than about $10^{-9}\text{m.s}^{-1}$ below 150 m depth, flow lines related to topography can be drawn. Borehole C, at its hilltop location, yielded recently recharged waters at deep levels. Most Altnabreac springs lie at the ends of short and shallow flowpaths. The chemistry of samples from shallow boreholes is related to their location and is determined by local topography and lengths of flowpath. These parameters control the mixing proportions of young and old groundwaters in the samples. The deeper zones in borehole B (and borehole A, which is not shown in the diagram) yielded old groundwater samples characterised by low $^{14}$C contents, low $^3$H contents and high excess $^4$He levels. These long and essentially horizontal flowpaths eventually discharge in the river valleys.

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REFERENCES


RECHERCHES ISOTOPIQUES
SUR LES EAUX SOUTERRAINES
DES FORMATIONS POREUSES
DE LA PARTIE ORIENTALE
DE LA DEPRESSION PANNONIENNE

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Abstract—Résumé

ISOTOPIC STUDIES ON GROUNDWATER IN THE POROUS FORMATIONS OF THE
EASTERN PART OF THE PANNONIAN DEPRESSION.

The study in question covered the terraced system of aquifers in the north-eastern end of
the Pannonian Depression situated in the western part of Romania. A topical arrangement has
been used to discuss the results (based on analyses of \(^{2}H\), \(^{14}C\), \(^{2}H\), \(^{18}O\) and \(^{13}C\)), since this kind
of arrangement makes it possible to describe the regional situation and to show the specific
procedures by which the isotope techniques were applied. As far as meteoric water is concerned,
determinations were made of the input signal values and of the variability in the isotopic
composition of the water as a function of temperature and altitude. An anomaly in the
continental effect was detected in the region. In the case of groundwater, certain aspects were
considered: isotopic stratification, regional inter- and intra-system circulation, origin and
genesis. In connection with the first aspect, a clear stratification for the first four types of
water was established throughout the region. Interesting results were obtained on intra-system
circulation with the help of radiocarbon. The analyses made it possible to consider the
applicability of the various models under geochemical conditions characterized by penetration
of large amounts of CO\(_{2}\). Isochrone maps showed that radiocarbon could satisfactorily reflect
the hydrodynamic situation. It was established that groundwater originated from local
infiltration, whereas the water of the aquifers of medium depths I and II was recharged at
average altitudes of 200 and 500 m. The origin and genesis of deep water are more complex.
In origin it is a mixture of two components — meteoric palaeo-infiltration water and
syngenetic water — in proportions varying according to the size of the surface. The \(\delta^{18}O\) — Cl
parabolic correlation revealed genetic changes in certain types of water due to isotopic exchange
with the matrix.

RECHERCHES ISOTOPIQUES SUR LES EAUX SOUTERRAINES DES FORMATIONS
POREUSES DE LA PARTIE ORIENTALE DE LA DEPRESSION PANNONIENNE.

L'objet de cette recherche est le système étagé d'aquifères de l'extrémité nord-est de la
dépression Pannonienne, région qui correspond à la zone occidentale de la Roumanie. Pour
l'exposition des résultats (fondés sur des analyses de \(^{2}H\), \(^{14}C\), \(^{2}H\), \(^{18}O\) et \(^{13}C\)), on a adopté une
structure thématique permettant une description de la situation régionale et la mise en
evidence des modalités spécifiques de l'application des méthodes isotopiques. En ce qui

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concerne les eaux météoriques, on a déterminé les valeurs du signal d’entrée et la variabilité de la composition isotopique de ces eaux en rapport avec la température et l’altitude. On a fait ressortir pour la région la présence d’une anomalie de l’effet de continentalité. En ce qui concerne les eaux souterraines, on a traité certains aspects: stratification isotopique, circulation régionale inter et intrasystème, origine et génèse. En relation avec le premier aspect, on a constaté la présence, dans toute la région, d’une stratification nette pour les quatre premiers types d’eaux. Quant à la circulation intrasystème, des résultats intéressants ont été obtenus à l’aide du radiocarbone. Les analyses ont permis un examen de l’applicabilité de divers modèles dans des conditions géochimiques caractérisées par la pénétration de quantités considérables de CO₂. Les cartes aux isochrones ont démontré que le radiocarbone peut refléter de façon satisfaisante la situation hydrodynamique. On a établi que les eaux phréatiques sont des eaux d’infiltration locale, tandis que les eaux des aquifères de moyenne profondeur I et II sont rechargées à des altitudes moyennes de 200 et 500 m. Les aspects d’origine et de génèse des eaux de profondeur sont plus complexes. Du point de vue de l’origine, elles représentent un mélange, en proportions variables en aréal, de deux composantes: paléo-infiltrations météoriques et eaux syngénétiques. La corrélation parabolique δ¹⁸O – Cl⁻ a rendu manifestes des modifications génétiques de certaines eaux par l’échange isotopique avec la matrice.

Le présent mémoire expose en bref quelques aspects d’hydrogéologie isotopique concernant les eaux souterraines cantonnées dans les dépôts poreux de la plaine occidentale de Roumanie (fig. 1), une région dont la surface est d’environ 14 000 km². Pour notre étude, nous avons traité plus de 1 250 analyses isotopiques et 400 analyses hydrochimiques effectuées au cours de différentes phases entre 1972 et 1982.

L’approche par une étude isotopique de tous les aquifères poreux de la région nous a semblé intéressante et nous a tenté en raison du volume considérable de données isotopiques et du dégrou poussé des connaissances en hydrogéologie.

A ces raisons, on pourrait ajouter l’intérêt d’ordre scientifique que les particularités géologiques et la disposition étagée des aquifères confèrent à la région étudiée.

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**Fig. 1. Localisation de la zone étudiée.**
FIG. 2. Sections géologiques schématiques à travers la région (leur position est indiquée sur la figure 3); Crs = fondement cristallin; N1 = Miocène non-différéntié; m = Pliocène inférieur; p - Q = Pliocène-Quaternaire.

Les aspects essentiels abordés envisagent la stratification isotopique des eaux sur la verticale, la circulation régionale des eaux souterraines et leurs interrelations avec les eaux de surface, de même que l’origine et la genèse des eaux souterraines.

1. GENERALITES SUR LES CONDITIONS GEOLOGIQUES ET HYDROGEOLOGIQUES REGIONALES

1.1. Cadre géologique

Du point de vue géologique, la région étudiée constitue la limite nord-est de la dépression Pannonienne, une unité structurale qui s’est formée suite aux mouvements mésocrétaciques.

Le fondement de la région est constitué de schistes cristallins qui s’enfoncent graduellement et à peu près continuellement à partir de la bordure de la dépression vers l’ouest (fig. 2) et des dépôts sédimentaires mésozoïques dont la présence est seulement locale dans le tiers septentrional, dans la zone du graben Giris-Oradea.

La couverture post-tectonique est constituée du Sénenien et du Paléogène, développés de façon discontinue, après lesquels le Néogène, représenté par les Miocène et Pliocène en faciès pannonien, est disposé de façon transgressive et discordante. Les épaisseurs de ce dernier terme, qui constituent environ 90% du remplissage du bassin, sont très variables dans la région; des épaisseurs de l’ordre de quelques mètres vers la bordure atteignent 2900 m au sud de la localité.
TABLEAU I. PARTICULARITES HYDROGEOLOGIQUES DES AQUIFERES

<table>
<thead>
<tr>
<th>No.</th>
<th>Aquifère</th>
<th>Profondeurs (m)</th>
<th>Niveau piézométrique</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Holocène (phréatique)</td>
<td>2 – 30</td>
<td>libre</td>
</tr>
<tr>
<td>2.</td>
<td>Pléistocène</td>
<td>50 – 120</td>
<td>ascensionnel</td>
</tr>
<tr>
<td></td>
<td>(moyenne profondeur I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Pliocène supérieur</td>
<td>150 – 400</td>
<td>ascensionnel, artésien local</td>
</tr>
<tr>
<td></td>
<td>(moyenne profondeur II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Pontien inférieur</td>
<td>500 – 2000</td>
<td>artésien</td>
</tr>
<tr>
<td></td>
<td>(de profondeur)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Satu Mare et dépassent 3000 m dans la zone Sinnicolau Mare. Du point de vue litho-facial, on peut généralement, dans les dépôts pliocènes, séparer deux séries: l’une inférieure, à prédominance pélitique, et l’autre supérieure, à fréquentes intercalations psamitiques. Cette deuxième série est considérée comme appartenant au Pontien, avec des passages probables aussi vers les termes plus récents du Pliocène.

La série des dépôts qui constituent le remplissage post-tectonique s’achève par le Quaternaire qui couvre toute la région. Il est représenté par des dépôts pléistocènes et holocènes disposés en continuité de sédimentation, ayant des épaisseurs cumulées qui augmentent graduellement vers l’ouest jusqu’à plus de 400 m (les zones de Sinnicolau Mare et du sud de Salonta).

1.2. Cadre hydrogéologique

Les formations poreuses quaternaires et pliocènes sont les principaux collecteurs d’eaux souterraines de la région [1, 2]. On peut séparer dans les formations signalées quatre aquifères caractérisés par une disposition étagée, une bonne continuité aréale et une individualisation assez nette, et par des paramètres géométriques, litho-faciaux, hydrodynamiques et physico-chimiques (tableaux I et II).

La morphologie de la surface piézométrique du phréatique, exposée dans la figure 3 est représentative de la situation hydrodynamique de tous les aquifères. La carte met en évidence l’orientation générale E–O de l’écoulement souterrain (à l’exception d’une zone confinée, située au sud-ouest de la localité de Carci) et des gradients hydrauliques variables entre 0,4 et 5%.

Du point de vue physico-chimique, une caractérisation sommaire des aquifères peut ressortir des données synthétiques portées au tableau II. Ainsi, du point de vue thermique, les deux premiers aquifères sont athermaux, le
TABLEAU II. PARTICULARITES PHYSICO-CHIMIQUES DES EAUX SOUTERRAINES

<table>
<thead>
<tr>
<th>No.</th>
<th>Aquifère</th>
<th>Température (°C)</th>
<th>Minéralisation totale (mg/L)</th>
<th>Type hydrochimique</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Holocène (phréatique)</td>
<td>12–13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>600</td>
<td>bicarbonaté-sulfaté-calcique-magnésien</td>
</tr>
<tr>
<td>2.</td>
<td>Pléistocène (moyenne profondeur I)</td>
<td>13–19</td>
<td>390</td>
<td>bicarbonaté-sodique-calcique</td>
</tr>
<tr>
<td>3.</td>
<td>Pliocène supérieur (moyenne profondeur II)</td>
<td>17–25</td>
<td>410</td>
<td>bicarbonaté-sodique</td>
</tr>
<tr>
<td>4.</td>
<td>Pontien inférieur (de profondeur)</td>
<td>50–88&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2450</td>
<td>bicarbonaté-sodique et chlorure-sodique</td>
</tr>
</tbody>
</table>

<sup>a</sup> Valeurs moyennes régionales.
<sup>b</sup> Température moyenne annuelle.
<sup>c</sup> Températures mesurées à l’émergence.

Pliocène supérieur athermal avec des transitions vers le hypothermal, tandis que le dernier est hyperthermal.

Quant à la teneur en sels dissous et au type hydrochimique, l’évolution sur la verticale dans les quatre aquifères (fig. 4) est normale, compte tenu des conditions géologiques et des profondeurs où sont situés les aquifères.

Pour rendre complète l’image hydrochimique générale, il serait opportun de signaler deux faits concernant la variabilité aréale:

- a) On observe un accroissement de la minéralisation à partir de l’est vers l’ouest en concordance avec la direction du flux souterrain, accroissement plus marqué aux aquifères de profondeur moyenne au sud de Mureș par suite du trajet plus long de l’eau souterraine.
- b) En ce qui concerne les aquifères phréatiques et de moyenne profondeur, on peut constater un accroissement graduel de la minéralisation totale du nord au sud, tandis que, dans le cas de l’aquifère de grande profondeur, la situation est inverse.

2. RESULTATS DES RECHERCHES ISOTOPIQUES

2.1. Composition isotopique des eaux météoriques

La détermination de la composition isotopique des eaux des précipitations dans cette région a été justifiée par le fait que la station du réseau AIEA/OMM la plus rapprochée se trouve à Vienne, à une distance dépassant 450 km.
En ce qui concerne le tritium, on a donc réalisé une série multiannuelle de données pour les précipitations et pour la rivière Crișul Repede (fig. 5). On a pu ainsi observer que les concentrations obtenues des eaux des précipitations diminuent, de 550 UT en 1970 à environ 50-60 UT en 1982 [3].

Quant aux isotopes stables D et 18O, les analyses effectuées sur les précipitations collectées à Oradea et en six autres stations auxiliaires ont permis de déterminer tous les paramètres isotopiques.

On a ainsi établi que l’équation de corrélation des valeurs δD - δ18O (fig. 6) s’exprime par:

\[ \delta D = 6,7 \delta^{18}O - 3,1 \]  \hspace{1cm} (1)

On a calculé les valeurs moyennes pondérées de la composition isotopique à la station Oradea, lesquelles au niveau annuel sont: δD = -56,1 ‰; δ18O = -8,1 ‰; pour la saison froide (pendant laquelle on considère que les précipitations ont un apport efficace dans la recharge du souterrain), elles sont: δD = -81 ‰ et δ18O = -11,6 ‰ [2, 4].

En corrélant la composition isotopique avec différents paramètres météor-climatiques, on a confirmé la relation essentielle de celle-ci avec la température. Bien que le mode de répartition des points dans le diagramme δ18O - T (fig. 7)
FIG. 5. Teneurs en tritium des eaux de précipitation à Oradea (2) et des eaux de la rivière Criul Repede (3). La courbe (1) exprime le tritium dans les eaux météoriques à Vienne.

FIG. 6. Corrélation δD - δ18O pour les eaux de précipitation de la région (a); droite (b): précipitations à l'échelle mondiale [5].

suggère une corrélation non linéaire, ce qu'on doit spécialement aux précipitations d'été qui dépassent 65 mm, l'équation de régression calculée analytiquement:

\[ \delta^{18}O = 0.57 T - 15.72 \]  

(2)
a néanmoins un bon coefficient de corrélation. Il faut remarquer le fait que la forme de l'équation ci-dessus est pratiquement identique avec celle calculée pour tout l'hémisphère nord [5].
On a aussi établi la variation de la composition isotopique des précipitations en rapport avec l’altitude. Les teneurs moyennes annuelles calculées de façon pondérée pour sept stations de la région, situées à des altitudes entre 136 et 1250 m (tableau III), ont permis d’obtenir une équation de dépendance du deutérium de l’altitude (fig. 8) dont la forme est:

\[
\delta D = -0.017 A - 57.86
\]

(3)

Il en résulte un gradient d’altitude de 1,7 \(\delta D/100 \text{ m} \), qui correspond à un gradient de 0,21 \(\delta ^{18} \text{O}/100 \text{ m} \) pour l’oxygène 18.

Une comparaison des valeurs moyennes pondérées annuelles de la station Oradea avec celles des stations Valentia, Stuttgart et Vienne [5], toutes les quatre situées approximativement à la même latitude, a permis de constater que l’effet de continentalité, conformément aux résultats de Sonntag et al. qui ont calculé des gradients sur une distance d’environ 2000 km sur le territoire européen (d’après [5]), subit des perturbations à l’est de Vienne. C’est ainsi qu’à Oradea les précipitations sont plus riches en isotopes lourds qu’à Vienne, les valeurs étant comparables avec la station de Stuttgart tant pour le deutérium et l’oxygène 18 que pour l’excès en deutérium (\(d = 7.5\)).
TABLEAU III. VARIATION SELON L’ALTITUDE DES VALEURS $\delta$D$^a$

<table>
<thead>
<tr>
<th>No.</th>
<th>Station</th>
<th>Altitude (m)</th>
<th>Quantité annuelle de précipitations (mm)</th>
<th>$\delta$ D‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Oradea</td>
<td>136</td>
<td>583</td>
<td>-60,8</td>
</tr>
<tr>
<td>2.</td>
<td>Borod</td>
<td>333</td>
<td>761</td>
<td>-62,4</td>
</tr>
<tr>
<td>3.</td>
<td>Rimeti</td>
<td>482</td>
<td>1126</td>
<td>-67,0</td>
</tr>
<tr>
<td>4.</td>
<td>Leș</td>
<td>500</td>
<td>1272</td>
<td>-66,5</td>
</tr>
<tr>
<td>5.</td>
<td>Iedut</td>
<td>950</td>
<td>1754</td>
<td>-75,1</td>
</tr>
<tr>
<td>6.</td>
<td>Galbena I</td>
<td>1100</td>
<td>1918</td>
<td>-77,4</td>
</tr>
<tr>
<td>7.</td>
<td>Galbena II</td>
<td>1250</td>
<td>1907</td>
<td>-79,4</td>
</tr>
</tbody>
</table>

$^a$ Ces valeurs sont calculées en tant que moyennes annuelles pondérées.

Cette remarque attire spécialement l’attention sur la modération dont il faut faire preuve dans l’extrapolation des tendances ou même des lois pour l’interprétation des situations actuelles ou paléo-climatiques [3].

2.2. Résultats de la recherche isotopique concernant les eaux souterraines

Dans ce qui suit, nous allons présenter quelques uns des résultats des recherches isotopiques, structurés sur trois catégories de problèmes.

2.2.1. Stratification isotopique

Sans constituer un sujet de recherche en soi-même, la stratification isotopique a néanmoins une portée scientifique et pratique particulière vu le fait que, tout en étant un reflet de certaines lois de répartition, elle pourrait être envisagée comme une prémisse indispensable à la connaissance des relations intersystèmes. En raison de cette situation, elle est présente dans à peu près toutes les études isotopiques régionales.

Ainsi que nous l’avons déjà signalé auparavant (§ 1.2), il existe dans la plaine occidentale un système étage d’aquifères dont les eaux de surface pourraient être envisagées en tant qu’un premier «étage».

Les recherches poursuivies entre 1972 et 1973 au sud de la rivière Crișul Repede ont fait ressortir la présence d’une stratification isotopique évidente dans les quatre premiers «étages», en ce qui concerne tant le tritium que le deutérium.
Le sens général de l'évolution y est normal, c'est-à-dire vers la diminution des concentrations en rapport avec la profondeur, la dispersion maximale étant observée dans les cas du phréatique et de l'aquifère de moyenne profondeur I.

Par la diversification de la gamme d'analyses et par l'extension en superficie et en profondeur du domaine étudié, les recherches effectuées au cours de la période 1976–1979 ont permis d'obtenir une image complète. Les résultats de cette étape, systématisés sur les tableaux IV et V, démontrent la possibilité, pour les isotopes du milieu, de caractériser les types d'eau dans une certaine région, même si les écarts de moyennes calculées déterminent une superposition des valeurs aux limites.

Le sens de l'évolution des concentrations en isotopes stables avec la profondeur reste normal jusqu'au niveau de l'aquifère de moyenne profondeur II (fig. 9); dans l'aquifère de profondeur, on constate un accroissement marqué du deutérium et de l'oxygène 18, ce qui le détache nettement des autres aquifères. Il faut noter également le fait, en ce qui concerne l'excès en deutérium (d), que l'aquifère de profondeur est une entité tout à fait distincte (tableau IV).

Les teneurs en tritium et 14C marquent elles aussi une différenciation des aquifères dans les limites d'applicabilité de chaque méthode (tableau V); il faut remarquer les âges radiométriques anciens des eaux de moyenne profondeur II et aussi le nombre moindre d'échantillons des eaux de moyenne profondeur I, à teneur en tritium décelable.

2.2.2. Circulation régionale des eaux

Les problèmes qui se rapportent au mouvement des eaux souterraines présentent généralement deux aspects distincts: la circulation intersystème, dans laquelle on peut comprendre également les interrelations des aquifères avec les eaux de surface, et la circulation intrasystème.
TABLEAU IV. STRATIFICATION DES TENEURS EN OXYGÈNE 18 ET DEUTÉRIUM PAR TYPE D’EAU

<table>
<thead>
<tr>
<th>No.</th>
<th>Type d’eau (aquitère)</th>
<th>Oxygène 18</th>
<th>Deutérium</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>n</td>
<td>δ</td>
<td>σ₀</td>
</tr>
<tr>
<td>1.</td>
<td>De surface</td>
<td>8</td>
<td>-9,65</td>
<td>0,92</td>
</tr>
<tr>
<td>2.</td>
<td>Phréatique</td>
<td>24</td>
<td>-10,20</td>
<td>0,74</td>
</tr>
<tr>
<td>3.</td>
<td>Moyenne profondeur I</td>
<td>38</td>
<td>-11,18</td>
<td>1,14</td>
</tr>
<tr>
<td>4.</td>
<td>Moyenne profondeur II</td>
<td>30</td>
<td>-12,13</td>
<td>0,95</td>
</tr>
<tr>
<td>5.</td>
<td>De profondeur</td>
<td>44</td>
<td>-8,87</td>
<td>1,97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Type d'eau (aquifère)</th>
<th>Tritium</th>
<th></th>
<th>Carbone 13</th>
<th></th>
<th>Carbone 14</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>n écart</td>
<td>$\bar{A}$ (UT)</td>
<td>n $\delta$</td>
<td>$\sigma_n$</td>
<td>n Age radionucléique</td>
</tr>
<tr>
<td>1.</td>
<td>De surface</td>
<td>15</td>
<td>72–115 95</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>Phréatique</td>
<td>37</td>
<td>6–178   58</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Moyenne profondeur I</td>
<td>51</td>
<td>Bgd-17,8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>Moyenne profondeur II</td>
<td>55</td>
<td>Bgd (&lt;5)</td>
<td>14</td>
<td>-11,7</td>
<td>4,7</td>
</tr>
<tr>
<td>5.</td>
<td>De profondeur</td>
<td>94</td>
<td>Bgd (&lt;5)</td>
<td>-</td>
<td>-4,3</td>
<td>2,2</td>
</tr>
</tbody>
</table>


b 91% du nombre d'analyses, Bgd (<5 UT).
Nous avons abordé certains aspects particuliers des relations intersystèmes concernant la plaine occidentale de Roumanie. Quant aux relations régionales d’interéchange sur la verticale, la conclusion la plus importante est fondée sur la présence du tritium décelable par scintillation liquide. Sur le tableau V, le tritium n’apparaît que jusqu’au niveau des eaux de moyenne profondeur I, ce qui démontre le fait qu’un échange actif d’eaux avec la surface se produit jusqu’à la profondeur d’environ 100 m.

Quant à la circulation intrasystème, les seuls résultats notables ont été obtenus par le radiocarbone.

Ainsi qu’on peut le voir sur le tableau V, l’âge radiométrique moyen calculé pour l’aquifère de profondeur est de 34 900 ans, ce qui permet de conclure que ces eaux sont stagnantes. En même temps, l’uniformité des valeurs ($\delta_n = 3800$ ans) a exclu la possibilité d’une interprétation aréale satisfaisante de ces analyses.

L’âge radiométrique moyen de l’aquifère de moyenne profondeur II, 27 900 ans, et l’écart relativement grand des valeurs individuelles ($\delta_n = 7500$ ans) démontrent le fait que ces eaux participent dans une large mesure au circuit hydrologique actif et offrent ainsi la possibilité d’élaborer des cartes aux isochrones.

Pour illustrer l’apport des méthodes isotopiques dans la solution du problème de la circulation intrasystème, nous avons choisi la zone septentrionale, Oradea-
Satu Marc, où l’on dispose d’un nombre satisfaisant d’analyses isotopiques ($^{14}\text{C}$, $^{13}\text{C}$ et $^{3}\text{H}$) et hydrochimiques ainsi que d’une situation hydrodynamique relativement complexe. Toutes les analyses de radiocarbone exécutées pour les aquifères de moyenne profondeur II et de grande profondeur ont été traitées en calculant les âges au moyen de cinq méthodes différentes. Les moyennes des résultats ont été rapportées pour chaque aquifère et chaque méthode (tableau VI). Pour le calcul de ces âges, on a utilisé, en dehors des données analytiques, les constantes et valeurs suivantes:

- la période de $^{14}\text{C}$: 5730 ans;
- l’activité en $^{14}\text{C}$ du CO$_2$ du sol de la région, $A_p = 100\%$;
- l’activité en $^{14}\text{C}$ du carbonate solide de la matrice de l’aquifère, $A_M = 0\%$;
- la teneur en $^{13}\text{C}$ du carbonate solide de la matrice de l’aquifère, $\delta_M = +1,0\%$;
- la teneur en $^{13}\text{C}$ du CO$_2$ du sol de la région, $\delta_p = -24,0\%$;
- le facteur d’enrichissement isotopique en $^{13}\text{C}$ du carbonate dissous (calculé par la formule de P. Deines et al. [6], $\epsilon = -11,4$).

L’interprétation des données ainsi obtenues a permis d’aboutir à certaines conclusions intéressantes de deux points de vue, notamment:

- sur la mesure dans laquelle les analyses du radiocarbone peuvent refléter l’image hydrodynamique d’un système aquifère;
- sur le degré d’applicabilité des différentes méthodes de correction en conditions géochimiques particulières.

En ce qui concerne le premier aspect, la comparaison des cartes aux isochrones de l’aquifère de moyenne profondeur II (fig. 10) avec la carte hydrogéologique de la fig. 3 rend manifeste la similitude des spectres d’isolines, ce qui démontre que la situation hydrodynamique peut être fidèlement reflétée par des données isotopiques.

En ce qui concerne le deuxième aspect, les données du tableau VI mettent en évidence, comme observation d’ordre général pour la région, le fait que la variation des âges moyens calculés à l’aide des cinq méthodes est de 35\% au maximum. On a également constaté, que, étant donné les conditions géochimiques particulières de cette région, les modèles de calcul Pearson et Fontes-Garnier n’ont pas été opérationnels en certaines situations.

Ainsi, nous n’avons pu appliquer la méthode Pearson au cas d’une analyse où $\delta^{13}\text{C} = +0,8\%$, tandis que le modèle Fontes-Garnier a posé de grandes difficultés pour sa mise en pratique à l’aquifère de profondeur; aux valeurs $\delta^{13}\text{C} \approx -3,0 (\ldots) -4,0\%$, qu’on rencontre fréquemment en cet aquifère, l’activité initiale calculée ($A_0$) devient négative. C’est, de plus, une confirmation concrète des limites théoriques du modèle fourni dans [7]; la raison de l’impossibilité d’appliquer la méthode dans ce cas est la particularité géochimique apparue comme suite de la pénétration dans le système de certaines quantités de CO$_2$. Une analyse, où la teneur est $\delta^{13}\text{C} = -4,1\%$ PDB semble indiquer...
<table>
<thead>
<tr>
<th>No.</th>
<th>Méthode de calcul de l'âge</th>
<th>Aquifère de moyenne profondeur</th>
<th>Aquifère de profondeur (thermal)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$n \sum_{i=1}^{n} \frac{t_i}{n} \pm a_n$</td>
<td>$n \sum_{i=1}^{n} \frac{t_i}{n} \pm a_n$</td>
</tr>
<tr>
<td>1.</td>
<td>Age radiométrique</td>
<td>14 28 700 ± 7 400 100,0</td>
<td>16 36 600 ± 3 400 100,0</td>
</tr>
<tr>
<td>2.</td>
<td>Modèle Vogel</td>
<td>14 27 400 ± 7 400 95,5</td>
<td>16 35 200 ± 3 400 96,2</td>
</tr>
<tr>
<td>3.</td>
<td>Modèle Tamers</td>
<td>14 23 200 ± 7 500 80,8</td>
<td>16 30 800 ± 3 400 84,2</td>
</tr>
<tr>
<td>4.</td>
<td>Modèle Pearson</td>
<td>14 21 800 ± 7 900 75,9</td>
<td>15a 23 600 ± 3 900 64,5</td>
</tr>
<tr>
<td>5.</td>
<td>Modèle Fontes-Garnier</td>
<td>12b 22 500 ± 8 600 78,4</td>
<td>15c 23 600 ± 3 900 64,5</td>
</tr>
</tbody>
</table>

\[\text{a} \quad \text{Une analyse du total de 16, dont la valeur est } \delta^{13}\text{C} = +0,8\%, \text{ a franchi les limites d'applicabilité de la méthode.}\
\[\text{b} \quad \text{Deux analyses du total de 14, dont les valeurs sont } \delta^{13}\text{C} \approx -3,0\%, \text{ ont franchi les limites d'applicabilité de la méthode.}\
\[\text{c} \quad \text{On n'a pas eu la possibilité de mettre en pratique le modèle de calcul par l'accroissement des valeurs du } \delta^{13}\text{C} (\delta^{13}\text{C} = -4,3\%, \text{ tableau V).}\

l’origine endogène-magmatique du CO₂, mais on ne pourrait pas exclure cependant la présence d’une certaine quantité de carbone endogène sédimentaire [8].

Pour l’aquifère de moyenne profondeur II, le modèle Fontes-Garnier est en général opérationnel (tableau VI); il fournit des âges moyens qui peuvent être situés entre les modèles de Tamers et de Pearson. La transposition des valeurs individuelles sous forme d’isochrones (fig. 10 b) montre une allure qui n’est pas différente de façon significative de celle des âges radiométriques, l’unique différence notable étant la valeur absolue des âges.

2.2.3. Origine et genèse des eaux souterraines

A côté des problèmes du mouvement de l’eau souterraine, la détermination de l’aire, du mode et du taux de recharge, c’est-à-dire des aspects touchant l’origine, constitue les questions essentielles à caractère pratique de l’hydrogéologie des eaux de profondeur.

Dans la période 1972–1973, nous n’avons pas réussi à traiter d’une manière satisfaisante la question de l’origine des eaux souterraines de la plaine occidentale de Roumanie, en l’absence des analyses systématiques nécessaires à la détermination du signal d’entrée. On a quand même observé que les concentrations en deutérium dans la partie méridionale de la région étaient plus faibles, pour le même aquifère, que dans les zones centrale et septentrionale. Cette situation a mené à une série de conclusions sur les zones de recharge mais, naturellement, seulement qualitatives.
Les informations supplémentaires acquises à partir de 1976 pour les aquifères souterrains (tableau IV) et sur les eaux des précipitations (§ 2.1.) ont permis de rendre plus complète l'image de l'origine des eaux souterraines.

Dans un diagramme schématique $\delta D - \delta^{18}O$ (fig. 11), dressé pour une corrélation des valeurs moyennes pluriannuelles de toute la région, on constate la disposition linéaire des points 1–4, c'est-à-dire des quatre premiers types d'eaux du tableau IV; elles se situent sur la ligne des précipitations régionales (b), aux teneurs en deutérium et oxygène 18 qui encadrent asymétriquement la fonction d'entrée (B). Certainement, la composition isotopique des eaux de surface est une fonction complexe (de la saison de prélèvement, de la quantité de précipitations et, implicitement, des relations entre la rivière et le souterrain, etc.) et, par conséquent, elle est variable dans le temps. Les compositions isotopiques moyennes des trois aquifères souterrains sont cependant des valeurs représentatives, en général à variation lente. La position des points de corrélation sur le diagramme démontre l'accroissement progressif de la hauteur d'origine des eaux d'alimentation en rapport avec la profondeur de l'aquifère.

Compte tenu de ce que nous avons signalé au § 2.1., les eaux phréatiques pourraient être considérées en tant qu'eaux d'infiltration locale (eaux météoriques
et des rivières), les eaux de profondeur moyenne I correspondant à des alimentations par précipitations tombées à l'altitude moyenne de 200 m, tandis que les eaux de l'aquifère de profondeur moyenne II pourraient être envisagées comme étant rechargées à l'altitude de 500 m environ.

La position particulière de la composition isotopique moyenne des eaux de profondeur dans le diagramme de la fig. 11 peut conduire, dans une première estimation, à admettre le phénomène de l'évaporation comme la cause de l'enrichissement en isotopes lourds. A l'appui de cette conclusion s'ajoutent le coefficient angulaire, d'approximativement 5, et le fait que ces eaux sont thermales (températures de 50–85°C).

Une analyse plus détaillée de la corrélation δD – δ¹⁸O (fig. 12) permet de constater que le mode de distribution des points le long de la droite d'équation δD = 5,35 δ¹⁸O – 18,34 donne la possibilité de délimiter certaines zones qui ont également une signification territoriale précise. Vers le domaine des valeurs négatives sont situées les eaux de la partie méridionale de la région (zone Arad-Timisoara), tandis que la zone septentrionale (Oradea-Satu Mare) se situe au-dessus du point B. En même temps, on peut constater une inversion du sens de variation isotopique dans les deux zones: à partir de l'est vers l'ouest, dans la première zone, les valeurs deviennent plus négatives et, dans la deuxième, elles sont de plus...
en plus positives. Cette situation s'explique par des mécanismes différents
d'alimentation [4].

Nous allons insister un peu sur la zone Oradea-Satu Mare, intéressante aussi
du point de vue de l'origine et de la genèse des eaux de profondeur. De l'examen
de la fig. 12 et des âges déterminés par radiocarbone, il semble ressortir que les
eaux de profondeur de cette zone ont une origine mixte, étant des paléoinfiltrations
météoriques en mélange avec des eaux syngénétiques de type saumâtre (S). La
composition isotopique de cette dernière composante a été estimée comme à peu
près égale à celle de la Mer Noire (δD = -33,0‰; δ18O = -3,0‰). Les proportions
du mélange ont une variation aréale; dans la situation hydrodynamique actuelle,
la composante météorique est prépondérante dans la subzone orientale, vers la
limite de la dépression, tandis que la composante syngénétique l'est dans la
subzone occidentale. Par conséquent, la pente de la droite de régression apparaît
comme étant engendrée par la présence du mélange entre les deux composantes
et non par le phénomène d'évaporation.

Cette image succincte de l'origine des eaux de profondeur dans la zone
Oradea-Satu Mare est confirmée aussi par des arguments génétiques. A partir
d'une idée suggérée par H. Craig [9] nous avons corrélé, sur la fig. 13, la compo-
sition isotopique (deutérium et oxygène 18) avec celle chimique (l'anion Cl-).
Les diagrammes obtenus ont rendu manifeste la présence de deux familles différentes d’eaux: F₁, qui correspond aux eaux de la subzone orientale dont l’origine est à prédominance météorique, et F₂, qui représente la famille des eaux des subzones centrale et occidentale dans lesquelles apparaissent d’importantes quantités d’eaux syngénétiques. Sur la fig. 13a, on observe que la corrélation δD – Cl⁻ est linéaire pour les deux familles, tandis que la corrélation δ¹⁸O – Cl⁻ (fig.13b) est linéaire pour F₁ mais parabolique pour F₂.

La forme linéaire de la corrélation δD – Cl⁻ atteste le fait qu’on se trouve en présence d’un phénomène de mélange de deux composantes chimique et isotopique distinctes, qui sont les eaux fossiles météoriques infiltrées dans la bordure orientale et les eaux syngénétiques des sédiments pontiens. La corrélation de forme parabolique entre δ¹⁸O et Cl⁻ pour la famille d’eaux F₂ met en évidence l’apparition de certains enrichissements prononcés en ¹⁸O, lesquels n’apparaissent qu’après des délais de résidence très longs. Dans la zone orientale, où sont prédominantes les eaux fossiles d’origine météorique (famille F₁), la corrélation δ¹⁸O – Cl⁻ se maintient linéaire, en raison de l’âge relativement plus récent de ces eaux.

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COMPARATIVE STUDY OF DIFFERENT AQUIFER TYPES IN CENTRAL EUROPE, USING ENVIRONMENTAL ISOTOPES

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Abstract

COMPARATIVE STUDY OF DIFFERENT AQUIFER TYPES IN CENTRAL EUROPE, USING ENVIRONMENTAL ISOTOPES.

Hydrological studies using environmental isotopes were carried out in the porous, inhomogeneous Younger Tertiary aquifer of the Bavarian molasse basin, the Keuper sandstone of Fränkisches Albvorland, which is a low-permeability porous aquifer traversed by fissures, and the karst aquifer of the molasse basin in Oberschwaben. From 1976 to 1983, water samples were taken from about 300 wells and springs for hydrochemical and isotope analyses ($^2$H, $^3$H, $^{13}$C, $^{14}$C, $^{18}$O). It was possible to approximately determine a coherent zone of young, tritium-containing groundwater in the porous Younger Tertiary aquifer. Locally, tritium was found at great depths of the fractured aquifers of the Fränkisches Albvorland and Oberschwaben, revealing a rather inhomogeneous flow pattern. In all three areas investigated, low $^{14}$C contents of groundwater are associated with low $\delta^2$H and $\delta^{18}$O values which are considered to be due to the colder climate during recharge in the glacial period. Attempts were also made to correlate $\delta^2$H and $\delta^{18}$O values of precipitation and young groundwater with those of old groundwater.

For this purpose, a few values of groundwater formation temperatures determined from noble-gas measurements were taken into account. In the Keuper sandstone aquifer, different $^{14}$C dating models were compared for calculating the initial $^{14}$C contents of groundwater and for deducing groundwater flow velocities. In the Younger Tertiary and Keuper sandstone aquifers an exchange between alkaline-earth and alkali-metal ions is observed, the time-scale of which is roughly estimated from the associated decrease of the $^{14}$C content of the groundwater.
Furthermore, empirical relationships between nitrate and tritium contents and chloride and 
$^{14}$C contents are presented. Hydrological conclusions were drawn for the groundwater flow 
pattern in the areas under investigation.

INTRODUCTION

Hydrological studies using environmental isotopes were carried out in three 
south-German areas (Fig. 1) representing hydrogeologically different types of 
aquifers:

- The Younger Tertiary aquifer in the Bavarian molasse basin ('area t'). This 
  porous aquifer is formed of gravel and sand with intermediate clay and silt 
  lenses.
- The Keuper sandstone of the Fränkisches Albvorland ('area k'). This aquifer 
  is partially covered by thick clay layers and is considered to be a low-
  permeability porous aquifer which is traversed by fissures.
- The karst aquifer of the north-western part of the molasse basin in Ober-
  schwaben ('area m'). The heavily karstified limestone aquifer belongs to 
  the Upper Malm and dips towards the south-east below molasse sediments.

The object of the isotope hydrological investigation in area t was mainly to 
explore the groundwater flow pattern in the deep porous aquifer of the Younger 
Tertiary and thus to contribute to establishing a groundwater balance [1]. The 
field investigations in area k were aimed at examining different $^{14}$C groundwater 
dating models for their applicability in this area. Besides isotope measurements 
on samples of groundwater, solid carbonate and soil gas, extensive hydrochemical 
analyses were carried out [2]. In area m, regional and local information on the 
flow system of the Malm karst aquifer will be gained with a view to utilizing 
geothermal energy\(^1\).

From 1976 to 1983, water samples were taken, in part repeatedly, from 
about 300 wells and springs for hydrochemical and isotope analyses ($^2$H, $^3$H, 
$^{13}$C, $^{14}$C, $^{18}$O).

HYDROGEOLOGICAL SITUATION

The investigation area t covers a great part of the unfolded molasse in the 
Bavarian molasse basin. The investigations were concerned with the layers of the

\(^1\) Investigation performed partly in the framework of the geothermal project Saulgau 
(project manager Dipl.-Ing. J. Fritz, Urach), with financial support by Bundesministerium für 
Forschung und Technologie and the Commission of the European Communities.
Obere Süßwassermolasse (OSM), which are an aperiodic sequence of gravel, sand, silt and clay (Fig. 2). The available water yield is related to gravelly and sandy horizons which reach a thickness of up to 150 m and have permeabilities of $10^{-4}$ to $10^{-6}$ m/s; the intermediate layers have permeabilities of $10^{-7}$ to $10^{-10}$ m/s. Recharge takes place mainly in the southern and middle part of the molasse basin, whilst in the north the deep groundwater rises to overlying local aquifers or small receiving water courses. The main receiving water course for this aquifer is the Danube, in the eastern part also the Inn and the lower Isar.

In the upper layers of the OSM the Ca-Mg-HCO$_3$ type of groundwater dominates, whereas with increasing depth the Na-HCO$_3$ type prevails because of cation exchange. The groundwater samples were taken from wells with depths between 41 and 288 m. The filter sections of the wells are in most cases distributed over the depth, with total lengths of between about 20 and 110 m.

The investigation area $k$ covers parts of the Südliche Frankenalb with its Jurassic deposits and, adjacent to the north-west, parts of the Keuper foreland (Fränkisches Albvorland). The Keuper aquifer investigated is tapped by many wells and characterized by sandstone sequences which are separated by clayish interlayers of slight extension. The sandstones crop out in a part of the investigation area (unconfined area), but are covered by thick clay layers of the upper Middle Keuper (Feuerleuten), Lias and Dogger (confined area) below the Fränkische Alb and its immediate foreland. The south-eastern part of area $k$ drains to the Danube, whereas the north-western part belongs to the Rhine system.

According to laboratory experiments the following data can be assumed for the Keuper sandstone: a permeability of about $10^{-5}$ m/s [3], a mean drainable
porosity of about 20% [4] and a joint volume of 0.5–1% [5]. The permeabilities of the clayey layers of the overlying cover vary between 10^{-8} and 10^{-12} m/s [4]. The water-table gradient has a value of 0.8‰ in the confined zone [6] and a mean value of 5‰ in the unconfined zone.

Samples for analysis were taken from production wells with depths of between 26 and 225 m which receive their water from the Keuper sandstone, and from springs which are fed by groundwater in the layers overlying the sandstone Keuper. The water belongs to the Ca-HCO_3 or Ca-Mg-HCO_3 type.

The investigation area m is situated in the north-western marginal part of the molasse basin in Oberschwaben where during the Tertiary Period sediments were deposited on the limestone sequence of the Malm. The simplified geological cross-section (Fig. 2, area m) shows how the partially strongly karstified Malm dips down deeply below the molasse sediments from the Schwäbische Alb toward the Alps. Below the molasse sediments the active karstification is restricted to the upper 20–50 m of the massive limestone (Kimmeridge). The Malm karst water belongs to the Ca-Mg-HCO_3 type, has drinking-water quality (mineralization less than 1000 mg/L) and a temperature of 40–55°C (the groundwaters in the aquifers above and below the Malm are highly mineralized). Recharge takes place in the north-western part of area m (Meßkirch, Fig. 8) where the Malm crops out. The receiving water course is mainly the Danube in Bavaria and partially the Danube south-west of Ulm. Most of the karst water samples analysed were taken from wells or boreholes which have filters only within the Malm aquifer.

RESULTS OF TRITIUM MEASUREMENTS

The tritium contents found are between about 0 and 130 TU and characterize those groundwaters which — at least partially — have relatively short mean residence times.

In the porous aquifer of area t, relatively high tritium contents are found, as expected, in wells which take groundwater from the Quaternary and/or the upper Younger Tertiary. On the other hand, the water from many of the investigated wells contains no tritium or only very little (≤ 1.5 TU) although the upper filter edge of some of the wells lies only about 30 m below ground-level. In Fig. 2 (area t) a line is drawn below which, according to the measurement results and hydrogeological considerations, no tritium is to be expected within the investigation period. The real position of the boundary line (or area) between tritium-containing and tritium-free groundwater cannot be indicated exactly because of the poor depth resolution which is caused by the large filter lengths of the existing wells. It is, however, estimated to lie between 20 and 40 m below ground-level.
in the cross-section given in Fig. 2 (area t), and between 40 and 60 m below ground-level in another cross-section investigated (Landsberg-Augsburg). The position of the boundary area depends strongly on hydrogeological and hydraulic factors, such as permeability, groundwater gradient and pumping rate. A hydrogeologically reasonable value of the mean groundwater recharge rate was estimated on the basis of the depth down to which bomb-produced tritium has penetrated the aquifer [7].

In the fissured and porous aquifer of area k with its alternating sandstone and clay layers, the isotope contents differ considerably, even in neighbouring wells of similar construction. For example, a tritium content of 5 TU and a $^{14}$C content of 10% modern were found in the one well and about 1 TU and 80% $^{14}$C modern in the other, reflecting the inhomogeneity of the aquifer.

In the karst area m, tritium was found in almost all wells and even in water samples with $^{14}$C contents below 10% modern. This shows that there is a mixing of water with large age differences, at least within the wells, but possibly also in the aquifer down to depths larger than those into which tritium penetrates in area t.

RELATIONSHIP BETWEEN CARBON-14 AND CARBON-13 CONTENTS

In each of the three different investigation areas, $\delta^{13}$C of the dissolved inorganic carbon (DIC) increases with decreasing $^{14}$C contents of the groundwater samples. In area t, for example, $\delta^{13}$C increases from −15 to −9‰, whilst the $^{14}$C contents decrease from 103% to less than 0.6% modern. This is primarily ascribed to the change in pH which is connected with an exchange between alkaline-earth and alkali-metal ions. This exchange is taken into account when calculating the initial $^{14}$C content. In contrast to the situation in area t, in area m the change of $\delta^{13}$C in the groundwater can be explained by carbon isotope exchange between DIC and carbon in the rock. In area k, $\delta^{13}$C increases from −23.1 to −10.7‰ with decreasing $^{14}$C content. This can be explained mainly by the corresponding increase of the saturation indices for calcite, aragonite and dolomite, but a carbon isotope exchange between water and rock cannot be excluded.

Model calculations of the initial $^{14}$C contents of DIC depend, among other things, on $\delta^{13}$C of the carbonate in the aquifer matrix. The average $\delta^{13}$C values determined from many solid carbonate samples are for area t at −3.0‰ ($−8.2 \text{ to } +1.5‰$) and for area m at +2‰ (0 to +3‰). In area k, the samples from the Keuper formations have a mean $\delta^{13}$C value of −7.9‰ (−14.0 to −3‰), whereas the corresponding value for samples from the Jurassic formations is +1.0‰ (0 to +2‰). Considering a possible carbon isotope exchange, the $^{14}$C model ages resulted from the $^{14}$C contents of between recent values (the lower $^{14}$C dating limit being of the order of 1500 years b.p.) and at least 35 000 years b.p.
FIG. 2. Characteristic, schematic geological cross-section of the investigation area 1 (Younger Tertiary aquifer in the Bavarian molasse basin), k (Keuper sandstone of the Frankisches Albvorland), and m (karst aquifer of the upper Malm, Oberschwanen). For location, see Fig. 1. Wells with filter sections are indicated. Th.B. Saulgau 1 and 3 are projected into the plane of the cross-section (Th.B. = thermal-water borehole).

OMM = Oberer Meerwassermolasse (upper sea-water molasse)
USM = Untere Süßwassermolasse (lower fresh-water molasse)
RELATIONSHIP BETWEEN CARBON-14 AND TRITIUM CONTENTS

Figure 3 shows which groundwaters are 'young' (with mean residence times of years or decades) and which groundwaters contain an admixture of older, tritium-free groundwater which often has low $^{14}$C contents. Groundwater with tritium contents of $>60$ TU and $^{14}$C contents of $>80\%$ modern are certainly young as a whole. Groundwater which contains tritium (for example, $<60$ TU in the investigation period) and $^{14}$C less than about $60\%$ modern can be considered in most cases as a mixture of young and old groundwaters. No definite statement is possible for groundwater with tritium contents of less than about $30$ TU and $^{14}$C contents of more than about $60\%$ modern, this being the possible range of initial $^{14}$C values which are not necessarily influenced by currently recharged groundwater.
The $^{14}\text{C}$/tritium relationship reflects clearly the different groundwater flow patterns in the different types of aquifers which cause different degrees of mixing between young and old groundwaters. In the porous aquifer of area t, $^{14}\text{C}$ contents of less than about 40% modern — which are distinctly lower than recent values — are associated with low or not detectable tritium contents, thereby indicating no essential mixing. In contrast, the groundwater samples from the fissured aquifer of area m contained tritium even in most of those cases where the $^{14}\text{C}$ content was low, thus indicating that mixing between old and young groundwaters had taken place. The broad range of mixing in area k, indicated by the scattering of the measuring points in Fig. 3, is considered to reflect qualitatively the porous/fissured type of aquifer, with its flow characteristics being a mixture of those of areas t and m.

RELATIONSHIP BETWEEN DEUTERIUM AND OXYGEN-18 CONTENTS

As can be seen from Fig. 4, most of the $\delta^2\text{H}-\delta^{18}\text{O}$ values of the groundwater in all three investigation areas lie slightly below the general meteoric water line 

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10,$$

a fact which was also observed in other south-German regions. For comparison with young groundwater having tritium contents of, for instance, more than 20 TU, $\delta$-values for precipitation were used which were obtained by interpolation of $^2\text{H}$ and $^{18}\text{O}$ measuring results of monthly samples from the precipitation collection stations Hohenpeißenberg, Neuherberg (near Munich), Regensburg, Würzburg, Stuttgart and Constance (Fig. 1). The monthly $\delta$-values were weighted with the precipitation amount (neglecting evaporation) and were averaged essentially over the period 1978–1982. The five-year means of the $\delta$-values were weighted with the distance to the relevant investigation areas (Fig. 4). In areas k and m the mean $\delta$-values of precipitation and young groundwater are nearly equal, whereas in area t the mean $\delta$-value of young groundwater is greater by about 7‰ in $\delta^2\text{H}$ or 0.9‰ in $\delta^{18}\text{O}$ than the mean $\delta$-values of precipitation.

It is obvious that the stable-isotope content of young groundwater depends on the stable-isotope content of the infiltrating part of precipitation recharging the groundwater. Therefore, besides the seasonal variation of the isotope content of precipitation, the stable-isotope content of the recharged groundwater is determined by the seasonal distribution of the precipitation amount, the evaporation (which is possibly connected with isotopic fractionation) and the surface runoff. In the frame of this paper the complicated interrelationships between the different parameters can be dealt with only briefly in a very simplified and empirical way. The agreement of the mean $\delta$-values of precipitation and groundwater in areas k and m points to groundwater recharge occurring over the whole year. This concurs with the hydrogeological expectation for area m, whereas in area k mainly winter recharge was expected. In area t the mean $\delta$-values of young
groundwater equal the mean δ-values of precipitation if, for example, the precipitation of December, January and February is assumed not to contribute to recharge. There is indeed a hydrological indication for preferential recharge during summer [8]. Another possibility of explaining the difference between the mean δ-values of precipitation and groundwater is that the precipitation periods investigated were too short compared with the ‘age’ of the groundwater samples referred to. However, assuming that the stable-isotope content of precipitation at a given collection station (for example Hohenpeißenberg) is mainly dependent on the mean air temperature, the stable-isotope content should not have varied by more than about ±3‰ in δ²H during the last two centuries, as the ten-year averages of temperature have not varied by more than about ±1°C within this period [9].
RELATIONSHIP BETWEEN CARBON-14 AND OXYGEN-18 CONTENTS

In Fig. 5, a clear decrease of δ¹⁸O (or δ²H) with decreasing ¹⁴C contents — below certain limits of the ¹⁴C contents — can be recognized for groundwater samples from all three investigation areas. The limits of the ¹⁴C contents are about 25, 10 and 8% modern, respectively, for areas t, k and m. Above these limits the mean δ¹⁸O value lies at around −10% in all three areas.

Low values of δ²H and δ¹⁸O of groundwater or of precipitation from which the groundwater is formed can have different reasons, among which the temperature during water evaporation and vapour condensation plays an important role. In addition to the isotope altitude effect and the influence of season on the stable-isotope content of infiltrating water, in Middle Europe a decrease in the δ-values of precipitation is observed with increasing distance from the Atlantic coast (continental effect; see, for example, Ref. [10]). For an interpretation, the
simplifying assumption is made that the origin of the air masses from which the precipitation originated remained unchanged within the time span represented by the age of the groundwater under investigation. As a consequence, and in keeping with the relatively high $^{14}C$ model ages, the low $\delta^2H$ and $\delta^{18}O$ values of deep water in the areas under investigation suggest that these groundwaters had formed in whole or in part under colder climatic conditions than have prevailed during the last few thousand years until present. Such an interpretation was applied, for example, to groundwater in North Africa [11, 12], the Styrian basin [13] and east England [14].

Among the various hypotheses explaining the decrease of the $\delta$-values there is chiefly the simplifying assumption that in the past the stable-isotope content of precipitation depended mainly on temperature in the same way as at present. This leads to semi-quantitative estimates of the temperature depression in the glacial period.

In order to correlate $\delta$-values of present precipitation with the mean air temperature, empirical linear relationships were established for 11 meteorological stations located between the North Sea coast and the Alps, covering the years 1978–1982. The mean $\delta^2H$ temperature gradient turned out to increase from about $1\%$ per $1^\circ C$ temperature increase in Cuxhaven (North Sea coast) to about $3\%$ per $1^\circ C$ in Garmisch-Partenkirchen (northern border of the Alps) and at higher altitudes to about $5\%$ per $1^\circ C$ on Patscherkofel (2045 m a.s.l., near Innsbruck).

The low $\delta^2H$ and $\delta^{18}O$ values of groundwater samples with low $^{14}C$ contents can be interpreted by assuming that the present mean $\delta$-temperature gradients are also applicable for the glacial period. Noble-gas measurements\(^2\) [15] on a few selected groundwater samples from area t revealed a difference of about $7^\circ C$ between the groundwater infiltration temperatures in Holocene and the glacial period. If one relates this with the mean air temperature at which precipitation is formed, and if also the difference between the $\delta$-values of the ocean water (as the source of precipitation water) during Holocene and during the glacial period is considered, one arrives at $\delta^2H \approx -84$ to $-80\%$, using the $\delta$-temperature gradients assumed to be relevant for the investigation area. The lowest $\delta^2H$ value of $-98\%$ measured is reached if one allows for an admixture of about 30 to 50$\%$ of melt water from glaciers in the past (the $\delta^2H$ values of the melt water being $-130$ to $-110\%$ according to a rough estimate). No contribution of glacial melt water to the groundwater recharge in areas t and m is needed for explaining the difference between the $\delta$-values of young and old groundwaters if the $\delta$-temperature gradient valid at present for the Alpine region is applicable to the pre-Alpine region during the glacial period.

In area k, the measured difference between the $\delta^2H$ values of groundwater from the Holocene and the glacial period is about $12\%$. Allowing for the mean

\(^2\) The authors thank Dr. J. Rudolph and Dr. C. Sonntag, Heidelberg, for their co-operation.
$\delta^2$H value of ocean water in the glacial period and using the recent $\delta$-temperature gradient mentioned above, again a difference of about 7°C results for the groundwater infiltration temperatures.

Among the groundwater samples from area 1 with very low or not detectable $^{14}$C content are those which have the lowest $\delta^{18}$O values (~13.3%) and the lowest formation temperatures deduced from noble-gas measurements (2°C). These samples are assumed to represent old groundwater from the glacial period. Other groundwater samples belonging to this group display higher $\delta^{18}$O values, between ~12.1 and ~12.5%, with a representative sample among them on which a relatively high formation temperature of 4.5°C was determined. The $^{13}$C and hydrochemical analyses do not indicate any marked dilution of the $^{14}$C content in the aquifer which may have existed before sampling. In view of the elevated formation temperature and not in disagreement with hydrogeological considerations, one could assume that this water is, at least partially, older than about 60 000 years, but in most cases it appears realistic to assume that samples with $\delta^{18}$O values below about ~10.5% are mixtures of Holocene and Pleistocene groundwaters.

Those groundwater from area 1 which have the highest $\delta^2$H and $\delta^{18}$O values and a $^{14}$C content of about 40% modern (Fig. 5) have also a special position in the $\delta^2$H-$\delta^{18}$O diagram (Fig. 4). From this position, one would be inclined to conclude that these groundwaters underwent some evaporation, but there is no hydrogeological support for such an assumption.

Even though the above considerations appear to be realistic, they are only rough estimates which have to be examined further.

### RELATIONSHIP BETWEEN CARBON-14 AND ALKALI ION CONTENTS

Cation exchange is linked to clay minerals with exchangeable groups. These minerals occur in the investigation areas 1 and k, but they are missing in area m. Correspondingly, an increase of the alkali concentration in groundwater from areas 1 and k is observed which is due to ion exchange and goes along with a decrease in the $^{14}$C content (Fig. 6). In area m the cation exchange between rock and groundwater occurs with water coming from the layers that lie over the Malm karst. It takes place slowly (for example, an increase from 0.2 to 0.4 mmol [Na$^+$ + K$^+$ + Cl$^-$] takes a few thousand years in area k) and requires long residence times of the water in the aquifer.

### FURTHER RELATIONSHIPS BETWEEN ISOTOPE AND ION CONTENTS

Nitrate and partly chloride can be considered as representing an anthropogenic burden of the groundwater in the investigation areas. Groundwater samples
with high tritium contents mostly contain relatively high nitrate and chloride concentrations, but no strong correlation was found. Especially the nitrate concentration in groundwater depends strongly on the hydrochemical environment, besides depending on the amount introduced. Relatively high concentrations of chloride are found even in groundwater with low $^{14}$C contents (Fig. 7). It is possible that the chloride originates also from the aquifer matrix. This is certainly the case in area k with groundwater samples having 1–1.5 mmol Cl$^-$/L and a $^{14}$C content of less than 25% modern.

HYDROLOGICAL RESULTS

In area t, it was not possible to use isotope measurements for establishing the depth profiles of the groundwater flow velocities (and flow directions) as the aquifer is too inhomogeneous and most of the wells do not allow sampling from a well-defined depth. However, the zone of the aquifer could be determined
approximately by tritium analyses, in places where the groundwater in part or as a whole is young (Fig. 2). In principle, anthropogenic toxic pollutants such as tritium could also penetrate the aquifer under similar hydrological conditions within comparable time spans, if the pollutants were not eliminated, retarded or at least strongly diluted in the aquifer, as seems to be usually the case in practice.

High $^{14}$C model ages of 25 000 years b.p. and more, which were found for the groundwater from some deep wells located at both ends of the cross-section shown in Fig. 2 (area t), are in accordance with rough hydrological estimates of flow times.

Isotope hydrological and hydrogeological investigations of the deep aquifer supplemented each other effectively and formed, together with a mathematical flow model [16], the basis for establishing a groundwater balance [7].
FIG. 8. Map of investigation area m (karst aquifer), indicating the probable flow direction deduced from isotope hydrological considerations (→→), compared with the main flow direction based on hydrogeological studies (→) (after Ref. [17], modified). —— groundwater contours (m a.s.l.), —— north boundary of the confined karstified aquifer,  —— northern boundary of the molasse cover,    —— north boundary of the Faltenmolasse, ———— groundwater divide between Rhine and Danube, ——— Danube total infiltration zone, ==⇒ assumed recharge of the thermal Malm karst water through the overlying molasse.

In area k, large differences resulted when different models were used for calculating the initial $^{14}$C contents of young tritium-containing groundwater as well as of relatively old groundwaters with low tritium and $^{14}$C contents [2]. On the other hand, there was fairly good agreement between the groundwater flow velocities deduced from the differences of the groundwater ages that were derived from the different models; in the confined aquifer the flow velocities are comparable with those derived from hydrological parameters.

In area m, the isotope measurements together with the hydrochemical analyses confirm in general the groundwater flow pattern assumed by Strayle et al. [17], and complete and refine this picture for some parts of the investigation area (Fig. 8). For example, it is concluded from $^2$H and $^{18}$O measurements that the presumable catchment area of a part of the deep groundwater is not restricted to the area of Meßkirch but extends to an area east of Sigmaringen. The results of $^{14}$C and hydrochemical analyses point to a recharge of the thermal Malm karst
water through the molasse from the south. Furthermore, it is concluded from
$^{14}\text{C}$ and $^{13}\text{C}$ analyses that in the area of Ulm the groundwater flow which is
directed north-east is diverted within a narrow zone by groundwater flowing
south-east. The study in area m has not yet been finished.

CONCLUDING REMARKS

In the Younger Tertiary aquifer (area t) of the Bavarian molasse basin the
investigation of tritium penetration made it possible to approximately determine
the coherent zone of young groundwater, since the aquifer is porous although it
contains intermediate low-permeable lenses. Such a coherent zone of young
groundwater does not exist in the unconfined part of area k, and in area m where
young groundwater can locally reach great depths containing the fractured
aquifers consisting of sandstone in the Fränkisches Albvorland (area k) and of
limestone of the upper Malm in Oberschwaben (area m).

From the comparison of tritium and $^{14}\text{C}$ contents in groundwater samples,
mixtures of young and old groundwater can be recognized under certain conditions.
The mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of young groundwater (with $^{14}\text{C}$ contents of
$> 40\%$ modern) are nearly equal in the three investigation areas. The lowest $\delta^2\text{H}$
and $\delta^{18}\text{O}$ values measured are, however, different. As these $\delta$-values are connected
with low $^{14}\text{C}$ contents, the pertinent groundwater is considered to be in part or
as a whole of Pleistocene origin. On the basis of the tritium contents of recent
groundwater and the difference between the $\delta^2\text{H}$ or $\delta^{18}\text{O}$ values of Holocene and
Pleistocene groundwaters, an attempt was made to estimate the mixing ratios of
groundwaters of three different age ranges [1]. Krypton-85 analyses can be very
helpful in those cases where it is not possible to use only tritium and carbon-14
measurements for determining the proportion of the young component of mixed
waters and the relevant mean residence times. Krypton-85 analyses were used,
for example, in investigations of two wells in area k [18].

A comparison of the various isotope measurement results with each other and
with hydrochemical data gave information about the origin of the pumped ground-
water or at least of one of its components, for example, for groundwater of large
$^{14}\text{C}$ model ages containing chloride and alkali ions.

In all three investigation areas, repeated sampling and analyses were carried
out for a number of wells at large time intervals. As expected, no essential change
of the isotopic and chemical composition of old groundwater was observed in
general. Where such changes occurred they were attributed to alterations of the
hydraulic sampling conditions, such as the position of the pump within the well or the
pumping rate. In wells with long filter sections, generally samples should be taken
preferably at depths with maximum groundwater inflow into the well or borehole.
Such zones can be determined by flowmeter or tracer measurements.
On the whole, the isotopic investigations and hydrogeological studies complemented each other in furnishing information on the origin and flow pattern of shallow and deep groundwaters. This is a valuable contribution to establishing the groundwater balance.

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Abstract—Аннотация

STUDY OF THE GENESIS AND DYNAMICS OF UNDERGROUND WATERS USING NATURALLY OCCURRING ISOTOPES: RESULTS OF RESEARCH AND INTERPRETATION OF DATA.

The paper examines examples of using system models to solve hydrogeological and palaeohydrogeological problems. It shows the possible applications of various naturally occurring isotopes in studying the hydrogeological conditions of large semi-arid regions such as the southern lowlands of Western Siberia. In the region studied, the distribution of hydrogen (D,T), oxygen (18O) and carbon (13C, 14C) isotopes is used to detect the presence of waters with low isotope levels (δD = −140‰, δ18O = −18.1‰) in the lower Miocene aquifer; these are compared with contemporary atmospheric precipitation (δD = −87‰, δ18O = −11.4‰) which stays in the aquifer for about 20,000 years. The paper notes that in localized areas this level is fed from contemporary lakes and also from water courses which existed in the region studied during an earlier Holocene. Dynamic tritium studies of thermal waters of Kunashir Island (one of the Kurile island chain) have shown that the water exchange rate averages 100 years and that the base temperatures, measured by an oxygen-sulphate geothermometer, are significantly higher than the exit temperatures. During hydromeliorative studies of irrigation in the Asha massif (western part of the Fergana Basin) isotope data were used to split up the sources of salinization of the irrigated lands. It is shown that the basement Neogenic strata add only an insignificant amount of salts to the massif and that the main source of salinization is evaporative concentration of salts added by irrigation waters. This is confirmed (as the mineralization of underground waters increases) by the reduction of the excess parameter δ = 8518O - δD, by the increase in tritium concentration and the reduction in water-soluble helium. The maximum age of underground waters, determined with 14C, is 3700 years. Isotope research conducted in the Sevan basin has shown that the proportion of lake waters in the Atarbekyan and Makrovan springs does not exceed 25%. Given that the flow rate of the springs is 2.4 m³/s, the annual underground discharge of lake water is 20 million m³, which satisfactorily agrees with independent balance calculations.
ИЗУЧЕНИЕ ГЕНЕЗИСА И ДИНАМИКИ ПОДЗЕМНЫХ ВОД С ИСПОЛЬЗОВАНИЕМ ПРИРОДНЫХ ИЗОТОПОВ: РЕЗУЛЬТАТЫ ИССЛЕДОВАНИЙ И ИНТЕРПРЕТАЦИЯ.

Рассмотрены примеры использования системных моделей для решения гидрогеологических и палеогидрогеологических задач. Показана перспективность использования комплекса природных изотопов при изучении гидрогеологических условий крупных регионов с плавучим климатом на примере ваг Западно-Сибирской низменности. По распределению изотопов водорода (D, Т), кислорода (18O) и углерода (13C, 14С) установлено присутствие на исследуемой территории в нижнемоценовом водоносном горизонте вод облегченного изотопного состава (D = −140%, δ18O = −18.1%) по сравнению с современным атмосферными осадками (D = −87%, δ18O = −11.4%). Время пребывания которых в водоносном горизонте составляет примерно 20 тыс. лет. На локальных участках отмечено течение этого горизонта из современных озер, а также из водотоков, существовавших на исследуемой территории в раннем голоцене. Исследование динамики термальных вод о. Кунашир (Курильская островная дуга) с использованием трития показали, что время водообмена в среднем составляет около 100 лет, а базовые температуры, определенные по кислородно-сульфатному геотермометру, значительно превышают температуры на выходе. При гидрометрических исследованиях на Ашхарском массиве орошения (западная часть Фернгской долины) по изотопным данным проведено расчленение источников заселения орошаемых земель. Показано, что привнос водей на массив из подстилающей неогеновой толщи незначителен, а основным источником заселения является испарительное концентрирование соей, приносимых с просительными водами. Это подтверждается (по меру возрастания минерализации подземных вод) уменьшением эквивалента компонент d = 86°С = 4D, увеличением концентрации трития и снижением содержания водородсодержащего гелия. Максимальный возраст подземных вод, вычисленный по углероду-14, составляет 3700 лет.

Изотопные исследования, проведенные в Северской котловине, позволили оценить долю озерных вод в Атабексийских и Макровских родниках, которая не превышает 25%. При дебите родника 2.4 м3/с годовая подземная разгрузка озерных вод составляет 20 млн. м3, что удовлетворительно согласуется с независимыми балансовыми расчетами.

ВВЕДЕНИЕ

При интерпретации результатов изотопных исследований природных вод широко используют физико-математические модели. Начало разработки таких моделей было положено работами Бегемана и Лаббса [25], Эркссона [29], Дениера и Пейна [28], Брауна [26]. В дальнейшем применительно к изотопным исследованием подземных вод модели развивались и использовались целым рядом специалистов: Аллисоном и др. [24], Гатом [31], Лубеничем [18], Поляковым [15], Мартинсем и др. [36], Пшеворским и др. [41], Романовым и др. [16].

Опознавать частных и общих моделей переноса изотопов в гидрогеологических системах возможно найти в работах [16-20, 29, 30, 33, 39]. При этом наблюдается тенденция применения не только простых одноизометричных, но и структурно-сложных динамических моделей на базе достижений обшей теории структурно-сложных систем [1, 4, 5, 10, 34, 40, 41]. При интерпретации приводимых ниже результатов изотопных исследований авторы использовали теоретические и методические предпосылки, которые подробно рассмотрены в работах [6, 7, 8, 9, 18, 31, 33, 39].
1. ИСПОЛЬЗОВАНИЕ КОМПЛЕКСА ЕСТЕСТВЕННЫХ ИЗОТОПОВ ПРИ ИЗУЧЕНИИ ГИДРОГЕОЛОГИЧЕСКИХ УСЛОВИЙ КРУПНЫХ РЕГИОНОВ

1.1. Задачи исследований и гидрогеологические условия района

При изучении гидрогеологических условий крупного региона (40 тыс. км²), расположенного на юге Западно-Сибирской низменности, был проведен комплекс исследований с использованием изотопов водорода, кислорода и углерода.

Целью изотопных исследований явилось решение следующих задач:

1. Уточнение условий формирования подземных вод различной минерализации в отложениях нижнего миоцена.

2. Оценка времени водообмена на различных участках нижнемиоценового водоносного горизонта.

3. Определение величин локального и регионального питания этого горизонта и величины подземного стока.

4. Установление взаимосвязи между поверхностными (озерами) и подземными водами.

Территория исследований представляет пологоволнистую слабодренированную озерно-аллювиальную равнину, сложенную осадочными породами палеогена и неогена и перекрытую маломощным чехлом суглинков и супесей четвертичного возраста (рис. 1).

Рис. 1. Схематический геологический разрез одного из участков территории исследований на юге Западно-Сибирской низменности по линии 1-1 (рис. 2):

Поверхность изобилует пресными и соленными озерами различной величины, большей частью приуроченными к днищам древних долин стока. Климат — резко континентальный, засушливый. Среднегодовая температура воздуха — +1 °C, количество осадков — 300-350 мм/год, испарение свыше — 900 мм/год [3].

В гидрогеологическом отношении район работы является частью Тобольского и Иртышского артезианских бассейнов [13]. Региональная водоупорная толща глин чеганской свиты разделяет водонесущие горизонты и комплексы на два этажа. Нижний этаж содержит напорные воды, приуроченные к палеозойским, трiasовым, меловым и палеоцен-эоценовым отложениям, верхний — преимущественно безнапорные воды в отложениях олигоценового, миоценового и четвертичного возрастов (рис. 1, 2).

Основным объектом изучения при съемочных работах были водонесущие горизонты верхнего этажа, главным образом, водонесущий горизонт в отложениях бешелукской свиты нижнего миоцена (N1.3), в котором ранее встречены линзы пресных и солоноватых вод. Этот горизонт на изучаемой территории имеет посещаемое распространение и является практически единственным водонесущим горизонтом, который может быть использован для питьевого водоснабжения. Водообильность горизонта достаточно высока. Дебиты скважин достигают 4 л/с при понижениях 5-8 м. Минерализация воды изменяется от 0,4 до 20 г/л и более.

Пробы воды для изотопного анализа отбирались в основном из бешелукского водонесущего горизонта и озер различной минерализации.

Интерпретация изотопных данных проводилась с учетом ранее имевшейся и полученной при съемке геологической, гидрогеологической и другой информации.
1.2. Распределение дейтерия и кислорода-18

Средневзвешенные на годовой основе значения δD и δ¹⁸O для атмосферных осадков составляют −87‰ и −11,4‰, соответственно. Усреднение по холодным сезонам года (октябрь-май), когда испарение минимально, дает значения δD = −108‰ и δ¹⁸O = −14,2‰. Наиболее "тяжелыми" по изотопному составу являются воды озер, что связано с процессами неравновесного испарения в условиях поларного климата. Изотопный состав подземных вод, приуроченных к отложениям башкирской свиты неогена (N₁bS₁), изменяется в значительных пределах: от −65 до −139‰ по дейтерию и от −7,5 до −18,1‰ по кислороду-18. Графическая зависимость изотопного состава всех исследованных вод в координатах δ¹⁸O–δD представлена на рис. 3. Из рис.3 видно, что точки, характеризующие изотопный состав атмосферных осадков, расположены вблизи прямой метеорных вод. Точки, характеризующие изотопный состав озерных вод, группируются вблизи прямой δD = 3,28 δ¹⁸O − 51, что связано с кинетическими (неравновесными) факторами изотопного фракционирования при испарении воды. Анализ зависимости δ¹⁸O−δD позволяет выделить по условиям формирования четыре типа подземных вод нижнемиоценового (N₁bS₁) водоносного горизонта. К первому типу относятся воды, значительно облегченные по изотопному составу по сравнению с современными...
атмосферными осадками. Как правило, это воды с минерализацией выше 3 г/л (до 12,6 г/л) хлоридно-натриевого состава. Второй тип вод по изотопному составу близок к современным атмосферным осадкам. Минерализация этих вод редко превышает 1 г/л, тип воды — гидрокарбонатно-натриевый.

В третий тип вод, точки которых расположены вдоль прямои неравновесного испарения (II), попадают все озерные воды, а также подземные воды низкимиохлодного водоносного горизонта, вскрытые скважинами, пробуренными недалеко от озер. Минерализация этих вод изменяется от 0,6 до 5,6 г/л. Тип воды по минерализации 2 г/л — гидрокарбонатно-натриевый, выше — хлоридно-натриевый.

К четвертому типу можно отнести подземные воды, изотопный состав кислорода у которых утяжелен за счет процессов испарения (прямая III), но по содержанию дейтерия эти воды тяготеют к первому типу. Преобладающими ионами в этих водах являются хлор и натрий, а их минерализация изменяется от 2,5 до 5,0 г/л.

Опираясь на общие предпосылки, используемые при интерпретации изотопных данных [17, 19, 20, 42], можно сделать следующие выводы:

1. Формирование естественных запасов подземных вод, выделенных по изотопному составу в первый тип, происходило в более холодных, чем современные, климатических условиях без заметных испарительных процессов при инфильтрации через зону аэрации. Повышенная минерализация этих вод обусловлена вышелачиванием солей из водопроявляющих толщ в результате длительного контакта воды с горной породой.

2. Второй тип вод формируется в современных климатических условиях также без существенного испарения при инфильтрации.

3. Формирование третьего типа подземных вод связано с питанием из существующих озер.

4. Четвертый тип вод, вероятно, формировались в холодную климатическую эпоху за счет питания из ранее существующих, но исчезнувших к настоящему времени озер.

1.3. Построение изотопий изотопного состава

На основании данных об изотопном составе подземных вод беучылского водоносного горизонта на исследуемой территории построены линии равных концентраций кислорода-18 и дейтерия. Эти изотопии характеризуют время водообмена на различных участках исследуемого горизонта. Переход к временным параметрам водообмена был осуществлен с использованием моделей полного перемешивания системы, описывающей изменение изотопного состава воды во времени при скачкообразном увеличении концентраций дейтерия и кислорода-18 в атмосферных осадках 1 лет тому назад в результате быстрого изменения климата. Для исследуемой территории такой границей является время потепления климата после окончания зырянского оледенения. Можно допустить, что после деградации толщи многолетнемерзлых пород, существовавших на исследуемой территории в позднем плейстоцене, произошло быстрое восполнение запасов подземных вод за счет временных поверхностных водоисточников с изотопным
составом С1. После потепления климата, которое имело место на исследуемой территории 8-10 тыс. лет тому назад [21], в водноносный горизонт стали поступать воды с изотопным составом С2. Величину С1 можно принять, исходя из экспериментальных данных. Минимальные величины δD и δ18O определены в водах отложений олигоцена: δD = -170‰, δ18O = -21,4‰. Эти значения приняты нами как С1. Величина С2 может быть охарактеризована средневзвешенным изотопным составом современных атмосферных осадков (δD = -87‰, δ18O = -11,4‰). Время t, прошедшее с момента изменения климата от условий, характерных для ледникового периода, до современных, можно оценить примерно в 8000 лет (максимальный откорректированный возраст подземных вод в биотурбационном горизонте, полученный по углероду-14). Пример построения изохор приведен на рис. 3. Изохоры для интервала от 0 до 1000 лет рассчитаны по концентрациям трития, от 1000 до 20 000 лет – по данным о содержании в подземных водах дейтерия и кислорода-18. Как видно из рис. 3, для значительных участков бещебельского водноносного горизонта характерны большие времена пребывания подземных вод. Рядом скважин выходят реликтовые воды, сформировавшиеся в раннем голоцене из временных поверхностных озер и водотоков, исчезнувших к настоящему времени. Таким образом, повышенная минерализация подземных вод на ряде участков нижнеморенового водноносного горизонта может быть объяснена крайне затрудненным водообменом на обширных по площади территориях.

Используя уравнения Дистерда [27], связывающие среднегодовые температуры с усредненным стоячим составом атмосферных осадков (δD = (5,6 t – 100)‰, δ18O = (0,7 t – 13,6)‰), можно оценить среднегодовые температуры, характерные для данного региона в период позднеплейстоценового (зарвасского) оледенения. Поставлено минимально зафиксированное значение δD = -170‰ и δ18O = -21,4‰, получим t = [(-10) + (-12)]°C. Эти температуры ниже среднегодовых современных температур (приблизительно -7°C) центральной Якутии, где в настоящее время существует толша многотолочковых пород. Среднее время пребывания подземных вод на всей исследуемой территории (t) может быть оценено величиной примерно в 5000 лет. Если предположить, что изучаемый водноносный горизонт находится в динамическом равновесии, т. е. qнит = qсток, можно рассчитать среднемноголетнюю питание и сток с единицы исследуемой территории по формуле:

$$q_{нит} = q_{сток} = \frac{H \cdot n \cdot 1000}{t} \frac{мм}{год},$$

где, H, n, t – средние значения мощности, пористости и времени пребывания. Средняя многолетняя величина питания составляет примерно 0,3 мм/год, а подземный сток – 3⋅10² м³ в год с 1 кв. км площади (при расчетах использованы значения H = 5, n = 0,3, полученные по результатам бурения). С использованием индикаторного трогия установлено, что величина инфильтрационного питания на трех репрезентативных площадках изменяется от 0 до 40 мм/год.
1.4. Тритий

Концентрация трития в подземных водах бещеульского водоносного горизонта незначительна. Она изменяется от 0 до 14 Т.Е., увеличиваясь на участках, расположенных вблизи современных озер. Концентрация трития в озерах изменяется от 85 до 112 Т.Е. в зависимости от времени водообмена и условий питания. Расчеты по модели полного перемешивания с использованием данных о содержании трития в атмосферных осадках исследуемой территории, начиная с 1952 г., дают среднее время пребывания подземных вод в нижнемиоценовом водоносном горизонте, равное 500 годам и более. Для озер время водообмена, рассчитанное по тритию, лежит в пределах от 0 до 30 лет.

1.5. Изотопы углерода

Концентрация радиоуглерода в подземных водах нижнемиоценового водоносного горизонта изменяется от 35 до 90% стандарта современного углерода. Значения δ¹³С изменяются от −7,7 до −15,4% (РДВ). Концентрация углерода-14 в озерах лежит в пределах от 44 до 123%, а δ¹³С изменяется от +4,6 до −6,7% в зависимости от условий питания озер (поверхностное или подземное) и времени водообмена. Максимальный откорректированный возраст подземных вод, рассчитанный по углероду-14, составляет примерно 8000 лет. Коррекция возраста производилась по изотопному составу стабильного углерода с использованием известных приемов [14]. Между содержанием трития и радиоуглерода имеется прямо пропорциональная связь (рис. 4). Подобная же связь отмечена между величинами δD(δ¹⁸O) и концентрацией углерода-14 для участков нижнемиоценового водоносного горизонта, где он перекрыт слабопроницаемыми отложениями.

Рис. 4. Соотношение между содержанием трития и углерода-14 в подземных водах нижнемиоценового горизонта.
Рис. 5. Соотношение между содержанием дейтерия (кислорода-18) и углерода-14 в подземных водах нижнемиоценового горизонта на участках слабого артезианского режима.

Рис. 6. Соотношение между содержанием дейтерия (кислорода-18) и радиоуглерода в подземных водах нижнемиоценового горизонта на участках с грунтовым (безапорным) режимом.
Рис. 7. Соотношение между минерализацией \( M \) и изотопным составом водорода \( \delta D \) в подземных водах нижнемиоценового горизонта. Пролеживает зависимость минерализации с увеличением среднего времени пребывания \( \tau \) подземных вод, что связано с выщелачиванием солей из водоемещающих пород. Выделены линии пресных вод, перспективные \( I \) и неперспективные \( II \) для водоснабжения: 1 — озеро; 2 — подземные воды.

товолжской свиты \((N_1 tv)\) и лагунными осадочными породами \((IaQ_3)\) (рис.5). Это свидетельствует в пользу предположения (см. раздел 1.3) о разбавлении "реликтовых" вод современными атмосферными осадками.

На участках, где нижнемиоценовый водоносный горизонт переходит в безнапорный режим и перекрыт породами зоны аэрации, корреляционная связь между изотопным составом воды и концентрацией углерода-14 не прослеживается (рис.6). Для этих же участков значения \( \delta^{13}C \) практически не зависят от содержания растворенных карбонатных компонентов \( \delta^{13}C = -11.0 \pm 0.5\%_o \). Все это указывает на непрерывный процесс формирования изотопного состава карбонатной системы подземных вод за счет обмена с углекислым газом почвенной атмосферы. В связи с этим производить определение возраста подземных вод этих участков по углероду-14 некорректно, так как в данном случае не выполняется главная предпосылка радиоуглеродного датирования, согласно которой все воды считаются "современными" в пределах радиоуглеродной возрастной шкалы независимо от времени реального существования, если они имеют активный

обмен с почвенной атмосферой (условие открытой системы). Ранее подобное явление изотопного обмена между бикарбонат-ионом грунтовых (безнапорных) вод и почвенным углекислым газом для районов с аридным и полуаридным климатом наблюдал Гей [32]. На ряде участков, где по изотопам водорода и кислорода отмечается питание подземных вод из озерных котловин, прослеживается "утяжение" изотопного состава стабильного углерода карбонатной системы подземных вод (813С возрастает от −12,5 до −7,7‰).

1.6. Условия формирования естественных запасов, ресурсов и химического состава подземных вод

Анализ полученной изотопной информации позволяет сделать следующие выводы о формировании естественных запасов и химического состава подземных вод:

1. Время водообмена (среднее время пребывания) подземных вод нижнемиоценового водоносного горизонта изменяется от 500 до 20 тыс. лет. Прослеживаются обширные области распространения "реликтовых" вод, естественные ресурсы которых нитожны. Среднемноголетнее распределение по площади питание горизонта в условиях современного климата оценено величиной 0,3 мм/год, а подземный сток — величиной 3·10² м³ с 1 км² в год.
<table>
<thead>
<tr>
<th>Водопункт</th>
<th>Тритий Т.Е.</th>
<th>Среднее время пребывания в т. год</th>
<th>Температура на выходе °C</th>
<th>δ¹⁸O₀₂</th>
<th>δ¹⁸О₂</th>
<th>Расчетная базовая температура °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Верхнеменделеевский источник №12</td>
<td>57 ± 4</td>
<td>55 ± 5</td>
<td>93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Горячий плюс, скв. №26</td>
<td>18 ± 2</td>
<td>100 ± 10</td>
<td>175</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Горячий плюс, скв. №3</td>
<td>36 ± 3</td>
<td>80 ± 5</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Горячий плюс, скв. №5</td>
<td>32 ± 3</td>
<td>85 ± 5</td>
<td>74</td>
<td>+ 9,1</td>
<td></td>
<td>— 7,4</td>
</tr>
<tr>
<td>Нижнеменделеевский источника №6</td>
<td>26 ± 2</td>
<td>90 ± 5</td>
<td>91-98</td>
<td></td>
<td>+ 5,8</td>
<td>— 6,9</td>
</tr>
<tr>
<td>Верхневодокорский источник</td>
<td>19 ± 2</td>
<td>95 ± 10</td>
<td>50-60</td>
<td>+10,1</td>
<td></td>
<td>— 6,9</td>
</tr>
<tr>
<td>Менделеевский участок, скв. №32</td>
<td>11 ± 2</td>
<td>130 ± 15</td>
<td></td>
<td></td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>Источник Прибрежный (кислый)</td>
<td>0 ± 1</td>
<td>&gt;500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. На отдельных участках нижнemerоценоового водоносного горизонта установлено его питание из существовавших в раннем голоцене и современных озер.

3. Главным процессом формирования химического состава подземных вод является вышелачивание солей из водовмещающих пород в условиях загрунтованного водообмена. Испарительное концентрирование солей отмечено лишь на трех участках, где уровни грунтовых вод нижнemerоценоового горизонта залегают на глубине менее 2 м.

4. По изотопным данным в нижнemerоценоевом горизонте выявлены линии пресных вод, перспективные (с современным питанием) и неперспективные ("реликтовые") для целей питьевого и промышленного водоснабжения (рис. 7).

2. ИЗУЧЕНИЕ ТЕРМАЛЬНЫХ ВОД О. КУНАШИР

2.1. Гидрогеологические условия и задачи исследований

О. Кунашир, самый южный из Курильских островов, как и вся островная дуга, входит в состав Курило-Камчатской зоны современного вулканизма и характеризуется интенсивной гидротермальной деятельностью, проявляющейся выходами горячих минеральных источников и парогазовых струй. Современная геологическая структура острова сформировалась под влиянием неоген-четвертичного вулканизма. В гидрогеологическом отношении неоген-четвертичный вулканогенно-осадочная толща, слагающая остров, представляет собой ряд типичных трещечно-жильных водоносных систем, в которых циркуляция термальных вод происходит по вулканическим трещинам, выходам термальных источников и парогазовых струй. Опробованные водопонятки относятся к гидротермальной системе вулкана Менделеева, расположенного в центральной части острова (рис. 8). В пределах рассматриваемой гидротермальной системы разружаются различные генетические типы термальных вод, представляющие практически все группы гидротерм, встречающихся в областях современного вулканизма: кислые и ультракислые сульфатные воды на фумарольных полях (к их числу относится Верхнемендельевский источник №12), сульфатно-хлоридные и хлоридно-сульфатные кислые воды (Докторские и Нижнемендельевские группы источников), щелочные термы хлоридно-натриевого состава (источники Горячего Пляжа). Минерализация исследуемых вод изменяется от 2,2 до 7,8 г/л.

В районе Горячего Пляжа происходит разгрузка термальных вод системы вулкана Менделеева на Тихоокеанском побережье. Гидрогеологический разрез изучен бурением до глубины 760 м [11].

Задачи исследований сводились к решению следующих вопросов:

1. Определение времени пребывания термальных вод с использованием данных о распределении тридат в термальных водах и атмосферных осадках.
2. Оценка базовых температур гидротермальной системы с использованием кислородно-сульфатной изотопной геотермометрии.

Результаты исследований приведены в таблице I.
2.2. Дейтерий и кислород-18

Содержание дейтерия и кислорода-18 в водах исследованных источников изменяется в пределах от $-61$ до $-69\% (8D)$ и от $-5,2$ до $-7,4\% (8\text{O})$. Наибольший изотопный свинг зафиксирован в скважине №2, воды которой имеют самую высокую температуру и наиболее время пребывания. Наименьший свинг характерен для низкотемпературных вод, выводимых скважиной №5. Генетически все воды связаны с местными атмосферными осадками, хотя в некоторых гидротермах хлоридно-натриевого типа не исключается присутствие небольшой доли океанических вод (см. следующий раздел).

2.3. Тритий

Во всех пробах термальных вод (за исключением источника Прибрежного) тритий присутствует в заметных количествах, которые превосходят его содержание в атмосферных осадках прибрежных районов в "дотермоядерную эпоху" (см. табл.1). Расчет времени пребывания подземных вод выполнен по модели полного перемещения. Концентрация трития в атмосферных осадках с 1951 г. восстановлена по методике, изложенной в работе [12]. Аппроксимация гидротермальной системы моделью резервуара с полным перемешиванием, по всей вероятности, не вполне адекватна реальным гидродинамическим условиям, однако циркуляция вод по сложной системе тектонических трещин, равнозначно распределенных в пространстве, и питье гидротермальной системы на обширной территории восточного склона вулкана позволяет с большим основанием использовать модель полного перемешивания, чем, например, дисперсно-пористую. Рассчитанное в рамках этой модели среднее время пребывания термальных вод приведено в табл.1. В случае реализации дисперсно-пористого механизма движения подземных вод, что, вероятно, более достоверно, можно констатировать, что метеорические воды поступали в гидротермальную систему после 1953 г. Достоверность определения параметра $\delta D$ для прибрежных гидротерм хлоридно-натриевого состава ниже, чем для вод сульфатно-натриевого типа в связи с тем, что изучаемая гидротермальная система, по всей вероятности, имеет два "входа", одним из которых являются атмосферные осадки, другим — океанические воды, содержание трития в которых незначительно. Такое предположение подтверждается симпатией роста и минерализации в подземных воях Горячего Пляжа, вскрываемых скважинами №26, №3 и №5 (скв. №3: $M = 4,7$ г/л; $\delta D = -69\%$; скв. №26: $M = 5,7$ г/л; $\delta D = -64\%$; скв. №5: $M = 7,8$ г/л; $\delta D = -61\%$). По кислороду-18 подобная зависимость не прослеживается, что, вероятно, связано с изотопным обменом в системе порода — вода при повышенных температурах.

2.4. Сульфатно-кислородная изотопная гидрогеотермометрия

Изотопный геотермометр, основанный на температурной зависимости кислородно-изотопного обмена между водой и растворенными сульфат-ионами, использован
для определения базовых температур некоторых участков гидротермальной системы о. Куншир. Для расчета температуры применяна формула Мизутани и Рафтера [38], описывающая температурную зависимость изотопного кислородного обмена в системе бисульфат–вода, которая с поправкой на новое экспериментальное значение коэффициента фракционирования изотопов кислорода между водой и углекислым газом (при $e = 1.0412$ и $t = 25^\circ C$) имеет вид: $1000 \ln a = 2.88 (10^5/T^2) - 3.6$ (для $t = 100 \div 200^\circ C$). Как известно [35], скорость реакции изотопного обмена кислорода между сульфатом и водой при постоянной температуре сильно зависит от pH среды. Наиболее медленно обмен протекает в нейтральных и щелочных средах. Из исследованных водопунктов два (Нижнеменделеевский и Верхнеходорский источник) выделяют кислые термальные воды, а скважина №5 на Горячем Пляже вскрывает хлоридно-натриевые воды с pH близким к нейтральному. При pH = 7 изотопный кислородный обмен между растворенным сульфатом и водой протекает на 99,9% при $t = 200^\circ C$ за 18 лет [37]. Среднее время пребывания исследуемых вод в рамках любой из рассмотренных моделей (полного перемешивания или поршневой) превышает этот временной интервал, поэтому можно допустить, что в гидротермальной системе имеет место изотопное равновесие между растворенными сульфат-ионами и водой. В заключение отметим, что базовые температуры, определенные по изотопному геотермометру, во всех случаях превышают температуру воды на выходе.

3. ИСПОЛЬЗОВАНИЕ ИЗОТОПНЫХ МЕТОДОВ ПРИ ГИДРОМЕЛИОРАТИВНЫХ ИССЛЕДОВАНИЯХ

3.1. Гидрогеологические условия. Задачи исследований

Комплексные изотопные исследования были проведены на Аштском массиве орошения, расположенном в западной части Ферганской депрессии на правобережье р. Сыр-Дарья. Основная часть изучаемой территории приуручена к предгорной равнине, простирающейся между грядой, сложенной породами неогенового возраста (алаты Кзыл-Джар, Суле-Гуз), и Курашпинским хребтом. В гидрогеологическом отношении это Самгир-Камышкурганский заливной бассейн, приурученный к одноименной системе впадин. Основным объектом исследований явился водоносный комплекс четвертичных отложений конусов выноса, который включает взаимосвязанные воды горизонтов средней и верхнеплейстоценового возраста. На севере четвертичные отложения залегают на палеозойском кристаллическом фундаменте и в пределах впадины подстилаются слабопроницаемыми песчано-глинистыми породами верхнеплейстоценового и нижнеплейстоценового возраста. Схема территории исследований представлена на рис. 9, а геологический разрез, рассекающий заливную впадину в ее центральной части в меридиональном направлении, приведен на рис. 10. В пределах изучаемой территории выделено четыре гидродинамических зоны.
Рис. 9. Схема территории исследования Аштского орошаемого массива: 1 — водопритоки по свяям; 2 — границы гидродинамических зон; 3 — скважины дренажных рядов; 4 — увлажнные участки.

Зона формирования подземных вод (I) сложена валуно-гравийными и гальечниковыми отложениями мощностью от 10 до 250 м с песчаным и супесчаным заполнителем, образующим однослойную толщу. Для этой зоны характерны изолированные подземные потоки, формирующиеся за счет паводкового стока по свяям в весенний период. Расход питания со стороны Кураннинского хребта оценивается величиной 5,65 м³/с. Зона грандиционного подземного вод (II) занимает центральную часть впадины. Мощность водонамывающихся отложений, представленных гальечниками с песчаным и супесчаным заполнителем, равна 400-500 м. Глубина залегания грунтовых вод составляет от 150-250 м на севере до 5-10 м на южной границе зоны. Влияние водосбора, производительность которого достигла в 1981 г. 8,7 м³/с, сказывается на снижении уровня грунтовых вод лишь в восточной части бассейна, где сформировались депрессионные воронки глубиной до 25 м. Зона разгрузки подземных вод (III) расположена на юге территории исследования. Здесь гравийно-галечниковые отложения сменяются толщей слоенонепрерывно-следующих озерно-проливных глин, суглинков, песков и аллювиальных гальечников.

В этой зоне выделяются несколько напорных водоносных горизонтов, не выдержанных по площади и в разрезе. Разгрузка подземных вод происходит путем испарения и частично оттоком непосредственно в р. Сыр-Дарью. Направление потока — с северозапада на юго-восток.
Зона трешин и прямой разгрузки в р. Сыр-Дарью (IV) представляет однослоиную толщу песчано-галечниковых отложений конусов выноса мощностью 400-600 м. Единый грунтовый поток свободно разгружается в р. Сыр-Дарью. Водопроводимость толщи — 500-2000 м²/сут.

В ненарушенных условиях минерализация подземных вод в зонах I, II и IV вариировалась от 0,2 до 0,4 г/л с преобладанием ионов Na⁺ и HCO₃⁻. Минерализация грунтовых вод закономерно увеличивалась по мере движения потока впадины от 0,4 до 30 г/л в южной части гидродинамической зоны III. Состав вод изменялся от гидрокарбонатно-натриевого до хлоридно-натриевого.

Подземные воды четвертичного водоносного комплекса используются для орошения, а также для водоснабжения населенных пунктов. Отбор вод осуществляется скважинами, играющими роль вертикального дренажа, расположенными двумя рядами: верхним и нижним (см. рис. 9). Глубина скважин — 100-150 м. С 1979 г. для поливов используется также вода р. Сыр-Дарьи с расходом около 6 м³/с во время вегетационного периода. Минерализация подземных вод, отбираемых скважинами дренажных рядов, непрерывно возрастает во времени: в 1978 г. она составляла в среднем 0,78 г/л, а к
1981 году достигла 1,3 г/л. В отдельных скважинах отмечен более интенсивный рост концентрации солей до 3,5-5,0 г/л с преобладанием в химическом составе аннонов хлора и SO42-

Изотопные исследования на Аштском массиве орошения преследовали цель установления удельного вклада различных источников засоления подземных вод. На массиве было изучено распределение изотопов водорода (D, T), кислорода (18O), углерода (13C, 14C), урana (234U/238U), а также проведена водно-геохимическая съемка. Минерализация подземных вод определялась портативным резистивиметром.

Были рассмотрены следующие возможные причины изменения качества подземных вод при их интенсивной эксплуатации: 1 — вымывание накопленных в зоне аэрации "вековых" запасов солей поливными водами; 2 — подтягивание к скважинам нижнего дренажного ряда сформировавшихся в естественных условиях соленых вод из зоны перетекания; 3 — активизация испарительного концентрирования солей за счет орошительных мероприятий и поступление их в водоносный горизонт с возвратными водами; 4 — поступление на некоторых участках вод повышенной минерализации из нижерасположенных водоносных горизонтов.

Ниже кратко рассмотрены результаты изотопных исследований.

3.2. Дейтерий и кислород-18

Содержание дейтерия и кислорода-18 в исследованных водах изменяется от -99 до -45‰ (δD) и от -12,6 до -3,6‰ (δ18O). Наиболее "тяжелыми" по изотопному составу являются воды озер и грунтовые воды с высоким стоянием уровня. Прямая испарения описывается уравнением:

$$\delta D = 5,0 \delta^{18}O - 31.$$

Средние величины δD и δ18O в зоне формирования (I), характеризующие изотопный состав атмосферных осадков областей питания, составляют -82 ± 11‰ и -11,2 ± 1,6‰, соответственно. В скважинах дренажных рядов содержание дейтерия и кислорода-18 изменяется в пределах от -95 до -78‰ и от -12,8 до -9,7‰, соответственно, т.е. эти вариации близки к таковым в водах зоны формирования. Четкой связи величин δD и δ18O с минерализацией подземных вод не прослеживается. Более детальные изотопные исследования были проведены на четырех "узловых" участках, расположение которых приведено на рис. 9. В пределах каждого из участков опробованные скважины, расположенные на сравнительно небольшом расстоянии друг от друга, выводят воду, различающуюся по минерализации. Участки поровну распределены между верхними и нижними дренажными рядами (по 2) и характеризуют западную, центральную и восточную части массива. Анализ роли испарительного концентрирования солей в увеличении минерализации подземных вод проведен путем построения графической зависимости в координатах d—M. Здесь d — экцесс-параметр, определяемый как
d = δD - 8 δ18O [42]. Для атмосферных осадков "нормального" формирования и связанных с ними подземных вод d близко к 10. Неравновесное испарение приводит к
Рис. 11. Зависимость параметра d = δD - 8° от величины минерализации подземных вод.
1-4 — номера угловых участков.

Кинетическому фракционированию изотопов, что эквивалентно параллельному смещению прямой δD = 8 δ° от исходной линии. В этом случае величина параметра будет обратно пропорциональна длительности процесса неравновесного испарения и, как следствие этого, минерализации. Применение экспресс-параметра d (а не величины δD и δ°) удобно потому, что d не зависит от начальных значений δD и δ°, которые могут меняться в результате естественных изменений погодных и климатических условий, а также вследствие антропогенного воздействия на режим подземных вод. Изменение параметра d при формировании минерализации воды за счет процессов испарения прослеживается на Аштском массиве орошения. Так, в области питания (воды сев) среднее значение параметра d равно 9%, а для вод соленых озер оно уменьшается до -17%. Изменение параметра d в зависимости от минерализации подземных вод показано на рис. 11. Как видно, для всех угловых участков наблюдается уменьшение параметра d с ростом минерализации, приводя до определенного предела, выше которого, по всей вероятности, рост минерализации подземных вод определяется главным образом вышелачиванием солей из зоны аэрации. Интересно отметить, что на третьем участке в одной из скважин рост минерализации сопровождается увеличением параметра d, который становится равным 8,8, т.е. приближается к "нормальному" значению. Поэтому логично предположить, что воды этой скважины имеют глубинное формирование
(без участия испарительных процессов), а их минерализация целиком обусловлена вышелачиванием пород, подстилающих четвертичные отложения. Такое предположение подтверждается также высоким содержанием растворенного гелия (1,06·10^-2 мл/н), повышенной на общем фоне температурой воды, "нулевой" концентрацией трития, низким, по сравнению с другими исследованными водопунктами, содержанием углерода-14 (63% стандарта современного углерода) и облегченным составом (изотопным) стабильного углерода (δ13С = -10,2‰ против среднего значения, равного -7,8 ± 1‰). Отношение активностей четных изотопов урана (3,5 ± 0,1) в водах этой скважины также выше среднего значения по массиву (2,5 ± 0,1).

3.3. Тритий

Содержание трития в подземных водах массива изменяется от 0 до 100 Т.Е. Наибольшие концентрации характерны для зон I и IV, а также для западного участка зоны II. В напорных водах зоны III содержание трития крайне низкое (0-5 Т.Е.). Тритий практически отсутствует также в водах гидродинамической зоны II, минерализация которых не превышает 0,4 г/л. Как правило, рост минерализации сопровождается увеличением концентрации трития. На рис. 12 графически изображена зависимость концентраций трития от минерализации воды для исследованных участков. Видно, что на участках 1, 2 и 4 рост минерализации подземных вод сопровождается увеличением
в них трития. На участке 3 такой закономерности не прослеживается. На основании этого, а также с учетом данных, приведенных в разделе 3.2, можно заключить, что основным источником засоления подземных вод массива являются поливные воды, минерализация которых возрастает в результате испарения и вымывания накопленных солей из зоны аэрации. На третьем участке наблюдается привление полей водами относительно глубинного формирования, однако в общем водо-солевом балансе эта составляющая для массива не превышает 1%. Рост концентраций трития, как правило, сопровождается уменьшением количества растворенного в воде геля за исключением нескольких скважин в районе третьего участка. В восточной части массива в скважинах нижнего дренажного ряда в процессе эксплуатации отмечен рост минерализации, который однако не сопровождается увеличением содержания геля и трития. Это свидетельствует в пользу предположения о том, что в данном районе засоление обусловлено поступлением в скважины нижнего дренажного ряда "старых" соленных вод из периферийной части гидродинамической зоны III в результате сформировавшейся глубокой воронки депрессии.

3.4. Изотопы углерода

Содержание углерода-14 в водах четвертичных отложений изменяется от 63 до 111‰ стандарта современного углерода, а величина δ13С изменяется от −6,6 до −10,2‰. Откорректированный возраст подземных вод, рассчитанный по порционной модели, изменяется от 0 до 3700 лет. Наибольший возраст характерен для участка 3, где прослеживаются гелиевая и термическая аномалии. В ряде проб воды с "радиоуглеродным" возрастом около 2000 лет обнаружен тритий (до 10 Т.E.), что указывает на смещение разновозрастных вод в некоторых частях исследуемой гидрогеологической системы. Вероятно, что это связано с проведением мелиоративных мероприятий. Как указывалось ранее в разделе 3.2, на участке глелиевой и термической аномалии карбонатная система подземных вод обеднена изотопом углерода-13 по сравнению со средним значением (−10,2‰ против среднего значения −7,8 ± 1‰). Вероятно это связано с поступлением более глубоких вод, несущих "облегченный" по изотопу углерода-13 углерод, связанный с деструкцией органического вещества пород неогеновых или палеогеновых отложений, к которым в восточной части Ферганской долины приурочены нефтяные месторождения.

3.5. Результаты исследований

Проведенные изотопные исследования позволяют сделать вывод о том, что основной вклад в процесс засоления подземных вод при существующей методике эксплуатации массива вносят процессы испарения оросительных вод из поверхностных водотоков и зоны аэрации. Вторым по значимости источником засоления является вымыв накопленных в зоне аэрации "вечных запасов" солей и подтягивание к скважинам нижнего дренажного ряда естественных запасов соленых вод с периферийной части зоны пере-
сляния. Последний механизм засоления характерен для восточной части массива. Привлечение на массив солей "глубинными" составляющими водного баланса в настоящее время ничтожно, однако этот источник необходимо учитывать при планировании последующих мелиоративных мероприятий.

4. ИЗОТОПНЫЕ ИССЛЕДОВАНИЯ В БАССЕЙНЕ ОЗЕРА СЕВАН

4.1. Гидрогеологоческие и гидрологические условия исследований

Изотопные исследования в бассейне оз. Севан являются частью комплексной программы изучения водного баланса озера и влияния различных естественных и техногенных факторов на водообмен в Севанской котловине. Бассейн оз. Севан расположен в северо-восточной части Армянской ССР на высоте около 2000 м над уровнем моря. Горное обрамление котловины представлено на западе вулканическим Гегамским, на юге Варденисским, на северо-востоке и востоке Арегунийским и Севанским хребтами. Хребты имеют среднюю высоту 2500-2800 м над уровнем моря, а высота отдельных вершин превышает 3000 м. С целью эффективного использования статических (вековых) и динамических запасов вод озера для нужд народного хозяйства (производства электроэнергии и орошения земель) в 40-е годы была принята программа постепенного понижения уровня воды в озере на 50 м и сокращения его площади в 7 раз с целью значительного снижения потерь воды на испарение и увеличения стока через р. Раздан для снабжения энергоресурсами ирригационно-энергетического Севано-Разданского каскада. До начала спуска воды площадь озера равнялась 1415 км², запасы вод — 58,7 млрд. м³. В озеро впадает 28 небольших рек и временных водотоков, а вытекает лишь одна р. Раздан. Годовой водный баланс оз. Севан при естественном режиме имел следующие составляющие [23]:

<table>
<thead>
<tr>
<th>Приход</th>
<th>млн.м³</th>
<th>Расход</th>
<th>млн.м³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Поверхностный приток</td>
<td>770</td>
<td>Испарение</td>
<td>1210</td>
</tr>
<tr>
<td>Выпадение осадков</td>
<td>550</td>
<td>Сток через р. Раздан</td>
<td>50</td>
</tr>
<tr>
<td>на зеркало озера</td>
<td></td>
<td>Подземный сток</td>
<td>60</td>
</tr>
<tr>
<td>Всего</td>
<td>1320</td>
<td>Всего</td>
<td>1320</td>
</tr>
</tbody>
</table>

Потери воды на испарение составляли 92% поступающей в озеро воды, поэтому значительное снижение этой расходной статьи путем уменьшения поверхности озера в 40-е годы казалось экономически выгодным мероприятием. С начала 70-х годов в республике появились новые источники электроэнергии, были построены ТЭЦ и АЭС,
что позволило удовлетворить нужды промышленности в энергоресурсах без привлечения вод оз. Севан. К началу 1970 г. статические запасы озера уменьшились на 22 млрд. куб. м, а уровень озера понизился на 17,25 м. Было принято решение прекратить дальнейший спуск озерных вод и сохранить его уровень на отметке 1989 м, т.е. понизить всего на 18 м. В результате этих мероприятий площадь поверхности озера уменьшилась на 12%, испарение снизилось на 340 млн. м³, сток через р. Раздан увеличился на 110 млн. м³, а подземный отток по гидрометрическому балансу снизился примерно в 3 раза. Увеличение оттока воды через р. Раздан достаточно для удовлетворения нужд сельского хозяйства. Изотопные исследования были направлены на уточнение подземной составляющей расходной части водного баланса озера и проводились в районе современной фильтрации из озера (рис. 13) [2].

Район расположен в западной части Севанской котловины. Он представляет собой вулканическое плато со ступенчато-увалистым рельефом, сложенным молодыми сильно трещиноватыми андезито-базальтовыми лавами. Поверхностный сток в пределах участка практически отсутствует. Атмосферные осадки инфильтруются в водонесущие горизонты и в соответствии с уклоном палеополини Раздана направляются в сторону селения Атарбекян, где частично разружаются в виде групп родников с суммарным дебитом 2,37 м³/с. На участке бурением вскрыты два слабошарнированных водоп...
носных горизонта (рис. 14), сложенных пористыми трещиноватыми андезито-базальтами и их обломочными и отщеповатыми разностями, а также валуно-галечниковыми отложениями. Уровни напорных вод устанавливаются на глубинах от 16,6 до 58,4 м, причем с удалением скважин от озера наблюдается снижение абсолютных отметок залеганий уровня, что косвенно указывает на возможность поступления озерных вод в водоносные горизонты. Нижний водоупор представлен песчанистыми глинями сарматского возраста и тufопорфиритами сречного эоцен.

Целью исследований являлось уточнение доли вод оз. Севан в Азарбайджанских и Макрованских родниках, а также уточнение условий подземной инфильтрации вод из озера. Результаты изотопных исследований приведены в табл. II и графически представлены на рис. 15.

4.2. Дейтерий и кислород-18

Средний изотопный состав атмосферных осадков по режимным наблюдениям на метеостанции Севан может быть охарактеризован следующими величинами:
\[ \delta D = -81\%_\circ, \delta^{18}O = -10,6\%_\circ. \] Воды озера значительно обогащены тяжелыми изотопами водорода и кислорода за счет процессов неравновесного испарения в условиях поларного климата. Их средний изотопный состав характеризуется величиной \[ \delta D = -27\%_\circ, \delta^{18}O = -2,6\%_\circ. \] Линия неравновесного испарения может быть описана уравнением \[ \delta D = 5,28\delta^{18}O - 19. \]

Содержание дейтерия и кислорода-18 в подземных водах, вскрываемых скважинами и родниками, изменяется от \(-75\%_\circ\) до \(-33\%_\circ\) и от \(-3,6\%_\circ\) до \(-9,2\%_\circ\), соответственно. Отметим, что на других участках, где происходит разгрузка подземных вод в озеро, их изотопный состав несколько "облегчен" тяжелыми изотопами, по сравнению с исследуемыми подземными водами района современной фильтрации из озера. (Например, в районе нижнего течения р. Дзескента для подземных вод характерны величины \[ \delta D = -90 \pm 5\%_\circ \] и \[ \delta^{18}O = -12,0 \pm 0,4\%_\circ. \]) Это обстоятельство качественно указывает на присутствие озерных вод в водоносных горизонтах и родниках района исследований.

4.3. Тритий

Концентрация трития в озерных водах примерно одинакова по глубине (80 и 81 Т.Е.), в истоках р. Раздан она несколько выше (87 Т.Е.). Среднее время водообмена, рассчитанное по тритию по модели полного перемешивания с учетом распределения трития в атмосферных осадках, составляет около 50 лет, что превышает независимые гидрологические оценки (45 лет до спуска воды и примерно 30 лет для современных условий). Такое расхождение, по-видимому, может объяснить несколькими факторами: неточностью задания входной функции, малым рядом режимных наблюдений за распределением трития по глубине и площади озера, а также и тем обстоятельством, что в питании озера существенную роль играют реки. Концентрация трития в их водах ниже, чем в атмосферных осадках за счет разгрузки подземных вод.

В подземных водах изучаемого района концентрация трития изменяется от 6 до 41 Т.Е., т.е. она ниже, чем его концентрация в современных озерных водах.

4.4. Изотопы углерода

Наиболее высокие концентрации радиоуглерода (до 115% стандарта современного углерода) зафиксированы в водах озера. Расхождение в содержании радиоуглерода в поверхностных водах Малого Севана и в истоках р. Раздан пока не поддается однозначному объяснению, хотя в этих пробах наблюдается симпатичное увеличение содержания трития. За исключением родников, карбонатная система озерных и подземных вод обогащена углеродом-13 практически до равновесного значения с изотопным составом углерода в атмосферном углекислом газе, что косвенно указывает на генетическую связь подземных и поверхностных вод. Карбонатная система воды, вскрываемая скважиной №7, вероятно, формируется за счет растворения карбонатного цемента древних озерных отложений, хотя в Севанской котловине "тяжелый" изотопный состав углерода...
<table>
<thead>
<tr>
<th>Водопункт</th>
<th>M (г/л)</th>
<th>δD (%)</th>
<th>δ18O (%)</th>
<th>Тритий, Т.Е.</th>
<th>[HCO₃⁻] (мг/л)</th>
<th>[14C] %совр.станд.</th>
<th>δ13C РВБ %</th>
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<tbody>
<tr>
<td>Озеро Севан:</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>с поверхности</td>
<td>0,80</td>
<td>-20</td>
<td>-1,8</td>
<td>80 ± 4</td>
<td>454</td>
<td>105</td>
<td>-0,3</td>
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<tr>
<td>с глубины</td>
<td>0,78</td>
<td>-28</td>
<td>-2,1</td>
<td>81 ± 4</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>р. Раздан (истоки)</td>
<td>0,79</td>
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<td>-2,1</td>
<td>87 ± 3</td>
<td>446</td>
<td>115</td>
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<tr>
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<td>-75</td>
<td>-9,2</td>
<td>20 ± 3</td>
<td>220</td>
<td>105</td>
<td>-6,3</td>
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<tr>
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<td>-8,0</td>
<td>18 ± 4</td>
<td>182</td>
<td>107</td>
<td>-5,7</td>
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<tr>
<td>Скважина №3</td>
<td>1,50</td>
<td>-49</td>
<td>-4,6</td>
<td>6 ± 3</td>
<td>360</td>
<td>88</td>
<td>+0,4</td>
</tr>
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<td>Скважина №4</td>
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<td>-3,6</td>
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<td>102</td>
<td>-0,2</td>
</tr>
<tr>
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<td>-71</td>
<td>-7,6</td>
<td>31 ± 3</td>
<td>376</td>
<td>64</td>
<td>+2,4</td>
</tr>
<tr>
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<td>1,30</td>
<td>-49</td>
<td>-4,9</td>
<td>35 ± 3</td>
<td>190</td>
<td>81</td>
<td>+0,5</td>
</tr>
<tr>
<td>Скважина №7</td>
<td>1,40</td>
<td>-33</td>
<td>-4,0</td>
<td>19 ± 4</td>
<td>414</td>
<td>95</td>
<td>-0,1</td>
</tr>
</tbody>
</table>
Рис. 15. Соотношение между содержанием кислорода-18 и дейтерия в исследованных водах Северной озера (точки указаны скважины и родники):  
I — линия метеорных вод; II — подземные воды с питающим за счет атмосферных осадков; III — воды озера.

подземных вод не является редкостью и на участках, не затронутых фильтрацией из озера, что характерно для сейсмически активных районов. Концентрация углерода-14 в водах двух групп родников превышает 100%, однако изотопный состав углерода их карбонатной системы обеднен по углероду-13 по сравнению с другими водами. Отметим, что в подземных водах, вскрытых скважинами, расположенными в нижнем течении р. Дзекнагет, т. е. в районе, где современной фильтрацией из озера нет, содержание радиоуглерода составляют от 13 до 57%, а значение δ13С для этих вод изменяется от −11 до −13%.

4.5. Обсуждение экспериментальных данных

Анализируя изотопные (и гидрохимические) данные, приведенные в табл. II и графически представленные на рис. 15, не представляет труда сделать качественный вывод о том, что в исследованным районе имеет место подземная фильтрация вод из озера, причем доли озерных вод резко уменьшаются в более глубоком водонапорном горизонте.
Для точных расчетов данных недостаточно (работы в этом направлении будут продолжены), однако можно произвести приближенную оценку доли озерных вод, участвующих в питании родников. Если принять, что в смешении принимает участие две составляющие (это противоречит гидрогеологическим данным), одной из которых являются воды озера, а другой — подземные воды, связанные с инфильтрацией атмосферных осадков, то максимальная доля озерных вод в родниках по содержанию дейтерия и кислорода-18 может быть оценена величиной 25% (18 ± 7%). Большая погрешность обусловлена значительными вариациями изотопного состава атмосферных осадков, формирование которых может происходить на различных высотных отметках и в различные сезоны года. Оценка по стабильному углероду позволяет сделать вывод о том, что карбонатная система родниковских вод "разбавлена" примерно в два раза "озерным" углеродом (δ13С ос. = -1%, δ13С п.в. = -12%), что с учетом среднего содержания растворенных карбонатных компонентов в озере, приблизительно равного 450 мг/л, а в подземных водах "нормального" формирования – приблизительно 230 мг/л, дает значение доли озерных вод, также примерно равное 25%. Если доля озерных вод в родниках составляет около 25%, то для согласования данных по радиоуглероду и тритию нужно допустить, что содержание трития в подземных водах "нормального" формирования стремится к 0, а концентрация углерода-14 – к 100%. Однако подобных вод с минерализацией ниже 0,3 г/л в районе не встречено. Подземные же воды, генетически связанные с озером, при низких концентрациях трития (6 Т.E.) имеют сравнительно высокую минерализацию (1,5 г/л), поэтому их участие в формировании родникового стока гидрохимически обосновано быть не может. Разбавление озерных вод атмосферными осадками, что наблюдается, например, в скважине № 5, сопровождается увеличением содержания в них трития. Изложенные факты косвенно указывают на то обстоятельство, что фильтрация вод из озера происходит лишь в локальной зоне, а не на всей площади района исследования. Вероятно также, что эта зона совпадает с руслом Прираздана, расположение которого на исследуемой площади в настоящее время точно не известно. Лучшее согласование экспериментальных результатов по оценке доли озерной воды в родниках можно получить, если предположить, что озерная вода добегает до селения Артбеки примерно за 15-20 лет и количество трития (в отличие от радиоуглерода) в них уменьшается примерно в 3 раза за счет радиоактивного распада. Тогда второй составляющий смешения могут являться водами с концентрацией трития около 20 Т.Е. и концентрацией радиоуглерода, равной 100%, которая характерна для "современных" вод массивов силикатных пород.

Если принять долью озерных вод в родниках равной 25%, а суммарный их дебит 2,4 м³/c, то подземный отток вод из озера в современных условиях составляет около 20 млн.м³, что согласуется с независимыми гидрометрическими измерениями [23].

В заключение доклада авторы считают своим долгом выразить искреннюю благодарность своим коллегам Ю.Б. СЕЛЕЦКОМУ, Н.В. ПИТНИЦКОМУ, Н.Н. КРИШТАЛ, А.Е. ТКАЧЕНКО, Н.В. ИСАЕВУ, Н.С. ОТМАН, Ю.Л. ЛАГОЗИНУ, В.В. РОМАНОВУ, Ю.М. БЕЛИКОВУ, А.С. НИХАЯ, П.Е. КАРАПЕТЯНУ и другим товарищам, без активного участия которых эта работа не могла бы быть выполнена.
ЛИТЕРАТУРА

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HIDROLOGIA ISOTOPICA DE LAS AGUAS SUBTERRANEAS DEL PARQUE NACIONAL DOÑANA Y ZONA DE INFLUENCIA

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Abstract—Resumen

ISOTOPE HYDROLOGY OF GROUNDWATERS IN THE DOÑANA NATIONAL PARK
AND THE ASSOCIATED ZONE OF INFLUENCE.

The authors describe a study, using environmental isotopes, of the groundwaters of a complex hydrological system formed by a free recharge zone with a multi-layer structure, a confined zone with connate waters trapped by the deposition of a thick clay layer in a coastal pool environment, and a series of both recent and ancient highly permeable dune formations. Attempts have been made, using tritium of thermonuclear origin, to determine the approximate average recharge rate during the last 28 years in the free aquifer zone. Despite the difficulties encountered, the value of 78 mm/a obtained, which is 13.2% of the average precipitation, is very similar to that obtained using conventional methods (approximately 84 mm/a). As was expected, there was no tritium in the confined zone. Carbon-14 was used to determine the reduced velocity of the underground stream and to confirm the network of streams deduced from conductivity measurements. The age-correction methods proposed by Tarnows, Pearson, Mook and Fontes were compared. The differences in age between the last method and the first two are reasonable and can be explained by the isotopic interchange between the CaCO₃ of the rock formation and the gaseous CO₂ included in Fontes' model. On the other hand, the differences found with the Mook method are considerable, particularly for sample values below δ¹³C. The last model is more sensitive to changes in δ¹³C, and the interval of this parameter for which this model gives reasonable values of age is very small. In addition, the δ¹⁴C made it possible to determine the sedimentation velocity of clays in the swamp zone. The stable isotopes in the water confirmed the hypothesis that the underground waters in the confinement zone are a mixture of fresh water which has infiltrated into the recharge zone and of connate water trapped by the deposition of the clay layer.

HIDROLOGIA ISOTOPICA DE LAS AGUAS SUBTERRANEAS DEL PARQUE NACIONAL DOÑANA Y ZONA DE INFLUENCIA.

Se describe un estudio, con isotopos ambientales, de las aguas subterráneas de un complejo sistema hidrológico formado por una zona de libre recarga con textura de multi-
capa, una zona confinada con aguas congénitas atrapadas por deposición de una potente capa de arcilla en un ambiente de albufera y un conjunto de formaciones dunares, recientes y antiguas, de elevada permeabilidad. A partir del tritio de origen teronuclear se ha tratado de determinar, de forma aproximada, la recarga media habida durante los últimos 28 años en la zona de acuífero libre. A pesar de las dificultades encontradas, el valor obtenido de 78 mm/a, que representa un 13.2% de la precipitación media, es muy similar al obtenido por métodos convencionales, aproximadamente 84 mm/a. Como era de esperar, no hay tritio en la zona confinada. El carbono 14 ha permitido determinar la reducida velocidad del flujo subterráneo y confirmar el esquema de flujos deducido de las medidas de conductividad. Se ha realizado una comparación de los métodos de corrección de la edad propuestos por Tamers, Pearson, Mook y Fontes. Las diferencias de edad entre este último método con los dos primeros son razonables y se justifican por el intercambio isotópico entre el CO₂ en el medio rocoso y el CO₂ gaseoso incluido en el modelo de Fontes. En cambio, las diferencias con el método de Mook son muy elevadas, sobre todo para valores bajos de δ¹³C de la muestra. Este último modelo es muy sensible a los cambios de δ¹³C y el intervalo de este parámetro para el que proporciona valores razonables de la edad es muy pequeño. Por otra parte, el ¹⁴C ha permitido también determinar la velocidad de sedimentación de las arcillas en la zona actual de marismas. Los isótopos estables del agua han confirmado la hipótesis de que las aguas subterráneas existentes en la zona de confinamiento son mezcla de agua dulce infiltrada en la zona de recarga y del agua congénita atrapada por deposición de la capa de arcilla.

1. INTRODUCCION

El Parque Nacional Doñana es una reserva ecológica que goza de protección oficial y que se halla situada en el extremo sur de España. Su posición geográfica, así como dos de sus límites geográficos naturales, como son el río Guadalquivir y el océano Atlántico, le proporcionan su característica de punto de reposo para las aves migratorias que van de Europa a África. Existe un proyecto para el aprovechamiento agrícola de una amplia zona de marismas colindante con el borde norte del Parque Nacional, que incluye la utilización de aguas subterráneas. Durante los últimos años se han realizado numerosos estudios de todo tipo sobre la viabilidad de este proyecto y sobre su posible influencia en la alteración del ecosistema del Parque. Entre estos últimos pueden citarse los Proyectos SF/SPA 9 y 16, patrocinados por el Programa de las Naciones Unidas para el Desarrollo (PNUD) [1, 2].

Como complemento a los estudios realizados, se consideró que las técnicas basadas en la medida de los isótopos ambientales del agua, tritio, carbono 14, deuterio y oxígeno 18 podían aportar nuevos datos sobre el comportamiento de las aguas subterráneas y servir de confirmación de otros datos ya conocidos. El presente trabajo recoge los resultados obtenidos con estas técnicas.
2. GEOLOGIA

La zona objeto del estudio tiene una superficie de unos 3500 km² y forma parte del delta del Guadalquivir. Esta limitada al norte por el afloramiento de los materiales impermeables tortonienses (margas azules), al sureste por este río y al suroeste por el océano Atlántico (Fig. 1).

Durante el Secundario, el mar ocupa casi la totalidad del delta actual, depositando grandes espesores de margas triásicas y calizas jurásicas. En el Terciario se acentúa la subsistencia y con ello la penetración del mar tortoniense. A finales de este período se inicia la regresión general del mar, que prosigue hasta el Cuaternario. En primer lugar, se depositan facies detríticas de base, sobre las cuales se apoyan potentes sedimentos margosos y, sobre éstos, nuevas facies detríticas regresivas. Posteriormente, se depositan los sedimentos continentales del Plioceno.

Durante el Cuaternario antiguo y medio, el mar que ocupa la zona de la marisma (Q₁ y Q₂ en la Fig. 1, exceptuando la franja litoral) comienza a cerrarse por formación de una barra o cordón arenoso, que corresponde a esta franja litoral, formándose una amplia albufera que, posteriormente, se rellena con los sedimentos transportados por el río Guadalquivir. Este proceso de colmatación dura hasta épocas históricas. Se originan así las actuales marismas, formadas por depósitos arcillosos de origen fluvial que llegan a tener espesores mayores de 80 metros. El área cubierta por estas marismas es de unos 1400 km².

3. HIDROGEOLOGIA

Las formaciones permeables de la zona son: a) arenas y areniscas de facies marina depositadas durante el Mioceno Terminal; b) depósitos continentales
del Plioceno formados por arenas más o menos arcillosas, gravas y cantos rodados; c) niveles más profundos de los depósitos fluvio marinos del Cuaternario reciente y d) cordón litoral de dunas y playas antiguas y recientes. Todas estas formaciones constituyen un acuífero único, que es libre en las zonas de afloramiento de las mismas y confinado en la zona cubierta por la capa arcillosa de las marismas. La potencia máxima del acuífero se aproxima a los 200 m en sus límites sur y este. Debido al carácter sedimentario de la mayor parte de los materiales, se trata de un acuífero del tipo multicapa, exceptuando la franja litoral de dunas y playas antiguas. Muchas de estas dunas conservan aún su movilidad y, en la parte sur, están cabalgando sobre las arcillas de las marismas y el flujo subterráneo descarga parcialmente sobre éstas.

El substrato impermeable está formado por las margas azules tortonienses que afloran a pocos kilómetros al este del río Guadalquivir y en el límite norte del acuífero. La recarga del acuífero se realiza por infiltración directa de las precipitaciones en la zona de acuífero libre, de unos 2000 km² de superficie. La descarga se produce parte en el mar, una pequeña fracción en el río Guadalquivir y en otros ríos locales y otra pequeña fracción como evapotranspiración en las zonas donde el nivel freático es poco profundo.

La pluviometría media es del orden de 590 mm/a, de los cuales cerca del 90% tiene lugar durante el período comprendido entre octubre y abril. La evapotranspiración potencial es del orden de 1050 mm/a. La precipitación supera a esta evapotranspiración potencial sólo durante el período de noviembre a febrero, siendo el exceso del orden de 200 mm/a. Los recursos renovables en el área de acuífero libre se estiman en un valor del orden de 160 hm³/a.

Las zonas más bajas de las marismas permanecen inundadas durante una parte del año debido a agua aportada por los ríos o arroyos locales y a las precipitaciones directas. Este agua es aprovechada por las aves migratorias. Las marismas se secan en verano en su mayor parte, pero suelen quedar unos puntos, denominados localmente "Ojos de las Marismas", por los cuales continúa aflorando un reducido caudal de agua, a veces imperceptible. Estos "Ojos de las Marismas" han sido explicados por algunos hidrólogos como puntos de descarga del acuífero confinado profundo. Los resultados obtenidos en este trabajo desmienten esta hipótesis.

4. TRITIO

4.1. Concentración en las precipitaciones locales

Las concentraciones medias de tritio en las precipitaciones locales se han obtenido a partir de los datos de las dos estaciones más próximas (Gibraltar y Madrid) [3]. Los datos conocidos para estas dos estaciones son incompletos.
CUADRO I. OSCILACIONES ESTACIONALES RELATIVAS DE LA CONCENTRACION DE TRITIO EN LAS PRECIPITACIONES DEL HEMISFERIO NORTE

<table>
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<tr>
<th>Mes</th>
<th>CR (%)</th>
<th>DT (%)</th>
<th>Mes</th>
<th>CR (%)</th>
<th>DT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enero</td>
<td>5,90</td>
<td>1,95</td>
<td>Julio</td>
<td>12,35</td>
<td>4,01</td>
</tr>
<tr>
<td>Febrero</td>
<td>7,09</td>
<td>2,17</td>
<td>Agosto</td>
<td>9,82</td>
<td>2,76</td>
</tr>
<tr>
<td>Marzo</td>
<td>8,76</td>
<td>2,15</td>
<td>Septiembre</td>
<td>6,11</td>
<td>1,93</td>
</tr>
<tr>
<td>Abril</td>
<td>10,12</td>
<td>3,49</td>
<td>Octubre</td>
<td>4,89</td>
<td>2,10</td>
</tr>
<tr>
<td>Mayo</td>
<td>12,92</td>
<td>2,90</td>
<td>Noviembre</td>
<td>4,26</td>
<td>1,95</td>
</tr>
<tr>
<td>Junio</td>
<td>14,32</td>
<td>3,54</td>
<td>Diciembre</td>
<td>3,47</td>
<td>1,49</td>
</tr>
</tbody>
</table>

*a CR = concentración relativa.
*b DT = desviación típica o estándar (σ).

En el caso de Gibraltar, comprende el período 1962-75 y, en el caso de Madrid, el período 1970-82. La distribución pluviométrica de Gibraltar durante el período 1962-75 fue muy similar a la del área del estudio, lo cual indica que las precipitaciones proceden de los mismos frentes nubosos y que, por esta razón, pueden esperarse concentraciones de tritio muy parecidas. No obstante, para obtener las concentraciones medias anuales ponderadas (CMAP) se han tenido en cuenta las distribuciones pluviométricas a lo largo de cada año medidas en la zona del estudio, que difieren algo de las de Gibraltar. Es decir, se ha supuesto que las concentraciones mensuales ponderadas de las precipitaciones fueron idénticas a las de Gibraltar durante el período 1962-75, pero el cálculo de la CMAP se realizó con la distribución pluviométrica local. Lo mismo se ha hecho para calcular las concentraciones ponderadas referidas al período útil de recarga (de noviembre a febrero). Cuando los datos mensuales de Gibraltar estaban incompletos, los valores que faltaban se han obtenido por interpolación de los existentes, de acuerdo con el modelo de distribución mensual del Cuadro I.

Los valores correspondientes al período 1954-61 se han calculado a partir de los valores anteriores deducidos de los de Gibraltar y de un modelo general de distribución de la concentración de tritio en las precipitaciones, válido para el Hemisferio Norte, obtenido a partir de los datos de 54 estaciones comprendidas en la red OIEA-OMM [3] y que se muestra en el Cuadro II. Con cada uno de los valores obtenidos para el período 1962-75, se han calculado los valores correspondientes a todos los años del período 1954-61, haciendo uso de los factores de proporcionalidad del Cuadro II, calculándose a continuación la media aritmética de estos 14 valores. Por último, los valores para el período
<table>
<thead>
<tr>
<th>Año</th>
<th>CAMR (%)</th>
<th>DT (%)</th>
<th>Año</th>
<th>CAMR (%)</th>
<th>DT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1954</td>
<td>103.4</td>
<td>9.6</td>
<td>1970</td>
<td>67.6</td>
<td>7.7</td>
</tr>
<tr>
<td>1955</td>
<td>15.2</td>
<td>8.0</td>
<td>1972</td>
<td>61.9</td>
<td>9.0</td>
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<td>1956</td>
<td>49.5</td>
<td>9.3</td>
<td>1973</td>
<td>44.6</td>
<td>9.9</td>
</tr>
<tr>
<td>1957</td>
<td>40.9</td>
<td>9.3</td>
<td>1974</td>
<td>37.0</td>
<td>9.0</td>
</tr>
<tr>
<td>1958</td>
<td>150.1</td>
<td>25.5</td>
<td>1975</td>
<td>42.5</td>
<td>13.8</td>
</tr>
<tr>
<td>1959</td>
<td>134.0</td>
<td>16.1</td>
<td>1976</td>
<td>32.6</td>
<td>12.4</td>
</tr>
<tr>
<td>1960</td>
<td>52.5</td>
<td>7.4</td>
<td>1980</td>
<td>75.0</td>
<td>6.1</td>
</tr>
<tr>
<td>1961</td>
<td>46.7</td>
<td>14.5</td>
<td>1981</td>
<td>80.3</td>
<td>9.6</td>
</tr>
</tbody>
</table>

CAMR = concentración anual media relativa.
DT = desviación típica o estándar (δ).
(x) Sólo había 1 dato.
CUADRO III. CONCENTRACIONES DE TRITIO MEDIAS PONDERADAS PARA EL PERIODO NOVIEMBRE-FEBRERO EN EL AREA DEL ESTUDIO

<table>
<thead>
<tr>
<th>Año</th>
<th>UT*</th>
<th>Año</th>
<th>UT*</th>
<th>Año</th>
<th>UT*</th>
<th>Año</th>
<th>UT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1954</td>
<td>59</td>
<td>1961</td>
<td>27</td>
<td>1968</td>
<td>59</td>
<td>1975</td>
<td>18</td>
</tr>
<tr>
<td>1957</td>
<td>23</td>
<td>1964</td>
<td>279</td>
<td>1971</td>
<td>44</td>
<td>1978</td>
<td>16</td>
</tr>
<tr>
<td>1958</td>
<td>86</td>
<td>1965</td>
<td>161</td>
<td>1972</td>
<td>25</td>
<td>1979</td>
<td>8</td>
</tr>
<tr>
<td>1959</td>
<td>88</td>
<td>1966</td>
<td>81</td>
<td>1973</td>
<td>16</td>
<td>1980</td>
<td>10</td>
</tr>
</tbody>
</table>

* UT = unidad de tritio.

1976—80 se han obtenido a partir de los datos de Madrid. La relación entre los valores de Madrid y los calculados para el área del estudio para el período 1971—75 da un factor de proporcionalidad medio de 0,489 ± 0,032. El producto de este factor por los datos de Madrid del período 1976—80 da los valores correspondientes al área del estudio. La validez de estos valores se ha confirmado a través de la medida directa de algunas muestras de precipitaciones de los últimos 8 años, acumuladas en aljibes de diversas casas. El resultado completo de la evaluación se muestra en el Cuadro III.

4.2. Determinación de la recarga en la zona de acuífero libre

Como se ha indicado anteriormente, el acuífero es confinado en el área ocupada por las marismas, debido a la potente capa de arcilla. El resto de la zona, cuya extensión es de unos 2000 km², es de libre recarga y en ella se observa la presencia de tritio de una forma casi general, con concentraciones que varían entre 0 y 28,9 UT. La ausencia de tritio está relacionada siempre con la presencia esporádica de niveles superiores impermeables. Se analizaron 35 muestras de agua extraídas de pozos distribuidos por toda la zona. Casi todos estos pozos penetraban hasta el sustrato impermeable.

A pesar de las dificultades derivadas de la condición de acuífero multicapa, de la irregular distribución de los pozos y de la gran variabilidad de las concentraciones de tritio, se ha tratado de estimar la recarga por el conocido
método de integración de perfiles verticales de concentración [4]. De acuerdo con este método, la recarga media $R$ viene dada por la expresión:

$$ R = \frac{\int_{0}^{h_{0}} p(h) C(h) \, dh}{\int_{1954}^{t} \frac{R(t')}{R} C_{0}(t') e^{-\lambda(t-t')} \, dt'} $$  \hspace{1cm} (1) $$

Siendo $p(h)$ y $C(h)$ las funciones que definen la variación de la porosidad y de la concentración de tritio con la profundidad $h$, $C_{0}(t')$ la función de variación de esta concentración en las precipitaciones locales, dada por el Cuadro III, y $R(t')$ la variación de la recarga durante el período comprendido entre 1954 y el año actual representado por $t$. Los límites de integración $0$ y $h_{0}$ corresponden, respectivamente, al nivel piezométrico y al muro de la formación permeable. La relación $R(t')/R$ puede obtenerse suponiendo que la recarga es proporcional a la precipitación local $P$, mejor aún, a los cambios de nivel piezométrico entre las estaciones seca y húmeda. En nuestro caso, hemos considerado $(R(t')/R) = (P(t')/P)$, debido a la falta de datos completos del nivel piezométrico.

El numerador de la expresión (1) se ha obtenido para cada pozo de acuerdo con los criterios siguientes:

1) Se ha supuesto que la cantidad de tritio presente en la zona no saturada es despreciable frente a la existente en la zona saturada. Esto es cierto en la mayoría de los casos, debido a la escasa profundidad del nivel piezométrico y a la elevada permeabilidad de los materiales superficiales.

2) Cada pozo ha sido objeto de un análisis individual para determinar la longitud del tramo del mismo que suministra el agua extraída, teniendo en cuenta el espesor de los estratos permeables atravesados, la posición de los filtros existentes y la zona de influencia de cada tramo de filtros según las leyes hidráulicas convencionales. La expresión $\int_{0}^{h_{0}} C(h) \, dh$ se ha sustituido por el producto de esta longitud y la concentración media de tritio en el agua extraída del pozo.

3) Para la porosidad se ha tomado un valor constante igual a 0.25, que se considera adecuado para la litología y textura de los materiales.

El denominador de la expresión (1) se ha calculado discretizando las funciones correspondientes para períodos de 1 año, es decir, transformando la expresión integral en un sumatorio de 27 términos (período 1954—80). El valor obtenido asciende a 783,2 UT · a. Si se hubiera supuesto una recarga anual media constante, este valor habría sido 673,3 UT · a.
CUADRO IV. VALORES DE LA RECARGA ANUAL MEDIA PARA EL PERIODO 1954–80

<table>
<thead>
<tr>
<th>Pozo</th>
<th>UT (^a)</th>
<th>(\Delta h) (m) (^b)</th>
<th>(\bar{R}) (mm/año)</th>
<th>Pozo</th>
<th>UT (^a)</th>
<th>(\Delta h) (m) (^b)</th>
<th>(\bar{R}) (mm/año)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5,2</td>
<td>84</td>
<td>139</td>
<td>29</td>
<td>9,2</td>
<td>(\approx 58)</td>
<td>170</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>(\approx 84)</td>
<td>0</td>
<td>30</td>
<td>0,8</td>
<td>33</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>2,1</td>
<td>70</td>
<td>47</td>
<td>31</td>
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<td>90</td>
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<td>6</td>
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<td>181</td>
<td>32</td>
<td>1,1</td>
<td>125</td>
<td>4</td>
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<tr>
<td>7</td>
<td>14,7</td>
<td>31</td>
<td>145</td>
<td>33</td>
<td>2,3</td>
<td>(\approx 70)</td>
<td>51</td>
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<td>9,3</td>
<td>36</td>
<td>103</td>
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<td>5,5</td>
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<td>65</td>
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<td>11</td>
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<td>22</td>
</tr>
<tr>
<td>12</td>
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<td>46</td>
<td>37</td>
<td>1,0</td>
<td>136</td>
<td>43</td>
</tr>
<tr>
<td>15</td>
<td>4,2</td>
<td>(\approx 58)</td>
<td>78</td>
<td>38</td>
<td>1,0</td>
<td>136</td>
<td>43</td>
</tr>
<tr>
<td>18</td>
<td>17,4</td>
<td>(\approx 23)</td>
<td>128</td>
<td>39</td>
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<td>–</td>
<td>&gt;100</td>
</tr>
<tr>
<td>20</td>
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<td>28</td>
<td>174</td>
<td>40</td>
<td>0</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>0,3</td>
<td>39</td>
<td>4</td>
<td>41</td>
<td>0,3</td>
<td>(\approx 90)</td>
<td>9</td>
</tr>
<tr>
<td>24</td>
<td>0,8</td>
<td>(\approx 25)</td>
<td>6</td>
<td>42</td>
<td>1,3</td>
<td>81</td>
<td>34</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>66</td>
<td>0</td>
<td>43</td>
<td>3,4</td>
<td>78</td>
<td>85</td>
</tr>
<tr>
<td>26</td>
<td>0</td>
<td>52</td>
<td>0</td>
<td>44</td>
<td>2,3</td>
<td>47</td>
<td>35</td>
</tr>
<tr>
<td>27</td>
<td>4,5</td>
<td>46</td>
<td>66</td>
<td>45</td>
<td>1,5</td>
<td>(\approx 45)</td>
<td>22</td>
</tr>
<tr>
<td>28</td>
<td>1,9</td>
<td>53</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Valor medio = 58,7 mm/año

\(^a\) UT = unidad de tritio.
\(^b\) \(\Delta h\) = espesor saturado.

Los resultados obtenidos se presentan en el Cuadro IV. La segunda columna muestra la concentración de tritio en el agua extraída, y la tercera el espesor de acuífero que aporta este agua. Se observa que tanto las concentraciones de tritio como los valores de la recarga obtenidos a partir de las mismas varían dentro de límites muy amplios. Esto se explica, principalmente, por los cambios de permeabilidad de los estratos superiores responsables de la recarga en el entorno de cada pozo. Resulta claro que, como consecuencia de esta gran variabilidad, la recarga media obtenida depende fuertemente de cuál sea la distribución de los pozos elegidos para el muestreo y del número total de ellos.
En nuestro caso, se ha tratado de realizar un muestreo lo más uniforme posible, pero se ha tropezado con la dificultad de la falta de pozos en algunas zonas. El muestreo realizado ha sido casi exhaustivo, si se exceptúan algunas áreas de gran densidad de pozos, donde el muestreo ha sido parcial.

El valor de la recarga calculado como promedio de todos los datos del Cuadro IV asciende a 58,7 mm/a. Este valor representa un 10% de la pluviometría anual media y es inferior en, aproximadamente, un 30% al obtenido por técnicas convencionales, que es del orden de 84 mm/a [2]. Sin embargo, el valor de la recarga proporcionado por el tritio puede hacerse más representativo si el efecto negativo derivado de una distribución irregular de los pozos de muestreo se compensa atribuyendo a cada uno de estos una representatividad que corresponda a una fracción de área delimitada por una línea que pasa por la mitad de la distancia existente entre éste y los pozos contiguos. De esta forma, donde hay mayor densidad de pozos, la representatividad de cada uno de ellos corresponde a un área menor, y viceversa. La recarga media se calcula entonces por la expresión \( R = \frac{\Sigma R_i S_i}{\Sigma S_i} \), siendo \( S_i \) la superficie representada por cada pozo. En nuestro caso, el valor de \( R \) calculado por este procedimiento ha sido de 78 mm/a, que es similar al obtenido por métodos convencionales.

Por otra parte, en la zona de dunas y playas antiguas, el agua de los pozos y de las fuentes presenta una concentración de tritio mucho más homogénea, como corresponde a la mayor homogeneidad de estos materiales. En un total de 20 puntos de muestreo, la concentración media de tritio fue de 34,6 UT, con un valor mínimo de 14,8 UT y máximo de 73,7 UT y una desviación típica o igual a 15,2 UT. Pero, en este caso, no pudo obtenerse información sobre la recarga, debido a tratarse de pozos manuales de escasa penetración por debajo del nivel piezométrico. Una recarga igual a la obtenida para el resto de la zona (78 mm/a) sería coherente con un espesor medio de la lámina de agua de 1,77 m y, por tanto, con un espesor medio saturado del orden de 7,0 m, que parece razonable.

5. CARBONO 14 Y CARBONO 13

5.1. Datación del sistema confinado

Se ha utilizado el carbono 14 para estudiar la renovación del agua en la zona de confinamiento definida por la capa de arcilla de la marisma. En la zona de libre recarga el agua presenta una conductividad que varía entre 0,2 y 1 mS/cm. En la zona de confinamiento la conductividad crece bruscamente en el sentido oeste a este y hacia el sur, tal como se muestra en la Fig.2, alcanzando valores de más de 20 mS/cm. Esta distribución de la conductividad sugiere el sentido del flujo que se muestra en la figura. Las aguas de mayor salinidad se consideran
aguas congénitas, es decir, aguas atrapadas al comienzo de la deposición de los materiales arcillosos. Las conductividades intermedias representan mezclas de este agua congénita con agua dulce más reciente procedente de la zona de recarga.

Los resultados obtenidos con el carbono 14 son coherentes con este esquema de flujos. Dichos resultados se muestran en el Cuadro V, donde se incluyen los valores de \( \delta^{13}C \) y las edades del agua calculadas según los métodos de corrección propuestos por Tamers [4], Pearson, Jr. [5], Mook [6] y Fontes [7]. La Fig.3 muestra la relación existente entre la actividad específica de \( ^{14}C \), \( A^{14}C \), expresada en tanto por ciento de carbono moderno y la desviación isotópica de \( ^{13}C, \delta^{13}C \), en tanto por mil. Los números indicados entre paréntesis corresponden a la concentración total de carbono expresada en milimoles/litro. Se observa que las aguas modernas de la zona de libre recarga y de algunos puntos ubicados en el borde del sistema confinado se sitúan próximos a la recta de ecuación \( A^{14}C = -4 \delta^{13}C \), que corresponde a un modelo de simple disolución de CO\(_2\)Ca sin intercambio para \( \delta CO_2 = 0, \delta CO_2 = -25\% \) (ciclo de fotosíntesis de Calvin) y actividad específica inicial de \( ^{14}C \) en el CO\(_2\) del suelo igual al 100%.

Dentro de la zona de libre recarga, los valores más próximos al origen de coordenadas corresponden a muestras con mayor concentración de carbono.
CUADRO V. EDADES OBTENIDAS CON EL CARBONO 14

<table>
<thead>
<tr>
<th>Punto</th>
<th>Carbono 14 (% C Mod.)</th>
<th>( \delta^{14}C ) (%o)</th>
<th>Edad calculada (años)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tamers</td>
</tr>
<tr>
<td>PR-2</td>
<td>73,2 ± 1,8</td>
<td>-20,3</td>
<td>-1 700</td>
</tr>
<tr>
<td>PR-4</td>
<td>93,5 ± 2,9</td>
<td>-15,1</td>
<td>-4 500</td>
</tr>
<tr>
<td>PR-8</td>
<td>41,1 ± 1,2</td>
<td>-10,7</td>
<td>2 050</td>
</tr>
<tr>
<td>PR-9</td>
<td>62,3 ± 1,3</td>
<td>-16,5</td>
<td>-1 300</td>
</tr>
<tr>
<td>PR-11</td>
<td>59,3 ± 1,3</td>
<td>-12,7</td>
<td>-1 400</td>
</tr>
<tr>
<td>PR-12</td>
<td>67,7 ± 1,7</td>
<td>-14,2</td>
<td>-2 750</td>
</tr>
<tr>
<td>OM-1</td>
<td>33,7 ± 1,4</td>
<td>-15,1</td>
<td>3 300</td>
</tr>
<tr>
<td>OM-3</td>
<td>83,6 ± 3,3</td>
<td>-6,8</td>
<td>-4 150</td>
</tr>
<tr>
<td>OM-5</td>
<td>55,5 ± 1,8</td>
<td>-8,7</td>
<td>-850</td>
</tr>
<tr>
<td>PM-1</td>
<td>10,1 ± 1,8</td>
<td>-14,6</td>
<td>13 250</td>
</tr>
<tr>
<td>PM-3</td>
<td>19,3 ± 4,5</td>
<td>-13,2</td>
<td>7 900</td>
</tr>
<tr>
<td>PM-4</td>
<td>7,4 ± 1,3</td>
<td>-10,5</td>
<td>15 850</td>
</tr>
<tr>
<td>PM-5</td>
<td>25,0 ± 1,5</td>
<td>-18,6</td>
<td>6 000</td>
</tr>
<tr>
<td>PM-6</td>
<td>46,8 ± 1,7</td>
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<td>650</td>
</tr>
<tr>
<td>PM-7</td>
<td>23,1 ± 1,4</td>
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<td>6 500</td>
</tr>
<tr>
<td>PM-9</td>
<td>41,6 ± 2,2</td>
<td>-17,3</td>
<td>2 200</td>
</tr>
<tr>
<td>PM-11</td>
<td>27,6 ± 1,7</td>
<td>-13,0</td>
<td>4 950</td>
</tr>
<tr>
<td>PM-12</td>
<td>78,8 ± 1,7</td>
<td>-20,1</td>
<td>-2 800</td>
</tr>
<tr>
<td>PM-13</td>
<td>45,5 ± 3,0</td>
<td>-14,7</td>
<td>800</td>
</tr>
<tr>
<td>PM-15</td>
<td>14,1 ± 3,1</td>
<td>-9,6</td>
<td>10 550</td>
</tr>
<tr>
<td>PM-16</td>
<td>8,1 ± 1,2</td>
<td>-11,1</td>
<td>15 050</td>
</tr>
<tr>
<td>PM-18</td>
<td>33,5 ± 1,3</td>
<td>-9,0</td>
<td>3 350</td>
</tr>
<tr>
<td>PM-19</td>
<td>15,7 ± 2,8</td>
<td>-4,0</td>
<td>9 600</td>
</tr>
<tr>
<td>PM-20</td>
<td>19,0 ± 2,7</td>
<td>-12,4</td>
<td>8 050</td>
</tr>
<tr>
<td>PM-24</td>
<td>15,6 ± 2,4</td>
<td>-3,1</td>
<td>9 650</td>
</tr>
<tr>
<td>PM-27</td>
<td>18,7 ± 2,1</td>
<td>+2,4</td>
<td>8 400</td>
</tr>
<tr>
<td>PM-29</td>
<td>10,8 ± 2,2</td>
<td>-0,1</td>
<td>12 750</td>
</tr>
</tbody>
</table>

(1) Actividad específica inicial \( A_0 > 100\% \).
(2) Actividad específica inicial \( A_0 < 0 \).
PR = pozos de zona libre de recarga.
OM = ojos de marismas.
PM = pozos de zona de confinamiento.
FIG.3. Relación entre los parámetros $A^{14}C$ y $\delta^{13}C$.

total. Estos datos parecen indicar que los valores de $\delta^{13}C$ y $A^{14}C$ pueden justificarse, más o menos, con este modelo de simple disolución. Por el contrario, los puntos correspondientes a la zona confinada se sitúan a la izquierda de esta recta, es decir, en la zona de aguas antiguas. La concentración de carbono total en estas muestras es muy homogénea, indicando una gran estabilidad química del agua. Por último, las muestras situadas a la derecha de la recta contienen concentraciones muy elevadas de carbono total, debido, probablemente, al aporte local de CO$_2$ procedente del ataque con ácidos húmicos de carbonatos recientes de origen marino con $\delta^{13}C \approx 0$ (los restos de moluscos tienen este valor de $\delta^{13}C$) y $A^{14}C$ elevado. Estos puntos corresponden, principalmente, a Ojos de las Marismas y los ácidos húmicos están ligados a las arcillas de la capa confinante. El agua debe proceder de lentejones arenosos existentes en dicha capa.

Para obtener las edades del agua subterránea con los métodos de corrección indicados anteriormente, se han utilizado los siguientes parámetros:

a) Método de Tamers: concentraciones de CO$_2$ y CO$_3^-$, obtenidas experimentalmente en campo.
b) Método de Pearson: \( \delta\text{CO}_3\text{Ca} = 0, \delta\text{CO}_2 = -25\%_o \) y \( \text{A}^{14}\text{CO}_2 = 100\% \).

c) Método de Mook: los mismos valores anteriores y, además, según nomenclatura del autor \( A_{\text{a0}} = A_{\text{b0}}, \delta_{\text{a0}} = \delta_{\text{b0}}, A_1 = 0 \) y \( \epsilon_g = -9\%_o \) (unos 16°C de temperatura de intercambio). Los valores de las relaciones \( a/\Sigma \) y \( b/\Sigma \) se han calculado a partir del pH medido experimentalmente, teniendo en cuenta el efecto de la salinidad total sobre las constantes de disociación de las especies carbonatadas.

d) Método de Fontes: los mismos valores anteriores y además \( \epsilon = +8,889\%_o \). Este valor del coeficiente de fraccionamiento se ha calculado por la expresión \( \epsilon = \epsilon_{K} + \epsilon_{a} (1 + \epsilon_{K}/10^3) \), siendo \( \epsilon_{K} \) el coeficiente de fraccionamiento de la calcita con respecto al \( \text{CO}_2 \) disuelto (aproximadamente, igual a +10\%o) y \( \epsilon_{a} \) el coeficiente de fraccionamiento del \( \text{CO}_2 \) disuelto con respecto al \( \text{CO}_2 \) gaseoso (-1,10\%o para una temperatura de 15°C). La concentración de carbono muerto \( C_{M} \) se ha obtenido por la expresión \( mC_{M} = m\text{Ca}^{++} + m\text{Mg}^{++} + m(\text{Na}^{+} + \text{K}^{+} - \text{Cl}^{-})/2 - m\text{SO}_4^{2-} \). La concentración de carbono total es la determinada experimentalmente.

Las edades calculadas se comparan entre sí en la Fig.4, donde se representa la variación del incremento de edad con respecto a la obtenida con el modelo de Fontes frente al valor de \( \delta^{13}\text{C} \) del carbono total de las muestras analizadas. Estas curvas pueden obtenerse también, fácilmente, por vía analítica. Las tres curvas se cortan en un punto próximo a \( \Delta t = 0 \) y \( \delta^{13}\text{C} = -12,5\%_o \). Esto resulta lógico porque, para este valor de \( \delta^{13}\text{C} \), el término de las ecuaciones de Mook y Fontes que corrije la actividad específica inicial por efecto del intercambio isotópico se aproxima a cero y entonces intervienen sólo los términos de disolución de \( \text{CO}_3\text{Ca} \), los cuales conducen a resultados similares en los cuatro modelos. Para valores de \( \delta^{13}\text{C} \) más negativos que, aproximadamente, –12,5\%o, el término de intercambio en la ecuación de Fontes toma un valor positivo, con lo cual la actividad inicial \( A_{0} \) y las edades calculadas aumentan y los incrementos \( \Delta t \) con respecto a los modelos de Tamers y Pearson se hacen negativos. Lo contrario sucede con valores de \( \delta^{13}\text{C} \) menos negativos de, aproximadamente, –12,5\%o.

Los incrementos de edad con respecto al modelo de Mook reflejan una gran dependencia de las edades obtenidas con éste, del valor de \( \delta^{13}\text{C} \) de la muestra y, en su caso, de \( \delta\text{CO}_3\text{Ca} \). Si se determinan por medio de la ecuación de Mook los valores de \( \delta_{\Sigma} \) (anotación del autor) para el carbono total de la muestra, correspondientes a valores de \( A_{\Sigma} \) iguales a 100 y a 0 se obtienen, respectivamente, ecuaciones del tipo

\[
(\delta_{\Sigma})_{100} = K_1 \frac{a}{\Sigma} + K_2 \frac{b}{\Sigma} + K_3
\]

y

\[
(\delta_{\Sigma})_0 = K_1 \frac{a}{\Sigma} + K_2 \frac{b}{\Sigma}
\]
donde $K_1$, $K_2$ y $K_3$ son constantes de signo negativo, suponiendo que los parámetros que las definen no varíen de unos puntos a otros. La diferencia $(\delta_\Sigma)_{100} - (\delta_\Sigma)_0$ es igual a $K_3$ y equivale a la expresión:

$$K_3 = \frac{100 [\delta_{\Sigma_0} - \epsilon_\Sigma (1 + \delta_{\Sigma_0}/10^3) - 0,5 (\delta_{\Sigma_0} + \delta_1)]}{A_{\Sigma_0} (1 - 2 \epsilon_\Sigma/10^3) - 0,5 (A_{\Sigma_0} + A_1)}$$

(2)

El valor de $K_3$ está comprendido en la maya parte de los casos entre $-7$ y $-8$. Este es, por tanto, el intervalo de variación de $\delta_\Sigma$ correspondiente a un intervalo de $A_\Sigma$ comprendido entre 0 y 100%. Este dato explica la alta variabilidad de $A_\Sigma$ en función de $\delta_\Sigma$. En nuestro caso, el valor de $(A_\Sigma)_0$ se tenía para $\delta_\Sigma \cong -8,7\%$ y el de $(A_\Sigma)_{100}$ para $\delta_\Sigma \cong -16,6\%$. Esto sucedría considerando un valor de $\delta_1 = \delta CO_3Ca = 0$. Si se hubiera tomado el valor de
este parámetro obtenido experimentalmente igual a −4,7%, el intervalo habría sido mucho más corto y sólo unos pocos valores situados alrededor de −12,5% habrían dado edades coherentes con los otros modelos.

Las edades calculadas con el modelo de Fontes conducen a las líneas isocronas que se muestran en la Fig.5 y que son coherentes con las líneas de isoconductividad de la Fig.2. La isocrona para $t = 0$ coincide sensiblemente con los límites del acuífero cautivo, como era de esperar. La isocrona de 10 000 años presenta una protuberancia en su parte central que está basada en un solo dato. Por esta razón, no se sabe si corresponde realmente a una digitación del flujo subterráneo o se trata de una contaminación de la muestra con carbono procedente de agua más moderada. Desgraciadamente, la falta de pozos en la zona de aguas más salinizadas impidió completar el estudio para toda la extensión del acuífero cautivo.

5.2. Datación de la capa de arcilla

El carbono 14 se utilizó también para datar la capa de arcilla de la zona de marismas. Este isótopo se midió en restos de moluscos atrapados a distintas profundidades. Sólo pudo disponerse de cuatro muestras, que proporcionaron los resultados que se muestran en la Fig.6. La curva dibujada correspondería a una velocidad de sedimentación variable entre unos 5 y 2 mm/a para el período
comprendido entre unos 12 000 y 2000 años antes del momento presente, respectivamente. Los datos son coherentes con los obtenidos a través del hallazgo de diversos objetos arqueológicos. La albufera quedó totalmente desecada hace escasamente 2000 años.

6. **ISOTOPOS ESTABLES**

Se analizaron 61 muestras de agua. Los resultados completos no se incluyen por razones de espacio. Los pozos de la zona de libre recarga dieron los siguientes valores medios: $\delta D = -32,9\%$ y $\delta^{18}O = -5,13\%$. Estos valores son, aproximadamente, un 15\% más negativos que los deducidos a partir de los datos de Gibraltar para el período útil de recarga. En la zona de dunas los valores medios fueron $\delta D = -28,5\%$ y $\delta^{18}O = -4,66\%$. Las diferencias con los anteriores pueden explicarse por una posible evaporación parcial del agua en la zona no saturada durante el proceso de infiltración. Los llamados Ojos de las Marismas dieron resultados que reflejan, en casi todos los casos, una clara evaporación del agua, como puede verse en el diagrama de la Fig.7. Esto indica que los Ojos, al menos en su mayor parte, no se encuentran conectados con el acuífero profundo, sino que se trata de agua procedente de la recarga local de lentejones permeables incrustados en la capa de arcilla producida durante el período invernal en el que las marismas permanecen inundadas.

Por último, las aguas de la zona confinada presentan valores comprendidos entre los indicados para la zona de libre recarga y los valores extremos.
\( \delta D = -9.8\%_o \) y \( \delta^{18}O = -1.5\%_o \). En esta zona se observa la existencia de una clara correlación entre la concentración de los isótopos estables y la conductividad del agua, como se muestra en la Fig. 8. Este resultado sugiere que los valores intermedios de concentración de isótopos estables deben corresponder a mezclas de dos tipos diferentes de aguas, uno formado por el agua dulce infiltrada en la zona de libre recarga y otro por el agua congénita atrapada hace unos 30 000 años, cuando el sistema funcionaba en régimen de albufera. El agua de esta albufera sería, a su vez, una mezcla del agua aportada por los ríos que desembocaban en la misma y de agua del mar, que penetraba durante las mareas. La composición isotópica de esta agua podría corresponder, aproximadamente, a los valores extremos antes indicados de \( \delta D \) y \( \delta^{18}O \). La conductividad de este agua (20.5 mS/cm) sería coherente con una mezcla en las proporciones aproximadas de 45\% de agua del mar y 55\% de agua de los ríos. Suponiendo para el agua del mar un valor \( \delta D = 0 \) y para el agua de los ríos un valor medio del orden de \( \delta D = -30\%_o \), saldría para la mezcla de ambas un valor \( \delta D = -16.5\%_o \). La diferencia hasta \( \delta D = -9.8\%_o \) se podría justificar por evaporación del agua en la albufera.

7. CONCLUSIONES

Las concentraciones de tritio del agua extraída mediante bombeo de acuñeros libres pueden servir para la determinación aproximada de la recarga, si se cumplen, entre otras, las siguientes condiciones: a) número elevado de pozos de muestreo; b) distribución de éstos no demasiado irregular; c) actividad despreciable de tritio en la zona no saturada, con respecto a la zona saturada; d) corrección del espesor del acuñero de acuerdo con la longitud total de los filtros y de los diferentes niveles permeables, y e) ponderación de los resultados.
FIG. 8. Relación entre conductividad y δD para muestras de la zona confinada.

teniendo en cuenta la fracción de área representada por cada uno de los pozos con respecto a la superficie total del acuífero. El método proporciona mejores resultados cuanto más homogéneo sea el acuífero. El esquema de flujos deducido a través de las dataciones con 14C del agua subterránea en la zona de confinamiento es coherente, a grandes rasgos, con el que se deduce de las curvas de isoconductividad del agua. Los métodos de corrección de la edad propuestos por Tamers, Pearson, Mook y Fontes proporcionan resultados similares cuando el parámetro δ^13C de la muestra tiene un valor próximo a −12.5‰ para ciclo Calvin de fotosíntesis con δCO₂ = −25‰. Cuando δ^13C se desvía de este valor, las diferencias de edad se hacen cada vez mayores. Las diferencias entre los métodos de Pearson y Fontes son relativamente pequeñas y menores que con los otros métodos. El modelo de Mook conduce a resultados no utilizables cuando el valor de δ^13C es menos negativo de −9‰ o más negativo de −17‰, aproximadamente. Estos dos valores límites dependen de los valores que tengan los restantes parámetros que influyen en el modelo.

Se comprueba una vez más que los isótopos estables del agua constituyen un instrumento importante para identificar aguas de distintos orígenes. En el caso presente, han servido para diferenciar entre aguas de precipitación local, aguas congénitas atrapadas hace varias decenas de miles de años y aguas sometidas a fuerte evaporación. Dentro del acuífero confinado, han permitido definir la zona de transición entre el agua dulce de recarga reciente y el agua congénita de elevada salinidad.
REFERENCIAS


L'ALIMENTATION DES EAUX SOUTERRAINES
DE LA ZONE KOLOKANI-NARA AU MALI

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Abstract–Résumé

GROUNDWATER RECHARGE IN THE KOLOKANI-NARA REGION IN MALI.

The area studied is part of the Nara, Kolokani, Banamba and Koulikoro regions and lies between the Mauritanian frontier and Bamako. It is a Sahel zone devoid of active surface hydrography, the annual rainfall varying between 1000 mm in the south and 400 mm in the north. The altitude decreases from 600 m to 250 m from the Mandingues Plateaux to the Nara plain. The Nara area consists of a basin filled with Cambrian schists containing seams of dolomitic limestones and sandstones cemented by limestone. The thickness of the series is thought to be about 300–500 m. The area of the Mandingues Plateaux is composed of Lower Cambrian sandstone-schist formations with a thickness of several hundred metres, covered with a crust of weathering. The two formations have aquifers of the same type — they are discontinuous with predominantly fissure-type permeability. The permeable zones in the Cambrian schist aquifers are more discontinuous than those in the Cambrian sandstones and are less developed in depth. The recharge conditions, on the other hand, are quite good on account of the sand cover which allows rapid infiltration of rain water. The Lower Cambrian aquifer is highly heterogeneous but much less discontinuous. The transfer of groundwater takes place at the level of small local sub-basins over short distances. The hydrogeological and hydrogeochemical data point to the existence of recent recharge and mixing with older water. The groundwater renewal rate indicates, in many cases, limited water reserves. Infiltration is associated, in some cases, with storms of greater intensity and, in other cases, also with small sudden showers. Under natural conditions, the infiltrated water is generally used up by evapotranspiration. Under conditions of exploitation, a fraction of this recharge is recovered either almost directly or indirectly by replacement of the water taken from the fissured zones of the substratum.
L’ALIMENTATION DES EAUX SOUTERRAINES DE LA ZONE DE KOLOKANI-NARA AU MALI.

La région d’étude fait partie des cercles de Nara, Kolokani, Banamba et Koulikoro; elle est située entre la frontière mauritanienne et Bamako. Il s’agit d’une zone sahélienne dépourvue d’hydrogramme superficiel active, dont la pluviométrie annuelle varie entre 1000 mm au sud et 400 mm au nord. Le relief décroît de 600 m à 250 m, des Plateaux Mandingues à la plaine de Nara. La zone de Nara est formée par une cuvette comblée par des schistes cambriens à passées de calcaires dolomitiques et de grès à ciment calcaire. L’épaisseur de la série serait de 300–500 m environ. La zone des Plateaux Mandingues est constituée par des formations grès-schisteuses de l’Infracambrien avec plusieurs centaines de mètres d’épaisseur, recouvertes par une cuirasse d’altération. Les aquifères des deux formations sont du même type, discontinus et à perméabilité d’origine fissurale prédominante. Dans les aquifères des schistes cambriens, les zones perméables sont plus discontinues que celles des grès cambriens et se développent moins en profondeur. Par contre, les conditions de recharge sont assez bonnes du fait de la couverture sableuse qui permet un affouissement rapide des eaux de pluie. L’aquifère infracambrien est très hétérogène mais beaucoup moins discontinu. Le transfert de l’eau souterraine se fait à l’échelle de petits sous-bassins locaux et sur de petites distances. Les données hydrogéologiques et hydrogéochimiques ont permis de mettre en évidence l’existence d’une recharge actuelle et d’un mélange avec des eaux plus anciennes. Le taux de renouvellement des eaux souterraines implique dans de nombreux cas l’existence de réserves hydriques limitées. L’infiltration est liée dans certains cas aux orages de plus forte intensité, dans d’autres cas aux petites averses. En régime naturel, les eaux infiltrées sont en général reprises par évapotranspiration; en régime d’exploitation, une fraction de cette recharge est récupérée soit quasi directement, soit indirectement en remplaçant des eaux prélevées dans les zones fissurées du substratum.

1. INTRODUCTION

La région d’étude est située entre 13° et 15° 30’ de latitude Nord et 7° et 8° 30’ de longitude Est (Cercles de Nara, Kolokani, Banamba et Koulikoro) à 150 km environ au nord de Bamako. Elle est caractérisée par une saison sèche, comprise entre octobre et mars, et une saison humide pour le reste de l’année atteignant son maximum en été. La durée de la saison humide diminue du sud du pays vers le nord parallèlement à la hauteur des pluies. La pluviométrie étant d’environ 1000 mm par an au sud, elle décroit jusqu’à 400 mm par an vers les zones sahéliennes. La durée de l’hivernage dans ces mêmes zones est de quatre mois seulement.

La température de l’air mesurée à Bamako montre des variations saisonnières. D’octobre à mars, elle varie entre 25 et 32°C; des températures de 31 à 32°C sont enregistrées en mai et juin; en juillet, août et septembre, on mesure 26 à 27°C.

Du point de vue morphologique, on peut distinguer deux secteurs ayant des caractéristiques propres: la plaine de Nara et les plateaux Mandingues. Le premier secteur est caractérisé par une vaste zone de plaine située entre 250 et 300 m d’altitude en partie ensablée avec des alignements de dunes. Les plateaux
Mandingues, par contre, ont une morphologie plus variée. L’altitude décroît de 600 à 350 m en allant vers le nord. Un réseau hydrographique dense ravine ces plateaux mais les cours d’eau sont exclusivement temporaires. Même pendant la saison des pluies, la plupart du ruissellement de surface, naissant sur les plateaux Mandingues, s’infiltre avant d’atteindre les fleuves Niger et Baoulé.

2. CADRE GEOLOGIQUE ET HYDROGEOLOGIQUE

2.1. Secteur Nord

Il est limité approximativement par le parallèle 14° 30’ et la frontière mauritanienne (fig. 1). Il fait partie du domaine sahélien et correspond à une vaste zone de plaine structurellement située sur le prolongement du fossé de Nara, orienté ENE-WSW. La zone est caractérisée par une séquence de roches (série de schistes de Nioro et Nara) d’âge Cambrien, formée par des schistes (argiles et siltstones) à passées de calcaires, dolomitiques et de grès à ciment calcaire. L’épaisseur de cette série serait de 200 m sur la bordure de la cuvette de Nara, près de Nioro, et d’un millier de mètres au centre de la cuvette même. Les schistes sont souvent métamorphosés, durcis et fracturés par des intrusions doléritiques. Ces venues magmatiques se sont mises en place au Permien, lors des mouvements hercyniens.

Sur les schistes repose en discordance la formation du «Continental Intercalaire», d’âge Crétacé, à faciès gréseux et argilo-sableux, d’épaisseur variable (de quelques mètres à 400 m). Le passage entre les deux formations est mis en évidence par des niveaux conglomératiques peu épais et discontinus.

Du point de vue hydrogéologique, on peut faire les remarques suivantes.

A) Par suite de la mise en place de dolérites et lors des mouvements tectoniques associés, les schistes ont acquis localement une certaine perméabilité de fissures avec une petite capacité d’emmagasinement. Ils renferment donc une nappe discontinue caractérisée par de faibles productivité. Seules de rares conditions favorables montrent des débits supérieurs à 15 m³ h⁻¹ (Dilly-Campement Modibo et Keybani). Les venues d’eau rencontrées dans les forages productifs varient entre 20 et 70 m de profondeur et près de 70% des données révèlent des localisations de moins de 40 m [1]. La profondeur des niveaux statiques varie entre 4 et 24 m. Les cotes piézométriques sont comprises entre 235 et 265 m d’altitude, les cotes les plus basses étant localisées dans la zone de la Vallée du Serpent. Les essais de pompage montrent un débit moyen de 5,4 m³ h⁻¹, avec des débits spécifiques variant entre 0,3 et 6,4 m³. Les forages productifs représentent seulement 36% du nombre total des forages [1].

B) La formation du Continental Intercalaire représente un très bon aquifère par ses niveaux conglomératiques grossiers, perméables par porosité d’interstices. Pour
cette formation, on ne dispose que d’un seul forage (forage de Tendyé, 169 m de profondeur) qui donne un débit de 5 m$^3$.h$^{-1}$.

C) Les sables dunaires jouent un rôle important dans l’infiltration des eaux météoriques. Leur forte perméabilité permet aux pluies de s’infiltrer rapidement et de rejoindre les nappes des formations sous-jacentes. Les niveaux piézométriques de la nappe superficielle sont proches des niveaux mesurés dans la nappe du substratum. Les fluctuations ont été de 5 m en moyenne pendant la période 1980–82 [1].
FIG. 2. Localisation des points d'eaux échantillonnés pour des analyses chimiques et isotopiques.
### TABLEAU I. DONNEES CHIMIQUES DES EAUX SOUTERRAINES DANS LES REGIONS DE NARA ET DES PLATEAUX MANDINGUES (MALI)*

<table>
<thead>
<tr>
<th>N°</th>
<th>Localité</th>
<th>Date</th>
<th>Tempér. (°C)</th>
<th>Conductiv. (µS·cm⁻¹)</th>
<th>pH terrain</th>
<th>pH laborat.</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>CO₃²⁻</th>
<th>HCO₃⁻</th>
<th>CI⁻</th>
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Les échantillons 209 et 210 ont été prélevés lors de deux essais de pompage et analysés: a: après 1 h; b: après 12 h; c: après 18 h.
FIG. 3. Relation entre alcalinité et conductivité.
2.2. Secteur Sud

Cette zone, représentée par les plateaux Mandingues, est caractérisée par une formation grése-schisteuse subtabulaire du Pré cambrien terminal fréquemment altérée sur plusieurs mètres. Il s’agit de grès cimentés compacts passant à des quartzites et de grès schisteux et schistes sur plusieurs centaines de mètres d’épaisseur. Le recouvrement est en général épais d’une dizaine de mètres mais peut atteindre 25 à 30 m. Il est essentiellement de nature latéritique, avec des horizons cuirassés le plus souvent vacuolarisés en surface, reposant sur une lithomarge argilo-sableuse [2]. Des intrusions doléritiques sont fréquentes, soit sous forme de batholites de plusieurs centaines de kilomètres carrés soit sous forme de dykes et de filons-couches qui s’interstratifient dans les séries grése-schisteuses.

Les conditions hydrogéologiques sont caractérisées par la présence d’un système aquifère bicouche composé d’une nappe superficielle de type intergranulaire, associée aux formations de recouvrement et à la frange altérée du substratum, et d’une nappe principale localisée dans le substratum grése-schisteux essentiellement de type fissural.

Il a été montré [3] que les axes de drainage apparaissant sur les cartes piézométriques correspondent à des fractures majeures longues de plusieurs dizaines de kilomètres.

La nappe superficielle est alimentée soit par infiltration directe des précipitations soit indirectement à partir de « marigots » à fond sableux ou argileux par infiltration progressive des eaux de ruissellement. Les deux nappes sont hydrauliquement interconnectées comme en témoignent les fortes fluctuations piézométriques et les phénomènes de drainage enregistrés lors de nombreux essais de pompage sur des forages exploitant la nappe du substratum gréseux [1]. Les essais de pompage effectués sur 48 forages ont montré, pour 45% des forages, des débits variant entre 1 et 3 m³·h⁻¹, pour 48%, entre 3 et 10 m³·h⁻¹, le restant (7%) présentant un débit supérieur à 10 m³·h⁻¹ [1].

3. CARACTERISTIQUES CHIMIQUES DES EAUX

Des analyses chimiques effectuées par l’AIEA et par le Laboratoire de chimie de la Direction nationale de l’hydraulique et de l’énergie de Bamako ont porté sur 78 points d’eau (forages équipés de pompes manuelles ou puits traditionnels) (fig. 2 et tableau 1).

3.1. Secteur Nord

Les valeurs de conductivité mesurées sont en général inférieures à 600 μS·cm⁻¹ avec 60% des valeurs en salinité comprises entre 0,4 et 0,6 g·L⁻¹ et 16% entre
0,6 et 4,0 g·L⁻¹. Des eaux saumâtres ont été rencontrées dans deux forages situés aux environs de Nara pour lesquels la salinité atteint 17 g·L⁻¹ (n° 4 dans tableau I).

Les eaux sont toujours légèrementbasiques avec des pH variant entre 7,1 et 8,2; leur température est comprise entre 28 et 32°C. Les faciès chimiques sont fonction de la valeur du résidu sec: les eaux peu chargées ont un faciès bicarbonaté calcique, avec des teneurs en magnésium et en sodium parfois très élevées. Les eaux contiennent fréquemment, comme souvent en pays sahélien, des nitrates avec des concentrations pouvant dépasser, dans certains cas, 2500 ppm (n° 111 dans tableau I). Les teneurs en silice varient entre 14 et 77 ppm. Les eaux à résidu sec élevé ont un faciès sulfaté sodique avec des teneurs en chlorures importantes. L’origine de ces importantes salinités doit être recherchée dans le lessivage de dépôts salins secondaires présents dans la zone non saturée.

**Fig. 4.** Relation entre hauteurs moyennes des pluies mensuelles et valeurs moyennes pondérées en oxygène 18 des précipitations à la station de Bamako pour la période 1965–1978 [5].
L'alcalinité et la conductivité montrent une bonne corrélation dans la quasi-totalité des forages (fig. 3), indiquant que la charge saline est en général contrôlée par la mise en solution des silicates (phénomène d'hydrolyse). L'excès en bicarbonates pourrait être expliqué par la mise en solution de carbone organique dont les couches superficielles sont riches. Par contre, les fortes conductivités et l'alcalinité relativement faible seraient dues à la présence de minéraux solubles localisés surtout dans les environs de Nara (forages de Nara et Tanganagaba).

3.2. Secteur Sud

Les eaux du Précambrien terminal sont en général très peu chargées en sels: la conductivité est de l'ordre de 200 µS·cm⁻¹ avec des valeurs en résidu sec d'environ 0,1 à 0,2 g·L⁻¹ (fig. 3) [1, 4]. Les variations de salinité sont essentiellement dues à la lithologie: dans les quartzites et les grès, la conductivité varie entre 30 et 300 µS·cm⁻¹; dans les grès pélitiques, les schistes gréseux, les pélites et les dolérites, entre 100 et 800 µS·cm⁻¹. Le pH des eaux est souvent acide avec une valeur moyenne de 6,0; la température varie entre 28 et 30°C. Le faciès chimique des eaux est bicarbonaté calcique et magnésien, ou sodique, avec des teneurs en chlorures et en sulfates très faibles, particulièrement dans les formations gréseuses. Les teneurs en silice varient entre 13 et 50 ppm. Il faut noter que les eaux moins chargées sont alcalines, celles plus chargées sont calciques, en bon accord avec le plus grand degré d'altérabilité des plagioclases et des micas par rapport aux feldspaths alcalins.

4. DONNEES ISOTOPIQUES

4.1. Précipitations

Dans les précipitations de la station météorologique de Bamako [5], la composition isotopique est minimale au cœur de la saison pluvieuse (juillet-septembre), comme dans tous les pays touchés par la mousson (fig. 4) [5–7]. L'évaporation et l'humidité jouent ici un rôle important vis-à-vis des teneurs en oxygène 18. En 1972, par exemple, année de la grande sécheresse des régions sahéliennes, les précipitations ont montré un comportement, du point de vue isotopique, analogue aux précipitations relatives aux périodes du début et de la fin de l'hivernage (fig. 5) [8, 9]. Les valeurs isotopiques des précipitations s'inscrivent dans le diagramme δD − δ¹⁸O (fig. 6) sur la droite:

\[ \delta D = (5,79 \pm 0,27) \delta ^{18}O - (0,92 \pm 1,37) \]
L’enrichissement dû à l’évaporation est relativement fort, surtout pendant les mois à faible pluviosité (coefficient angulaire égal à 5,79). La teneur moyenne pondérée en oxygène 18 des précipitations à Bamako (sur la période 1962—1978) s’établit à −4,06% vs V-SMOW pour une lame d’eau de 14 770 mm. Si l’on considère seulement les précipitations mensuelles supérieures à 30 mm, ce qui pourrait donner naissance à une recharge significative, la teneur moyenne pondérée en $^{18}$O serait de −5,00% pour une lame d’eau de 13 900 mm [5].

**FIG.5.** Variations des teneurs moyennes mensuelles pondérées en oxygène 18 des pluies et variations des hauteurs moyennes mensuelles des pluies à la station de Bamako pour la période 1963—1975 (d’après [7]).
4.2. Les eaux souterraines

4.2.1. Les isotopes stables de l'eau

Les teneurs en isotopes stables des eaux souterraines varient entre $-48.9$ et $-17.7\%$ pour le deutérium et $-7.09$ et $-2.36\%$ pour l'oxygène 18 (tableau II). La figure 6 met en évidence trois familles différentes d'eaux : des eaux liées aux apports météoriques locaux (droite de Bamako), des eaux rechargées sous conditions climatiques différentes (pente 8 et ordonnée à l'origine +6), et des eaux plus ou moins évaporées (pente 5.2 et ordonnée à l'origine $-8$).

Cette division confirme la distinction géographique en secteurs sud et nord, faite pour la zone d'étude. En effet, les eaux de la région nord sont en général évaporées, tandis que les eaux collectées dans la zone sud s'inscrivent sur la droite météorique locale; dans cette région les eaux de la zone de Banamba et Boro (fig. 6) semblent être affectées par une recharge sous des conditions climatiques relativement différentes.

Le diagramme montrant l'excès en deutérium en fonction de la conductivité permet de tirer d'importantes observations pour la compréhension de la circulation hydrique souterraine.
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* c.a.: couverture d'altération; gr: grès; qz: quartzites; sch: schistes; F: forage; P: puits.
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* c.a.: couverture d’altération; gr: grès; qz: quartzites; sch: schistes; F: forage; P: puits. Les échantillons 209 et 210 ont été prélevés lors de deux essais de pompage et analysés: a: après 1 h; b: après 12 h; c: après 18 h.
4.2.1.1. Secteur Nord

Cette région est caractérisée par des situations hydrogéologiques très différentes quant à l’infiltration des eaux souterraines. Sous certaines conditions lithologiques, les eaux s’infilrent rapidement, comme c’est le cas des forages dans les sables dunaires (Goumbou, Dounguel). Ces sables favorisent l’infiltration rapide des eaux météoriques même lors d’orages de faible intensité. Les eaux montrent ainsi un enrichissement en isotopes lourds sans augmentation de la charge saline (fig. 7).

Dans d’autres situations hydrogéologiques, les eaux présentent une relation entre enrichissement en isotopes lourds et teneur en sels dissous. La charge saline importante qui caractérise certains forages (Nara, Tanganagaba, Safintara) serait due à la présence de sels secondaires très solubles. Dans les zones à niveaux piézométriques relativement profonds, il est peu vraisemblable que les eaux souterraines subissent des enrichissements en oxygène 18. Ces phénomènes d’enrichissement isotopique et salin ne prennent une grande importance qu’au moment de l’infiltration des eaux dans les zones des schistes et les dépôts quaternaires anciens très peu perméables.
FIG. 8. Relation entre profondeurs des niveaux statiques (N.S.) et valeurs en δ¹⁸O des eaux souterraines du secteur nord (zone de Nara).

Sur la base des variations en oxygène 18 en fonction de la profondeur des niveaux statiques (fig. 8), on peut concevoir que le fractionnement isotopique par évaporation a lieu jusqu’à une profondeur de 10 m. La recharge se ferait suivant un style «piston flow», c’est-à-dire que l’eau serait poussée chaque année vers le bas.

Alors qu’en régime naturel les eaux infiltrées sont en grande partie reprises par évapotranspiration, en régime d’exploitation une fraction de cette recharge est récupérée, soit quasi directement, soit indirectement en remplacement des eaux prélevées dans les zones fissurées du substratum. Le développement de l’exploitation conditionne l’accroissement de la fraction utilisable du potentiel de recharge en la soustrayant à l’évaporation par suite du rabattement des niveaux induits par les pompages et par l’amorce d’une circulation au sein de l’aquifère qui, en régime naturel, est très réduite [1].

4.2.1.2. Secteur Sud

La teneur en sel des eaux souterraines est pratiquement constante: aucune corrélation n’apparaît entre l’excès en deutérium et la conductivité, ce qui confirme que la charge saline est contrôlée par hydrolyse des silicates (fig. 9). Le faible enrichissement en isotopes lourds qui caractérise les eaux souterraines amène à envisager une alimentation liée aux orages de plus forte intensité, bien que des enregistrements limnigraphiques montrent une alimentation probable
mêmes par les petites averse. La recharge est d'autant plus remarquable que l'on s'approche des intrusions dolériques où les fractures sont plus développées.

4.2.2. *Les isotopes radioactifs*

4.2.2.1. *Le tritium*

Les valeurs en tritium varient entre 0 et 46 UT. Si l'on compare les teneurs en tritium dans les pluies à Bamako [4], corrigées pour la décroissance radioactive, on peut envisager que les eaux souterraines dont les teneurs en tritium varient entre 20 et 46 UT (soit 50% du total) correspondent à des eaux rechargées après 1968. Les eaux avec une activité en tritium inférieure à 20 UT correspondaient à un mélange entre eaux actuelles et les eaux plus anciennes, quoique relativement récentes comme en témoignent les activités élevées en carbone 14. Les teneurs souvent importantes en tritium sont aussi l'indice de réserves relativement faibles puisque les eaux pompées lors de deux essais de pompage sont en grande partie des eaux actuelles ou subactuelles, avec des valeurs constantes en tritium dans le temps.
4.2.2.2. Carbone 14 et carbone 13

Les teneurs en carbone 13 du carbone total dissous varient entre −10,9 et −18,7% référé au PDB. Les eaux souterraines de la zone de Nara sont affectées par un échange isotopique avec les carbonates solides; au contraire, les eaux souterraines des plateaux Mandingues représentent un système totalement ouvert à l'atmosphère avec des valeurs en $^{13}$C semblables à celles évoquées pour l'Afrique occidentale par certains auteurs [9]. Puisque les modèles de détermination des activités initiales s'appliquent exclusivement aux systèmes où se produit un mélange de carbone organique avec le carbone minéral, nous pouvons considérer que les activités en carbone 14 mesurées sont, en première approximation, égales aux activités réelles [10].

Les eaux ayant une activité en carbone 14 supérieure à 85% ont des teneurs en tritium relativement importantes (>5 UT). Les activités en carbone 14 inférieures à 50% indiqueraient une recharge ancienne dans des conditions météorologiques différentes. Les pôles extrêmes (fig. 10) de ce mélange seraient représentés par des eaux anciennes d’âge supérieur à 10 000 ans caractérisées par une composition en oxygène 18 de −7‰ vs V. SMOW, et les eaux actuelles par une activité en carbone 14 de 120% pour une valeur en $^{18}$O de −5,00‰. Ce fait confirmerait la présence d’une stratification en âge, verticale, entrevue déjà par de nombreux essais de pompage.
5. CONCLUSIONS

Les données hydrogéologiques, la chimie des eaux et la composition isotopique permettent d’atteindre les conclusions suivantes sur l’alimentation des eaux souterraines:

- Les teneurs en tritium et carbone 14 confirment en général l’existence d’une recharge actuelle et le mélangé avec des eaux plus anciennes quoique relativement récentes.
- Le recyclage des eaux d’infiltration récentes est favorisé par le développement de l’exploitation. Cependant, ce taux de renouvellement souvent élevé implique des réserves relativement limitées.
- La dispersion des teneurs en deutérium et oxygène 18 indique que l’infiltiration est liée aussi aux petites averse (Goumbou, Douguel). Dans d’autres situations hydrogéologiques, les teneurs appauvries en isotopes lourds semblent indiquer des conditions d’alimentation plus strictes. Seuls des orages de forte intensité pourraient contribuer à la recharge (Kolokani, Banamba). Une autre raison de cette dispersion des teneurs vient de l’infiltiration plus ou moins rapide à partir des marigots qui réalimentent les nappes grâce à la fracturation.
- En régime naturel, les eaux infiltrées sont reprises par évapotranspiration (ex.: zone de Nara). En régime d’exploitation, une fraction de la recharge est récupérée soit quasi directement (zone de Nara), soit indirectement en remplacement des eaux prélevées dans les zones fissurées du substratum (zone de Kolokani). Le développement de l’exploitation conditionne l’accroissement de la fraction utilisable du potentiel de recharge en la soustrayant à l’évaporation par suite du rabattement des niveaux induit par le pompage et par l’amorce d’une circulation au sein de l’aquifère qui, en régime naturel, est très réduite.

REMERCIEMENTS


REFERENCES


HYDROLOGIE ISOTOPIQUE ET HYDROCHIMIE DES AQUIFÈRES DISCONTINUEN DES LA BANDE SAHELienne ET DE L’AÎR (NIGER)

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Abstract—Résumé

ISOTOPE HYDROLOGY AND HYDROCHEMISTRY OF THE DISCONTINUOUS AQUIFERS IN THE SAHEL STRIP AND THE AIR REGION (NIGER).

The study deals with the aquifers in the outcrops of the crystalline and metamorphic basement in Western Niger: Liptako-Gourma, Maradi, Zinder and Air regions. The hydrochemical data (major ions) demonstrate the predominant role played by the weathering of silicates in the acquisition of the salt content of the water. Moreover, comparison of these data with the natural variations in stable-isotope contents (oxygen-18 and deuterium) yields similar hydrogeological conclusions for all the sectors: (1) the regional aquifers are compartmentalized into isolated circulations and are characterized by specific modes and periods of recharge; (2) these aquifers are recharged rapidly, without evaporation, during rains and exceptionally heavy flooding; (3) the stagnant parts of the drainage system are fully lost to evaporation and do not participate in the recharge; (4) homogenization is rapid and total in each system.

A study of the $^{13}$C and $\text{Ca}^{++}$ contents indicates that there is no dilution in $^{14}$C activity by dead carbon. Estimates of the recharge periods suggested by the tritium contents can be refined by analysing the radiocarbon measurements. Recent water, which has infiltrated over a few decades, is mixed with water hundreds and thousands of years old in some sectors.

HYDROLOGIE ISOTOPIQUE ET HYDROCHIMIE DES AQUIFÈRES DISCONTINUEN DES LA BANDE SAHELienne ET DE L’AÎR (NIGER).

L’étude porte sur les aquifères contenus dans les affleurements du socle cristallin et métamorphique de la partie occidentale du Niger: Liptako-Gourma, régions de Maradi, Zinder et massif de l’Air. Les données hydrochimiques (ions majeurs) mettent en évidence le rôle prépondérant de l’altération des silicates dans l’acquisition de la charge saline des eaux. Elles conduisent en outre, par comparaison avec les variations naturelles des teneurs en isotopes...
stables (oxygène 18, deutérium), à des conclusions hydrogéologiques similaires pour tous les secteurs: 1) les aquifères régionaux sont compartimentés en circulations isolées et caractérisés par des modes et des périodes d'alimentation spécifiques; 2) la recharge de ces aquifères à partir d'épisodes pluvieux et de crues exceptionnels est rapide, sans évaporation; 3) les parties stagnantes du réseau hydrographique sont reprises totalement par l'évaporation et ne participent pas à la recharge; 4) l'homogénéisation dans chaque système parait rapidement et totalement effectuée. L'absence de dilution de l'activité en carbone 14 par un carbone mort est déduite de l'examen des teneurs en $^{13}$C et $^{14}$C. La discussion des mesures de radiocarbone permet d'affiner les estimations des périodes de recharge suggérées par les teneurs en tritium. L'eau récente, infiltrée depuis quelques dizaines d'années, est mêlée d'eaux séculaires et millénaires dans certains secteurs.

1. INTRODUCTION

Les roches cristallines de socle (plutoniques ou métamorphiques) occupent de vastes secteurs de l'Afrique intertropicale. En zone humide, ces roches sont recouvertes d'un manteau d'altérates dont le remaniement par les eaux et le vent donne naissance à des colluvions et des alluvions. Les eaux souterraines s'installent alors dans la porosité de ces niveaux superficiels. En zone tropicale sèche, le couvert poreux s'amincit, parfois au point de disparaître. C'est le cas dans la "bande sahélienne" centrée sur $13^\circ + 2^\circ$ entre Sénégal et Tchad, zone très sensible à la sécheresse parce qu'encore fortement peuplée, à la limite des domaines traditionnels d'occupation des pasteurs et des cultivateurs de mil. Cette situation concerne notamment le Mali, la Haute-Volta, le Niger. Dans les régions franchement arides ou semi-arides, les roches cristallines se trouvent le plus souvent enfouies sous les dépôts sédimentaires. Elles n'affleurent que dans les régions montagneuses où les pentes des versants provoquent leur mise à nu par le fort ruissellement qui accompagne les épisodes pluvieux exceptionnels. C'est le cas du moelle de vieilles roches de socle du Sahara Central (Hoggar) et de ses dépôts méridionaux, les massifs de l'Adrar des Iforas au Mali, de l'Aïr au Niger et du Tibesti au Tchad. Cette étude concerne deux secteurs d'aquifères en roches de socle au Niger. Le territoire de ce pays offre la possibilité d'examiner l'hydrogéologie des zones de socle sur plus de 1500 km d'extension de la "bande sahélienne", avec les secteurs du Liptako-Gourma qui ont fait l'objet d'investigations détaillées complétées par des données sur les régions de Maradi et Zinder (fig. 1). Les informations livrées par ces zones sont à comparer à celles que l'on tire de l'étude d'une reconnaissance du massif de l'Aïr quelques 500 km plus au nord.
FIG. 1. Situation géographique des zones étudiées. Les isohyêtes sont indiquées en pointillé et les températures moyennes annuelles en trait continu.
2. CONDITIONS HYDROGÉOLOGIQUES

2.1 La bande sahélienne

Le socle cristallin qui remonte dans le Liptako, à Maradi et à Zinder est anté et précambrien. Le matériel est divers: granites, granodiorites, gneiss, schistes métamorphiques et quartzites. Les accidents méridiens liés aux structures panafriques sont souvent injectés de filons et d'INTRUSIONS BASIQUES (dolérites) [1].

La tectonique majeure s'est exprimée en plusieurs phases, toutes antérieures au Cambrien. Les roches métamorphiques, intensément fracturées, sont aussi profondément altérées et pénéplanées. De loin en loin, quelques hauteurs tabulaires de dépôts secondaires ou tertiaires dominent la plaine de quelques dizaines de mètres.

A différents degrés, tous les faciès sont altérés avec une composante argileuse qui confère au manteau d'altération d'épaisseur variable (0 à 20 m) une certaine imperméabilité. Une couche d'alluvions ou de colluvions (0 à 5 m) complète souvent les dépôts superficiels.

En tous points, les gradients hydrauliques sont faibles. Le réseau hydrographique intermittent (les "koris") est fait d'un chevelu divagant dont les bras se tronçonnent progressivement après la saison des pluies, au fur et à mesure que l'eau de surface s'évapore ou s'infiltre.

Les pluies sont le produit de la mousson qui vient du golfe de Guinée. En été, poussées par les haute pressions engendrées aux haute latitudes australes, les masses d'air maritime humide migrent vers le nord et viennent buter sur les haute pressions sahariennes. Elles s'élèvent alors et atteignent le profil de condensation. Les pluies tombent de juin jusqu'à septembre, époque de la migration inverse des masses d'air méridionales délestées de leur humidité. La hauteur d'eau annuelle moyenne précipitée, légèrement plus forte à l'ouest en Liptako-Gourma (650 mm), diminue à Maradi (550 mm) et plus encore à Zinder (500 mm). L'évapotranspiration est mal connue mais dépasse probablement 2000 mm dans ces régions à végétation naturelle de steppe et de savane à épines avec des cultures vivrières et du mil dans les secteurs aux sols les mieux développés.

Dans ces conditions, les points d'eau permanents sont rares ("mare" de Madaroumfa près de Maradi, point
d'aboutissement méridional du trafic caravanser) et le recours à l'eau souterraine est une obligation. Dans la tradition villageoise et pastorale, l'eau souterraine est recherchée selon la technique du "puisard" qui consiste à surcreuser les lits de koris dans les zones les plus humides, à la poursuite du sous-écoulement en voie d'infiltration.

Depuis quelques années, plusieurs campagnes de forage ont permis de livrer de nombreux points d'eau à l'alimentation des villages. Ce sont ces ouvrages qui ont donné lieu aux échantillonnages.

2.2 L'Aïr

Le socle cristallin de granites et granodiorites précambriens est affecté d'accidents distensifs qui ont ouvert la voie à un volcanisme complexe d'âge tertiaire et quaternaire [2]. Les oueds intermittents, dont l'orientation est guidée par celle du réseau de fractures, ont disséqué les reliefs et creusé de profondes vallées souvent frangées de terrasses et encombrées d'alluvions fluviales grossières et de sables éoliens. L'érosion mécanique due aux écarts de température journalière est très importante tandis que l'altération chimique est fort limitée. Les roches cristallines et volcaniques affleurent largement, le plus souvent à nu, dans les têtes de bassins et à l'écart des lits d'oueds. La pluviosité bénéficie de l'effet d'altitude et, peut-être, d'un effet de relief isolé. Elle s'inscrit en moyenne annuelle à près de 200 mm [3]. L'évapotranspiration potentielle dépasse largement les deux mètres mais l'évapotranspiration réelle est très difficile à apprécier par suite de la rareté d'une végétation à épineux qui se borne à coloniser les fonds de vallées parfois barrées par des coulées récentes et se développe en oasis à dattiers dans les bas-fonds où s'étendent les crues. Comme l'écoulement, la rétention de surface n'est qu'intermittente et l'eau souterraine représente la seule ressource. Elle parvient parfois à soudre naturellement au pied de certains reliefs et en fuite de barrages naturels (Timia), mais la plupart du temps elle doit être prélevée dans des ouvrages de type puisard ou puis traditionnels dans les axes de vallées. L'étude s'est limitée aux mêmes points d'accès à l'eau souterraine.

3. OBJECTIFS DE L'ETUDE ET METHODES

Les moyens classiques et éprouvés de l'hydrogéologie sont difficiles à mettre en œuvre dans le cas des systèmes aquifères liés aux roches cristallines:
- la continuité hydraulique, l'une des exigences de base pour l'emploi des lois de l'hydraulique souterraine, ne peut être établie avec certitude (on emploie volontiers dans la littérature l'expression d' "aquitères discontinus");

- les gradients sont extrêmement faibles dans le cas de la bande sahélienne et l'établissement de cartes piézométriques nécessiterait des nivellements de haute précision pour chaque ouvrage;

- perméabilité et porosité de la roche fracturée et de son couvert poreux varient fortement en fonction de la densité de la fracturation et de son style (compression ou distension), de la puissance du manteau d'altération et de dépôts meubles, de sa granulométrie et de sa teneur en minéraux argileux.

Les techniques de l'hydrochimie et de l'hydrologie isotopique sont censées permettre d'aborder les problèmes:

- d'origine des eaux souterraines et de leur mode de recharge (avec ou sans évaporation);
- d'homogénéisation des masses d'eau et de leurs relations mutuelles;
- de temps de séjour et de renouvellement des ressources en eaux souterraines.

En chaque site, les prélèvements sont destinés à la mesure des teneurs en oxygène 18, deutérium et tritium, à la détermination des teneurs en ions majeurs et en silice sur échantillons filtrés à travers une membrane colloïdale (diamètre moyen des pores: 0,25 micromètres) dont une partie aliquote est traitée par HCl suprapur pour la mesure des teneurs en cations alcalino-terreux susceptibles de se précipiter ou d'être adsorbés dans le laps de temps qui sépare la collecte de l'analyse et qui peut atteindre plusieurs semaines. Dans le même temps que les prélèvements, les mesures suivantes sont réalisées in situ: température, pH, conductivité et alcalinité.

Sur certains sites choisis en fonction des données et des mesures de terrain, un échantillon de carbone inorganique total dissous (CITD) est précipité selon la méthode de l'AIEA afin d'en mesurer les teneurs en $^{14}$C et $^{13}$C.

On trouvera sur les tableaux I, II, III et IV les résultats des analyses chimiques et isotopiques des échantillons prélèvis respectivement dans le Liptako, les régions de Maradi, de Zinder et du massif de l'Aïr.
4. LES DONNEES HYDROCHIMIQUES ET LEURS ENSEIGNEMENTS

4.1 Mesures in situ

La température est en général très proche des valeurs atmosphériques annuelles moyennes: 30 à 31°C dans la bande sahélienne, 28 à 29°C dans l’Air. Les eaux souterraines ne correspondent apparemment pas à des circulations qui s’enracinent à grande profondeur, ou, si cela était, la remontée serait suffisamment lente pour autoriser la mise en équilibre thermique avec la matrice de l’aquifère.

La conductivité varie très largement et avec elle la charge saline des eaux souterraines: 60 à près de 2500 microS·cm⁻¹. Les eaux les moins salées se trouvent dans le Liptako (secteur de Torodi) à Maradi et dans certains puits de l’Air. Le gisement de ces eaux faiblement chargées en sels correspond à des faciès de granites, granulites et autres roches acides.

En revanche, les eaux du secteur de Téra dans le Liptako-Gourma, ainsi que celles de Zinder, sont les plus riches en sels. Cette charge saline apparaît associée à des circulations dans des roches basiques (gabbros, intrusions doléritiques) ainsi que dans des faciès métamorphiques comme les schistes et les gneiss.

Les pH s’inscrivent dans des gammes relativement faibles: 6,2 à 7,4 dans le secteur de Torodi du Liptako, 5,2 à 6,6 à Maradi, 6,1 à 7,9 dans l’Air, 5,8 à 6,8 à Zinder, et 6,8 à 7,6 dans le secteur de Téra du Liptako. Ces valeurs peuvent témoigner que l’hydrolyse des silicates (qui a pour effet de libérer des ions alcalins et de porter le pH vers des valeurs hautes) n’est pas très active. Cela peut être le cas de l’Air où le climat n’est pas propice à l’hydrolyse par suite de la faible présence d’eau dans la zone aérée des sols où le phénomène est le plus actif en présence de CO₂.

Une autre possibilité est que la teneur en CO₂ des sols soit suffisante pour assurer la stabilisation du pH à des valeurs faibles.

L’alcalinité, elle aussi, montre de très larges variations: 1,10 à 6,50 mèg.·l⁻¹ dans le Liptako (Torodi), 1,65 à 9,20 à Téra, 0,27 à 4,37 à Maradi, 1,18 à 8,14 à Zinder, 0,72 à 4,92 dans l’Air. De plus, l’alcalinité est la composante anionique essentielle des eaux, ainsi que l’indique la corrélation généralement bonne avec la conductivité (fig. 2). Ceci indique que la salinité est surtout acquise dans les horizons aérés du sol où se
### TABLEAU I(a). LIPTAKO OCTOBRE 1980

<table>
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<th>Ech.</th>
<th>Localité</th>
<th>Prof. (m)</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>Conduct. (µS cm⁻¹)</th>
<th>Alcal. (mEq Lt⁻¹)</th>
<th>δ¹⁸H % SMOW</th>
<th>δ¹⁴H % SMOW</th>
<th>δ¹³C PDB</th>
<th>δ¹⁴C ppm</th>
<th>δ¹⁴C corr.</th>
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<td>Diagoga</td>
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-24.6 | -16.4 | 83.6 | 85.0

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# TABLEAU I(b). LIPTAKO MARS 1981

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produisent les réactions d’altération des silicates qui conduisent à la kaolinite, à la gibbsite et aux bicarbonates.

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 3\text{H}_2\text{O} + 2\text{CO}_2 \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4
\]

Anorthite

Kaolinite

\[
\text{NaAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{HCO}_3^- + \text{Na}^+ + 3\text{SiO}_4\text{H}_4 + \text{Al(OH)}_3
\]

Albite

Gibbsite

L’altération a évidemment une influence considérable sur la perméabilité et la porosité des fissures et des horizons meubles. Elle est variable selon les secteurs, en fonction de la composition minéralogique de la roche.

En conclusion de l’examen des résultats des analyses de terrain, on soulignera surtout :

- la variabilité du chimisme qui met en évidence l’hétérogénéité des masses d’eau ;
- la part prépondérante jouée par les réactions d’altération dans la formation du résidu sec.

4.2 Teneurs ioniques

Les compositions chimiques des eaux seront discutées plus longuement par ailleurs. Dans l’ensemble, les eaux de la bande sahélienne et de l’Air ont un faciès bicarbonate calcique, sodique et magnésien. Le dominance cationique change selon les secteurs ce qui reflète encore la variété des cortèges minéralogiques soumis à l’altération. Les fortes teneurs en magnésium confirment la participation des roches basiques à l’acquisition de la charge saline. La faiblesse relative des teneurs en ions d’origine météorique (chlorures) suggère que les phénomènes évaporatoires ne jouent pas un grand rôle dans la salinisation des eaux souterraines. Cela conduit à penser que l’infiltration est, d’une façon générale, un phénomène relativement rapide à l’échelle régionale.

Les sulfates sont toujours présents en teneurs souvent plus fortes que ne l’autoriserait une simple origine météorique. L’oxydation des pyrites des roches cristallines peut représenter une source pour cet ion. Cela pourra être examiné dans la suite de l’étude par détermination des teneurs en $^{34}S$ et $^{18}O$ des sulfates. Enfin, les concentrations, variables mais souvent importantes en

*Suite du texte p.383.*
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FIG. 2. Corrélation entre la conductivité (exprimée en μS·cm⁻¹) et l'alcalinité (en mèq·L⁻¹) mesurées sur le terrain. Les figures correspondent aux échantillons du Liptako (points), de Maradi (croix), de Zinder (étoiles), de l’AP (ronds).

nitrate, semblent pouvoir être attribuées à des venues de surface et à des retours de la surface à proximité des ouvrages utilisés pour l’abreuvement des troupeaux.

5. TENEURS EN ISOTOPES STABLES

5.1 Mode de recharge

Plusieurs faits sont à relever:

- Dans tous les cas, les variations au sein d’une même région, sont supérieures aux écarts moyens que l’on peut relever d’une région à l’autre. L’hétérogénéité des circulations, supposée à l’examen des analyses chimiques, se trouve confirmée par des différences de teneur en isotopes stables liée à la nature des eaux et donc à leur origine.

- Dans le diagramme δ²H-δ¹⁸O (fig. 3), réalisé à partir d’un nombre encore restreint d’analyses de deutérium, les points s’ordonnent à proximité de la droite d’équation δ²H = 8 δ¹⁸O + 10 qui traduit la relation générale dans les eaux météoriques applicable à cette région d’Afrique, comme en
FIG.3. Corrélation oxygène 18–deutérium (points; Liptako; ronds; Aïr). Les valeurs s'alignent à proximité de la droite des eaux météoriques d'équation $\delta^2H = 8.5\delta^{18}O + 10$. Seul le point NAIR 7 présente les signes d'une évaporation attribuable à une réinfiltration à partir d'une mare (Aguelman) qui draine les versants.

témoigne la chronique du réseau AIREA-OMM de la station de Bamako, au Mali [4]. Il s'ensuit que les eaux souterraines se sont infiltrées sans avoir subi de modification de leur teneur en isotopes lourds sous l'effet de l'évaporation. Ceci est en accord avec les hypothèses auxquelles conduit l'examen des compositions chimiques.

- Les variations de teneur en oxygène 18 et deutérium dans les aquifères sont strictement le reflet des différents événements pluvieux qui ont rechargé les nappes.

- Les compositions isotopiques élevées ($\delta^{18}O = -5$ à $-12$% vs SMOW) traduisent le fait que les épisodes distincts appartiennent au système de mousse. Cela est normal dans la bande sahélienne mais permet d'exclure la participation des pluies de fronts polaires dans la recharge des nappes superficielles de l'Aïr.
Les eaux des mares et des bras stagnants de koris sont, comme attendu, fortement enrichies en isotopes lourds. Ces eaux à cachet évaporé ne se retrouvent pas dans la nappe. L'infiltration est donc négligeable dans les fonds des lits colmatés par le dépôt des minéraux argileux. La recharge des nappes intervient soit par infiltration directe, soit pendant la montée de crue dans les parties poreuses des berges.

5.2 Discontinuité des aquifères, homogénéité des masses d'eau

Les teneurs en isotopes stables n'administrent la preuve définitive de l'indépendance des circulations que si l'on peut également prouver que les différences observées d'un point d'eau à l'autre ne résultent pas d'une stratification ou d'un déplacement par "effet piston" des épisodes successifs de recharge au sein d'un même ensemble hydraulique.

La figure 4 apporte cet argument. Elle consigne les résultats des mesures de teneurs en oxygène 18 réalisées sur différents forages du Liptako à plusieurs mois d'intervalle. Les points représentatifs s'ordonnent sur une droite de pente l ou à toute proximité de celle-ci. Il s'ensuit deux conséquences importantes:

- au sein d'une masse d'eau considérée, la dispersion est achevée et conduit à un mélange extrêmement homogène;
- chaque masse d'eau ainsi homogénéisée est rigoureusement indépendante des circulations avoisinantes du secteur.

La bonne dispersion ne peut guère être due qu'à l'intervention d'un filtre poreux dans la circulation. C'est la zone non saturée de la couverture d'alluvions et d'altérations qui joue ce rôle.

L'isolement des circuits implique des épontes imperméables. C'est au système de fractures non connectées hydrauliquement qu'il faut attribuer cette fonction. Dans la logique de cette interprétation, il faudrait concevoir que la circulation de fracture, réputée non dispersive, est limitée au seul drainage de la couche de colluvions et d'alluvions.

Il faut souligner également qu'une autre preuve de l'indépendance des circulations est fournie par le fait que les eaux souterraines de l'Aïr affichent un effet d'altitude
qui témoigne que les infiltrations des parties hautes ne parviennent pas en proportion notable dans les zones basses des bassins.

6. TRITIUM, ISOTOPE DU CARBONE ET APPROCHE DES TEMPS DE SEJOUR DES EAUX SOUTERRAINES

6.1 Les informations du tritium

Toutes les eaux de l'Air contiennent du tritium (entre 20 et 80 UT). Bien que les chroniques de référence manquent dans ce secteur, on peut néanmoins considérer, par comparaison avec la station de Bamako, que ces eaux souterraines sont récentes (postérieures à l'âge des essais thermonucléaires aériens) en leur plus large part. Ceci est bien conforme à leurs conditions de gisement en systèmes aquifères isolés, superficiels et de dimensions restreintes, ainsi que suggéré par l'analyse des teneurs en isotopes stables.

On sait, d'autre part, qu'en tous lieux de l'hémisphère nord la distribution du tritium dans les précipitations marque un maximum dans les années 63-64. Théoriquement et compte tenu de la décroissance, les activités des eaux de l'Air pourraient être rapportées à la période antérieure à
1963. En considérant la situation hydrogéologique (réserves essentiellement localisées dans les sous-écoulements), il paraît plus vraisemblable de rapporter l'infiltration de ces eaux à une période postérieure à 1972. Le temps de séjour des eaux souterraines de l'Air, serait donc de l'ordre de quelques années à une dizaine d'années. Cette estimation devra être confrontée aux conclusions livrées par l'examen des teneurs en radiocarbone.

Les teneurs en tritium des eaux de la bande sahélienne s'inscrivent dans une assez large gamme: quelques UT à quelques centaines d'UT. Dans l'ensemble, les teneurs en tritium apparaissent distribuées en deux groupes, soit supérieures à 30 UT soit inférieures à 15 UT. Les unes seraient nettement marquées par l'apport récent, les autres peuvent contenir une forte proportion d'eaux antérieures à la période des essais thermonucléaires. Une venue d'eau, isolée grâce à un dispositif à prélèvement introduit dans un forage de la région de Zinder, a même affiché une activité $^3$H inférieure à 1 UT ce qui signifie que les eaux délivrées par la fissure ont plus de 30 ans.

La difficulté de pousser davantage l'interprétation des teneurs en tritium dans le cas où l'on ne dispose pas de prélèvements sérilés sur un temps suffisamment long, nous a conduit à tenter d'utiliser le carbone 14 concurremment au tritium afin de préciser les estimations sur les temps de séjour.

6.2 L'apport des isotopes du carbone

Les teneurs en carbone 14 du CITD sont variables et généralement élevées: 84 à 132% dans le Liptako-Gourma, 108 à 131% dans l'Air.

Les valeurs supérieures à 100% démontrent que:

- la plupart des eaux ont un CITD récent;

- le radiocarbone ne semble pas subir de dilution importante lors de son passage de la zone aérée des sols à l'aquifère (voir à ce sujet FONTES et GARNIER [5], MOK [6], FONTES [7], entre autres).

D'autres arguments en faveur de l'absence d'une dilution du carbone 14 par un carbone ancien peuvent être invoquées:

- Dans le diagramme $^{14}$C-$^{13}$C (fig. 5), il n'apparaît pas de corrélation, ni même de tendance. Aucun vieillissement du CITD ne semble
Fig. 5. Diagramme $^{14}C - \delta^{13}C$. L’absence de toute tendance conduit à admettre que l’activité du CITD n’est pas diluée par du carbone mort (étoiles: Liptako; ronds: Aïr).

pouvoir être attribué à un mélange avec une autre source de carbone que celle du CO₂ des sols. Ceci est important, en particulier dans le cas de l’Aïr, où la présence de volcanisme quaternaire pouvait laisser envisager des remontées de CO₂ profond et "mort". Dans le Liptako, cela est conforme aux données géologiques de ne pas trouver dans les eaux la trace de mise en solution de carbonates sédimentaires qui sont absents de la région. Toutefois, dans le Liptako comme dans l’Aïr, il faut remarquer que la mise en solution de carbonates néogénétiques qui pourraient se trouver dans les sols, ou tapiser les fissures, reste théoriquement possible. Ce phénomène ne pourrait être détecté dans un diagramme $^{14}C - ^{13}C$. En effet, le fractionnement isotopique est faible entre carbonate et bicarbonate. La mise en solution d’une calcite préalablement précipitée dans les sols n’affecterait guère la teneur en $^{13}C$ du CITD. A ce sujet, on peut simplement noter qu’il n’existe pas, non plus, de relation entre la teneur en $^{14}C$ du CITD et la teneur en calcium des eaux (fig. 6). Aucun vieillissement apparent ne semble pouvoir être mis en relation avec une dissolution de calcite. Cela est
également en accord avec l'état général de sous-saturation des eaux vis-à-vis de ce minéral. Les eaux souterraines sont, certes, susceptibles de dissoudre de la calcite pédogénétique mais on ne voit guère par quels mécanismes elles auraient préalablement pu la laisser déposer.

On admettra donc que les teneurs en $^{14}$C du CITD ne doivent pas être corrigées de la dilution et sont directement représentatives (au fractionnement près) de celles du CO$_2$ de l'atmosphère ainsi que cela a été proposé pour interpréter les teneurs mesurées dans les aquifères cristallins du Nord-Ghana [8]. La totalité du CITD provient donc du CO$_2$ des sols.

Les variations de teneurs en $^{13}$C ($-9 \text{ à } -18\%$o vs PDB) témoignent:

- de différences dans la nature du couvert végétal (influence plus ou moins grande des plantations de mil qui est une plante à cycle photosynthétique de Hatch et Slack et produit un CO$_2$ à teneur en $^{13}$C voisine de $-12\%$o);

- de l'intervention de mécanismes différents lors de la minéralisation du carbone: du point de vue isotopique, cela peut correspondre à tous les intermédiaires, depuis les équilibres de système.
ouvert entièrement régis par le CO₂ gazeux lorsque celui-ci est en forte concentration, jusqu'à la simple transformation en système fermé, molécule par molécule, du CO₂ en bicarbonate lors de l'altération des feldspaths dans un milieu où la production de CO₂ est faible [7].

La minéralisation du carbone de la zone des racines est un phénomène relativement rapide qui prend de zéro à deux ans [9]. Dans ces conditions, le carbone 14 représente un outil potentiel plus puissant que le tritium pour l'étude des eaux récentes en nappes libres. En effet le carbone 14 rend compte de la période d'infiltration sans présenter les inconvénients du tritium à savoir :

- la décroissance radioactive qui émousse les signaux ;
- la très forte baisse des teneurs dans les précipitations au cours des dix dernières années.

Avec le carbone 14 et pour autant que l'on puisse s'affranchir du problème de la dilution, on dispose d'un marqueur de temps de séjour qui présente une fonction entrée (la teneur en 14C du CO₂ de l'atmosphère) nette, immuable, homologue à l'origine de celle du tritium depuis 1952 et encore très au-dessus de l'activité de l'époque prénucléaire au début des années 80 [10].

Afin de comparer les teneurs en 14C du CITD à celles du CO₂ correspondant de l'atmosphère, il convient de procéder à la correction des fractionnements isotopiques qui interviennent dans les processus. Cela peut se faire d'une façon globale, approchée mais suffisante :

$$\frac{A_{atm}}{A_{CITD}} = 1 + \varepsilon^{14C}_{atm-CITD}$$

avec $\varepsilon^{14C} = 2,3 \varepsilon^{13C}$ [11]

et $\varepsilon^{13C}_{atm-CITD} = \delta^{13C}_{atm} - \delta^{13C}_{CITD}$ avec $\delta^{13C}_{atm} = -7\%$ [12]

Par exemple dans le cas de l'échantillon le plus appauvri en 13C :

LIP 32 : $\delta^{13C} = -18,12$ ; $A^{14C} = 107%$

$$A_{atm} = A_{CITD} \times 1,026 = 109,8\%.$$ Les valeurs ainsi calculées de l'activité du CO₂ équivalent au CITD sont
reportées sur les tableaux Ia et Ic. Elles sont supérieures de 0.7 à 2.7% aux activités mesurées.

7. INTERPRETATION

La discussion des teneurs en isotopes stables a mis en évidence la caractéristique spécifique de chaque masse d'eau et de son origine. Il est tentant d'envisager le principe d'épisodes de recharge isolés dans le temps à l'occasion, par exemple, de crues des koris. On est alors conduit à un essai de datation de ces éventuelles périodes, bien délimitées, d'infiltration.

Pour les échantillons à teneurs en $^{14}$C correspondant à des activités du CO$_2$ atmosphérique comprises entre 130 et 115%, il serait possible d'attribuer à la recharge une date d'infiltration entre 1975 et 1980 ou entre 1959 et 1961. Cela représente 14 échantillons du Liptako-Gourma et 3 de l'Aïr. Les teneurs en tritium seraient, de leur côté, compatibles avec ces attributions.

Pour les échantillons à teneur en $^{14}$C correspondant à des activités du CO$_2$ atmosphérique comprises entre 115 et 100%, soit 7 échantillons du Liptako et 1 de l'Aïr, l'interprétation en terme de recharge isolée dans le temps exige de faire intervenir des eaux infiltrées entre 1952 et 1958. Cela est peu réaliste dans la mesure où l'on ne voit pas pourquoi aucune eau infiltrée entre 1961 et 1975 (avec des teneurs en $^{14}$C du CO$_2$ atmosphérique de 130 à 180% [10]) n'aurait été détectée.

On est donc conduit à invoquer pour ces eaux (ACITD = 100 à 115%):

a) soit une dilution chimique et/ou isotopique du radiocarbone;

b) soit des mélanges faisant intervenir des eaux antérieures à la période des essais nucléaires aériens.

On a vu que rien dans les teneurs en alcalino-terreux et en carbone 13 ne permet de faire appel à une dilution et, devant l'absence d'arguments en sa faveur, nous continuons à éliminer l'hypothèse (a). Il reste donc à admettre que des contributions multiples et successives portant sur plusieurs dizaines d'années peuvent s'homogénéiser au sein de chaque système. Cela oblige à revoir également le cas des CITD à
forte teneur en $^{14}\text{C}$. Ces eaux seraient elles aussi des mélanges où les eaux récentes dominerent mais où la contribution antérieure à 1952 ne saurait être exclue.

Il faut enfin envisager le cas des eaux dont l'activité du CITD est nettement inférieure à 100%, soit 2 échantillons provenant de deux forages de la même localité du Liptako (Sirifikouara):

LIP 76 : $^{14}\text{C} (\text{CO}_2\text{ atm.}) = 95,7% ; \, ^3\text{H} = 14,6\text{ UT}$

LIP 77 : $^{14}\text{C} (\text{CO}_2\text{ atm.}) = 85,4% ; \, ^3\text{H} = 8,1\text{ UT}$

Ici, la participation post-nucléaire est attestée par la présence de tritium. En revanche, le radiocarbone du CITD aurait sensiblement décru par effet d'âge. On peut alors considérer que l'eau à activité la plus forte (Pengona):

LIP 23 : $^{14}\text{C} (\text{CO}_2\text{ atm.}) = 134,2% ; \, ^3\text{H} = 77\text{ UT}$

est représentative de la recharge post-nucléaire sans participation d'eaux vieilles de plus de 30 ans. Le bilan de tritium indique que LIP 76 et LIP 77 contiennent respectivement environ 10% et 20% d'eau récente. Comme l'alkalinité est différente en LIP 23, LIP 76 et LIP 77 (2,8, 3,3 et 3,6 mèg.l$^{-1}$ respectivement), on doit en tenir compte dans les bilans de mélange pour l'évaluation de l'alkalinité m de la composante ancienne

LIP 76 : $0,1 \times 2,8 + 0,9 \times m = 3,3 \quad m = 3,35 \text{ mèg.l}^{-1}$

LIP 77 : $0,2 \times 2,8 + 0,8 \times m = 3,6 \quad m = 3,80 \text{ mèg.l}^{-1}$

Restent alors à calculer les activités de la composante prénucléaire A dans le CO$_2$ atmosphérique équivalent du CITD:

LIP 76: $0,1 \times 2,8 \times 134 + 0,9 \times 3,35 \times A = 3,3 \times 85,4 \quad A=81\%$

LIP 77: $0,2 \times 2,8 \times 134 + 0,8 \times 3,80 \times A = 3,6 \times 98,6 \quad A=92\%$

En ce secteur, les eaux anténucléaires afficheraient donc un vieillissement moyen de 1700 ans en LIP 76 et 700 ans en LIP 77. Des eaux séculaires et même millénaires participeraient ici aux réserves exploitées par les forages. On doit noter que ces ouvrages sont les plus profonds qui aient été échantillonnés (environ 80 m). Il est difficile de dire si la réserve est ici beaucoup plus importante qu'ailleurs ou bien si l'exhaure s'adresse à une réserve ancienne peu renouvelée.
Dans l'ensemble, la tendance positive entre les teneurs en $^3\text{H}$ et en $^{14}\text{C}$ (fig. 7) rend compte du mélange qui se produit dans chaque circulation entre des eaux ante et post nucléaires.

8. CONCLUSIONS

L'ensemble des données de la chimie et des isotopes du milieu conduit à des conclusions hydrogéologiques convergentes aussi bien dans l'Aïr que dans la bande sahélienne:

- L'indépendance des modes de recharge et des circulations dans des aquifères isolés alimentés par infiltration rapide en dehors de toute évaporation. Cela était prévisible pour l'Aïr où les eaux ne stagnent ni sur les versants, ni dans les bas fonds à remplissage grossier. C'est une information importante dans le cas de la bande sahélienne où la planéité topographique engendre, on l'a vu, la stagnation des eaux dans les cours tronçonnés des "koris".

- L'extrême homogénéisation des eaux au sein de chaque système, ce qui implique l'intervention d'un écran dispersif entre les aires de recharge et les fractures circulantes; cette partie dispersive des
systèmes pourrait être la zone non saturée du couvert d’altérations et de sédiments meubles.
- L’acquisition d’une charge saline variable par altération de silicates (feldspaths) conduisant à une alcalinité dominante sur le reste de la charge ionique.
- La participation d’eaux infiltrées sur plusieurs dizaines d’années dans la plupart des systèmes avec présence d’eaux séculaires ou même millénaires dans certains secteurs.

Du point de vue géochimique, il convient d’insister sur les possibilités d’application de la technique du radiocarbone à l’étude des eaux souterraines récentes, lorsque l’on se trouve en présence de terrains dépouvus de carbonates comme cela peut être le cas pour les roches cristallines.

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ISOTOPE HYDROLOGY AND HYDROCHEMISTRY
OF THE GREAT ARTESIAN BASIN, AUSTRALIA

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Abstract

ISOTOPE HYDROLOGY AND HYDROCHEMISTRY OF THE GREAT ARTESIAN BASIN, AUSTRALIA.

Environmental isotope and hydrochemical results used to study the dynamic behaviour of the regional groundwater system in the Great Artesian Basin, Australia, have confirmed recharge areas and regional groundwater flow patterns. Samples downgradient from the recharge areas show percentages of modern carbon between 26 and 1%, and carbon-14 derived isochrones can be determined. Further basinwards only ‘dead’ $^{14}$C was found, though ‘hydraulic ages’ have been confirmed by $^{36}$Cl data. The carbon isotope ratio $^{13}$C/$^{12}$C increases basinwards from about −18‰ to about +1‰, and the variation of $^{13}$C is closely related to the changes in HCO$_3$. Most Lower Cretaceous–Jurassic confined aquifers in the eastern and central parts of the Basin contain Na-HCO$_3$-Cl type water, and these ions contribute more than 90% of the total ionic strength of solutes in the main Basin area. Near the recharge areas, Ca, Mg and SO$_4$ concentrations are proportionally higher, but they decrease basinwards. In the south-western part of the Basin the groundwater is characterized by Na-Cl-SO$_4$ type chemistry. $^{13}$C values in this area, basinwards of the western recharge area, show trends similar to those downgradient of the main, north-eastern recharge area. Higher $^{13}$C values of −7‰ are found near the south-eastern recharge area.

INTRODUCTION

The Great Artesian Basin occupies 1.7 x 10$^6$ km$^2$, about one-fifth of the Australian continent (Fig. 1). It is a large, multi-layered confined groundwater basin, comprising aquifers in continental quartzose sandstones and confining beds of siltstone, mudstone and marine argillaceous sediments of Middle Triassic to Late Cretaceous
age [1]. The Basin is up to 3000 m thick, and forms a large synclinal structure, uplifted and exposed along its eastern margin and tilted southwest. Recharge occurs mainly in the eastern marginal zone, and large-scale groundwater movement is generally towards the southwestern, western and southern margins. Natural discharge occurs from springs in these areas. Minor recharge occurs in the western margin.

The Basin underlies arid and semi-arid regions where surface water is sparse and unreliable. Discovery of the Basin's groundwater resources around 1880 enabled settlement and the establishment of an important pastoral industry. Groundwater development and utilisation in the Basin have been reviewed by [1]. Aspects of groundwater assessment and effects of development are given in Habermehl & Seidel [2], Habermehl [1] and Seidel [3]. Traditional main usage of the artesian groundwater has been for pastoral, domestic and town water supplies, but future additional usage will probably be for mining projects located outside the Basin.

Groundwater has been exploited from about 4700 flowing artesian waterwells, which were drilled into the main Lower Cretaceous-Jurassic aquifers to depths of up to 2000 m, but average about 500 m. Flows from individual wells exceed 100 L·s⁻¹ and about 3100 wells remained
flowing during the 1970s. Non-flowing artesian waterwells in the Basin which tap a stratigraphically higher, Cretaceous aquifer number about 20 000 and are generally less deep. Groundwater in the Lower Cretaceous-Jurassic aquifers generally contains about 500 to 1500 mg·L⁻¹ total dissolved solids, and is dominated by sodium-bicarbonate-chloride type chemistry [1, 4].

A basin-wide hydrogeological study has been carried out by the Bureau of Mineral Resources, Geology and Geophysics (BMR) during the 1970s and 1980s [1, 4]. Potentiometric maps showing the conditions during the early years of development (Fig. 2) and the 1970s for the main aquifers in the Lower Cretaceous-Jurassic sequence [1] were prepared from the large number of historical pressure data available from most flowing artesian waterwells, using the (finite difference) GABHYD computer simulation model [3]. Delineation of the regional groundwater movement and of the recharge areas in the Basin has been largely based on the results of the hydrogeological study and model simulation of the Basin's hydrodynamics. Hydrochemical and isotope hydrology studies [4, 5, 6, 7] have been jointly undertaken by the Australian Atomic Energy Commission (AAEC) and BMR from 1974 to 1982 to complement and validate the earlier studies. Airey et al. [6] reported on the results from wells in the northeastern part of the Basin. They pointed out that the concentration of major ions appeared to correlate with the groundwater age and inferred that systematic differences reflected changes within the recharge area. The stable-isotope ratios D/H and ¹⁸O/¹⁶O were depleted relative to the rainfall in the intake area. The observed variability of the ratios was less than might have been inferred from expected changes in the palaeoclimate at recharge over the past few hundred thousand years. Explanations have been sought in terms of the opposing effects on stable-isotope ratios of different climatic determining parameters, or in terms of large-scale dispersion [8, 9].

The present study extends the interpretation to data from 176 representative flowing artesian waterwells sampled from the whole of the Basin during the period 1974 to 1980 (Figs 3, 4, 6).

A survey of the levels of chlorine-36 in groundwater from the Great Artesian Basin, to extend the dating technique beyond the ¹⁴C limits, has recently been completed. The ³⁶Cl/Cl ratios decrease with distance along the flowlines from 0.5-1.16 x 10⁻¹⁵ in the recharge area to 5.1 x 10⁻¹⁵ near
FIG. 2. Potentiometric surface of the main aquifers in the Lower Cretaceous–Jurassic sequence during 1880 (pre-development stage) and 1970. (Mean sea level; potentials relate to pure water at 15°C.)
the Queensland/South Australian border (a distance of about 700 km). The chlorine-36 isochrones were found to correlate well with groundwater ages calculated from hydraulic data [7].

Airey et al. [7] deal with results from other environmental isotopes, collected from 31 wells in the northeastern, central and south-central parts of the Basin.

The levels of iodine-129 from 2 wells have been measured. The $^{129}$I/I ratios were, in general, found to increase basinwards [10].

Many flowing artesian waterwells produce noticeable amounts of dissolved gases which include appreciable concentrations of light hydrocarbons, hydrogen, helium, oxygen, carbon dioxide, nitrogen and other gases [11]. The Lower Cretaceous-Jurassic aquifer sandstones are reservoir rocks for hydrocarbons which have been generated in the intervening fine-grained sediments.

Systematic measurements of $^{13}$C/$^{12}$C and D/H ratios in methane and ethane, of $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O ratios in carbon dioxide and of $^{15}$N/$^{14}$N ratios in nitrogen suggest a plurality of gas sources. For example, the hydrocarbon gases appear to be mixtures in various proportions of typical (Permian-Triassic) Cooper Basin natural gas and biogenic methane. Furthermore, although little isotopic variation in nitrogen has been observed, in all samples argon/nitrogen ratios are significantly greater than that of the present atmosphere. However, this could simply reflect the effects of degassing prior to sampling [7].

Noble-gas samples were collected during 1982, and noble-gas ratios, which might reflect palaeoclimate variations, will be examined.

An evaluation of the helium accumulation technique for the dating of groundwater is being made [12, 13]. The efficiency of transport of radiogenic helium to the groundwater is being monitored by the levels of dissolved radon [13].

REGIONAL GROUNDWATER MOVEMENT

Regional groundwater movement in the Basin has been interpreted from the potentiometric surface maps of the aquifers in the Lower Cretaceous-Jurassic sequences [1]. Large-scale groundwater movement is generally directed to
the west, southwest and south in the main part of the Basin; some flow is directed to the north (Figs 2 and 4). In the western part, regional groundwater movement is towards the southeast and south, and this groundwater mixes with west and southwest moving water. Recharge areas in the Basin have been interpreted from the potentiometric maps. The main recharge area is located in the elevated eastern margin within an, in part (at present), humid temperate and semi-arid climate. Natural discharge occurs from many springs in the southern, southwestern and western marginal areas of the Basin [14].

Groundwater flow rates are low, and based on hydraulic data around 1 m·year⁻¹; as hydraulic conductivities are low (0.1 to 10 m·day⁻¹), gradients are
FIG. 3. Hydraulic isochrones calculated from the 1880 potentiometric surface. Waterwells in shaded areas show significant levels of carbon-14 (>1% modern) (Fig. 3b).

low (typically between 1:1500 and 1:4000) and porosities of most aquifer sandstones are high (10 to 30 percent) [4]. Hydraulic data suggest very long residence times for the artesian groundwater. Hydraulic isochrones, based on the 1880 (pre-development) potentiometric surface map (Fig. 2), are shown in Figure 3. The major groundwater flow patterns interpreted from the potentiometric maps are consistent with the patterns derived from the chemical composition and concentration of major ions in the artesian groundwater, and isotope data support these findings [1, 4, 5, 6, 7, 11, 15].

HYDROCHEMISTRY

Groundwater in the main aquifers in the Lower Cretaceous-Jurassic sequence in the Basin contains usually about 500 to 1500 mg L⁻¹ total dissolved solids and is
chemically of the Na-HCO₃-C1 type. Near the recharge areas, Ca, Mg and SO₄ concentrations are proportionately higher, but these decrease basinwards, and Na, HCO₃ and Cl contribute more than 90 percent of the total ionic strength of solutes in the main Basin area (Figs 4, 5). In the southwestern part of the Basin the groundwater is characterized by Na-Cl-SO₄ type chemistry, probably derived from outcropping evaporitic and gypsiferous rocks near the western marginal recharge area, located in an (at present) arid region. Regional groundwater flow patterns interpreted from the potentiometric surface maps are in good agreement with the hydrochemistry in the southwestern part of the Basin. The two regional groundwater flow directions, with the westward flowing water being of the Na-HCO₃-C1 type, and eastward flowing water of the Na-Cl-SO₄ type, mix and are directed towards the main discharge area near the southwestern Basin margin. The combined groundwater flow is distinguished by Na-Cl-HCO₃ and Na-Cl-HCO₃-SO₄ type water [1, 4, 15].
Chemical data of about 200 flowing artesian water-wells representative for most parts of the Basin were collected from 1974 to 1982 as part of the present study. A multi-variate statistical technique was used to differentiate compositional groups from the major ion data of 151 wells. Three groups, 1, 2 and 6 in Figure 4, contain the majority of wells, with 116, 11 and 10 wells respectively. Most wells tap the same aquifer in the Lower Cretaceous-Jurassic sequence. Samples with relatively high Ca, Mg and SO₄ concentrations (groups 6 to 9, Fig. 4) are mainly from relatively shallow, low-temperature, artesian wells located near the Basin margins. The chemical evolution of the water in and near the recharge areas probably includes cation exchange and determines the composition of the groundwater basinwards. The wells downgradient from the recharge areas are deeper (up to 2000 m) and have higher temperatures (up to 100°C at the surface), and these wells, in groups 1 to 5, are dominated by Na-HCO₃-CI type chemistry. The hydrochemical composition in the Basin is relatively uniform on a regional scale and probably reflects the chemical inertness of the predominately quartzose and lithic sandstone aquifers. Gradations occur in the total dissolved solids concentrations, with a general increase along the flowlines [4]. Variations of the major ion concentrations and ratios occur along the flowlines in some parts of the Basin (Fig. 5). Na and HCO₃ generally increase in most areas. Cl and SO₄ concentrations decrease basinwards of the northeastern margin and then increase downgradient. Na and SO₄ concentrations are relatively constant in the southeastern part and SO₄ concentrations are generally constant in the northwestern part. The increase of HCO₃ and the decrease in SO₄ concentrations could be related to biochemical reduction of SO₄. The variations in concentrations downgradient of the northeastern recharge area are thought to reflect variations in the climatic conditions in the recharge area[6].

CARBON ISOTOPES

Several possible sources exist for the dissolved inorganic carbon content of groundwater [16]:

(1) atmospheric carbon dioxide (containing ¹⁴CO₂) dissolved in rainwater,
(2) carbon dioxide (also containing ¹⁴CO₂) produced by the decomposition of organic material in the soil or by root respiration in the unsaturated zone,
(3) solution of mineral carbonates within the saturated zone,
TABLE I. CLASSIFICATION OF GROUNDWATER WITHIN THE GREAT ARTESIAN BASIN BASED ON CARBON ISOTOPES

<table>
<thead>
<tr>
<th>Classification (Figs 3 and 6)</th>
<th>Wellhead temperature (°C)</th>
<th>Per cent modern carbon</th>
<th>δ13C (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25 to 50</td>
<td>27 to 0</td>
<td>-17 to -13</td>
</tr>
<tr>
<td>B</td>
<td>50 to 100</td>
<td>0</td>
<td>-13 to -2</td>
</tr>
<tr>
<td>C</td>
<td>30 to 50 up to 100</td>
<td>1 to 0</td>
<td>-12 to -6</td>
</tr>
<tr>
<td>D</td>
<td>30 to 50</td>
<td>6 to 0</td>
<td>-11 to -8</td>
</tr>
<tr>
<td>E</td>
<td>40 to 60</td>
<td>2 to 0</td>
<td>-7 to -6</td>
</tr>
</tbody>
</table>

(4) oxidation of organic materials present,
(5) reduction of sulphate by inorganic materials present,
(6) addition of carbonate to the groundwater if Ca²⁺ concentration is decreased by calcium-sodium exchange, thus maintaining the saturation of calcite.

Large variations of the radiocarbon activity and δ13C values¹, resulting from a combination of the above factors and the increasing residence time of the groundwater with distance from the recharge area, are observed (Table I). They can be used as a basis for the classification of groundwater into five divisions (Fig. 6).

RADIOCARBON

The radioactive isotope of carbon, radiocarbon or ¹⁴C (half-life 5730 years), is being continuously produced in the troposphere, principally by the interaction of secondary cosmic ray neutrons and nitrogen nuclei [18]. The ¹⁴C atoms are rapidly oxidised to form ¹⁴CO₂ molecules which subsequently enter the biosphere and hydrosphere.

¹ δ13C is defined as $\left[ \frac{\text{C}_{13}}{\text{C}_{12}} \text{ (sampled)} \right] \left[ \frac{\text{C}_{13}}{\text{C}_{12}} \text{ (standard)} \right]^{-1} \times 1000$

The PDB standard used is a sample of Belemnitella Americana found in the Cretaceous Pee Dee Formation of South Carolina [17].
Radiocarbon dating of groundwater was first introduced about 25 years ago [19, 20] and has since been used in hydrological investigations in the interpretation of groundwater flow systems.

Radiocarbon techniques are limited to dating groundwater residence times of less than 35,000 years and the shaded areas in Figure 3 indicate regions where the groundwater contains significant levels of $^{14}$C (> 1% modern). These regions delineate the recharge areas which are situated both in the eastern and western margins of the Basin. The presence of water containing modern carbon in the western part of the Basin, near the Queensland-Northern Territory border (in part of Division C), is surprising and indicates a local input of relatively modern water. It should be noted that there is evidence for massive recharge
FIG. 7. Groundwater flow rates between several non-flowing artesian waterwells near the northeastern recharge area.

to the Mereenie Sandstone aquifer south of Alice Springs in the Northern Territory about 1800 and about 6000 years ago [21].

In Division A, there are a number of non-flowing artesian waterwells near the eastern margin of the Basin, and for samples from these wells the $^{14}C$ specific activity has been interpreted as age, using the procedure of Salem et al.[22]. Results are shown in Figure 7 and a flow rate for groundwater moving in a southwestern direction has
been calculated to be $2.2 \text{ m m}^{-1}$. This value is in good agreement with the flow rate of $0.5 \text{ m m}^{-1}$ for the southwestern directed flow and $0.8 \text{ m m}^{-1}$ for the southern directed flow lines in Division B in the Basin when calculated from 36Cl dating techniques [7, 23].

**STABLE-ISOTOPE RATIOS $^{13}\text{C}/^{12}\text{C}$**

The $\delta^{13}\text{C}$ values of soil carbon dioxide show a bimodal distribution with modes close to $-24\%$ and $-17\%$ [24]. In the former case, the carbon dioxide arises principally from plants with the Calvin three-carbon-atom pathway to photosynthesis. In the latter case the carbon dioxide is dominated by plants with the Hatch-Stack four-carbon-atom cycle [25]. Carbonates of marine origin have a $\delta^{13}\text{C}$ value of $-0.4 \pm 2.2\%$ and freshwater carbonates resulting from evaporation processes in semi-arid regions have a $\delta^{13}\text{C}$ value of $-6.5 \pm 0.5$ [26].

The stable-isotope composition of dissolved inorganic carbon is the net effect of the six factors listed in the introductory paragraph of the section on carbon isotopes. The variation throughout the Great Artesian Basin of $\delta^{13}\text{C}$ values is illustrated in Figure 6. It was found that the $\delta^{13}\text{C}$ values of the dissolved carbonates in the water in the recharge areas of Divisions A, C, D and E have well-defined values (Table 1). In Division A, the main recharge area of the Great Artesian Basin, the climate is in part semi-arid and humid temperate, and $\delta^{13}\text{C}$ values for soil CO$_2$ of about $-25\%$ would be expected. Interaction of the soil CO$_2$ with carbonate of marine origin ($\delta^{13}\text{C} = -0.4 \pm 2.2\%$) within the aquifer sandstone would lead to a $\delta^{13}\text{C}$ value of the resulting bicarbonate consistent with that observed ($-17\%$).

In Divisions C and D (Figure 6) the climate is arid to semi-arid and a soil $\delta^{13}\text{C}$ between $-11$ and $-19\%$ could be expected as the vegetation tends to be dominated with plants exhibiting the Hatch-Stack photosynthesis cycle. Dissolution of freshwater carbonates could result in the observed $\delta^{13}\text{C}$ of $-12\%$ in the input groundwater. This value is in good agreement with the $-10.7\%$ found for the input groundwater of the Mereenie Sandstone aquifer, at Alice Springs, Northern Territory [21]. In Division E, the southeastern recharge area, the $\delta^{13}\text{C}$ value of $-7\%$ is unexpected and requires further investigation.
The variation of the $\delta^{13}C$ values downgradient of the principal northeastern recharge area (Division B) has been interpreted in terms of a two-component system [6] on which the bicarbonate from the recharge water ($\delta^{13}C=-17\%$) is increasingly diluted with dissolved mineral carbonate of marine origin ($\delta^{13}C=0\%$). As the two-component model predicts, $\delta^{13}C$ varies linearly with the reciprocal of the concentration of dissolved bicarbonate. Similar processes occur in Divisions C and D in the western parts of the Basin.

In some sections of flowlines in the deep, very hot regions of the centre of the Basin there is evidence for exchange of dissolved bicarbonate with the carbonate of the aquifer - systematic enrichment of the bicarbonate is observed without a corresponding increase in its concentration.

CONCLUSIONS

1. Important features of the hydrogeochemistry and isotope hydrology of the Great Artesian Basin, Australia, are consistent with the groundwater flow patterns interpreted from the potentiometric surface maps. Two regional groundwater flow directions, with westward water being of the Na-HCO$_3$-Cl type, and eastwards flowing water of the Na-Cl-SO$_4$ type, mix and are directed towards the main discharge area near the southwestern Basin margin.

2. A more detailed interpretation is possible with the stable carbon isotope data. Each of the important recharge areas have characteristic $\delta^{13}C$ values. Despite perturbations basinwards by the subsurface uptake of carbonate, and in the high-temperature regions by exchange, the $\delta^{13}C$ contours may be used to determine the extent of influence of the different intake areas. The isotope ratios near the western margins of the Basin are consistent with those found in other sandstone aquifers in Central Australia.

3. Radiocarbon techniques have been used to delineate intake areas near the margin of the Basin with greater resolution than would be possible from analysis of the potentiometric surfaces alone. Downgradient of the principal recharge area in the northeastern portion of the Basin, groundwater flow velocities have been calculated which are in acceptable agreement with those deduced from chlorine-36 dating techniques.
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ENVIRONMENTAL ISOTOPE STUDY OF A GROUNDWATER SUPPLY PROJECT IN THE KALAHARI OF GORDONIA

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Abstract

ENVIRONMENTAL ISOTOPE STUDY OF A GROUNDWATER SUPPLY PROJECT IN THE KALAHARI OF GORDONIA.

A feasibility study for a central fresh groundwater supply scheme in the Kalahari of the Gordonia district, South Africa, provided the opportunity to study fresh and saline water occurrences in detail with environmental isotopes. The isotopic and chemical signals show a clear contrast among groundwaters below a river bed, an extended fresh groundwater body and saline groundwaters in close proximity to the river. Carbon-14, tritium and stable-isotope data lead to a vertical rain recharge model rather than a regional flow mechanism for an understanding of the various water occurrences, their interrelationships and varied hydrochemistry.

1. INTRODUCTION

The district of Gordonia of the north Cape Province of South Africa forms the southern-most section of the Kalahari thirstland. It is a predominantly sheep-raising farming area with a carrying capacity of less than one sheep per two hectares, and relies for its water almost exclusively on groundwater, drilled for by individual farmers. Boreholes generally have poor yields; many are dry. Apart from certain areas, the water quality ranges from poor to impotable and rest levels may be deeper than 100 metres.

Recently, an intensive investigation was conducted to establish the feasibility of a central water supply to the individual farms, based on certain areas where good-quality groundwater was known to exist. This investigation involved borehole surveys, geophysical measurements, exploratory and supply borehole drilling and hydrochemical observations. An environmental isotope study was conducted in parallel with this investigation in order to assist in the interpretation of the other data and to elucidate the relationship between the different water bodies,
FIG. 1. Map of Gordonia showing locations of sampled boreholes, section lines (see Fig. 2), water quality and isotope data.
their movement and the development of the varied hydrochemistry. The paper gives an account of this study.

The area was previously studied by Levin [1], who summarizes the results of some earlier studies pertaining to other parts of Gordonia.

2. DESCRIPTION AND GEOLOGY

The most pervading feature of the Kalahari is the almost unbroken cover of aeolian sand which for the greater part is flat and featureless, but in certain areas, including Gordonia, forms parallel dunes which under present climatic conditions are largely fixed by vegetation.

The only features (Fig. 1) relating to surface waters are the beds of the ephemeral Kuruman, Molopo and Nossob Rivers, some minor drainage lines and the playas or pans, which may vary from a few tens of metres to several kilometres in diameter. These are normally dry, but may contain some surface water after heavy downpours in the rainy season which normally lasts from October to April. Mean annual precipitation is 200 mm, of which 60% falls between January and April [2].

During 1974–77 the Kuruman River flowed along its entire length after exceptional rains of three times the annual mean on its distant dolomitic catchment. An earlier flood is known to have occurred in 1920. Even earlier floods in 1891–92, 1896, 1915, 1917 and 1918 are referred to [2], but evidence of these is uncertain.

The underlying hard-rock geology [1] consists mainly of the Karoo sediments of shales and tillites. This formation and the earlier Nama sedimentary sequence were deposited in a basin of pre-Cambrian and earlier rocks, producing a shallow depression. On this surface the deposits of the Kalahari Formation have been accumulating since Tertiary times. The generalized section of this Formation consists of gravel, sandy clay and sandstone, red and yellow clay and crete, both calcareous and silicious. The surface is almost exclusively sand; other components occur locally. The thickness of the Kalahari Beds, often with sandstone lenses, can reach 100 m or more over palaeo-drainages in the Kalahari floor but thins considerably to the west and south-west where the Karoo becomes locally exposed.

In the extreme east of the basin the pre-Cambrian rocks are exposed in hills jutting from the Kalahari plain, which drops from an elevation of about 1000 m a.m.s.l. in the east to about 800 m in the south-west.

3. GEOHYDROLOGY

Groundwaters are generally unconfined to semi-confined. The piezometric levels range in depth from a few tens of metres to 160 metres and lie mainly within the pre-Kalahari rocks and occasionally in the lower sections of the Kalahari
Formation. Yields from successful farm boreholes range from less than 0.1 L/s in argillaceous sections to 1.3 L/s. Some production boreholes drilled for the central supply produced up to 7 L/s from semi-consolidated sands in the river bed.

Groundwater quality is good (less than 1000 mg/L TDS) in the aquifer below the Kuruman River, in the rock exposure areas to the east and in a few other areas. Towards the west and south-west there is a general deterioration of quality up to 30 000 mg/L TDS, with brines in some pan floors.

In an extensive study of an adjacent area of the Kalahari, Smit [3], following earlier studies by Martin [4], assumed that infiltrating rainfall is quantitatively lost by evapotranspiration before reaching the water-table in areas of thick (tens of metres) Kalahari Bed (particularly sand) cover. This approach, applied to the present study area by Levin [1], assumed that effective recharge would occur only along the river courses during infrequent floods and into bedrock exposure areas during heavy rains. Gradual salination would then occur during regional underflow.

Certain aspects of the hydrochemistry and the regional drainage of Gordonia, however, appear to be in conflict with this philosophy. Isotopic and hydrochemical evidence is put forward by Verhagen [5] who attempts to reconcile these conflicting features. The sand moisture profiles and conditions in an underlying aquifer were studied by Verhagen et al. [6] in analogous conditions. In this paper, some of the detailed evidence obtained during the study of the water supply project itself is examined.

4. PHASE I OF THE STUDY

From a borehole survey and early results of the geophysical investigation, it was known that a trough of deep Kalahari sediments (up to 120 m) stretches south-westwards away from the Kuruman River bed (Fig. 1). For a distance of some 30 km the groundwater in this trough is at TDS < 1000 mg/L, but this value rises abruptly at the south-western end as well as towards the sides of the trough. The rest level with a gradient of about 0.8% south-westwards lies for the greater part within the Kalahari Beds. This fresh-water body was considered as a possible source for exploitation in the central supply scheme.

The second possibility considered for exploitation was the aquifer under the river bed itself, composed mainly of sand which in places is more or less argillaceous. The majority of farms along the river have boreholes located on the river banks, providing good-quality groundwater. Some boreholes were sunk to relatively shallow depths (~ 50 m) into the river bed itself, encountering good supplies.

The fresh groundwater below the river was taken to be derived from periodic river flow. Following the regional underflow philosophy, it was assumed that the fresh water in the Kalahari trough was in its turn derived from this source.
FIG. 2. Sections A-A' and B-B' (Fig. 1) based on information from de Beer et al. [2], showing depth of sampling, water quality and isotope data.
A preliminary isotope study was undertaken in which some existing farm boreholes were sampled along the trough, the river and at some other sites. The results of this survey are discussed in detail by Verhagen [5] and can be summarized as follows:

(a) Groundwaters in the immediate vicinity of the river usually have radiocarbon concentrations of > 80 pmc and tritium concentrations of up to 4 TU, with \( \delta^{13}C \leq -8\%o \) and \( \delta^{18}O < 5.6\%o \). The groundwaters are mainly fresh (TDS \( \leq 500 \, \text{mg/L} \)), with Ca and Mg-HCO\(_3\) dominance. These results are compatible with infiltration from surface flow in, and rain falling on, the river bed.

(b) Groundwaters in the trough area, except those close to the river, gave radiocarbon concentrations in the range 35–75 pmc, with low (\( \leq 0.5 \, \text{TU} \)) tritium concentrations and \( \delta^{13}C \) in the range \(-4.5\%o \) to \(-10\%o \). No clear geographical trends are observable in these data, such as a systematic decline in \(^{14}C\) values away from the river bed.

(c) Observations on some other boreholes, notably in the extreme north-west of the study area (see Fig. 1) indicated that salinities of up to 10 000 mg/L could be found in some very recent (<20 a) groundwaters. This proved that salinity was not necessarily coupled to long residence times or distance of underflow.

The above results were obtained from existing farm boreholes on which generally scant information was available. The penetration depth of the saturated zone is usually unknown, and the possibility that minor perched groundwaters had been intersected is not proven.

5. PHASE II OF THE STUDY

During this phase, observation boreholes were sunk as benchmarks for the geophysical survey and aquifer evaluation. Samples for isotopic and chemical analysis were obtained from these boreholes if and when conditions allowed. The sampled boreholes are shown in Fig. 1 as well as those existing boreholes which were sampled during both phases of the study.

Samples were taken (a) of ‘first-strike’ waters during drilling, (b) at various depths below the water-table, also during drilling, and (c) during pump tests.

Although these samples were considerably better documented than under Phase I, conditions were rarely ideal. Saturation might only be noticed several metres below the static water level. ‘First-strike’ waters therefore may refer to the top few metres of the saturated zone. Even at slow sampling rates, some mixing with deeper water could occur. Leakage past the casing makes the integrity of deeper samples progressively more uncertain.
6. DISCUSSION OF DATA

6.1. Data from profile A-A' of Fig. 2

Profile A-A' of Fig. 2 was chosen to incorporate a maximum of sampling points and roughly follows the Kalahari trough. Piezometric heights at individual boreholes for some distance follow the regional dip of about 0.8%. The piezometric surface shown may not be truly continuous because of the heterogeneity of the Kalahari Beds. Borehole 1, closest to the river, was found to be very low yielding as a result of the (local) considerable clay content of the aquifer. The high piezometric level may be an exaggerated mound, slowly descending since recharge during 1974–77 (see Section 6.2).

Each borehole on or close to the profile line has been projected onto the section, showing water quality and isotopic data.

The first-strike $^{14}$C value for borehole 1, below the river, is 86 ppmc. Away from the river, at boreholes 2, 3 and 4, the $^{14}$C concentrations are lower, representing more or less mean values for the saturated zone. At greater distances the $^{14}$C values become quite heterogeneous and do not parallel all the increase in salinity observed towards the south-west of the profile. Except possibly in its immediate vicinity (3–5 km) there is no geographical trend away from the river, confirming the Phase-I $^{14}$C data. On the other hand, first-strike waters gave $^{14}$C values of up to 77 ppmc where surrounding production wells produced considerably lower values. Although the data do not prove this unequivocally, there is a priori evidence of $^{14}$C and therefore age stratification within the saturated zone in some localities.

Moving away from the river the $\delta^{13}$C values rise slightly, but at some distance they become more uniform. This might be taken as evidence for dissolution/exchange reactions reaching equilibrium during underflow. However, local influences are observed, such as low $\delta^{13}$C values of $-10\%$ at boreholes 15 and 16, which are associated with average to high radiocarbon concentrations.

The $\delta^{18}$O values similarly show a rise away from the river where the values are below $-5.6\%$. Then, however, they become substantially uniform. In fact, they fall well within a narrow range of values for the rest of the trough samples, off the profile, as well as for large tracts of the rest of the study area, excluding the saline waters in the west (see Section 6.2).

A clear contrast is seen in the histogram between waters in, or close to, the river bed, with a maximum at about $-6.5\%$ (Fig. 3(a)), and those away from the river, with a maximum at about $-4.5\%$ (Fig. 3(b)). This histogram also contains some samples from hard-rock exposure areas away from the river and from slightly evaporated waters. The considerable difference in position of the maxima strongly suggests different recharge mechanisms for the two groups of waters.
FIG. 3. Histogram of $\delta^{18}O$ values in groundwaters (a) from the aquifer below or close to the Kuruman River and (b) elsewhere in the study area.

FIG. 4. Trilinear diagram of major ion composition of Kalahari trough waters, with $^{14}C$ concentrations and number of boreholes from Section A-A' of Fig. 2.
The chemical composition of waters along the trough is fairly heterogeneous. A trilinear diagram of major ion composition ratios in the trough area (Fig. 4) shows a scatter of points from Ca and Mg-HCO₃ dominance immediately below the river to NaHCO₃ and NaCl dominance. Again, there is no clear correlation, either with location or with ¹⁴C concentration.

6.2. Data from profile B-B' of Fig. 2

The western profile of boreholes was drilled across the river bed in the area of planned exploitation and continued south/south-westwards into the surrounding groundwaters (usually saline and alkaline). The piezometric surface (Fig. 2, B-B’) is almost entirely horizontal. A minor mound of a few metres is still observable below the river bed, some 5 years after the last flooding. The width of the river bed appears exaggerated as the profile was drilled obliquely across it.

The major surprise of this drilling programme was the limited extent of the fresh-water body and the abrupt transition from fresh to saline water. Only on close inspection [7] was a very fine clay layer observed in the drilling material which may produce the sharp separation of fresh and saline horizons.

The conductivities and isotope levels observed in spot samples and during pump tests are given in Fig. 2, B-B’. For holes 10–14, away from the river bed, very high salinities, up to near saturation values, go hand in hand with ‘heavy’ values of δ¹⁸O and relatively low ¹⁴C concentrations, ranging from 17 to 52 pmc. The δ¹³C values fall in roughly the same range as those for section A-A’ but trend to more positive values in the extremely saline waters. Many waters in the area have alkalinites of up to 300 meq/L (see Fig. 7) and pH values of up to 10. The chemical composition for borehole 11 (Fig. 5(a)) is typical for the area.

In the river bed, the fresh waters have generally high (84–103 pmc) ¹⁴C concentrations with 0.7–5.5 TU. However, lower values are also found, for instance in borehole 2, indicating that not all of the fresh-water lens was recharged during the recent flooding.

The deeper saline waters show chemical characteristics which are very similar to those found further to the south of the section. The δ¹³C values lie in the same range and radiocarbon concentrations are low. The δ¹⁸O values are considerably more negative, however, from −4.0‰ to −6.8‰, as compared with −2.6‰ to +8.0‰ for boreholes 10–14.

The mean of the tritium concentrations in the fresh-water section of boreholes 4, 5, 6 and 7 is 1.6 TU, while the mean for the saline section is 0.1 TU, with 1σ measurement errors of ±0.2 TU. The maximum contamination of the saline samples due to mixing in the borehole is therefore about 20%.

On the basis of this mixing estimate, the δ¹⁸O values in the saline waters in boreholes 4, 5, 6 and 7 would have been shifted by a maximum of about −1.3‰. The in situ values of δ¹⁸O in the saline waters under the river are therefore considerably ‘lighter’ than those in the saline waters further south along the section.
FIG. 5. Major ion compositions and total alkalinity (TAL) for water from different depths in (a) borehole 11 and (b) borehole 2 from section B-B' of Fig. 2.

The piezometric height of the fresh-water lens is somewhat higher than that of the saline horizon. Figure 5(b) shows the chemical composition at three different depths in borehole 2. As the samples were taken whilst drilling, there could have been no contamination due to sampling of the shallower sample by deeper saline water. The pattern suggests intrusion of the fresher waters by saline water probably before the flood, when the piezometric differential might have been reversed.

6.3. The oxygen-18/deuterium diagram

The oxygen-18 data are plotted against deuterium measurements for the whole study area in Fig. 6. The majority of points fall on or around the universal rain line [8].

No long-term isotope data are available for rainfall in the area. Records for Pretoria, some 700 km to the east [9], are used for comparison. The mean annual rainfall for Pretoria is 600 mm and for the study area 200 mm. However, both are summer rainfall areas with a substantial part falling late in the season; both are continental environments. The Pretoria weighted mean, although probably not identical with that of the study area, places the groundwater data in
perspective. Thus, all the waters fall in the ‘lighter’ sector of the diagram, with the exception of the saline waters in the west and south-west. The latter lie on an evaporation line and have undergone kinetic isotope enrichment. All normal groundwaters therefore appear to have experienced a degree of rainfall selection, i.e. recharging preferentially during heavier rainfalls. This effect is generally observed in the Kalahari [10, 11].

Most depleted are the river waters, i.e. those samples obtained from the aquifer below or close to the river. This depletion is compatible with conditions as expected during river flow. Much the same range of values was assumed for a tributary [6]. The highly infrequent flooding of the Kuruman River should occur, as it did in 1974–77, during exceptional weather, with rain falling during prolonged, overcast, cool and moist conditions. Although the points shown are associated mainly with recently recharged waters, any such recharge which occurred in the past should have carried a similar range of $\delta^{18}O/\delta^{2}D$ values. Mean values for Kuruman River head waters and for the major tributary during 1976–77 [12] are given for comparison. It is striking that after 300 km of surface flow under low gradients the infiltrated waters show no clear sign of evaporation.

As can also be seen in Figs 3 and 6 the Kalahari trough and associated waters form a much tighter group. They lie closer to the assumed mean precipitation value and somewhat off the rain line, suggesting a slight degree of surface evaporation. These characteristics are entirely compatible with rapid infiltration into dunes and some surface delay in the numerous small pans and pan-like areas that are found everywhere in the ‘streets’ or dune valleys. The surprising uniformity of the stable-isotope signal over such an extended area is probably controlled by its uniform physiography. Similar areal uniformity in $\delta^{18}O$ has been found in Namibia [13].

The stable-isotope signals in the highly saline waters of the western section of B-B' (Fig. 2) give an insight into their origins. The degree of evaporation seen in some cases is even more extreme than that which is associated with the saturated NaCl brines in the floors of major pans in the south-west (Fig. 6). The waters must have been exposed at the surface for some time, either as rain water before infiltration into the floors of minor pans which abound in the area, or possibly by the occasional rise of the relatively shallow water-tables during past extreme precipitation events to above surface level. Such a cyclical evaporation mechanism seems to be operative in the floors of some major salt pans.

Below the river, the saline section has assumed the $\delta D/\delta^{18}O$ signal of the overlying fresh water infiltrated from the river. The contrasting isotope signals suggest therefore that the evaporitic dissolved load is being mobilized by waters derived locally from the surface, carrying the characteristics determined by local surface conditions.

The isotopic evidence in the deeper saline waters and the chemistry of the fresh water overlying it indicate that the dividing clay layer is at best an aquitard, which may be effective only when the piezometric differentials are not too large.
6.4. Radiocarbon, tritium and carbon-13 data

Radiocarbon concentrations in fresh groundwaters close to the river are generally high (≥ 80 ppm), often with measurable tritium and generally low carbon-13 values (< −8‰). Away from the river, in the Kalahari trough area, \(^{14}C\) values are lower and variable, with no geographical trends observable and no correlation with salinity. Tritium concentrations are vanishing. Low \(\delta^{13}C\) values can appear locally. Some first-strike waters give distinctly higher \(^{14}C\) concentrations, strongly suggesting local stratification.

This combination of facts cannot support the concept of movement of groundwater away from the river bed as the only mechanism for the presence of fresh water. The facts can be reconciled by assuming vertical rain recharge, which is areally highly variable in both quantity and quality because of variable conditions in the unsaturated zone.

In the western profile B-B' (Fig. 2), high \(^{14}C\) and \(^{3}H\) values in the upper fresh section prove substantial recharge. Both drop to low levels in the saline section immediately below, as do the \(\delta^{13}C\) values. Laterally, where the saline waters present fairly shallow water-table conditions, \(^{14}C\) concentrations are likewise low with vanishing \(^{3}H\). However, during pump tests on several boreholes, \(^{3}H\) concentrations rose to just measurable levels (~1 TU) towards the end of the tests. Some recent water seems to be present in the saturated zone; as both salinity and \(\delta^{18}O\) remained largely unaltered during the tests, this water must have been salinized and evaporated before reaching the water-table.

Carbon-13 values are variable, with some anti-correlation with salinity. In one borehole just off the profile, an extremely low value of \(\delta^{13}C = -16\)‰ is observed (Fig. 1). Local effects seem to play as great a part here as in the eastern profile. This was independently seen in the discussion of the \(\delta D/\delta^{18}O\) data in Section 6.3.

6.5. High alkalinites and radiocarbon concentrations

As is shown by Verhagen [5] and has become clear from the above discussion, regional flow models do not appear to be valid in the Kalahari under present climatic conditions. This implies numerous local closed-basin conditions and salinity buildup.

Figure 7 shows the growth of alkalinity and chlorine in the extreme case of the western saline groundwaters (see Fig. 5). The maximum and minimum lines for chlorine and alkalinity concentrations have been drawn in as a guide. The most probable genesis is from an originally evaporitic environment, from which calcium and magnesium had largely precipitated. Any further development would have found sodium as the major cation, resulting in the roughly parallel development of chlorine and alkalinity, known as the common ion effect [14].
FIG. 7. Chemical development of western saline waters, showing a growth of $\text{Cl}^-$ and total alkalinity (TAL) with total dissolved ions (TDI).

Deviations from the trend lines show competing tendencies in the two anion concentrations.

The parallel trend in chlorine and alkalinity is already evident in relatively low ($\approx 10$ meq/L) concentrations. As the dominant cation in most groundwaters (even fresh ones) in the study area is sodium, it is possible that many of the groundwaters carry a dissolved inorganic carbon (DIC) concentration higher than the value in the infiltrating recharge water. This DIC already present therefore 'dilutes' the newly infiltrated carbonate. In this way, anomalously low radiocarbon concentrations can be produced. Such low values are observed in the western saline waters, even where they are under fairly shallow water-table conditions, with just measurable tritium. Great caution should therefore be exercised in interpreting $^{14}$C concentrations in terms of water and carbonate ages in this type of environment.
7. CONCLUSIONS

Hydrochemical and isotope data strongly suggest that in both the eastern and western profiles studied the demonstrable influence of river infiltration spreads laterally to the extent of at most a few kilometres.

In the western profile, active recharge is observed in the river bed largely as a result of flooding. The fresh-water lens is laterally and vertically restricted possibly by a semi-permeable clay layer. The chemical characteristics and isotope values provide a strong contrast with the surrounding and underlying saline waters. The former have a clear evaporation signal, which can be related to the density of pans in the area and the relatively shallow water-table. Although the $^{14}$C levels are low, alkalinity considerations and the appearance of just measurable tritium suggest that they do not signify great water antiquity.

In the Kalahari trough in the east, waters with characteristics different from those in the river aquifer are found. There is no ageing trend in the $^{14}$C data as we move away from the river, whilst individual values of 75–77 pmc suggest components of recent recharge. Because of unavoidable mixing during sampling, even higher $^{14}$C concentrations might be present at the top of the saturated zone. The $\delta^{18}$O values are highly uniform and different from those in the river aquifer. They are somewhat lighter than those of the probable mean present-day precipitation. This rules out the possibility that the groundwaters in the trough, as well as in most of the remaining study area away from rivers, are remnants of earlier 'pluvial' climatic periods. These should have carried isotope signals at least as light as those of water found in the river aquifer, which probably infiltrated mainly during the exceptionally wet period of 1974–77.

These results should sound a cautionary note on palaeoclimatic interpretations of stable-isotope concentrations in groundwaters in semi-arid environments and possibly elsewhere.

The one mechanism which reconciles all the available facts is vertical rain recharge. The absence of measurable tritium where the $^{14}$C data in the trough suggest active recharge does not present a contradiction: the delay in the unsaturated zone could run into several decades [6]. Where the water-table is shallower in the western profile, just measurable tritium is occasionally observed.

In both sections, there is no significant lateral movement of groundwaters under present climatological conditions. However, the contrasting water qualities may suggest conditions during earlier, wetter periods.

The existence of numerous pans in the west and south-west may indicate the earlier existence of an evaporitic basin in the region of confluence of the three rivers. Further evidence is the existence of extensive and thick calcareous deposits which are being incised by the rivers, alkaline saline groundwaters and saturated NaCl brines in major pan floors.
Wetter periods could, however, have leached the Kalahari Beds in the trough and the eastern area generally and temporarily set in motion regional drainage there. Lower transmissivities would have made such leaching much less effective in the bedrock aquifers. Aerosol deposition and enrichment in the unsaturated zone gradually salinize the water at present.

For a fresh-water supply that could be sustained for indefinite periods the groundwaters in the two areas studied do not appear promising. In the west, the lens of fresh water is obviously of limited extent and would require careful management in order to maintain its quality. In the eastern section, there is no evidence of major storage of infiltrated river water. In the Kalahari trough and elsewhere, the deep piezometric levels are being maintained predominantly by local, if at present very low, rain recharge.

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URANIUM SERIES DISEQUILIBRIUM IN ROCK/WATER SYSTEMS OF THE CANADIAN SHIELD

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Abstract

URANIUM SERIES DISEQUILIBRIUM IN ROCK/WATER SYSTEMS OF THE CANADIAN SHIELD.

A study of uranium series disequilibrium in groundwaters and fracture-filling materials from boreholes at Chalk River in the Canadian Shield has been undertaken to test its value in gaining information on the rate of movement of water from deep crystalline rock. Data for surface, shallow and deep waters are presented. An enhancement in $^{234}$U observed at shallow depths ($^{234}$U/$^{238}$U Activity Ratio (A.R.) = 1.5 to 2 at 10–20 m) correlates with $^{234}$U depletion in fracture coatings. In most boreholes studied, $^{234}$U enhancement appears to reach a limiting A.R. of about 3 at depths greater than 30 m. However, $^{234}$U/$^{238}$U activity ratios of up to 6 occur in the waters of one borehole. At no depth was equilibrium between the uranium activity ratio of fracture-filling material and that of coexisting water observed, even where it was likely that uranium was being incorporated into recrystallizing calcite. Speciation studies on water from the 60 m depth of this hole indicate that a portion of the uranium exists in the $^{4+}$ state with an activity ratio of about 2, in contrast to the major portion existing as $^{4+}$ with an activity ratio of 5–6. It is suggested that speciation may allow differentiation between uranium simply dissolved from mineralizations and that put into solution by isotope-discriminating processes associated with radioactive decay.

1. INTRODUCTION

Uranium isotopic disequilibrium has been studied extensively as a means of characterizing waters, and consideration has been given by many workers to its potential for dating deep groundwaters [1].
While the presence of flowing water is sufficient to effect many geochemical separations based on solubility differences, it is recognized that other mechanisms are required to explain isotopic separation. Those most commonly postulated for U-234/U-238 separation involve effects resulting from recoil of the daughter nucleus upon emission of an α particle and/or changes in oxidation state resulting from the radioactive decay process [2]. The cumulative effect of these processes is enhancement of U-234 in groundwaters and corresponding depletion in weathered surfaces. Conditions leading to high leach rates, e.g. oxidizing waters with high \( \text{CO}_2 \) partial pressures, tend to obscure these effects because of the predominance of non-discriminating dissolution.

Most of the groundwaters analyzed to date for U-234/U-238 activity ratios (A.R.) have been drawn from sedimentary terranes, either limestone or sand/shale. While some attempts have been made to utilize these data for water age estimates, Osmond and Cowart [3] have pointed out that the use of different models for the establishment, growth or decay of disequilibrium has led to widely conflicting results. Before these conflicts can be resolved the state of water-rock interrelationship within the fractures must be investigated.

As part of a continuing effort to provide the Canadian nuclear fuel waste management program with information on the rate of movement of water from deep crystalline rock, we have been studying the U series disequilibrium observed in groundwaters and fracture-filling materials from boreholes in the Canadian Shield. The data accumulated, in association with other isotope and hydrogeological information, should provide insights into the onset and subsequent evolution of this disequilibrium, and permit us to draw some conclusions as to the mobility of such deep groundwaters.

2. SITE DESCRIPTION

Bedrock at the Chalk River Nuclear Laboratories is too highly fractured to be considered suitable for long-term nuclear fuel waste disposal. However, it is a very convenient site for studying deep groundwater flow paths.

The regional high for the south side of the drainage basin of the Ottawa Valley is situated approximately 100 km to the south-west of Chalk River (Figure 1). A number of boreholes have been drilled to study fracture interconnections and to test methods of identifying groundwater discharge from bedrock.
FIG. 1. Study site location. Lines indicate some of the more extensive lineaments in the area evident from aerial photos and a topographic map.
A series of relatively shallow boreholes has been drilled into lineaments identified by aerial surveys and geophysical methods—sites where one might expect waters to be rising to the surface close to the regional topographic low.

CR 20, the borehole sampled most extensively during this study, extends 61 m into granodiorite rock, intersecting a thin pegmatite vein at approximately 48 m. It is situated on the edge of a lake that is very nearly at the regional topographic low. The strong upward hydraulic heads measured relative to the lake indicate this is a discharge zone, and that the waters sampled are probably representative of water recharged at some point that is spatially and temporally distant.

3. EXPERIMENTAL PROCEDURES

3.1. Field Sampling

Before sampling a borehole interval, several interval volumes were allowed to flow from, or were pumped from, the system and discarded.

A variety of sample containers was used, depending on subsequent purification procedures to be followed:

(a) 20 L rigid polyethylene bottles, well rinsed, for samples to be concentrated on ion exchange resin.

(b) 20 L glass bottles filled with N\textsubscript{2} prior to sampling to preserve the redox condition of the groundwater or subsequently retain Rn for Ra-226 measurement.

(c) 20 L heavy-walled polyethylene bags swept with N\textsubscript{2} and then collapsed prior to filling with samples to be precipitated as BaCO\textsubscript{3} or (U + Nd) fluoride.

3.2. Pre-concentration

For C-14 analysis, concentrated solutions of carbonate-free NaOH and BaCl\textsubscript{2} were added to the sample bag during collection.

For U\textsuperscript{4+} recovery, an acid solution of 1 g of pre-purified NdCl\textsubscript{3} and reduced U-232 yield tracer were added to the bag, followed by 20 mL conc. HF, taking care to avoid the introduction of air. The U-232 tracer was reduced with amalgamated Zn (a Jones reductor).
All other samples were acidified to pH 2 for Dowex 50 or to pH 6 for Hyphan (a proprietary cellulose-based complexing resin, supplier Riedel-de Haen AG, Seelze-Hanover, F.R.G.) and a U-232/Th-228 yield tracer added. The samples were either passed through a 100 mL column of Dowex 50 or allowed to equilibrate with 1 g Hyphan for 24 h. U and Th were recovered from the Dowex 50 column by elution with saturated oxalic acid, and from the separated Hyphan by elution with 1 mol·L⁻¹ HCl.

3.3. Purification

Carbonate and fluoride precipitates were recovered by decantation of the supernatants after a 24 h settling period. The collapsible bags allowed this to be done without exposure to the atmosphere. The final slurring out of the bag was done under a N₂ sweep. CO₂ released from the BaCO₃ with H₃PO₄ was absorbed in Packard “Carbosorb” and the C-14 measured by liquid scintillation counting in a low-background laboratory. It proved difficult to put the (U + Nd) fluoride precipitate into solution without excessive loss of U. The best technique found to date has been a Na₂CO₃ fusion.

Uranium was separated from thorium and the major cations present by adsorption on anion exchange resin from 9 mol·L⁻¹ HCl. Elution in 0.1 mol·L⁻¹ HCl was followed by extraction from saturated NH₄NO₃ into ethyl ether. Thorium was purified by a second anion exchange adsorption from 8 mol·L⁻¹ HNO₃.

3.4. Measurement

Both U and Th were electroplated from 0.04 mol·L⁻¹ ammonium oxalate - 0.16 mol·L⁻¹ HNO₃ solution onto polished stainless steel discs for measurement by α-spectrometry.

Tritium, carbon-14 and Rn-222 were measured by liquid scintillation counting. Tritium measurements had a 10 error of ± 3% with a lower limit of ± 10 TU.

4. RESULTS AND DISCUSSION

4.1. General

Uranium concentrations, U-234/U-238 activity ratios (A.R.) and tritium concentrations measured for surface, shallow and deep groundwater near Chalk River on the Canadian Shield are presented in Table I. The high levels of tritium in some samples result from releases of reactor tritium to the
TABLE I. TRITIUM AND URANIUM ISOTOPE CONTENT OF WATERS OF CHALK RIVER AREA

<table>
<thead>
<tr>
<th>Source</th>
<th>$^3$H concentration (TU)$^a$</th>
<th>$^{238}$U concentration ($\mu$g·L$^{-1}$)</th>
<th>$^{234}$U/$^{238}$U activity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ottawa River</td>
<td>80</td>
<td>0.04</td>
<td>1.3</td>
</tr>
<tr>
<td>Overburden 8 m depth</td>
<td>160</td>
<td>0.24</td>
<td>1.1</td>
</tr>
<tr>
<td>23 m depth</td>
<td>0</td>
<td>0.03</td>
<td>1.2</td>
</tr>
<tr>
<td>Domestic wells 54 m depth</td>
<td>770</td>
<td>0.15</td>
<td>1.1</td>
</tr>
<tr>
<td>71 m depth</td>
<td>10</td>
<td>1.3</td>
<td>2.7</td>
</tr>
<tr>
<td>Bedrock boreholes 18–60 m depth</td>
<td>0–3000</td>
<td>0.02–2.1</td>
<td>1.6–6.2</td>
</tr>
</tbody>
</table>

$^a$ 1 Tritium Unit (TU) = 0.12 Bq·L$^{-1}$.

atmosphere and to some localized groundwaters at this site. This serves to enhance the sensitivity of detecting recently infiltrated surface water in groundwaters. Waters showing major amounts of surface infiltration show little $^{234}$U enhancement. The A.R. of Ottawa River water demonstrates a significant contribution of deep groundwater to the streamflow.

Sampling from well-defined intervals of the bedrock was restricted to the CRNL site where specially drilled boreholes were fitted with packers and sampling lines. In all but one of the 13 boreholes sampled at this site dissolved uranium was less than 1 $\mu$g·L$^{-1}$ below the 20 m level. Under such conditions, one might expect to see recoil-enhanced $^{234}$U with increasing groundwater residence times. The analytical data for samples from 20 intervals of these boreholes are listed in Table II. Data for CR 20, of particular interest, are given in Table III. The $^{234}$U/$^{238}$U activity ratios are plotted vs depth interval in Figure 2.

The results illustrate:

(1) The presence of significant tritium (>20 TU) in most cases. Perhaps the surprising thing is the limited penetration of surface infiltration in view of the extensive fracturing in the area, only the major faults of which are shown in Figure 1.
TABLE II. TRITIUM AND URANIUM IN BEDROCK GROUNDWATERS

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Depth (m)</th>
<th>$^3$H concentration (TU)</th>
<th>U concentration ($\mu$g L$^{-1}$)</th>
<th>$^{238}$U/$^{238}$U activity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>FS 4</td>
<td>8–9</td>
<td>183</td>
<td>2.4</td>
<td>1.4 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>15–16</td>
<td>349</td>
<td>1.4</td>
<td>1.5 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>27–28</td>
<td>161</td>
<td>0.5</td>
<td>1.6 ± 0.08</td>
</tr>
<tr>
<td>CR 7</td>
<td>98–108</td>
<td>0.8</td>
<td></td>
<td>2.1 ± 0.10</td>
</tr>
<tr>
<td>CR 13</td>
<td>85–86</td>
<td>14</td>
<td>0.59</td>
<td>3.7 ± 0.10</td>
</tr>
<tr>
<td>CR 14</td>
<td>32–36</td>
<td>22</td>
<td>0.24</td>
<td>2.6 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>56–62</td>
<td>34</td>
<td>0.57</td>
<td>1.7 ± 0.04</td>
</tr>
<tr>
<td>CR 16</td>
<td>17–20</td>
<td>3070</td>
<td>1.0</td>
<td>1.5 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>35–38</td>
<td>101</td>
<td>0.6</td>
<td>1.9 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>56–62</td>
<td>3865</td>
<td>1.3</td>
<td>2.3 ± 0.10</td>
</tr>
<tr>
<td>CR 18</td>
<td>10–13</td>
<td>73</td>
<td>0.09</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>19–26</td>
<td>3</td>
<td>0.03</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>29–33</td>
<td>7</td>
<td>0.04</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>CR 19</td>
<td>9–16</td>
<td>46</td>
<td>0.38</td>
<td>2.6 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>18–24</td>
<td>23</td>
<td>0.44</td>
<td>3.2 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>28–31</td>
<td>42</td>
<td>0.30</td>
<td>2.7 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>34–41</td>
<td>58</td>
<td>0.20</td>
<td>3.4 ± 0.06</td>
</tr>
<tr>
<td>CR 21</td>
<td>60–65</td>
<td>38</td>
<td>0.28</td>
<td>2.0 ± 0.10</td>
</tr>
<tr>
<td>CR 22</td>
<td>17–20</td>
<td>40</td>
<td>2.3</td>
<td>2.7 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>52–56</td>
<td>39</td>
<td>2.1</td>
<td>2.9 ± 0.03</td>
</tr>
</tbody>
</table>

Precipitation in the area has a concentration of about 500 TU and Lake Maskinonge a concentration of 18 000 TU as a result of drainage from a nearby waste disposal site. Water from the surface or upper strata invariably is carried down to lower levels during drilling and takes considerable time to be flushed out. In most of the holes in Table II, tritium has persisted after extensive pumping and must indicate the continuing influx of a small portion of surface water. CR 20 is self-flowing and flushed itself free of tritium (less than 20 TU) in about two months after having been drilled.
TABLE III. CR 20 ANALYSES

<table>
<thead>
<tr>
<th>Depth interval (m)</th>
<th>E_h (mV)</th>
<th>Dowex 50</th>
<th>Hyphan</th>
<th>Dowex 50 after Hyphan</th>
<th>NdF_3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>U conc. (μg·L⁻¹)</td>
<td>A.R.</td>
<td>U conc. (μg·L⁻¹)</td>
<td>A.R.</td>
</tr>
<tr>
<td>18–21</td>
<td>43</td>
<td>0.02</td>
<td>1.6 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24–27</td>
<td>151</td>
<td>0.30</td>
<td>2.2 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27–30</td>
<td>–</td>
<td>0.05</td>
<td>4.1 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24–33</td>
<td>110</td>
<td>0.06</td>
<td>4.8 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36–39</td>
<td>165</td>
<td>0.08</td>
<td>5.3 ± 0.3</td>
<td>0.08</td>
<td>5.7 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08</td>
<td>5.9 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42–45</td>
<td>26</td>
<td>0.20</td>
<td>6.2 ± 0.2</td>
<td>0.27</td>
<td>5.7 ± 0.3</td>
</tr>
<tr>
<td>42–48</td>
<td>50</td>
<td>0.24</td>
<td>5.9 ± 0.2</td>
<td>0.27</td>
<td>5.7 ± 0.3</td>
</tr>
<tr>
<td>45–48</td>
<td>11</td>
<td>0.32</td>
<td>4.0 ± 0.2</td>
<td>0.26</td>
<td>6.0 ± 0.4</td>
</tr>
<tr>
<td>48–51</td>
<td>71</td>
<td>0.17</td>
<td>4.6 ± 0.2</td>
<td>0.17</td>
<td>5.9 ± 0.4</td>
</tr>
<tr>
<td>57–61</td>
<td>36</td>
<td>0.17</td>
<td>4.6 ± 0.2</td>
<td>0.14</td>
<td>5.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.18</td>
<td>4.6 ± 0.5</td>
<td>0.12</td>
<td>5.8 ± 0.2</td>
</tr>
</tbody>
</table>

^a 50% recovery estimated. For the 57–61 m interval, the data are consistent with the following speciation: total U conc. 0.17 μg·L⁻¹, U^4^ 0.11 μg·L⁻¹; A.R. ~ 6; U^4^ 0.06 μg·L⁻¹; A.R. ~ 2.

(iii) The general occurrence of disequilibrium even in shallow bedrock and in the presence of significant tritium. The conclusion is that the major part of the water sampled has passed through a long flow path and the tritium observed indicates a relatively minor contribution of local surface water.

(iii) A group of waters which shows no tendency for U-234 enhancement beyond the 2.5 to 3.2 A.R. achieved within the first 20 m depth. The absence of a relationship between depth and A.R. suggests that the A.R. has limited value in dating these groundwaters.

(iv) A group of waters, all from CR 20, which shows a rough A.R.-depth correlation and may be useful in studying the development of disequilibrium in this system.
4.2. CR 20 Water Samples

In CR 20, uranium concentrations near surface are the lowest observed (0.02 μg·L⁻¹) but increase gradually with depth. pH values are relatively steady (8.1–8.4). Eₘ values are lower than 160 mV (<100 mV below 39 m), cationic strength increases gradually, while chloride and sulfate increase much more dramatically with depth (<10–40 ppm). High unsupported Rn-222 values indicate considerable gaseous diffusion from this rock mass. The increasing trends of chloride and sulfate are indicators of older waters. While much higher activity ratios were observed in this drill hole than in the others studied, no concomitant decrease in U concentration was observed.

In the course of testing techniques for pre-concentrating U from these very dilute waters, it was found that a slightly different A.R. was obtained using Hyphan than when using Dowex 50. The literature [4] [5] shows Hyphan to adsorb UO₂⁺ much more strongly than Th⁴⁺ or La⁴⁺, suggesting that U⁴⁺ would not be strongly
adsorbed in contrast to the case with Dowex 50. Thus, there was a suggestion that the different species of U in solution might have different A.R.'s and it might be possible to measure them independently. At the E_h values observed below 45 m, uranium should be reduced to the 4+ state [6]; however, the rate of reduction may be very slow at the pH of these waters and UO_2^{2+} and U^{4+} may coexist.

An attempt has been made to isolate the U^{6+} and U^{4+} fractions in these samples in two ways:

(i) Co-precipitation of U^{4+} and a rare-earth fluoride with subsequent collection of U^{6+} from the supernatant on Dowex 50.

(ii) Collection of U^{6+} preferentially on Hyphan, followed by collection of the U^{4+}-enhanced remainder on Dowex 50. The results (Table III), though lacking in precision because of the low concentration of uranium, provide a strong suggestion of a reduced fraction with an A.R. about 2 occurring to the extent of <5% at the 36-39 m and 42-48 m intervals, but as much as 20-35% of the total U present at interval 57-61 m. Since the reduced fraction has an activity ratio so markedly different from that of the larger co-existing U^{6+} fraction, it must have been derived from a source other than in-situ reduction of U^{6+}. The host rock or the fracture-filling materials might contain the necessary leachable supply of uranium in the +4 state.

4.3. CR 20 Fracture-filling Materials

In order to investigate rock-water interactions in the fractures of CR 20, some calcite and clay minerals adhering to fracture surfaces have been selectively leached, and the solutions analyzed for U and Th (Table IV). The depletion of U-234 on the surfaces of the chlorite grains in the oxidizing portion of the system (24 m) indicates that at least some of the enhancement of this isotope in the contacting waters is being contributed by the fracture surfaces. More destructive leaching by aqua regia is believed to have dissolved underlying material that has served as a 'catcher' of U-234 recoiling inwardly from the surface material. Continued feed-in of freshly produced U-234 would prevent the Th-230/U-234 ratio from coming to equilibrium. (If, as suggested by Shirvington [7], surface depletion/interior enhancement of U-234 should be interpreted as reduced leachability of recoil-implanted U-234, it may be argued that the total of all Th-230 recovered should then be equal to the total U-234 found, assuming all U + Th are dissolved).
### TABLE IV. ACTIVITY RATIOS OF FRACTURE-FILLING MATERIALS

<table>
<thead>
<tr>
<th>Location and material</th>
<th>Treatment</th>
<th>U concentration (µg g⁻¹)</th>
<th>²³⁴U/²³⁸U</th>
<th>²³⁰Th/²³⁴U</th>
<th>Mean age (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay minerals, esp. chlorite, removed from fracture surface</td>
<td>9N HCl conc. HCl-HNO₃</td>
<td>10.0</td>
<td>0.55 ± 0.03</td>
<td>1.02 ± 0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>1.5 ± 0.09</td>
<td>0.63 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38 m</td>
<td>0.1N HCl calcite + clay minerals removed from fracture surface</td>
<td>2.0</td>
<td>3.9 ± 0.7</td>
<td>0.179 ± 0.05</td>
<td>20,600 ± 8000 (Th/U)</td>
</tr>
<tr>
<td></td>
<td>1N HCl</td>
<td>0.2</td>
<td>3.4 ± 0.4</td>
<td>0.48 ± 0.05</td>
<td>74,700 ± 16,000 (Th/U)</td>
</tr>
<tr>
<td></td>
<td>9N HCl</td>
<td>7.0</td>
<td>1.05 ± 0.2</td>
<td>&gt; 1.0</td>
<td></td>
</tr>
<tr>
<td>36–39 m</td>
<td>Dowex 50 Water</td>
<td>0.08</td>
<td>5.6 ± 0.3</td>
<td>4640 ± 560 (¹⁴C)</td>
<td></td>
</tr>
<tr>
<td>60 m</td>
<td>Sat(NH₄)₂CO₃ calcite + clay minerals removed from fracture surface</td>
<td>2.0</td>
<td>1.0 ± 0.3</td>
<td>1.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9N HCl</td>
<td>2.0</td>
<td>1.2 ± 0.3</td>
<td>1.2 ± 0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na₂CO₃ fusion whole rock</td>
<td>2</td>
<td>1.2 ± 0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57–61 m</td>
<td>Dowex 50 Water</td>
<td>0.17</td>
<td>4.6 ± 0.2</td>
<td>6580 ± 1140 (¹⁴C)</td>
<td></td>
</tr>
</tbody>
</table>

The groundwater chemistry at the 38 m level indicates it to be a zone of calcite saturation. Undoubtedly, uranium is being incorporated in the surface layer of calcite where re-crystallization is occurring. The calcite shows decreasing uranium activity ratios with increasing degree of dissolution; increasing mean depositional times have been calculated from the Th-230/U-234 ratios measured. The difference that appears to exist between present-day waters and the outer layers of calcite (U-234/U-238 A.R. of 5.6 compared to 3.9) may be indicative of variability in the system during the last 20,000 years, or further proof of direct recoil of decay products across the solid-liquid interface similar to that postulated for the 24 m level.

At the 60 m level, rock-water disequilibrium is even more pronounced. This is a zone of calcite undersaturation, and it is possible that uranium laid down with these fillings is now being added to the waters as the calcites dissolve.
Table V presents estimates of water ages derived from C-14 and Th-230/U-234 measurements where data are available. Usually, Th/U ages for water are considered unreliable because of the high probability for thorium compounds to hydrolyze and precipitate out of solution, but we see agreement with C-14 ages. U-234/U-238 activity ratios of the oxidized fraction have been included for comparison of trends. Above the 48 m level, increasing activity ratios correlate quite well with increasing C-14 and Th-230/U-234 ages; however, at greater depths, even if the A.R.'s for the oxidized portion only are considered, a leveling-off is observed. If UO$_2^{2+}$ addition to the water from calcite dissolution is occurring at this depth, it may be difficult or impossible to separate the 'true' recoil component.

5. SUMMARY

Groundwater enhancement in U-234 is observed in the sub-surface zone (A.R. = 1.5 to 2 at 10-20 m). There is evidence in the fracture coatings of a recoil contribution to this enhancement. In samples containing measurable quantities of tritium, activity ratios rarely rise beyond 3. Where uranium and tritium concentrations are very low, the enhancement increases over a longer depth interval.
Despite the occurrence of reducing conditions \( E_h < 100 \text{ mV} \), \( \text{UO}_2^{2+} \) may continue to exist in such groundwaters if the rate of reduction is very slow. \( \text{U}^{4+} \) may co-exist with \( \text{UO}_2^{2+} \) up to the solubility limit for the reduced state (about 1 \( \mu \text{g} \cdot \text{L}^{-1} \) at pH 8). If this is the case, the contributions to the A.R. by recoil (\( \text{UO}_2^{2+} \)) and leaching (primarily \( \text{U}^{4+} \)) should be separable. However, dissolution of pre-existing calcite deposits may also add \( \text{UO}_2^{2+} \) to the groundwater, and this contribution would be difficult to estimate.

If, as seems likely, the activity ratios measured in older reducing waters result from a combination of recoil, enhanced dissolution, and valence-sensitive processes, with the contribution of each dependent on local conditions, it may not be possible to derive an actual "age" of groundwater from such data. However, a clearer understanding of these contributions will help identify 'old' water at the point of discharge from deep bedrock.

ACKNOWLEDGEMENTS

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REFERENCES

URANIUM ISOTOPES IN A SANDSTONE AQUIFER
Interpretation of data and implications for groundwater dating

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Bergakademie Freiberg,
Freiberg, German Democratic Republic

Abstract

URANIUM ISOTOPES IN A SANDSTONE AQUIFER: INTERPRETATION OF DATA AND IMPLICATIONS FOR GROUNDWATER DATING.

The $^{238}\text{U}$ activity concentration and the $^{234}\text{U}/^{238}\text{U}$ activity ratio have been measured in groundwater from 29 pumping wells of a Triassic sandstone aquifer. Carbonate and iron hydrochemistry as well as environmental isotopes ($^4\text{H}, ^{14}\text{C}, ^{13}\text{C}, ^{222}\text{Rn}$) have been examined. At pH values of about 7 the groundwater is generally unsaturated in calcite. The redox state of the groundwater is indicated by the iron concentration and the $^{222}\text{Rn}$ activity concentration has been used as a qualitative measure of the uranium distribution in the rock matrix. The kinetics of the uranium isotope evolution could be studied on the basis of the $^{14}\text{C}$ model age which covers a range of from a few hundred years to about 17,000 years. Under oxidizing conditions in the recharge area the $^{238}\text{U}$ and $^{234}\text{U}$ activity concentrations exhibit a linear increase of 100 and 150 mBq/L, respectively, during 1000 years. In transition zones, both the $^{238}\text{U}$ and the $^{234}\text{U}$ activity concentrations decrease exponentially according to a relaxation time constant of about 500 years. In reducing groundwater the $^{234}\text{U}$ activity concentration seems to increase according to a relaxation time constant of the order of 10,000 years, while the $^{238}\text{U}$ activity concentration remains at about 5 mBq/L. A phenomenological model for the evolution of the uranium isotopes in groundwater is derived from the transport (dispersion) equation, assuming that the sorption processes affecting $^{238}\text{U}$, $^{234}\text{Th}$ and $^{234}\text{U}$ are of first-order kinetics. On the basis of this model the experimental results are used to evaluate model parameters characterizing quantitatively the kinetics of the uranium isotope evolution in the local groundwater system. The model allows the specification and quantification of conditions concerning the applicability of groundwater dating by the uranium isotopes. From the model equations a generalized formula concerning radioactive (nuclear) groundwater dating by the uranium isotopes is derived which includes the formula for special cases known from the literature.

1. INTRODUCTION

The radioactive disequilibrium between the isotopes $^{238}\text{U}$ and $^{234}\text{U}$ has proved to be a very useful tool in hydrological investigations for identifying water masses, evaluating quantitatively their mixing and characterizing
qualitatively various aspects of groundwater flow regimes [1–3]. In principle, this disequilibrium can be used to determine the residence time of groundwater (groundwater age), provided enough is known about the local geochemistry of the processes affecting $^{238}$U, $^{234}$Th and $^{234}$U. In practice, however, the information concerning the geochemical system is not yet sufficient; therefore, only qualitative groundwater dating is possible at present. This paper is concerned with a study of the evolution of uranium isotopes in groundwater of a Triassic sandstone aquifer in the German Democratic Republic. Carbonate, iron and uranium isotope chemistry as well as the environmental isotopes of the groundwater are examined.

A phenomenological model for the evolution of the uranium isotope disequilibrium in groundwater is presented. On the basis of this model, the experimental results are used to evaluate parameters characterizing the uranium isotope evolution in the local groundwater system. Implications for the problem of groundwater age determination by the uranium disequilibrium are included.

2. THE INVESTIGATION AREA

The particular sandstone aquifer was chosen for this study because it had previously been investigated extensively by hydrogeological, geochemical and isotope hydrogeological methods [4]. The southern boundary of the investigation area (Fig.1) is given by a fault zone. The main flow direction of the groundwater is from south-west to north-east. The sandstone extends vertically over about 210 m. According to single-well radioactive tracer experiments the groundwater flow is practically restricted to the upper layer of about 100 m depth [5]. The flow porosity and the total porosity have values of the order of 0.1% and 10%, respectively. Samples for geochemical, environmental isotope and uranium isotope measurements were obtained from 100–150 m deep wells used for drinking water supply. The perforations of the wells extend almost over their total depth. The groundwater is of meteoric origin, infiltrating in the southern, south-eastern and partly also western regions of the studied area. A confined part of the aquifer, indicated by former artesian wells, extends from south-west to north-east along the main groundwater flow direction (Fig.1).

3. MEASURING RESULTS

The geochemical and environmental isotope investigations of this sandstone aquifer were initiated in the early 1970s. The data summarized in Table I
FIG.1. Position of the groundwater sampling wells (a) and geochemical zones of the studied sandstone aquifer (b).

represent in most cases mean values of several single measurements during this ten-year period. The errors of the tritium and $^{14}C$ values indicated in Table I are mean standard deviations from the average values of the long-term measurements. The environmental isotope measuring techniques used by us are described by Fröhlich et al. [6]. Uranium isotopes have been measured since 1979 [7].
<table>
<thead>
<tr>
<th>Well No.</th>
<th>pH</th>
<th>CO₂</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>Ca²⁺</th>
<th>Fe</th>
<th>δ¹³C</th>
<th>δ¹⁸O</th>
<th>δ³⁴S</th>
<th>δ²⁶⁰U</th>
<th>δ²³⁵U/δ²³⁰U</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>6.7</td>
<td>47</td>
<td>159</td>
<td>30</td>
<td>50</td>
<td>0.2</td>
<td>1</td>
<td>±1</td>
<td>12</td>
<td>30.0±1.1</td>
<td>1.27±0.02</td>
</tr>
<tr>
<td>102</td>
<td>6.9</td>
<td>48</td>
<td>280</td>
<td>24</td>
<td>80</td>
<td>2.3</td>
<td>-16.8</td>
<td>±0.5</td>
<td>4.5±0.5</td>
<td>28.9±1.2</td>
<td>1.12±0.02</td>
</tr>
<tr>
<td>103</td>
<td>6.9</td>
<td>48</td>
<td>280</td>
<td>24</td>
<td>80</td>
<td>2.3</td>
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* Single measurements, ±1 pmc.
4. DISCUSSION

4.1. Groundwater chemistry

The studied groundwaters are calcium bicarbonate dominated (Table 1). They have pH values from 6.6 to 7.4 and are generally unsaturated in calcite. Only two of the chemically analysed groundwaters approach calcite saturation as indicated by the calcite saturation index (Fig. 2).

In the range of the observed pH values and dissolved carbon contents of the groundwater, an abrupt increase of the iron solubility is known to occur when the redox potential changes from the oxidizing to the reducing state [8]. Under reducing conditions in this particular aquifer, iron concentrations in the range of about 1–10 mg/L should be expected. Consequently, the observed iron concentrations above about 1 mg/L clearly indicate reducing conditions. On the other hand, the groundwater is oxidizing if its iron concentration is substantially smaller than 1 mg/L.

According to the results of the iron concentration measurements (Table 1) the investigation area can be subdivided into oxidizing, transition and reducing zones. It should be emphasized that there are at least two spatially separated
oxidizing zones — one in the north-west and the other in the south to south-east part (Fig.1(a)). This situation can be understood as a consequence of the groundwater flow regime (flow direction). The reducing region of this sandstone aquifer generally corresponds to its confined part, while oxidizing groundwaters are found in the uncovered part (Fig.1(b)).

4.2. Environmental isotopes

According to the mean tritium values, which range from less than 1 TU to about 5 TU (Table I), the portion of young water in the groundwater samples is rather small and decreases slightly downflow from the recharge areas. The mean $^{14}$C content of the groundwater decreases considerably in the flow direction.

Besides this spatial change there is also a temporal variation of the environmental isotope content of the groundwater during the investigation period.
Two typical examples — one for rather young groundwater and the other for older groundwater — are shown in Fig. 3. This temporal change is due to the pumping of considerable amounts of groundwater [4]. Regarding the initial $^{14}C$ content of the groundwater, a value of 85 pmc has been obtained, both by plotting the mean $^{14}C$ values for wells 108, 104, 112 as a function of distance from the boundary of the recharge area along the flow direction and by correlating the $^{32}Si$ and $^{13}C$ contents of some groundwater samples [9]. Since there is relatively little change in the carbonate chemistry and no regular variation of the $\delta^{13}C$ values, this initial content of $^{14}C$ can be attributed to all groundwaters of the studied area.

4.3. Dissolved uranium in the sandstone groundwaters

Plotting the iron concentration of the groundwaters as a function of the $^{238}U$ activity concentration, three groups of groundwaters can be distinguished (Fig. 4(a)). The $^{238}U$ activity concentration of group-I groundwaters is very variable and ranges from about 10 to more than 200 mBq/L at low activity
ratios. The iron concentration values do not exceed 0.2 mg/L; thus, these
groundwaters are oxidizing. Group-II groundwaters exhibit a transitional
caracter, with both low uranium content at high activity ratios and high
uranium content at low activity ratios under more or less reducing conditions.
The third group is reducing groundwater, characterized by high iron con-
centration values and low uranium contents at moderate activity ratios.
Obviously, the sandstone aquifer pertains to what Osmond and Cowart call
"reducing barrier-recharge system" [1].

Compared with the $^{238}$U activity concentration of the groundwaters the
$^{222}$Rn activity concentration varies only slightly (Fig.4(b)). Assuming that
$^{238}$U/$^{226}$Ra/$^{222}$Rn equilibrium in the solid phase has been established, the $^{222}$Rn
activity concentration of the groundwater is proportional to the uranium content
of the rock. Therefore, Fig.4(b) suggests a rather uniform uranium content of
the sandstone in the studied area, both in oxidizing and reducing zones. Near
transition from oxidizing to reducing zones, however, the $^{222}$Rn activity con-
centration values of the groundwaters are somewhat higher, obviously because
of uranium accumulation in the solid phase.

In order to study the kinetics of the uranium isotope geochemistry in
the local groundwater system the measured activity concentrations of $^{238}$U and
$^{234}$U have been plotted as a function of the $^{14}$C model age $\tau_C$ (Fig.5). The
$^{14}$C model age used as a measure of the groundwater residence time is obtained
by the expression

$$\tau_C = \frac{1}{\lambda_C} \ln \frac{C_0}{C}$$  \hspace{1cm} (1)

where $\lambda_C$ is the $^{14}$C decay constant, C is the $^{14}$C content of the groundwater and
$C_0$ is the initial $^{14}$C content. Figure 5 demonstrates the following: The activity
concentrations of $^{238}$U and $^{234}$U rapidly increase with residence time when the
groundwater passes a recharge zone where oxidizing conditions prevail. The
increase is in the range of 100–200 mBq/L during 1000 years. With a still longer
residence time the $^{234}$U/$^{238}$U activity ratio approaches 1.0 or even less than 1.0.
Therefore, the preferential leaching of $^{234}$U due to its higher etch-rate constant
seems to be masked by the effect of increasing $^{238}$U content of the rock matrix
when the groundwater approaches a reducing barrier (uranium accumulation zone).

The etch processes diminish and precipitation of the uranium isotopes
becomes the dominating process when groundwater enters the reducing barrier.
Figure 5 suggests that the activity concentration values of $^{238}$U and $^{234}$U decrease
in this transition region according to a relaxation time constant of the order of
1000 years. Consequently, the change of the $^{238}$U activity concentration of
groundwater flowing through a frontal system can be described by a curve like
those shown in the inset of Fig.5. The different curves of the inset represent
frontal systems with different flow times of the groundwater through the
oxidizing zone. This variety of flow times is the reason for the spread of the measuring points for reducing groundwater in the range of 2000–4000 years. The value of the $^{238}$U activity concentration approaches about 5 mBq/L, both in relatively young (2000–4000 years) and in older (15 000 years) reducing groundwaters. Three of the studied older groundwaters have still enhanced $^{238}$U activity concentrations and one of them (well 401) has an iron content of only 0.5 mg/L, suggesting that these groundwaters are derived from transition zones.

When the groundwater has passed the transition zone the value of the $^{234}$U activity concentration is in the range of 5–20 mBq/L for younger groundwater and about 30 mBq/L for 15 000 years old groundwater. Consequently, the $^{234}$U/$^{238}$U activity ratio seems to increase with increasing groundwater residence time in the reducing zone.

5. PHENOMENOLOGICAL MODEL FOR THE URANIUM ISOTOPE EVOLUTION IN GROUNDWATER

5.1. Derivation and general discussion of the model

The model is based upon the transport equation, which in its one-dimensional form can be expressed by:
\[
\frac{\partial a_i}{\partial t} = D \frac{\partial^2 a_i}{\partial x^2} - v_f \frac{\partial a_i}{\partial x} - \lambda_i a_i + \lambda_i a_{i-1} 
\]

(2)

where \( D \) is the dispersion coefficient, \( v_f \) the specific flow rate, \( \lambda_i \) the decay constant of the radionuclide \( i \), and \( a_i \) the activity concentration of radionuclide \( i \) in the groundwater. The subscript \( i-1 \) indicates the radioactive parent nuclide. The activity of the radionuclide \( i \) per unit volume of the porous medium may be written as

\[
a_i = n R_i a_i + a_i^G
\]

(3)

where \( n \) is the porosity of the medium, \( R_i \) the retardation factor and \( a_i^G \) the activity of the radionuclide in the rock per unit volume of the porous medium.

The water/rock interaction is assumed to be characterized by sorption processes of first-order kinetics:

\[
\frac{\partial a_i^G}{\partial t} = -e_i a_i^G + r_i n R_i a_i - \lambda_i a_i^G + \lambda_i a_{i-1}^G
\]

(4)

where \( e_i \) is the solution rate and \( r_i \) the precipitation (removal) rate. With Eqs (3) and (4) the transport equation (2) becomes:

\[
n R_i \frac{\partial a_i}{\partial t} = D \frac{\partial^2 a_i}{\partial x^2} - v_f \frac{\partial a_i}{\partial x} - n R_i (\lambda_i + r_i) a_i
\]

\[+ n R_{i-1} \lambda_i a_{i-1} + e_i a_i^G
\]

(5)

In order to describe the evolution of \(^{238}\text{U}\) and \(^{234}\text{U}\) in groundwater, the differential equation system (5) has to be solved for the \(^{238}\text{U}\) decay series radionuclides \(^{238}\text{U}, ^{234}\text{Th}\) and \(^{234}\text{U}\) under the given initial and boundary conditions.

For the studied sandstone aquifer it can be assumed that a steady state \((\partial a_i/\partial t = 0)\) has been established and dispersion is negligible \([10]\). Assuming furthermore that the parameters of Eq. (5) do not change, the following solutions are obtained:

\[
a_S(\tau) = a_S + (a_{80} - a_S) e^{-K_S \tau}
\]

(6.1)

\[
a_T(\tau) = \frac{E_T + \lambda_T R a_S(\tau)}{R_T (\lambda_T + r_T)}
\]

(6.2)

\[
Y(\tau) = Y_S + (Y_0 - Y_S) e^{-K_S \tau}
\]

(6.3)
where $\tau$ is the groundwater flow (residence) time

$$\tau = \frac{n}{v_f}$$  \hspace{1cm} (7)$$

The following quantities have been used in Eqs (6):

$$K_8 = R_U(\lambda_8 + r_U), \quad K_4 = R_U(\lambda_4 + r_U)$$  \hspace{1cm} (8)$$

$$E_i = e_i a_i^0 / n$$  \hspace{1cm} (9)$$

where the subscripts $i = 8, T, 4$ and $U$ indicate $^{238}U$, $^{234}Th$, $^{234}U$ and uranium, respectively. The subscripts 0 and S indicate initial and saturation values, respectively. $Y$ is the 'generalized $^{234}U$ activity concentration excess' defined by

$$Y(\tau) = a_4(\tau) - \frac{\lambda_T}{\lambda_T + r_T} a_8(\tau)$$  \hspace{1cm} (10)$$

The saturation values are obtained from the expressions

$$a_{8S} = E_8 / K_8 \text{ and } a_{4S} = \bar{E}_4 / K_4$$  \hspace{1cm} (11)$$

where

$$\bar{E}_4 = E_4 + \lambda_4 \cdot R_T \cdot a_{TS}$$  \hspace{1cm} (12)$$

According to Eq.(10) the generalized $^{234}U$ activity concentration excess strongly depends on the removal rate of $^{234}Th$. If $r_T \gg \lambda_T$, $Y(\tau) \approx a_4(\tau)$; and if $r_T \ll \lambda_T$, $Y(\tau) \approx a_4(\tau) - a_8(\tau) = X$, where $X$ is the $^{234}U$ activity excess — a quantity discussed, for instance, by Osmond and Cowart [1].

The derived model allows the following conclusions:

1. Groundwater can, in principle, be dated by the uranium isotopes if the values of the relevant geochemical parameters are known for the local groundwater system (see Eqs (6.1) and (6.3)).

2. Regarding a genuine radioactive dating of groundwater on the basis of the uranium isotopes, a suitable equation can be derived from Eqs (6.1) and (6.3):

$$\tau_U = R_U \tau = \frac{1}{\lambda_4} \ln \left[ \frac{a_4 - a_{8S}}{a_{90} - a_{8S}} \cdot \frac{Y_0 - Y_S}{Y - Y_S} \right]$$  \hspace{1cm} (13)$$
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<td>( A U = A U_0 \cdot \exp (-\lambda_4 t) )</td>
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<td>( X = X_0 + (X_0 - X_0) \cdot \exp (-\lambda_4 t) )</td>
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<td>( A U = A U_0 + (A U_0 - A U_0) \cdot \exp (-\lambda_4 t) )</td>
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<td>( A U = 1 + (A U_0 - 1) \cdot \exp (-\lambda_4 t) )</td>
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</tr>
<tr>
<td>SHIRVINGTON (1980) [17]</td>
<td></td>
<td>( y_T &lt; \lambda_T, a_8 = \text{const.}, A U_L = 1 )</td>
</tr>
</tbody>
</table>

\(^a\) In all cases the following approximation was used: \( \lambda_4 - \lambda_8 \approx \lambda_4 \).

\(^b\) Originally in a linear approximation.
However, also in this case one has to take into account at least the effect of uranium retardation. If the retardation factor is unknown, the uranium model age \( r_U \) has to be regarded as an upper limit of the groundwater 'age' \( r \). Moreover, the practical applicability of Eq.(13) and thus of radioactive groundwater dating with the uranium isotopes requires that the uranium precipitation rate is small compared with the \(^{234}\text{U} \) decay constant. Finally, it should be emphasized that Eq.(13) is related to a groundwater flow corresponding to the piston-flow model.

(3) Equations (6) and (13) seem to represent rather universal uranium isotope dating formulae because they include the dating formulae for special cases known from the literature. In Table II these formulae are compiled and the special conditions of validity in relation to Eqs (6) indicated. Further considerations about dating range, dating accuracy and practical applicability are included in Ref.[18].

(4) If the rate constants \( K_4 \) and \( K_8 \) have (approximately) the same value, a linear relation between \( Y \) and \( a_8 \) is obtained from Eqs (6.1) and (6.3):

\[
Y(a_8) = Y_0 + \frac{Y_0 - Y_S}{a_{80} - a_{8S}} (a_8 - a_{8S})
\]

The relation \( K_4 \approx K_8 \) corresponds to the condition \( r_U \gg \lambda_4 \) (see Eq.(8)). However, also in cases of rather low values of the uranium precipitation rate, an approximately linear relationship between \( Y \) and \( a_8 \) can be expected if the condition \( K_4 r < 1 \) comes true. This condition corresponds to a situation where the groundwater is young compared with the \(^{238}\text{U} \) relaxation time \( 1/K_4 \). Therefore, linear relations, as discussed extensively by Osmond and Cowart [1], can be derived from the model for special cases.

(5) The \(^{234}\text{U}/^{238}\text{U} \) activity ratio of the groundwater reflects the effect of several isotope fractionation mechanisms. According to Eqs (11), (12) and (6.2), the saturation value \( A_{US} = a_4S/a_8S \) can be split into three terms: a leaching term \( (A_U)_L \), a recoil term \( (A_U)_E \) and a production term \( (A_U)_P \):

\[
A_{US} = (A_U)_L + (A_U)_E + (A_U)_P
\]

where

\[
(A_U)_L = (1 - \Delta_4) \frac{e_4}{e_8} \cdot A_{UG}
\]

\[
(A_U)_E = \Delta_T \Delta_4 \frac{e_T \cdot a_T^G}{e_8 \cdot a_{8T}^G} \frac{r_U}{\lambda_T}
\]
\[ AU_p = \Delta_T \Delta_4 \]  

(15.4)

The quantities \( \Delta_i = \lambda_i / (\lambda_1 + \tau_i) \) represent the portion of the radioactive decay of the total corresponding radionuclide removed from the liquid phase.

5.2. Evaluation of model parameters for the sandstone aquifer

In the studied area there are three geochemically homogeneous regions for which the model equations can be used to estimate the values of relevant parameters by means of the experimental data.

5.2.1. Oxidizing zones

Since the oxidizing zones generally correspond to the unconfined parts of the sandstone aquifer and the sampling wells are perforated nearly over their total depth, the problem of residence time distribution of the analysed groundwater has to be taken into account. The exponential residence time distribution function

\[ f(\tau) = \frac{1}{\tau_{EM}} e^{-\tau/\tau_{EM}} \]  

(16)

seems to be quite useful as a weighting function for the \(^{14}\)C and uranium isotope values. From

\[ C = \int_0^\infty C_0 e^{-\lambda_C \tau} f(\tau) \, d\tau \]  

(17)

we obtain the mean residence time of the analysed groundwater as a function of its \(^{14}\)C content:

\[ \tau_{EM} = \frac{1}{\lambda_C} \left( \frac{C_0}{C} - 1 \right) \]  

(18)

which, according to Eq.(1), can be related to the \(^{14}\)C model age. In analogy, from Eqs (6.1), (6.3) and (10) the following relations are obtained:

\[ \bar{a}_8 = a_{80} + a_{8S} K_8 \tau_{EM} \]  

(19)
\[ \bar{a}_d = a_{40} + a_{4S} K_4 - \Delta_T a_{8S} (K_4 - K_8) r_{EM} \]  

(20)

where the conditions \( a_{80} \ll a_{8S} , a_{40} \ll a_{4S} \) and \( K_8 \tau_{EM} \ll 1 \), \( K_4 \tau_{EM} \ll 1 \) have been taken into account. These conditions are realized in the case of young oxidizing groundwaters. Thus, the activity concentration of both \(^{238}\text{U}\) and \(^{234}\text{U}\) should linearly increase with the mean residence time of young oxidizing groundwater. This result derived from the model corresponds to the experimental results shown in Fig.5.

The values of the slopes of \( \bar{a}_d \) and \( \bar{a}_4 \) can be estimated using the experimental data of the oxidizing groundwaters (wells 108, 104, 122). In order to prevent an overestimation of the \(^{238}\text{U}\) solution rate, the groundwater values of well 112 should be excluded because this groundwater is derived from the \(^{238}\text{U}\) accumulation zone. Consequently, a linear regression yields for the slopes of Eqs (19) and (20) 0.10 and 0.15 mBq/L ⋅ a respectively. Considering Eq.(11), the \(^{234}\text{U}\) (etch) solution rate becomes \( E_8 = 0.10 \text{ mBq/L ⋅ a} \). Since \( a_{8S} \) can be assumed to be of the order of 1000 mBq/L or even higher (see Fig.5), \( 1/K_8 \) could be much higher than 10,000 years.

According to Eq.(20) an analogous estimation of the \(^{234}\text{U}\) solution rate requires that the geochemical behaviour of \(^{234}\text{Th}\) in terms of \( \Delta_T \) is known. The results of Hussain and Krishnaswami [19] indicate that \( \Delta_T \ll 1 \). Therefore, the slope of Eq.(20) corresponds to the \(^{234}\text{U}\) solution rate, which thus has a value of \( E_4 = 0.15 \text{ mBq/L ⋅ a} \), i.e. \(^{234}\text{U}\) is preferentially solved by a factor of 1.5 compared with \(^{238}\text{U}\).

5.2.2. Reducing barriers

According to Eqs (6.1) and (6.3) the uranium content of the groundwater should exponentially decrease when the groundwater passes a reducing barrier. The values of the rate constants \( K_8 \) and \( K_4 \), which characterize the decrease of \( a_8 \) and \( a_4 \), respectively, can thus be derived from the experimental data by exponential regression. Figure 5 suggests that the data of the samples from wells 115, 120 and BB should be excluded. Obviously, these groundwaters belong to partial frontal systems, with the groundwater having rather low contents of \(^{238}\text{U}\) and \(^{234}\text{U}\) when entering the reducing barrier.

Since the reducing zones of the studied area correspond to those parts of the aquifer which are generally confined, the piston-flow model (Eq.(1)) provides a proper estimation of the groundwater residence time. Furthermore, an adequate assumption for reducing conditions is \( \Delta_T \ll 1 \) and, thus, \( Y \approx a_4 \). Consequently, the data of wells 103, 113, 114, 117, 118, 124, 201-204 and W yield: \( K_8 = 2.0 \times 10^{-3} \text{ a}^{-1} \) and \( K_4 = 1.8 \times 10^{-3} \text{ a}^{-1} \) for \( a_{8S} = 5 \text{ mBq/L} \) and \( a_{4S} = 15 \text{ mBq/L} \), respectively. Within the accuracy of this estimation, which is not better than 25%, \( K_8 \) and \( K_4 \) have the same value. With Eq.(8) we
obtain $rR \approx 2 \times 10^{-3} \text{ a}^{-1}$, where $R \ll rR/k_4 \approx 700$. Finally, with Eqs (11) and (12) we obtain: $E_a = 0.01 \text{ mBq/L} \cdot \text{a}$ and $E_d \approx 0.03 \text{ mBq/L} \cdot \text{a}$. Therefore, precipitation of the uranium isotopes is the dominating process. Compared with oxidizing zones, the solution rates are one order of magnitude lower, whereby the preferential leaching of $^{234}\text{U}$ corresponds to a factor of three.

5.2.3. Reducing zone

This geochemically homogeneous region is indicated by the groundwaters of wells 115, 116, BB, 204 and 403. Their iron concentrations have the highest values and the $^{238}\text{U}$ activity concentrations the lowest values observed in the studied sandstone aquifer. The $^{234}\text{U}$ activity concentration, however, considerably increases with the $^{14}\text{C}$ model age (see Fig. 6).

Regarding a quantitative interpretation of these data, one has to take into account that the residence time of these waters in the reducing zone is shorter than the value indicated by the $^{14}\text{C}$ model age. Figure 5 suggests that the difference is about 1000 years for the groundwaters of wells 116, 115, BB and 204. In the case of well 403, however, the difference cannot be estimated because of the few measurements in this age range. Therefore, the value of $a_4S$ for pure reducing groundwater of this sandstone aquifer cannot be determined by exponential regression. Assuming that $a_4S$ is in the range of from 30 to 50 mBq/L, we obtain: $K_4 = (2.4 - 1.1) \times 10^{-4} \text{ a}^{-1}$ and $E_d = (7.1 - 5.7) \times 10^{-3} \text{ mBq/L} \cdot \text{a}$. This result
TABLE III. GEOCHEMICAL PARAMETERS OF THE STUDIED SANDSTONE AQUIFER AND OF THE CARRIZO SANDSTONE AQUIFER OF TEXAS (USA)

<table>
<thead>
<tr>
<th>Geochemical zone</th>
<th>$k_a$ (10$^{-3}$ a$^{-1}$)</th>
<th>$k_d$ (10$^{-3}$ a$^{-1}$)</th>
<th>$E_a$ (mBq/L·a)</th>
<th>$E_d$ (mBq/L·a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triassic sandstone aquifer</td>
<td>oxidizing</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.10</td>
</tr>
<tr>
<td>(German Democratic Republic)</td>
<td>transition</td>
<td>2.0</td>
<td>1.8</td>
<td>0.01</td>
</tr>
<tr>
<td>Carrizo aquifer</td>
<td>transition</td>
<td>0.93</td>
<td>2.4</td>
<td>$0.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>(Texas, USA)</td>
<td>reducing</td>
<td>–</td>
<td>0.1–0.2</td>
<td>–</td>
</tr>
</tbody>
</table>

shows that also under purely reducing conditions the rate constant $k_a$ is much higher than the decay constant of $^{234}$U, the factor being in the range of from 80 to 40. Thus, geochemical processes (precipitation and/or retardation) are still of paramount influence on the rate constant, the deciding quantity regarding applications for groundwater age determinations.

The value of the solution rate $E_d$ seems to represent the contribution of the recoil mechanisms to the $^{234}$U delivery because the observed constancy of the $^{238}$U activity concentration (see Fig.6) suggests that the solution rate of $^{238}$U is small compared with that of $^{234}$U.

Concerning the local geochemistry of the uranium isotopes, the studied sandstone aquifer can be compared with other groundwater systems on the basis of the characteristic geochemical parameters. The Carrizo aquifer of Texas (USA) has been very extensively studied both by uranium isotopes [1, 12] and by $^{14}$C [20]. From the published experimental results we could derive the values summarized in Table III. According to these results for both sandstone aquifers the K values of the corresponding geochemical zones are of the same order of magnitude. The solution terms, however, show significant distinctions, reflecting the large difference between the uranium concentration values of the two aquifers (Carrizo aquifer: $a_s \approx 0.1–0.01$ mBq/L).

6. CONCLUSIONS

(1) The uranium isotopes $^{234}$U and $^{238}$U have proved to be both isotopic and geochemical indicators in hydrogeological systems. Geochemical processes of
water/rock interaction play a vital role in the evolution of the uranium isotope content in groundwater.

(2) Using a simplified transport model, it is possible to describe the uranium isotope evolution in sandstone aquifers. Characteristic parameters of this model are the rate constants $K_A$, $K_B$ and the solution terms $E_A$, $E_B$. The rate constants include geochemical parameters (precipitation rate and retardation factor) as well as the corresponding decay constant. If, in a particular aquifer system, dispersion is not negligible, the dispersivity of the porous medium is also implied in the rate constants [10].

The knowledge of these parameters is an important prerequisite for a detailed hydrogeological interpretation of uranium isotope data including groundwater dating. Therefore, as a basis for further hydrogeological application of natural uranium isotopes, these geochemical parameters should be quantified in different aquifer systems.

(3) In order to gain the full information implied in the uranium isotope data a complex investigation, including environmental isotopes ($^{14}C$, $^{222}Rn$) as well as chemical conditions (Eh, $CO_2$), is advantageous. Especially, a combination of such studies with the application of well-established groundwater dating methods is highly recommended. An exact calculation of the generalized $^{234}U$ excess $Y$ requires measurements of the dissolved $^{234}Th$. To determine the portion of the recoil mechanism of the isotopic fractionation in a particular aquifer, the $^{234}Th$ in the sorbed phase should also be measured.

(4) Radioactive groundwater dating by uranium isotopes is possible if the uranium precipitation rate $r_Y$ is at least of the order of $\lambda_4$ or smaller. Such conditions can exist, for example, both in oxidizing zones and in deep reducing zones of sandstone aquifers. A very important prerequisite regarding uranium groundwater dating is the geochemical homogeneity of the aquifer.

(5) The relaxation times in sandstone aquifers are of the order of 1000 years in the transition zone, 10 000 years in the reducing zone, and $>10 000$ years in the oxidizing zone.

(6) The model results have considerable consequences for all applications of uranium isotopes in groundwater systems. For instance, a calculation of groundwater mixing ratios is only possible if the residence time of water in the mixing reservoir is small compared with the relaxation time $1/K$.

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REFERENCES

NOBLE GASES AND STABLE ISOTOPES IN $^{14}$C-DATED PALAEOWATERS FROM CENTRAL EUROPE AND THE SAHARA

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Abstract

NOBLE GASES AND STABLE ISOTOPES IN $^{14}$C-DATED PALAEOWATERS FROM CENTRAL EUROPE AND THE SAHARA.

Noble-gas studies in combination with environmental isotope investigations have been carried out in various aquifer systems in the Federal Republic of Germany and in northern Africa. Recharge temperatures were derived from the dissolved Ar, Kr and Xe content, using the strong temperature-dependent solubility of these noble gases. The noble-gas temperatures of the modern European groundwaters reflect the local mean annual temperatures of today, whereas palaeowaters ($^{14}$C ages > 15,000 years, depleted in $^{18}$O by 10–12%) show 5–7°C lower noble-gas temperatures. For the palaeowaters from the Eastern Sahara ($^{14}$C ages > 20,000 years), the recharge temperatures are only slightly lower (2–3°C) than the actual mean annual temperatures. All groundwaters of $^{14}$C age greater than 10,000 years were found to contain radiogenic helium. Groundwater ages of U(Th)/He derived from the radiogenic helium under the assumption of reasonable uranium and thorium concentrations in the aquifer rock are in general too high compared with the $^{14}$C ages.

1. INTRODUCTION

In recent years, environmental isotope investigations in various regions have yielded significantly lower $\delta^D$ and $\delta^{18}$O values of palaeowaters ($^{14}$C age > 10,000 years) compared with modern local groundwaters [1–5]; this has mostly been interpreted as being caused by cooler climatic conditions at the time of groundwater formation. In some cases, however, the palaeoclimatic interpretation has been doubted and the lower stable-isotope content of old groundwaters has been attributed to altitude effects or to the dominant infiltration of water from heavy rain events having lower $D$ and $^{18}$O contents than the mean annual precipitation (amount effect) [6].

Groundwater recharge temperatures derived from dissolved atmospheric noble gases (He, Ne, Ar, Kr, Xe) can provide valuable additional information for the interpretation of environmental isotope data from palaeowaters. The
noble-gas method first described by Mazor [7] is based on the strong temperature
dependence of the solubility of the heavy noble gases Ar, Kr and Xe. For
instance, the solubility of Xe decreases by a factor of two between 0 and 20°C,
whereas the solubility of Ne shows only a slight temperature variation and can
thus be used as a monitor for entrained air or degassing effects. Recharging
groundwater receives the temperature information when it equilibrates in the
unsaturated zone with the atmospheric noble gases. The temperature derived
from the dissolved noble gases is thus expected to reflect the mean annual soil
temperature above the water level rather than the mean annual temperature of
the atmosphere. After entering the aquifer the temperature information will be
preserved since the hydrostatic pressure overcompensates a possible temperature
increase caused by the geothermal gradient.

The only significant source for noble gases in the aquifer is the uranium and
thorium decay series producing radiogenic helium. The excess helium content
of groundwater can be used to derive U(Th)/He groundwater ages [8, 9]. The
calculation of U(Th)/He ages, however, is very dependent on aquifer parameters
such as rock density, porosity and uranium and thorium content, which are
only poorly known in most cases.

The aim of our study was to gain an understanding of how far δD and δ¹⁸O
in palaeowaters can be used as palaeoclimatic indicators. This is essential if
changes in the atmospheric circulation pattern are to be derived from changes in the
spatial distribution of δD and δ¹⁸O in groundwaters, which has been done for
instance for the continental effect in Saharian palaeowaters [10].

2. NOBLE-GAS DETERMINATIONS

About 40 cm³ of water were sampled in 10 mm copper tubes sealed with
pliers (Imperial Eastman 105ft) after the method of Weiss [11]. In most of the
modern wells the copper tube was connected pressure-tight to a tap at the well
head and samples were taken under pressure to prevent degassing.

In the laboratory, the samples were degassed and about 5% of the gas
fraction was admitted to the inlet system; the remainder was sealed in a glass
ampoule for later ⁴He/³²He analysis. In the inlet system the noble gases were
cleaned by titanium sponge at 800°C and separated by adsorption on activated
charcoal. Measurements were conducted on a 120 mm radius, 60° deflection,
static mass spectrometer (VG Instruments MM1200). Calibration was made by
measuring known amounts of atmospheric air.

Air equilibration temperatures were calculated from the measured noble-gas
concentrations after an altitude correction [12] using the IUPAC solubility
functions [13]. In nearly all samples, air excess corrections had to be made by
subtracting small amounts of noble gases of atmospheric composition [8].
FIG. 1. Recharge temperatures derived from dissolved noble gases plotted against uncorrected 
$^{14}C$ groundwater ages, based on an initial $^{14}C$ content of 85 pmC. Sampling sites in the Federal 
Republic of Germany: Lüchow (•), Kassel (○), Nürnberg (□), southern Bavaria (■), Heidelberg (X), Freiburg (+).

In accordance with the work of Heaton and Vogel [14], we found that air excess is not caused by entrained air during sampling, but is a general phenomenon in groundwater, possibly caused by fluctuations of the water level. The overall precision of the noble-gas temperature determination after air excess correction is $\pm 1^\circ C (2\sigma)$.

Measurements of $^3He/\Lambda He$ were conducted on a 300 mm radius, 90$^\circ$ deflection, static mass spectrometer with a split flight tube (VG Instruments MM3000), specially designed for $^3He$ analysis [15].

3. RESULTS

3.1. Groundwaters from the western part of the Federal Republic of Germany

We have carried out noble-gas studies in different aquifer systems in the Federal Republic of Germany (see map in Fig. 1): A lower Triassic sandstone aquifer in the Kassel region, a crystalline aquifer south of Freiburg, an upper Triassic sandstone aquifer north-east of Nürnberg (all in co-operation with M.A. Geyh, Hannover) and an upper Tertiary aquifer system in southern Bavaria (in co-operation with L. Eichinger and W. Rauert, Neuhäuser). More details on
the environmental isotope work in the latter two aquifer systems are presented in Refs [16, 17]. In addition, some samples from a Tertiary/Quaternary aquifer in Lüchow and a sample from the Heidelberg region have been measured.

In Fig. 1 the results of the noble-gas temperatures for all aquifers are plotted against uncorrected $^{14}$C ages based on an initial $^{14}$C content of 85 pmc. The noble-gas temperatures of the modern groundwaters reflect the actual mean annual temperatures in the respective recharge areas. The lower noble-gas temperatures for the palaeowaters of $^{14}$C ages of $>15,000$ years imply that the soil temperatures in the recharge areas have been lower by 5–7°C compared with the present local temperatures.

As can be seen from Fig. 2, presenting a plot of $\Delta$δD versus groundwater age, the δD values (and $\delta^{18}$O, not discussed here) show a similar pattern. Figure 2 shows that nearly all palaeowaters of late Pleistocene age are depleted in δD by 10–12‰ compared with modern groundwaters. Two groundwaters from the Munich region, however, are depleted by more than 20‰. This might be due to the influence of infiltrated glacial melt water having low δD and $\delta^{18}$O values.

The good correlation between δD and noble-gas temperature which can be expected from Figs 1 and 2 is demonstrated in Fig. 3, where the δD values of the samples from the Nürnberg region are plotted against noble-gas temperature. The slope of the regression line is 1.8‰/°C. In good agreement with the $^{14}$C and
FIG. 3. Plot of δD versus noble-gas temperature for the groundwaters from the Nürnberg region. The slope of the regression line is 1.8‰/°C.

hydraulic data, the correlation between δD and noble-gas temperature has been interpreted to be caused by a two-component mixture of young groundwater leaking through the confining strata and old groundwater formed during the last glacial period [16]. Nevertheless, as mixing is linear both for noble-gas temperature and stable-isotope content, this set of data can be used to establish a relationship between δD of (palaeo)precipitation and mean annual (palaeo)temperature. In doing this, the higher stable-isotope content of the glacial ocean water has to be considered, which has been estimated as δ18O = 0.5–1.5‰ and δD = 4–12‰ [18, 19]. This leads to a higher slope for the δD versus temperature relationship of Fig. 3, which then amounts to 2.4–3.2‰/°C. The δD and noble-gas temperature data for groundwaters from the Bunter Sandstone of the United Kingdom [5, 8] yield a slope of 1.9–3.0‰/°C, which fits quite well into this picture.

It should be mentioned that δD of modern precipitation and atmospheric water vapour in Central Europe shows a quite similar correlation with the local temperature [20]. Compared with this, the δD/temperature relationship used by Dansgaard [21] to calculate mean annual temperatures from the δD and δ18O of palaeowaters underestimates the temperature changes by about a factor of two.

3.2. Saharan palaeowaters

Most of the noble-gas samples from the Sahara originate from artesian wells in the Nubian sandstone system in the Western Desert of Egypt (see map in Fig. 4) [22]. In addition, some samples from eastern Libya, one sample from Algeria (Grand Erg Occidental), and two samples from Nigeria (Chad Basin) have been
FIG. 4. Plot of noble-gas temperature versus $^{14}$C groundwater age for the Saharan groundwaters: Western Desert of Egypt (●), eastern Libya (○), Algeria (Grand Erg Occidental) (□), Nigeria (Chad Basin) (▲).

measured. Figure 4 presents a plot of noble-gas temperature versus $^{14}$C age for the Saharan groundwaters. In contrast to Central Europe, no trend of noble-gas temperatures with $^{14}$C age is found. The 16 samples from Egypt show noble-gas temperatures of between 21.8 and 25.6°C, with a mean value of 23.7°C. The mean annual temperatures of today are between 21.8°C (Bahariya Oasis) and 23.5°C (Kharga Oasis). Contrary to the situation in Central Europe, however, the noble-gas temperatures are not expected to reflect the mean annual air temperatures. The mean annual soil temperature in the Sahara, determining the amount of noble gas dissolved in groundwater, is up to 4°C higher than the corresponding mean annual air temperature, depending on the latitude [23].

This may be caused by the high insolation and the missing heat loss due to evaporation. For Egypt and Libya, one can estimate a soil temperature excess of 2–3°C from the geographical latitude [23], which would imply at most 2–3°C lower mean annual air temperatures at the time of groundwater formation than today.

The samples from Algeria and Nigeria (all of a $^{14}$C age of > 35,000 years) show significantly lower temperatures compared with present values (see Fig. 4). The soil temperature excess can be estimated as 1–2°C for the Grand Erg Occidental and 3°C for the Chad Basin [23]. This results in temperature reductions at the time of groundwater formation of 4–5°C and 8°C, respectively. Moreover, the palaeowaters from the Chad Basin are depleted in δD by 20‰ compared with modern local groundwaters.
3.3. Uranium (thorium)/helium ages

All groundwaters of $^{14}$C ages greater than 1000 years were found to contain more $^4$He than the air equilibrium value after air excess correction. There are two possible sources for excess helium in groundwaters, which can be distinguished by their $^3$He/$^4$He isotope ratio R [24]: crustal helium with a lower $^3$He/$^4$He ratio than the atmospheric value ($R_3 = 1.384 \times 10^{-6}$ [25]) and mantle helium, which is enriched in $^3$He. Crustal helium, the dominant helium component in groundwaters, is produced by the decay series of uranium and thorium in the aquifer rock and has a $^3$He/$^4$He ratio lower than 0.1 $R_3$. Mantle helium, having a $^3$He/$^4$He ratio greater than $R_3$, is important only in geothermal systems. Another source which may alter the $^3$He/$^4$He ratio in groundwater is the tritiogenic production of $^3$He [26], but this is a significant contribution only for young groundwaters containing bomb tritium.

We have carried out $^3$He/$^4$He analyses on some of our samples in order to identify the source of helium in the aquifer. In most cases the excess helium was found to be of crustal origin, only in three samples from Libya significant amounts of mantle helium were found. This might be attributed to the sampling location, which is situated on a fault system at the margin of an African subplate [27].

For helium of radiogenic origin one can calculate the U(Th)/He ages from the excess helium, assuming that all helium produced in the rock is released to the interstitial water:

$$t = \frac{C_{He}}{P_{He}}$$

(1)

where $C_{He}$ is the concentration of radiogenic helium and $P_{He}$ is the helium production rate determined by:

$$P_{He} = \rho \cdot p^{-1} \cdot (1.19 \times 10^{-13} \cdot C_U + 2.88 \times 10^{-14} \cdot C_{Th})$$

(cm$^3$STP·a$^{-1}$ per cm$^3$H$_2$O) [8]

(2)

where $\rho$ is rock density (g·cm$^{-3}$), $p$ is fractional porosity, $C_U$ is uranium content of the rock (ppm) and $C_{Th}$ is thorium content of the rock (ppm).

Typical values of the above parameters for a sandstone ($\rho = 2$ g·cm$^{-3}$, $p = 0.3$, $C_U = 3$ ppm, $C_{Th} = 12$ ppm) result in a production rate of $P_{He} = 5 \times 10^{-12}$ cm$^3$ STP per gram H$_2$O and year. The calculation of the helium production rate (Eq. (2)) is very dependent on the aquifer radioelement content and porosity. Since it is not possible to derive values of these parameters which are representative for the aquifer, U(Th)/He groundwater ages will always bear an uncertainty of more than a factor of two.

Our helium results are plotted in Fig. 5 against uncorrected $^{14}$C ages. The two straight lines are for U(Th)/He ages = $^{14}$C ages calculated from reasonable
values of aquifer parameters ($\rho = 2 \text{ g cm}^{-3}, \rho = 0.3$) for two values of radioelement content (lower line: $C_\text{U} = 3 \text{ ppm}, C_\text{Th} = 12 \text{ ppm}$; upper line: $C_\text{U} = 15 \text{ ppm}, C_\text{Th} = 60 \text{ ppm}$). Although there is a tendency of an increase with $^{14}\text{C}$ age, most of the data points in the diagram are above the upper line; this cannot be explained by varying porosity and density and/or higher radioelement content. Even in the case of the upper Triassic aquifer north-east of Nürnberg, where we have measured uranium concentrations in arcosic inclusions of up to 700 ppm, the high radioelement content cannot explain the helium excess values of up to $10^{-5} \text{ cm}^3 \text{ STP per gram H}_2\text{O}$.

Another mechanism must be responsible for the high helium concentration in most of the groundwaters. Of course, strong dispersive mixing of young groundwaters and very old groundwaters (age > 100 000 years) that had accumulated helium could explain the discrepancy between U(Th)/He ages and $^{14}\text{C}$ ages. The distinct differences in $\delta^D, \delta^{18}\text{O}$ and noble-gas temperatures between young groundwaters and old palaeowaters, however, contradict such effective mixing. Moreover, there are nearly no differences in $\delta^D, \delta^{18}\text{O}$ and noble-gas temperatures in palaeowaters from the same region having helium excess values different by nearly two orders of magnitude. A possible explanation could be
the admixture of helium from deeper layers of the aquifer, where the concentration must be higher in order to drive the transport of helium degassing from the crust through a more or less stagnant pore water. Regional discontinuities in the aquifer causing variable vertical dispersion coefficients would thus be responsible for the highly fluctuating helium concentrations. Of course, preferential crustal degassing along basement fault zones [28] could also cause the spatial variability of excess helium in groundwater.

4. CONCLUSIONS

It has been shown that recharge temperatures derived from dissolved atmospheric noble gases in groundwater may give valuable information supporting the palaeoclimatic interpretation of differences in δD and δ18O between young groundwaters and palaeowaters from the same region. The relationship between mean annual temperatures deduced from noble gases and δD, δ18O of (palaeo)-precipitation was found to be very similar to δD versus temperature correlations for actual precipitation based on the seasonal temperature variations.

Groundwater ages of U(Th)/He derived from the content of radiogenic helium were in general too high compared with 14C ages. This discrepancy cannot be explained as being caused by higher radioelement content in the aquifer rock or by mixing processes.

ACKNOWLEDGEMENTS

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The noble-gas and 14C data from eastern Libya are preliminary results from an environmental isotope study in co-operation with the University of Benghazi, which is still under way. The authors are grateful to the Libyan authorities for the permission to present these data here.

Special thanks are due to K.H. Fischer who performed the 3He/4He measurements, and to C. Junghans who ran most of the D and 18O measurements. A. Mangini carried out the uranium and thorium measurements on the arcose inclusions from the Nürnberg region.

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REFERENCES


GROUNDWATER AGE DETERMINATION
AND RELATED PROBLEMS

(Session VI)
Chairman

J.A.P. SARROT-REYNAULD
France
THE GEOCHEMISTRY OF THE UITENHAGE ARTESIAN AQUIFER
Carbonate solution in a closed system

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Abstract
THE GEOCHEMISTRY OF THE UITENHAGE ARTESIAN AQUIFER: CARBONATE SOLUTION IN A CLOSED SYSTEM.
Isotopic and chemical data are presented from a detailed investigation of groundwater in the recharge area and in a confined artesian section of a quartzite aquifer near Uitenhage, South Africa. The recharge water has a very low pH and alkalinity and contains inorganic carbon derived only from the solution of gaseous soil CO₂. Downflow, in the confined section, a progressive increase in pH and alkalinity reflects the gradual solution of rock carbonate in an environment where there is no carbon exchange with the atmosphere. The groundwater chemistry in this aquifer therefore represents an unusual example of carbonate solution in a closed system. In addition, the water remains undersaturated with respect to carbonate. The interpretation of the ¹³C and ¹⁴C data is therefore greatly simplified. Carbon-14-derived ages are found to increase systematically downflow, up to 28,000 years, and a flow rate of 0.76 m/a is established. On this basis the water resources are estimated and it appears that <3% of the total recharge flows into the confined section of the aquifer; the remainder issues from springs at the edge of the recharge area.

1. INTRODUCTION

Information on the age of groundwater is of considerable value in a variety of studies, and ¹⁴C dating is the most widely used technique. The reliability of this method, however, is commonly hindered by two factors: (1) the difficulty of obtaining an uncontaminated sample from the aquifer being investigated (the apparent ¹⁴C age of old groundwater can be significantly affected if contaminated by very young groundwater), and (2) the lack of information on the development of the carbon chemistry (this has an important bearing on the interpretation of ¹⁴C data).

Artesian aquifers with free-flowing boreholes provide ideal conditions for the collection of uncontaminated samples. The only extensive aquifer of this type in South Africa is situated near Uitenhage (Fig. 1), and its boreholes and springs represent an important water supply for the town and rural community. In order
to safeguard this supply, the aquifer was declared part of a control area. A preliminary 14C investigation was conducted by Vogel [1]. The close linear relationship of 14C age versus distance that was found suggested that sampling of uncontaminated water was possible in this aquifer. In addition, it was discovered that the water had an unusual carbon chemistry which might be amenable to detailed interpretation.

The chemistry of the Uitenhage groundwater is examined here with particular emphasis on the carbon chemistry, and 13C and 14C contents. It is demonstrated that in this aquifer the carbonate dissolves very slowly and that this occurs in a closed system. The progress of this reaction, which is usually quite rapid in nature, can easily be followed here along the subsurface path of the water. A fairly simple interpretation of the 14C data is therefore possible. Subsequent calculation of the 14C ages enables the natural recharge rate within the aquifer to be evaluated and will also form the basis of investigations of the uranium-series geochemistry and palaeoclimate (papers in preparation).
2. STUDY AREA

The study area shown in Fig. 1 has been described previously [2–4]. Fractured, northward dipping Ordovician quartzite of the Table Mountain Group, representing the northern limb of an anticline, is exposed on the high ground around the town of Uitenhage. To the east of this outcrop area the quartzites are unconformably overlain by sandstones and shales of the Upper Jurassic/Lower Cretaceous Uitenhage Group, generally less than 300 m thick. Small 'hills' on the pre-Cretaceous weathering surface of the quartzite are represented by small isolated outliers piercing the Uitenhage Group (Fig. 1).

Fracturing and pre-Cretaceous weathering of the quartzite render it a permeable aquifer, with the groundwater maintained under pressure by the relatively impermeable sediments of the Uitenhage Group. Some phreatic water is extracted from local permeable horizons in the Uitenhage Group, but this study is concerned with the artesian water from the underlying quartzite.

Free-flowing boreholes, with the small natural flow sometimes augmented by pumping, tap the artesian water between the edge of the quartzite outcrop and the Indian Ocean. The most important supply of water from the quartzite, however, comes from the Uitenhage Springs at the edge of the outcrop area (located at sampling points 3, 9, 16 and 20, Fig. 1). Up to 1910 the Springs discharged at 7000 m$^3$/d, but this has since been reduced by half because of drilling in the aquifer [2, 4].

The southern boundary of the artesian aquifer is formed by the Uitenhage fault, to the south of which the Uitenhage Group is more than 1000 m thick (Fig. 1). A steeply dipping contact between the quartzites and overlying shales of the Bokkeveld Group essentially defines the northern boundary of the aquifer.

3. METHODS

Groundwater samples were collected in 1969, 1978 and 1981 from boreholes in the quartzite outcrop area, the Springs at the edge of the outcrop, and from free-flowing and pumped artesian boreholes in the confined section of the quartzite aquifer (Fig. 1 and Table 1).

Carbon-14 analyses were done using standard methods [5]. The total dissolved inorganic carbon (C$_T$ = CO$_2$ + HCO$_3$ + CO$_3^-$) and dissolved oxygen content of the water was extracted in the laboratory from vacuum flasks filled at the borehole [6]. Their concentrations and $^{13}$C/$^{12}$C ratio were measured by manometry and mass spectrometry.

The major ions were measured in the laboratories of the National Institute for Water Research in Pretoria. The pH and alkalinity were measured in the field immediately after collection of the sample. Low alkalinite (<0.5 meq/L) are
### TABLE I. BOREHOLE DETAILS AND ISOTOPIC RESULTS

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<th>$^{13}$C (‰ NBS)</th>
<th>Tritium (TU ± 1)</th>
<th>$^{14}$C (‰ PDB)</th>
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<td>24 600</td>
<td>21 100</td>
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</table>

¹ Artesian (Art) or phreatic (Phr) borehole, either pumped (pu) or free flowing (ff) or spring (spr).
² $^{13}$C measurement on CO₂ extracted for $^{14}$C measurement: less accurate than $^{13}$C measurement on extractions done from vacuum flasks.
³ Age corrections done as described in text.
### TABLE II. CHEMICAL PARAMETERS

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<th>pH</th>
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<th>O\textsubscript{2} (mg/L)</th>
<th>Ca (meq/L)</th>
<th>Mg (meq/L)</th>
<th>Na (meq/L)</th>
<th>K (meq/L)</th>
<th>Alk (meq/L)</th>
<th>SO\textsubscript{4} (mg/L)</th>
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<td>0.26</td>
<td>1.15</td>
<td>0.14</td>
<td>0.93</td>
<td>8.2</td>
<td>-2.5</td>
</tr>
<tr>
<td>UH 13b</td>
<td>-</td>
<td>-</td>
<td>2.02</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>UH 14</td>
<td>345</td>
<td>5.72</td>
<td>1.60</td>
<td>3.3</td>
<td>0.20</td>
<td>0.32</td>
<td>1.61</td>
<td>0.0</td>
<td>0.34</td>
<td>0.14</td>
<td>2.08</td>
<td>5.0</td>
<td>-3.9</td>
</tr>
<tr>
<td>UH 15</td>
<td>455</td>
<td>5.55</td>
<td>2.18</td>
<td>0.5</td>
<td>0.24</td>
<td>0.74</td>
<td>2.83</td>
<td>0.05</td>
<td>0.31</td>
<td>0.50</td>
<td>3.35</td>
<td>5.8</td>
<td>-4.0</td>
</tr>
<tr>
<td>UH 16</td>
<td>139</td>
<td>4.76</td>
<td>1.14</td>
<td>4.1</td>
<td>0.20</td>
<td>0.17</td>
<td>0.74</td>
<td>0.0</td>
<td>0.03</td>
<td>0.06</td>
<td>0.85</td>
<td>5.5</td>
<td>-5.8</td>
</tr>
<tr>
<td>UH 17</td>
<td>317</td>
<td>6.53</td>
<td>1.08</td>
<td>0.1</td>
<td>1.25</td>
<td>0.33</td>
<td>1.22</td>
<td>0.27</td>
<td>1.24</td>
<td>0.10</td>
<td>0.87</td>
<td>9.2</td>
<td>-1.6</td>
</tr>
<tr>
<td>UH 18</td>
<td>492</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
<td>0.08</td>
<td>4.78</td>
<td>0.10</td>
<td>2.76</td>
<td>0.23</td>
<td>2.00</td>
<td>2.00</td>
<td>8.3</td>
<td>-</td>
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<tr>
<td>UH 19</td>
<td>206</td>
<td>6.58</td>
<td>1.70</td>
<td>0.2</td>
<td>0.30</td>
<td>0.33</td>
<td>1.13</td>
<td>0.22</td>
<td>1.09</td>
<td>0.08</td>
<td>1.04</td>
<td>20.0</td>
<td>-2.3</td>
</tr>
<tr>
<td>UH 20</td>
<td>126</td>
<td>4.61</td>
<td>1.31</td>
<td>3.9</td>
<td>0.10</td>
<td>0.17</td>
<td>0.87</td>
<td>0.03</td>
<td>0.02</td>
<td>0.04</td>
<td>0.82</td>
<td>5.5</td>
<td>-6.4</td>
</tr>
<tr>
<td>UH 21</td>
<td>240</td>
<td>6.69</td>
<td>2.24</td>
<td>0.2</td>
<td>0.35</td>
<td>0.17</td>
<td>1.96</td>
<td>0.29</td>
<td>1.60</td>
<td>0.04</td>
<td>0.86</td>
<td>8.1</td>
<td>-1.8</td>
</tr>
<tr>
<td>UH 22</td>
<td>704</td>
<td>7.15</td>
<td>2.60</td>
<td>0.1</td>
<td>0.70</td>
<td>0.17</td>
<td>5.74</td>
<td>0.21</td>
<td>2.29</td>
<td>0.48</td>
<td>3.79</td>
<td>8.3</td>
<td>-1.0</td>
</tr>
<tr>
<td>UH 23</td>
<td>3 210</td>
<td>-</td>
<td>-</td>
<td>14.5</td>
<td>16.1</td>
<td>50.0</td>
<td>1.09</td>
<td>4.92</td>
<td>5.00</td>
<td>57.5</td>
<td>9.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UH 24</td>
<td>736</td>
<td>6.31</td>
<td>3.90</td>
<td>0.9</td>
<td>2.20</td>
<td>1.16</td>
<td>5.48</td>
<td>0.0</td>
<td>2.36</td>
<td>0.63</td>
<td>6.20</td>
<td>5.3</td>
<td>-1.3</td>
</tr>
<tr>
<td>UH 25</td>
<td>642</td>
<td>5.96</td>
<td>2.86</td>
<td>1.9</td>
<td>1.65</td>
<td>0.91</td>
<td>5.22</td>
<td>0.09</td>
<td>0.85</td>
<td>0.50</td>
<td>4.06</td>
<td>5.7</td>
<td>-2.4</td>
</tr>
<tr>
<td>UH 26</td>
<td>278</td>
<td>6.52</td>
<td>2.01</td>
<td>0.1</td>
<td>0.50</td>
<td>0.50</td>
<td>1.94</td>
<td>0.14</td>
<td>1.21</td>
<td>0.13</td>
<td>1.47</td>
<td>5.3</td>
<td>-2.1</td>
</tr>
<tr>
<td>UH 27</td>
<td>731</td>
<td>8.77</td>
<td>2.53</td>
<td>0.2</td>
<td>0.40</td>
<td>0.0</td>
<td>7.22</td>
<td>0.06</td>
<td>2.61</td>
<td>0.44</td>
<td>4.18</td>
<td>7.7</td>
<td>+0.3</td>
</tr>
<tr>
<td>UH 28</td>
<td>265</td>
<td>6.70</td>
<td>1.59</td>
<td>2.8</td>
<td>0.90</td>
<td>0.98</td>
<td>1.30</td>
<td>0.15</td>
<td>1.11</td>
<td>0.02</td>
<td>1.01</td>
<td>3.7</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

difficult to measure accurately. In these cases, alkalinity was calculated from the pH and C\textsubscript{T} [7]. The saturation index of the water [8] with respect to calcite (SI) was calculated using

\[
SI = \log_{10}[Ca^{2+}] [CO_3^{2-}] - \log_{10}K_{sp}
\]

where \(K_{sp}\) is the solubility product of calcite.

### 4. RESULTS

Chemical and isotopic data are presented in Tables I and II. Groundwater from the main central sampling profile of the aquifer is characterized by low
salinity — a feature found in water from the Table Mountain Group in other areas [9]. In contrast, higher salinities are found in groundwater from the northern edge of the sampling area (e.g. UH 15, 22 and 27; Fig. 1). It was shown earlier that the predominant direction of groundwater is from the quartzite outcrop area south-eastwards towards the ocean [11]. The present discussion of the chemical evolution of the water will therefore concentrate on the samples which were collected along the main sampling profile, with low salinities (i.e. <200 μS/cm in the west and <300 μS/cm in the east). These are in a line from the Springs UH 3, 9, 16 and 20 towards UH 21 (Fig. 1).

5. CHEMICAL DEVELOPMENT OF THE ARTESIAN GROUNDWATER

The changes in groundwater chemistry in the direction of flow are shown in Figs 2 and 3. Water in the quartzite outcrop area has an unusually low pH (<5)
at the Springs and no alkalinity (<0.03 meq/L). Downflow, the pH rises to about 6.5 and the alkalinity rises likewise to about 2 meq/L. The calcite saturation (SI) also gradually increases (Fig. 2), but nowhere is complete saturation reached (max. SI = −1). These changes are mirrored by an increase in the $^{13}$C/$^{12}$C ratio of the dissolved inorganic carbon ($C_T$) from −21 to −16%. The slow progressive increase of alkalinity is supported by an increase in Na and to a lesser extent K. The other ions, Ca, Mg, SO$_4$ and Cl, show little change in the course of groundwater flow.

5.1. Carbonate chemistry

The very low pH and negligible alkalinity of the groundwater in the quartzite outcrop area, as illustrated by the chemistry of the Uitenhage Springs (UH 9, 16 and 20), indicate that virtually no carbonate solution occurs during recharge in the unconfined section of the quartzite aquifer. The inorganic carbon, $C_T$, 

FIG. 3. Hydrochemical development of the low-salinity groundwater.
which is present is derived only from CO$_2$ in the soil atmosphere and ranges between 1.1 and 1.4 mmol/L (Table II).

Solution of carbonate, reflected by increasing alkalinity and pH, only starts to occur in the confined section of the aquifer (Fig. 2) where the groundwater is no longer in chemical contact with soil atmospheric CO$_2$. It would therefore appear that this aquifer represents an unusual model situation illustrating closed system carbonate solution [10]. The chemical data are quantitatively interpreted as follows.

Let $C_0$ be the inorganic carbon initially dissolved in the recharge water from soil CO$_2$, and let $C_L$ be the carbon later added to the water owing to limestone solution. Then for any water sample:

$$ C_T = C_0 + C_L $$

Limestone is dissolved by the reaction

$$ CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^- $$

with a similar reaction for the CO$_3^{2-}$ ion. It follows that half the alkalinity, $a$, is derived from limestone carbon and thus

$$ C_0 = C_T - a/2 $$

The data for $C_T$ and $a$ in Table II therefore allow the calculation of $C_0$ using the closed-system assumption. For the low-salinity samples throughout the aquifer, $C_0$ is between 1.1 and 1.5 mmol/L. These calculated $C_0$ values correspond to those actually measured in the recharge water (UH 9, 16 and 20) and imply CO$_2$ partial pressures of 3–4.5% in the soil atmosphere of the recharge area.

When interpreting the $^{13}$C data, let $\delta_0$, $\delta_L$ and $\delta_T$ be the corresponding $^{13}$C contents of the inorganic carbon components. Carbon-13 mass balance requires

$$ \delta_T C_T = \delta_L C_L + \delta_0 C_0 $$

from which

$$ \delta_T = \frac{C_0}{C_T} (\delta_0 - \delta_L) + \delta_L $$

A plot of $\delta_T$ as a function of $1/C_T$ should therefore show a straight line and have $\delta_L$ as an intercept [11]. This is illustrated in Fig. 4, where a relation is shown and a $^{13}$C value of about $-12\%$ for the added carbonate is suggested.
FIG. 4. Relation between the $^{13}$C content and the inverse of the dissolved inorganic carbon content ($C_T$). (For sample symbols, see caption to Fig. 1.) S denotes points presumed to result if the high-oxygen Uitenhage Springs (UII 9, 16, 20) were to convert the dissolved oxygen to additional CO$_2$. The broken lines represent least-squares approximations through solid circles only (I) or through solid and open circles (II).

In this carbon mass balance the fate of the dissolved oxygen in the water may be relevant. The recharge waters all contain about 4 mL C per litre oxygen, but virtually none is in the confined water (Table II). This is a common phenomenon presumed to be due to the oxidation of sulphur or carbon compounds by biological means in the water [12]. A slight increase in sulphate is in fact observed downflow of the Springs, but it is not sufficient to account for all of the oxygen removal. It is therefore likely that some CO$_2$ is produced by this means downflow of the Springs. Corrections of 0.17 to 0.20 mmol/L have therefore been made to the $C_T$ values of the Spring samples in Fig. 4. It was assumed that this additional carbon was derived from vegetation of the area and therefore would have the same $^{13}$C content as the bulk of the dissolved CO$_2$.

5.2. Major ions in the water

It might be expected that the solution of carbonate downflow would cause not only the observed increase in alkalinity but also an increase in calcium or magnesium. The Ca and Mg concentrations, however, remain fairly constant and the alkalinity increase is in fact more or less matched by an increase in both Na and K (Fig. 3). Such a feature is normally ascribed to ion exchange whereby Ca and Mg replace and release Na and K from clay minerals [13]. This
TABLE III. DISSOLVED OXYGEN AND IRON CONTENT OF THOSE BOREHOLE WATERS ON WHICH THE LATTER WAS MEASURED

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Fe</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(µg/L)</td>
<td>(mL/L)</td>
</tr>
<tr>
<td>UH 4b</td>
<td>&lt;25</td>
<td>0.1</td>
</tr>
<tr>
<td>7b</td>
<td>&lt;25</td>
<td>0.0</td>
</tr>
<tr>
<td>8b</td>
<td>370</td>
<td>0.2</td>
</tr>
<tr>
<td>9</td>
<td>&lt;25</td>
<td>4.7</td>
</tr>
<tr>
<td>10</td>
<td>&lt;25</td>
<td>1.1</td>
</tr>
<tr>
<td>11</td>
<td>&lt;25</td>
<td>0.7</td>
</tr>
<tr>
<td>12</td>
<td>1700</td>
<td>0.1</td>
</tr>
<tr>
<td>13a</td>
<td>55</td>
<td>0.5</td>
</tr>
<tr>
<td>14</td>
<td>40</td>
<td>3.3</td>
</tr>
<tr>
<td>15</td>
<td>&lt;25</td>
<td>0.5</td>
</tr>
</tbody>
</table>

process is unlikely to occur in the almost pure quartzite of the aquifer, but might take place if the water were in sufficient contact with shaley sediments of the overlying Uitenhage Group. Even then, it is not clear which geochemical control maintains the Ca and Mg concentrations at their near-constant levels throughout the flow history of the water.

The dissolved iron content of the artesian water is quite low, both in the oxidized and reduced water (Table III). The few high Fe values measured are probably caused by corrosion of old steel borehole casings and are of no geochemical significance.

5.3. Calculation of $^{14}$C ages

There is a large range of $^{14}$C concentrations, from 87% in the Springs to less than 2% in the south-east section of the aquifer. On the basis of the above model for the evolution of the carbon chemistry the $^{14}$C data are used to derive the groundwater age in the following manner.

Carbon-14 measurements are made on the total carbon, $C_T$. This represents:

1. the original dissolved soil gas CO$_2$, $C_0$, with an initial $^{14}$C content of 100%;
2. carbonate (0% $^{14}$C) from the aquifer, = a/2. Mass balance requires

$$A_0 e^{-\lambda t} \cdot (C_T - \frac{a}{2}) + 0 \cdot \frac{a}{2} = A \cdot C_T$$

or

$$A = A_0 e^{-\lambda t} \cdot \frac{C_T - \frac{a}{2}}{C_T}$$

(4)
where $A$ is the measured $^{14}$C activity, $A_0$ is the initial activity of the soil CO$_2$ (= 100%), $\lambda$ is the $^{14}$C decay constant (based on a half-life of 5568 years) and $t$ is the groundwater age (years).

It was noted above that a maximum of $\sim$0.2 mmol CO$_2$/L might be produced during removal of the dissolved oxygen from the groundwater. If this process involved oxidation of organic carbon in the aquifer with 0% $^{14}$C, the ages calculated from the above equation would be too young by up to 1600 years. A more likely source for the carbon, however, would be dissolved organic carbon in the water, which would presumably have an initial $^{14}$C content of 100%. This would require no correction to the above equation.

Equation (4) was proposed by Ingerson and Pearson [14], but fell into disrepute with the realization that isotopic exchange between soil gas and groundwater in an open system has an important influence on the $^{14}$C content of the water [15]. These exchange complications do not arise in the closed-system environment in which carbonate solution takes place, as in the Uitenhage aquifer. The ages are therefore calculated using Eq. (4), and are shown in Table I and used in the discussion. The corrections due to limestone dilution range up to 4000 years for the confined water. Where the artesian water appears 'contaminated' with higher-salinity water from above the aquiclade, larger corrections are manifested, resulting in younger ages (e.g. UH 8b and 22).

Some $^{14}$C measurements performed on samples collected in 1969 were later repeated on samples collected in 1978 and 1981. The reproducibility of samples 4, 6 and 7 seems quite good. UH 8 was sampled three times, with rather varying results (Table I). The water from this borehole had a slightly higher salinity than that typical of water from the central part of the sampled profile. It seems likely that a leaky casing may have allowed a small amount of higher-salinity younger water, from the overlying Uitenhage Group sediments, to mix with the slow-flowing artesian discharge in the borehole. The lowest $^{14}$C content measured for UH 8 is therefore considered the most reliable.

The quantitative reliability of the ages calculated in Table II is supported by $^{18}$O data, in that the $^{18}$O/$^{16}$O ratios of the post-10 000-years-BP groundwater are higher than those in the older water which recharged during the last ice-age (Talma, unpublished data). This effect, moreover, is found not only for the lower-salinity water from the main central profile of the sampled area but also for the higher-salinity water from the northern edge of the area.

6. GROUNDWATER FLOW PATTERN

The $^{14}$C-derived ages are plotted in Fig. 5 as a function of the distance of the sample from the edge of the main quartzite outcrop. The samples may be discussed in two groups.
FIG. 5. Carbon-14-derived ages of the Uitenhage groundwater as a function of the distance of the samples from Uitenhage Springs towards the Indian Ocean (symbols as for Fig. 1). A flow rate of 0.76 m/a is derived from the low-salinity water (solid circles).

6.1. Main central profile

The majority of samples were collected along a central sampling profile and show a close linear age/distance relationship, indicating a flow rate of 0.76 m/a (solid circles in Fig. 5). This linearity suggests that those physical properties of the aquifer which determine the flow rate (width, thickness and porosity) are relatively constant over the sampled length of 25 km and that a constant recharge has been maintained. In addition, the linearity implies no significant mixing of younger phreatic water from the overlying Uitenhage Group with the confined water in the quartzite.

The youngest samples in this group, which are less than 2000 years old, suggest that the recharge area is within the main quartzite outcrop area about 5–10 km north of the town of Uitenhage (i.e. in the vicinity of UH 14 and 24, Fig. 1).

6.2. Northern and fault boreholes

Samples from the upper reaches of the Coega river, near the northern edge of the quartzite outcrop area (UH 15, 25, 27 and 28, Fig. 1), tend to show relatively high ages in terms of their distance away from the quartzite outcrop
(crosses in Fig. 5). The data could imply that these samples are derived from recharge areas further away.

Alternatively, these samples may be derived from the same recharge area as those of the main profile, but represent northward flow at a slower rate. The permeability of the aquifer quartzite is due to fracturing, and hydrological evidence suggests that the fracture planes are aligned in the same, approximately east-west direction as the faults and fold-axes in this area [3, 4]. Permeabilities and groundwater flow rates can thus be much lower in a north-south direction.

Two samples were collected from boreholes close to, or tapping, the Uitenhage fault (UH 17 and 26, Fig. 1). The high age of UH 26 may reflect the same factors as those influencing the age of the northern samples. The low age of UH 17 (for instance relative to neighbouring UH 8, Figs 1 and 5) may reflect a higher permeability and flow rate along the fault.

6.3. Phreatic boreholes

Three boreholes (UH 10, 18 and 23) have been sampled from the Uitenhage Group, the lower part of which forms the aquiclude. These waters contain predominantly NaCl with varying amounts of other ions, producing a much more saline water. The relatively high age of UH 10 (10 850 years) and its high helium content, similar to that of UH 7 close by (Heaton, unpublished measurements), suggest that leakage into the 'aquiclude' does occur. This is a common problem, the aggressive artesian water having already corroded many steel casings of boreholes sunk as early as 1912. Not enough chemical data could be collected to attempt a quantitative approach to the leakage problem.

7. WATER RESOURCES

The long-term safe yield of an aquifer is dependent on its recharge rate, which may be calculated from the relationship

$$Q = v \cdot \phi \cdot w \cdot d$$ \hspace{1cm} (5)

where

- \(Q\) = recharge rate (m\(^3\)/a)
- \(\phi\) = aquifer porosity
- \(w, d\) = width and thickness of the aquifer (m).

For the confined section of the quartzite aquifer the data in Fig. 5 indicate a value of \(v = 0.76\) m/a. The maximum width of the aquifer, estimated from Fig. 1, is about 10 km, and the thickness of the water-bearing part of the quartzite is unlikely to be greater than 100 m.
7.1. Aquifer porosity

The estimation of the porosity of an aquifer, where this is largely related to fractures, is a notoriously difficult procedure. In the absence of any other information we have therefore made recourse to the use of radon data [16].

Radon-222 is generated in rocks by the decay of $^{226}$Ra (derived from $^{238}$U). Some of this $^{222}$Rn escapes from the solid rock into the groundwater, and with a short half-life of 3.8 days the $^{222}$Rn concentration in the groundwater rapidly establishes an equilibrium with the enclosing rock. In most cases, very little of the $^{222}$Rn is produced by dissolved $^{226}$Ra in the water. As an inert substance the $^{222}$Rn concentration in groundwater is therefore only dependent on the rate at which it is released by the rock and on the water/rock ratio, i.e. the porosity of the aquifer.

In laboratory experiments, two samples of quartzite from the Uitenhage aquifer showed $^{222}$Rn release rates of between 10 and 40 dis/min per kilogram rock, this being equivalent to 0.5% and 1.9% release of the total equilibrium $^{222}$Rn production rate [16]. For a median $^{222}$Rn content of 3200 dis/min per litre in the Uitenhage artesian groundwater, and a rock density of 2.7 g/cm$^3$, the two measured release rates suggested aquifer porosities, $\phi$, of 0.01 to 0.05 [16]. Such values are realistic, bearing in mind that the porosity of hand specimens of the quartzite ranges from 0.002 to 0.004 and that the bulk porosity of the fractured aquifer is unlikely to be more than 0.10. On this basis, supported by the radon data, a value of $\phi = 0.1$ is used as a liberal value for the porosity.

7.2. Recharge rates

The above values inserted into Eq. (5) show that the recharge rate for the confined part of the aquifer is unlikely to be more than $8 \times 10^4$ m$^3$/a or $\sim 200$ m$^3$/d. The rate at which the whole aquifer is being recharged, however, must also take into account the natural discharge from the springs at the edge of the outcrop area, particularly the Uitenhage Springs. Du Toit [2] reported that in the latter part of the 19th century these Springs probably yielded about 7000 m$^3$/d; subsequent reductions in flow, down to approximately 3000 m$^3$/d in the late 1950s, appear in many cases to be the direct consequence of the drilling of artesian boreholes in the confined section of the aquifer [2–4].

Figure 6 represents a schematic section of the quartzite aquifer. It is apparent that only a small fraction (<3%) of the total recharge flows into the confined section — either because the permeability of the quartzite as a whole is low or because there is a restriction to flow at the eastern-most end of the aquifer (the Indian Ocean). Most of the recharge overflows at the Springs, which will tend to act as a constant-level control on the hydrostatic pressure in the confined section.
FIG. 6. Schematic NW-SE section through the Uitenhage aquifer, showing the thickness of the aquiclude on the basis of the assumption that the artesian boreholes tap the uppermost part of the quartzite. The relative positions of the sampled boreholes are shown, with solid vertical lines representing the borehole depths when known. The amounts of water recharging the confined section of the aquifer and discharging from the spring are discussed in the text.

It should be emphasized that the recharge rate calculated for the confined section of the aquifer is based on the analysis of a long-term flow pattern established over 28,000 years. In contrast, the relatively young age of groundwater issuing from the Springs indicates that their discharge may be subject to short- or medium-term fluctuations in rainfall.

If the present rate of abstraction from the confined section of the aquifer exceeds ~200 m$^3$/d, the difference will be balanced either by 'mining' of this section of the aquifer (by lowering the piezometric surface) or by reduction of flow from the Springs. The response of the Spring outflow to the drilling, noted above, suggests a fairly rapid transmission of pressure effects; the latter situation therefore seems more feasible.

8. CONCLUSIONS

The investigation of the geochemistry and hydrology of this aquifer has shown some interesting features. There is a clear separation between the process of CO$_2$ solution into the water in the recharge area and the subsequent reaction of this aggressive water with solid carbonate in the confined part of the aquifer. The quartzite of the aquifer is a very pure rock and it is likely that the aquiclude material actually contains the carbonate which is then dissolved. The separation of the two steps of carbonate solution, supported by the carbon isotope data, enables an easy quantification of the chemical evolution of the water.
The chemical composition of the artesian water does not change significantly in the course of its flow, except by the addition of bicarbonate (from carbonate solution) and sodium (from ion exchange). The interpretation of the $^{14}$C values in terms of water age can therefore readily be done. ‘Corrections’ for carbonate addition to the water amount to at most 4000 years. The eventually calculated ages show a very regular age increase to 28 000 years, resulting in a flow rate of only 0.76 m/a. This regularity and the ease of sampling the artesian boreholes make this aquifer a near ideal study area for hydrochemical and palaeoclimatic investigations.

The extent of the water resources of this aquifer was estimated on the basis of rather crude assumptions of aquifer porosity and dimensions. It was concluded that the water flowing through the confined part of the aquifer, either to reach the Indian Ocean or to be pumped out, can at most amount to a few per cent of the discharge of the Uitenhage Springs at the head of the confined part of the aquifer (Fig. 6). In this respect the artesian water forms an insignificant portion of the water resources of the entire compartment. Proper determinations of the geohydrological properties of this aquifer will undoubtedly improve this ‘guessimate’ of the recharge rate and enable a prediction of the effects of exploitation to be made.

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ISOTOPE STUDY ON THE KEUPER SANDSTONE AQUIFER WITH A LEAKY COVER LAYER

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Abstract

ISOTOPE STUDY ON THE KEUPER SANDSTONE AQUIFER WITH A LEAKY COVER LAYER.

Analyses of $^{14}$C, $^3$H, $^{39}$Ar, $\delta^{13}$C and $\delta^{18}$O were performed on groundwater samples taken from the confined Keuper sandstone aquifer north of Nuremberg. The conventional $^{14}$C data apparently contradict the hydrodynamic concept that the age of the deep groundwater flowing from east to west increases in the same direction. A two-dimensional dispersion model is used to convert the conventional $^{14}$C groundwater ages to the regionally valid hydraulic conductivity coefficient of the leaky cover layer confining the aquifer. The basic assumption is that the deep groundwater has a water component which has percolated through the cover layer and which, on mixing, has changed the $^{14}$C ages of the deep groundwater. Therefore, the ratio of the water from 'leaky' recharge to the water from the catchment area plays an important role. Values of $\delta^{18}$O and recharge temperatures derived from the noble-gas content of the deep water indicate mixing of Holocene and Pleistocene groundwaters and confirm the model. The considerable differences between the $^{39}$Ar and $^{14}$C groundwater ages may be plausibly explained by the hydrodynamic situation if $^{39}$Ar production in the aquitard is assumed.

1. INTRODUCTION

Groundwater dating is often described in the literature as a valuable tool for determining groundwater velocities, for localizing catchment areas, or for obtaining other temporal information. However, such uses are restricted to closed systems and piston-like groundwater flow, which are seldom observed in nature.
Already in the 1960s, Wendt et al. [1] studied the effect on $^{14}$C groundwater dating when isotope exchange occurs between the soil CO$_2$ and the bicarbonate in the unsaturated zone. Münich [2] discussed open-system conditions resulting from isotope exchange between limestone in the aquifer and bicarbonate in the groundwater. The effect on $^{14}$C groundwater ages does not exceed a few per cent [3] in exploitable aquifers if isotope exchange occurs only with a monomolecular layer.

Wigley [4], Wigley et al. [5] and Reardon and Fritz [6] have stimulated discussions about whether hydrochemical reactions in the aquifer change the $^{14}$C content of the bicarbonate in groundwater. According to the results of theoretical reflections, a considerable effect is possible, but proof that such reactions occur in fresh-water systems is lacking [7–9].

In 1978, Geyh and Backhaus [10] presented a hydraulic model which quantitatively describes the effect on the $^{14}$C content of deep groundwater if groundwater percolates through an aquitard into a confined aquifer. Since then, theoretical studies have confirmed that hydrodynamic mixing of groundwaters with different ages has to be considered when interpreting $^{14}$C groundwater ages [11, 12].

2. TWO-DIMENSIONAL DISPERSION MODEL

A practice-oriented, two-dimensional dispersion model derived from the hydraulic model was used to interpret conventional $^{14}$C groundwater ages of a confined aquifer system (Fig. 1) with a thickness $H_2$ (m) and a porosity $P_2$ [10]. The groundwater velocity $V_2$ (m/a) is unknown. The $^{14}$C concentrations (pmc) of the water samples from two neighbouring wells are $C_2$(I) and $C_2$(II). The cover layer is semi-permeable, has a thickness $H_1$, a porosity $P_1$ and a hydraulic conductivity coefficient $K$ (m/s) as defined by Darcy’s Law (Eq.(1)). The groundwater in the unconfined shallow aquifer is assumed to be young. The hydraulic heads of the confined and unconfined aquifers differ by $P$ (m).

The $^{14}$C content of the groundwater in the confined aquifer is the result of mixing of the horizontal and downward fluxes. Diffusion flux is negligible [10]. The deep groundwater in the confined aquifer is assumed to be well mixed, since the samples were taken from pumped wells and convective water movement occurs in deep aquifers owing to the geothermal gradient [13]. The filter velocity $V_f$ of the vertical water flow follows from Darcy’s Law:

$$V_f = \frac{K \cdot P}{H_1} = V \cdot P_1$$

(1)

If $P$ is positive, water flows upwards from the confined aquifer into the shallow one, and the $^{14}$C concentration $C_2$ does not change. In the reverse case,
shallow groundwater flows downwards through the semi-permeable layer into the confined aquifer [14]. In this way, the $^{14}$C concentration $C$ decreases by radioactive decay, and at the boundary between the aquitard and the confined aquifer reaches the following value:

$$C = C_0 e^{-\lambda \cdot H_1^2 \cdot P \cdot \gamma / (K \cdot P)}$$

(2)

The continuity equation is as follows:

$$\frac{\partial C_2}{\partial t} = V_2 \cdot \frac{\partial C_2}{\partial X} - (\phi(X) + \lambda) \cdot C_2 + \psi(X) \cdot C$$

(3)

where $\phi(X)$ and $\psi(X)$ are functions of the geometric parameters of the aquifer system. The solution $C_2$ at well II is

$$C_2(II) = C_2(I) \cdot e^{-\lambda \cdot t} \frac{(1 - V_2 t \cdot \alpha e^{e_3})}{(1 - V_2 t \cdot \beta e^{e_3})} \frac{C_0 V_f}{H_2 P_2}$$

$$X \int_0^t \left( \frac{(1 + \kappa(X + V_2 \tau)) e^{-\lambda \cdot \tau} (1 - V_2 \tau \alpha e^{e_3})}{(1 + \alpha(X + V_2 \tau)) (1 + \beta(X + V_2 \tau)) (1 - V_2 \tau \beta e^{e_3})} \frac{\lambda H_1^2 \cdot P_1 (1 + \alpha(X + V_2 \tau))^2}{K \cdot P (1 + \kappa(X + V_2 \tau))} \right) d\tau$$

(4)
with

\[ \alpha = \frac{H_1(II) - H_1(I)}{X \cdot H_1(I)} \]
\[ \beta = \frac{H_2(II) - H_2(I)}{X \cdot H_2(I)} \]
\[ \kappa = \frac{P(II) - P(I)}{X \cdot P(I)} \]

\[ \epsilon_1 = \frac{1 + \kappa/\alpha}{\alpha - \beta} \]
\[ \epsilon_2 = \frac{1 + \kappa/\beta}{\alpha - \beta} \]
\[ \epsilon_3 = \frac{V_2}{V_2 \cdot H_2 \cdot P_2} \]

The ratio of the groundwater entering the confined aquifer through the semi-permeable layer between wells I and II and the horizontal flow is

\[ Q = \frac{-K \cdot P(I)}{H_1(I)} \left( \ln \left(1 + \alpha X \right) (1 - \kappa/\alpha + \kappa X) \right) \]

\[ \frac{H_2(I) \cdot P_2 \cdot V_2}{\alpha} \]

3. NUMERICAL EVALUATION

The first step of a numerical evaluation is to select profiles in the study area which perpendicularly cross the piezometric contour lines and pass as many wells as possible (see Fig. 3). In this way, each profile consists of several sections taken between adjacent wells.

The choice of the initial \(^{14}\text{C}\) content of the groundwater is not critical for the calculation of \(K\) as it is valid for both aquifers. The water age for the shallow unconfined aquifer is assumed to be near zero.

Unknowns in Eq. (4) are the hydraulic conductivity coefficient \(K\) of the aquitard and the actual groundwater velocity \(V_2\) in the confined aquifer. Newton’s iterative method is used to numerically evaluate \(K\), starting with an estimate:

\[ K(1) = 1 \times 10^6 \text{ (m/s)} \]

\[ K(n) = K(n-1) - \frac{C_2(II)}{\partial C_2 / \partial K} \]

The calculations are \(n\)-times repeated until \((K(n) - K(n-1)) \leq 3\%\).

The calculation is started for the section closest to the catchment area. \(K\) and \(Q\) are calculated for several reasonable, assumed water velocities \(V_2\) of between 0.1 and 8 m/a as well as for the percolation time and \(V_2(II)\). These calculated velocities are used as initial velocities \(V_2(II)\) in the calculation for the next section in order to simulate continuous groundwater flow. Assuming rather isotropic hydraulic properties of the aquitard, the actual, regionally valid hydraulic conductivity coefficient \(K\) is found for the initial groundwater
velocity for which the K values of all sections of the same profile agree with each other.

4. ACCURACY OF THE VARIOUS PARAMETERS

The effect of inaccurately known parameters on the calculation of K by Eq.(4) was studied for 42 examples. The value of each parameter was increased by 10%. There is a rough linear correlation between the variation in K and the shift in the value of the individual parameters. This shift is positive for H₁, H₂, P₁ and P₂, and negative for P and X; for A, it is both negative and positive.

H₂: The thickness of the confined aquifer is well known either from wells or from geological mapping. H₂ as well as K may be inaccurate by up to 20% if the wells do not reach the bottom of the aquifer.

H₁: The thickness of the cover layer is known to at least ± 1 m. However, there is a major problem if no shallow aquifer exists. Equation (4) still yields reasonable K values if a reasonable H₁ value is used, which can be obtained by taking into account the morphology and the shallow water levels of adjacent wells. The use of H₁ in this case is in agreement with the observation that initially dry wells in an aquitard often become filled to a certain level with seeping water. Hence, even if a shallow aquifer is not present, ‘leaky’ groundwater recharge into the confined aquifer may occur. A value of H₁ that is inaccurate by x% results in a correspondingly inaccurate K value.

P: The given difference in the hydraulic heads of the confined and unconfined aquifers may differ from the actual difference by several metres and the relative deviation may be large if P is small. Inaccurate P values are due to unknown water levels before the beginning of groundwater pumping or to the influence of the pumping cones of the adjacent wells. If no shallow aquifer exists, an apparent level must be determined, as described for parameter H₁. An uncertainty of +x% in the value of P results in a K value shifted by −x% and vice versa.

A: The conventional ¹⁴C ages of the water samples from the various wells show different temporal behaviour. Analyses have been run almost every two years since 1968. In 70% of the samples, the ¹⁴C ages agree within the range of their standard deviations, 20% show a decreasing trend and the remaining samples show increasing values. Decreasing ¹⁴C ages may reflect accelerated percolation of young groundwater through the aquitard due to a lowered hydraulic head of the confined aquifer as a result of groundwater withdrawal (‘mining effect’ [10]). Increasing ¹⁴C ages reflect the admixture of old mineralized groundwater from the aquifer below the Keuper sandstone aquifer through the underlying aquitard (Lehrberg clay). In this case, the hydraulic head of the Keuper sandstone aquifer decreased to below that of the underlying aquifer.
As the initially determined conventional $^{14}$C water age may not be valid for undisturbed natural conditions, A has an uncertainty of up to 10%. The calculated K values deviate correspondingly. If the admixed water is older (younger) than the deep groundwater, K will decrease (increase) with increasing age.

X: The shortest distance between wells I and II is used for the calculation, although the flow lines may be curved or sections may not perpendicularly cross the piezometric contour lines. The deviation does not, however, exceed ±20%, which is why K may be shifted by a maximum of ±15%.

$P_1$ and $P_2$: The choice of the porosity is very critical. The total porosity, which is equal to the total water content, and the effective porosity differ by up to two orders of magnitude. The uncertainties of ±10% between the analytical and the actual values are negligible; they correspond to a shift of ±5% in the value of K. The decision of whether the total or the effective porosity, or some value in between, must be used for the calculation of K is made on the basis of the results.

5. HYDROGEOLOGICAL SITUATION

A geological profile illustrating the hydrogeological situation of the aquifer system in our study area north of Nuremberg is shown in Fig.2. The Keuper
sandstone (ks) aquifer is confined by strata from Dogger (d), Liás (1) and Feuer-
letten (kf) whose hydraulic conductivity coefficients are less than $10^{-9}$ m/s, but
probably more than $10^{-10}$ m/s. There is a fault in the eastern part of the study
area where the Keuper sandstone aquifer and the unconfined Malm aquifer (m)
have a common hydraulic head. Both aquifers discharge towards the west into
the Regnitz river. The mean total porosities of the Keuper sandstone and the
Feuerletten clay are 24% and 30%, respectively. The corresponding effective
porosities are smaller and amount to 0.5–1.5% and 2–5%. Towards the west,
the hydraulic head of the unconfined aquifer generally exceeds that of the
confined one. Consequently, leaky recharge into the confined Keuper sandstone
aquifer occurs.

The sampling sites (see Table 1), the corresponding conventional $^{14}$C ages,
the piezometric contour lines of the confined aquifer, and the contour lines for
the differences between the piezometric surfaces of the shallow and confined
aquifers are shown in Fig. 3. Groundwater flow towards the east is evident. In
apparent contrast to this, the conventional $^{14}$C ages neither increase nor decrease
in any direction. The smallest $^{14}$C ages are found where the difference piezo-
metric contour lines form a peak and reflect maximum leaky recharge from the
shallow aquifer.

6. RESULTS OF THE CASE STUDY

The input data of our case study are compiled in Table 1. Applying Eqs (4)
and (6), the following results were obtained for profiles A and F, which are shown
in Fig. 4.

Because of the input of water from the shallow aquifer, the velocity along
profile A increases between #1 and #12 from 0.8 to 4.5 m/a, and decreases in
agreement with the gradient of the piezometric contour lines to 3.5 m/a. At #7,
near the discharge area, 90% of the water of the Keuper sandstone aquifer stems
from leaky recharge and only 10% from the catchment area in the east. The $K$
values of the sections have an average of $5.4 \times 10^{-10}$ m/s. The total water
content of both the aquitard and the aquifer was used in Eq. (4). Smaller values
near the effective porosity yielded lower $K$ values which are hydrogeologically
not acceptable. Hence, the $^{14}$C content of the water in the fine pores cannot
differ considerably from that in the large pores.

In order to check the influence of groundwater mining, the calculation for
sections #12 and #6 was repeated with a more recently measured $^{14}$C water age.
$K$ has apparently increased from $3.9 \times 10^{-10}$ m/s by 25% to $4.8 \times 10^{-10}$ m/s. The
initial $K$ value would have been obtained again if the present higher $P$ value had
been used. In the same way, the input of fossil mineral water from the deeper
aquifer can be studied if its hydraulic head and other necessary hydrogeological
data are known.
FIG. 3. Sampling sites (Table I), conventional $^{14}$C ages (a B.P.), piezometric contour lines (---) of the confined Keuper aquifer (m.a.s.l.), and contour lines $P$ (---) for the differences (m) between the piezometric surfaces of the shallow and confined aquifers.
It should be mentioned that an increasing input of relatively young water through the aquitard, resulting from a greater difference between the hydraulic heads, does not automatically increase the present risk of pollution from the surface as the percolation time may decrease from a few ten thousand years to only several thousand years.

According to Fig.4, the K values decrease from north to south. This finding is not in conflict with the geological situation. The aquitard seems to be more tight in the south.

Attempts to calculate K for pairs of wells between which no groundwater flows were not successful because either the integrals did not converge or the exponents exceeded the capacity of the computer.

7. δ¹⁸O VALUES, NOBLE-GAS PALAEOTEMPERATURES

The temperature at the time of groundwater recharge correlates with the δ¹⁸O value [15, 16] as well as the noble-gas content [17, 18]. The two correlations are in good agreement (Table I). In Central Europe, the δ¹⁸O values for Pleistocene and Holocene groundwater differ by more than 1‰.

A plot of our δ¹⁸O values and the noble-gas temperatures versus the conventional ¹⁴C ages shows a linear correlation (Fig.5, left-hand side) rather than the expected two bands. There are various possibilities for a qualitative explanation: The apparent change of the ¹⁴C ages can be due to:

- chemical reactions in the aquifer [5, 6]
- aquitard diffusion [12]
- various residence times of the pore water [11]
- 'chromatographic' delay of the bicarbonate [19].

The dispersion model yields a plausible quantitative explanation.

Equation (5) can be used to estimate the proportions of Holocene and Pleistocene groundwater in the samples. An exact calculation is not possible as the groundwater recharge was interrupted for a rather inaccurately known time during the last glacial period owing to permafrost [15, 20]. In addition, for the area between the wells, the difference between the hydraulic heads can be obtained only by extrapolation, which hampers an exact delineation of the area where only Holocene water entered the Keuper sandstone aquifer.

However, plotting the estimated proportions of Pleistocene water in the samples versus the conventional ¹⁴C ages (Fig.5, right-hand side) yields the linear correlation expected for two-component mixing. The extrapolated maximum recharge temperature of 9–10°C for Holocene water agrees well with the mean of 10.2°C for the young water samples from our study area and the temperature ((9.4 ± 0.5)°C) of karst water in the Frankonian Alb.
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<th>$H_2$ (m)</th>
<th>$P$ (m)</th>
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<th>$\delta^{13}C$ (%)</th>
<th>$\delta^{18}O$ (%)</th>
<th>Ar (pmc)</th>
<th>T ($^\circ$C)</th>
<th>$Q_p$ (%)</th>
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<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Greding 1</td>
<td>11</td>
<td>13</td>
<td>0.4</td>
<td>22 920 c</td>
<td>-11.8</td>
<td>-10.6</td>
<td>17.2</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in brackets are estimates.

a = assumed, c = constant, r = rising, f = falling, u = unknown.
Summarizing, the δ¹⁸O values, noble-gas palaeotemperatures and conventional ¹⁴C ages should be interpreted as being the result of two-component mixing of Holocene and Pleistocene groundwater of different properties.

8. DISCREPANCIES BETWEEN ³⁹Ar AND ¹⁴C GROUNDWATER AGES

Loosli and Oeschger [21] published discrepant and linearly correlated ¹⁴C and ³⁹Ar water ages, deviating by two orders of magnitude. Known effects do not explain the discrepancy [19]. The assumed methodological errors in the ¹⁴C groundwater dating due to, for example, hydrochemical reactions in the aquifer [5] or isotope exchange [2] are questioned as both the ¹⁴C groundwater ages and δ¹⁸O values reflect the change in groundwater-recharge conditions from the interstadial to the post-glacial period, and the groundwater velocities derived from the ¹⁴C ages agree with the hydraulic situation.
FIG. 5. $\delta^{18}O$ values (‰) and noble-gas temperatures (°C) versus the conventional $^{14}$C groundwater ages (left-hand side). Pleistocene water content, $Q_p$, plotted versus the conventional $^{14}$C groundwater ages (right-hand side). $\bigcirc = \delta^{18}O$ values, $\bullet =$ temperature.

Methodological errors of $^{39}$Ar groundwater dating are as follows:

(a) Admixture of young water from the shallow aquifer:
Equation (4) was used to calculate K, but the results were not within the range of $10^{7}$ to $10^{12}$ m/s. The reason for this is that $^{39}$Ar from the shallow aquifer decays, in general, completely during its percolation through the aquitard.

(b) Argon-39 production in the aquifer [19]:
The $^{39}$Ar content increases in the direction of flow by a factor of four between wells #2 and #3, and decreases by a factor of six in the south between wells #19 and #25 (Table I). The uranium content in the Keuper sandstone should change correspondingly, for which geological evidence is lacking [22].

(c) Argon-39 production in the aquitard:
Argon-39 production in the aquitard results in saturation of the pore water since the half-life of 269 years for $^{39}$Ar is, in general, short compared with its residence time in the aquitard. The groundwater will transport $^{39}$Ar towards the confined aquifer and in this case the $^{39}$Ar concentration of the deep groundwater will depend mainly on the quantity of percolating groundwater. With this very simple concept, the $^{39}$Ar saturation concentration in the aquitard can be calculated from the measured $^{39}$Ar concentrations $C_2$ and the corresponding hydraulic data (Table I) as follows:

$$C_s = \frac{\lambda \cdot H_1 \cdot H_2 \cdot P_2 \cdot C_2}{K \cdot P} \left(1 - e^{-\lambda \cdot MRT}\right)$$  \hspace{1cm} (7)
The mean residence time (MRT) of the seeping water is calculated by Eq. (1). The \( C_s \) values (Table 1) were obtained with \( K \) values of \( 5.8 \times 10^{-10} \) m/s for the northern wells and \( 2.5 \times 10^{-10} \) m/s for the southern wells. In most cases where \( P \) is smaller than 15 m, the saturation concentrations are grouped in a very narrow range around \( (1550 \pm 125) \) pmc \(^{39}\)Ar. In the other cases, the \( C_s \) values are smaller. This may be explained by degassing, since for these well sites the upper part of the aquitard contained no pore water under pressure.

Because of the very simple model, the narrow scattering of the estimated \( C_s \) values for the above-mentioned cases should be stressed rather than their high absolute values. Thus, the principal validity of our interpretation of the discrepant \(^{14}\)C and \(^{39}\)Ar values is highly supported.

As in the case of the \( \delta^{18}\)O values and the noble-gas palaeotemperatures, the dispersion model accounts for two-component mixing, which explains the linear correlation between the \(^{14}\)C and \(^{39}\)Ar water ages.

9. CONCLUSIONS

The two-dimensional dispersion model shows that the conventional \(^{14}\)C groundwater ages of a confined aquifer system may strongly depend upon the hydrodynamic situation and leaky recharge may predominate in the confined aquifer. In spite of this, there may be no risk of pollution. Under such circumstances, \(^{14}\)C ages can be transformed into maximum hydraulic conductivity coefficients. The model explains \( \delta^{18}\)O values and noble-gas groundwater palaeotemperatures resulting from the mixing of young Holocene water percolating through the aquitard with Pleistocene water from the catchment area. Most of the discrepant \(^{39}\)Ar and \(^{14}\)C groundwater ages can be explained by \(^{39}\)Ar production in the aquitard and transport of it to the confined Keuper sandstone aquifer.

ACKNOWLEDGEMENT

Dr. C. Newcomb critically read the manuscript.

REFERENCES


ISOTOPE HYDROLOGICAL STUDY WITH CARBON-14 AND ARGON-39 IN THE BUNTER SANDSTONES OF THE SAAR REGION

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Abstract

ISOTOPE HYDROLOGICAL STUDY WITH CARBON-14 AND ARGON-39 IN THE BUNTER SANDSTONES OF THE SAAR REGION.

Argon-39, carbon-14 and other isotopes have been measured in a sandstone aquifer in the Saar region (Federal Republic of Germany) where already chemical and isotopic investigations had been carried out. From measurements of two samples showing no detectable $^{39}$Ar it was clear that subsurface production of $^{39}$Ar can be neglected in this aquifer. For the other three samples, the determination of isotope concentrations (including the usual corrections for the initial concentration of $^{14}$C) gave consistent results within the errors of determination and correction. The discussion of the results led to the conclusion that, in addition to $^1$H, $^2$H, $^{18}$O, $^{13}$C and $^{14}$C determinations, the $^{39}$Ar and $^{85}$Kr methods should be applied for isotope hydrological investigations. This is evident especially in systems where mixing of waters with different ages takes place. First steps in investigations of the subsurface production of $^{39}$Ar using neutrons for irradiating core material, as well as in elaborating a computer program for calculating isotope production (e.g. $^{35}$Cl and $^{37}$Ar) in parallel with $^{39}$Ar, are briefly mentioned.

1. INTRODUCTION

The isotope $^{39}$Ar has a half-life of 269 years, which is between the half-lives of $^{85}$Kr, $^3$H and $^{14}$C. Argon-39 is therefore well suited for groundwater dating in the range of 100 - 1000 years [1]. As a noble-gas isotope, $^{39}$Ar is chemically inactive and does not pose problems such as those affecting the initial isotope concentration of, for instance, $^{32}$Si and $^{14}$C. Until now, environmental $^{39}$Ar activities ($\leq 0.03$ dis/min per m$^3$ H$_2$O) can be measured only at the Physics
Institute of the University of Berne where the necessary detection limits are reached in an underground laboratory [2, 3].

Former investigations of $^{39}\text{Ar}$ concentrations in groundwaters were carried out in a sandstone aquifer in the foreland of the Frankenalb and in wells near Ingolstadt (Federal Republic of Germany), and in some thermal waters in Switzerland and in the Federal Republic of Germany [3, 4]. The groundwater ages derived from the $^{39}\text{Ar}$ concentrations were different from those calculated from the measured $^{14}\text{C}$ concentrations. Argon-39 concentrations above the atmospheric values were obtained in a few thermal waters [5]. For some aquifers the apparent $^{39}\text{Ar}/^{14}\text{C}$ discrepancy can be explained by subsurface production of $^{39}\text{Ar}$ from the reaction $^{39}\text{K}(n, p)^{39}\text{Ar}$ (see Appendix). Eichinger [6] showed that one reason for the $^{39}\text{Ar}/^{14}\text{C}$ age discrepancy could be an incorrect assumption of the initial $^{14}\text{C}$ concentration. In his investigations the usually assumed initial $^{14}\text{C}$ concentration of 85 pmc\(^1\) turned out to be too high, indicating the necessity to calculate the initial $^{14}\text{C}$ concentration by the use of correction models.

In this situation it seemed to be worth undertaking a new comparison between $^{39}\text{Ar}$ and $^{14}\text{C}$ age determinations in an area where subsurface production of $^{39}\text{Ar}$ could be excluded. The aquifer to be investigated should also have a known chemical evolution of the carbon content in order to demonstrate the range of corrections which would have to be applied for the determination of the initial $^{14}\text{C}$ content. Both conditions were nearly reached in a deep sandstone aquifer in the Saar region (Federal Republic of Germany) which is described in the following. Since the number of $^{39}\text{Ar}$ and $^{85}\text{Kr}$ samples was restricted, only five $^{39}\text{Ar}$ and $^{85}\text{Kr}$ determinations were carried out. In this paper, mainly the chemical and isotope data from these five samples are discussed, but all results of the extensive isotope investigation are considered. Details of the isotope investigations of this area will be published later. A similar, independent $^{39}\text{Ar}$ investigation is described in these Proceedings by Andrews et al. [7].

2. HYDROGEOLOGICAL SITUATION

Figure 1 gives a geological survey of the area under investigation. The sandstone aquifer under investigation reaches a thickness of up to 400 m and lies above the Lower Permian. Above the Middle Bunter follow sandstones of the Upper Bunter. Both sandstones are free of or very poor in carbonates. These layers are covered with calcareous sandstones, limestones and evaporites of Muschelkalk.

\(^{1}\text{pmc} = \text{per cent modern carbon.}\)
The Muschelkalk deposits remained uneroded in the southern part of the area under investigation and confine the Bunter sandstones [9–11]. In the northern part of this area the Muschelkalk is missing and therefore the sandstones are uncovered (Fig. 2). The pore volume of the sandstone aquifer is about 8% [12]. The relative height of the limestone recharge area above the wells explains the occurrence of artesian sandstone waters in some wells.

Because of the hydrological situation the deep-lying groundwater system is recharged with limestone waters and also with waters from distant sandstone recharge areas. From the geological situation it can be expected that the groundwater from the wells Kirkel, Altheim 1 and Altheim 2 represent a mixing system of shallow and deeper waters in the uncovered (Kirkel) and covered sandstone aquifer (wells Altheim 1, 2; see Fig. 2). Wells Altheim 1 and 2 are only about 400 m apart. Because of the different drilling and casing depths of the boreholes, mixing systems can be expected where in general the mean groundwater ages should
FIG. 2. Drilling depths and casings of the wells which were investigated with isotope techniques including $^{39}$Ar and $^{85}$Kr (solid circles in Fig. 1). This figure can only give a rough and schematic draft of the real hydrogeological situation (from Refs [9–11]).

grow as deeper aquifer regions are reached. The groundwaters from the wells Blieskastel and Blickweiler represent the deep-lying groundwaters in the covered and uncovered areas, respectively. From the drilling depths and borehole casings the mean groundwater residence times are expected to be higher than in Altheim and Kerkel.

Low U and Th concentrations have been detected in the different geological deposits [9, 10, 13]. These low concentrations have been confirmed by analyses of the U, Th and K contents in core material from boreholes of the wells under investigation. The results of seven samples show values of between 0.8 and 1.6 ppm for U, between 1.8 and 3.4 ppm for Th, and between 1 and 4% for K. From these values, the subsurface, alpha- and neutron-induced production of $^{39}$Ar has been estimated (see Appendix) to increase the measured $^{39}$Ar concentration by maximum 2% modern $^{39}$Ar, which is within the measuring-detection limit (3% modern $^{39}$Ar) and can be neglected. In view of this, the area seemed to be suited for carrying out a study combining different isotope techniques.
3. CHEMICAL AND ISOTOPIC INVESTIGATIONS

3.1. Evolution of the Ca/Mg ratio and the $^{13}$C content

As could be expected from the hydrogeological situation, the waters from more than 30 wells show a clear chemical evolution. A nearly continuous increase of the mineralization is observed in groundwaters from the uncovered part in the northern aquifer (Kirkel) to those from the Muschelkalk-covered Bunter (Blickweiler, Altheim); this is confirmed, for instance, by the measured Mg$^{2+}$ concentration. Chemical data are given in Table I.

The limestone of the Saar region contains a high amount of dolomite. The solution of dolomite therefore is expected to be the main reason for the increasing Mg$^{2+}$ and Ca$^{2+}$ ion concentrations. As shown in Fig.3, the results of Ca$^{2+}$ and Mg$^{2+}$ measurements in water follow a line which indicates a Ca/Mg ratio of around one in limestone. A comparable Ca/Mg ratio has been stated also for rock material from a dolomitie limestone drilling core [14].

The dolomitie limestone of the Saar region contains 20–40 g C (inorganic carbonate) per kilogram rock, while the sandstone has carbon contents of only up to 20 mg C per kilogram rock. The increasing dissolution of dolomite, visible by the Mg$^{2+}$ and Ca$^{2+}$ ion concentrations, therefore is expected to be a source of the increasing inorganic carbon dissolved in water. Since plots similar to that of Fig.3 (checking the corrected solution of calcite and gypsum) give no correlation, the solution of dolomite from the overlying limestone is assumed to be the main source of inorganic carbonate and carbon isotopes dissolved in water from the covered part of the aquifer.

Assuming the above-mentioned chemical evolution of these groundwaters, an analogous carbon isotopic evolution is expected. Therefore, the $^{13}$C concentrations of the two main rock components limestone and sandstone (Middle Bunter and Upper Bunter can be regarded as having approximately the same composition) determine the evolution of $^{13}$C dissolved in water.

The dolomitie limestone layers showed $\delta^{13}$C values varying slightly around 1%. The $^{13}$C concentration in sandstone was determined to be within the range of from $-5$ to $-7\%$. It can be calculated that the $\delta^{13}$C values of the carbonates in aqueous solution should increase with increasing solution of dolomite, from biological values ($-25\%$) to values for higher $^{13}$C contents, which correspond to the waters under the limestone covering. Figure 4 gives the measured $\delta^{13}$C values of inorganic carbon dissolved in water and shows the evolution of the $^{13}$C concentration caused by the solution of dolomite. The smaller gradient of the $\delta^{13}$C increase with increasing Mg$^{2+}$ ion concentration from medium- to high-mineralized waters may be an indication that more sandstone water with more negative $\delta^{13}$C values is admixed and/or that secondary calcite is precipitated.
<table>
<thead>
<tr>
<th>Name</th>
<th>Date</th>
<th>Sample No.</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>O₂ (mg/L)</th>
<th>CO₂ (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>Ca²⁺ (mg/L)</th>
<th>Mg²⁺ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kirkel</td>
<td>17.8.81</td>
<td>40</td>
<td>10.8</td>
<td>5.6</td>
<td>8</td>
<td>24</td>
<td>12</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>Altheim 1</td>
<td>7.8.82</td>
<td>110</td>
<td>12</td>
<td>7.1</td>
<td>2</td>
<td>37</td>
<td>428</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>Altheim 2</td>
<td>23.4.82</td>
<td>113</td>
<td>13</td>
<td>7.2</td>
<td>2</td>
<td>40</td>
<td>360</td>
<td>73</td>
<td>44</td>
</tr>
<tr>
<td>Blickweiler</td>
<td>14.8.81</td>
<td>77</td>
<td>14</td>
<td>6.8</td>
<td>≤0.3</td>
<td>37</td>
<td>288</td>
<td>53</td>
<td>28</td>
</tr>
<tr>
<td>Blieskastel</td>
<td>12.8.81</td>
<td>63</td>
<td>14.6</td>
<td>6.5</td>
<td>≤0.2</td>
<td>35</td>
<td>122</td>
<td>14</td>
<td>8</td>
</tr>
</tbody>
</table>
3.2. Initial $^{14}$C concentrations

Figure 5 shows the initial $^{14}$C concentrations $A_0$ of the groundwaters as they were calculated from the WATEQF computer program [15] in a modified version [6], which takes into account effects of carbon isotope exchange. It is assumed in this model that any exchange of carbon isotopes is detectable by $^{13}$C and/or HCO$_3^-$ changes in the water. Further calculations of the initial $^{14}$C content were carried out to compare the results of other correction models [16–18]. Table II shows that different correction models give no significant differences in their results (± 5 pmc). In groundwaters where comparatively high $^{13}$C and low (a few pmc) $^{14}$C concentrations indicate possible carbon isotope exchange (e.g. sample No. 104 in Fig.5) the $A_0$ results from the correction models showed differences. Therefore, in all cases the isotope exchange model has been used to calculate the initial concentration of $^{14}$C. For comparison, $A_0$ results are given in Fig.5 for the very old groundwater sample in Herbitzheim, which were calculated with the chemical mixing model (No. 103) and the isotopic exchange model (No. 104). As shown by the results of repeated measurements after one year of utilization of the wells, the calculated initial $^{14}$C concentrations are constant within the errors of the $^{14}$C measurement.

Table II summarizes the mean values of the calculated initial $^{14}$C concentrations as they were derived for waters of the uncovered, the intermediate and the covered areas of the aquifer. Results are given separately for the correction models of isotope mixing, isotope exchange and chemical mixing.

Initial $^{14}$C concentrations of typically 55 ± 11 pmc were calculated for waters from wells in the covered aquifer region. The error must be assumed
FIG. 4. Variation of $^{13}$C content in groundwaters in relation to the Mg$^{2+}$ concentration which rises with the thickness of the overburden and therefore with the solution of dolomite. The numbers indicate groundwaters for which isotope data are given in Section 3.3 (see Table III).

FIG. 5. Initial $^{14}$C concentration, $A_0$, in relation to the total dissolved inorganic carbon, calculated with the isotope exchange model [6]. This figure shows that the calculated initial $^{14}$C concentrations are decreasing as the concentration of carbonate increases. Results with arrows indicate repeated measurements after one year of utilization of the well. Groundwater numbers with brackets denote probable carbon isotope exchange. No. 103 gives the initial $^{14}$C concentration calculated with the chemical mixing model [17] in comparison with the result for No. 104.
TABLE II. CALCULATED MEAN INITIAL $^{14}$C CONCENTRATIONS $A_0$ IN DIFFERENT REGIONS OF THE AQUIFER

<table>
<thead>
<tr>
<th>Aquifer area</th>
<th>Calculated initial $^{14}$C concentrations (pmc)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_{0\text{(im)}}$</td>
</tr>
<tr>
<td>Uncovered</td>
<td>$101 \pm 12$</td>
</tr>
<tr>
<td>Intermediate</td>
<td>$74 \pm 11$</td>
</tr>
<tr>
<td>Covered</td>
<td>$56 \pm 10$</td>
</tr>
</tbody>
</table>

$^a$ $A_{0\text{(im)}}$ denotes the correction based on the isotope mixing model, $A_{0\text{(ie)}}$ and $A_{0\text{(cm)}}$ stand for the isotope exchange model and the chemical mixing model, respectively.

to reach $\pm 11$ pmc, although good reproducibility was obtained in different samplings. This is due to the uncertainties of chemical ion determination, related field measurements and calculation of the initial $^{14}$C content [6].

The measured $^{14}$C concentrations of groundwaters from the area under investigation lie within the limits of $(90 - 100) \pm 5$ pmc and $0.8 \pm 0.7$ pmc, covering the range of model ages from recent to older than 10 000 years B.P. and reflecting a situation similar to that investigated by Blavoux and Olive [19] in a neighbouring sandstone aquifer in France. It is obvious that the measured $^{14}$C concentrations strongly depend on parameters like depth and casing of the borehole as well as on the admixture of different components in the aquifer. Therefore, the $^3$H and $^{85}$Kr concentrations in waters from wells in the covered and uncovered parts of the aquifer were taken as indicators of recent water contribution to the deep groundwater system. Referring only to waters from boreholes of more than 200 m depth containing no $^3$H, it can be concluded that the mean corrected groundwater age increases as the sandstone aquifer becomes more overlain by limestone.

3.3. Measurement and interpretation of argon-39 concentrations

Because of the great efforts in the field and laboratory necessary for $^{39}$Ar investigations, the number of $^{39}$Ar determinations was restricted to five $^{39}$Ar samples (see Table III). The sampling points were chosen so as to achieve a distribution of the $^{39}$Ar measurements over the entire range of chemical evolution
<table>
<thead>
<tr>
<th>Name</th>
<th>Date</th>
<th>Sample No.</th>
<th>δ²H (‰)</th>
<th>δ¹⁸O (‰)</th>
<th>δ¹³C (‰)</th>
<th>Calculated initial (^{14})C concentration (pmc)(^b)</th>
<th>(^{14})C measured (pmc)</th>
<th>(^{3})H (TU)</th>
<th>(^{39})Ar (% mod.)</th>
<th>(^{85})Kr (dis/min per mL Kr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kirkel</td>
<td>22.10.80</td>
<td>39</td>
<td>-57.4</td>
<td>-8.4</td>
<td>-22.2</td>
<td>97 ( A_{0(cm)} ), 100 ( A_{0(im)} ), 93 ( A_{0(iso)} )</td>
<td>94.5 ± 4.0</td>
<td>17.1 ± 1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kirkel</td>
<td>17. 8.81</td>
<td>40</td>
<td>-58.2</td>
<td>-8.3</td>
<td>-22.1</td>
<td>93 ( A_{0(cm)} ), 100 ( A_{0(im)} ), 96 ( A_{0(iso)} )</td>
<td>91 ± 6.5</td>
<td>17.3 ± 1.4</td>
<td>75.5 ± 4.8</td>
<td>1.4 ± 5%</td>
</tr>
<tr>
<td>Altheim 1</td>
<td>12. 5.81</td>
<td>108</td>
<td>-56.8</td>
<td>-8.3</td>
<td>-12.5</td>
<td>53 ( A_{0(cm)} ), 58 ( A_{0(im)} ), 54 ( A_{0(iso)} )</td>
<td>61 ± 3.1</td>
<td>29.7 ± 2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Altheim 1</td>
<td>7. 8.82</td>
<td>110</td>
<td>-57.0</td>
<td>-8.2</td>
<td>-12.8</td>
<td>55 ( A_{0(cm)} ), 60 ( A_{0(im)} ), 56 ( A_{0(iso)} )</td>
<td>62 ± 3.5</td>
<td>30.4 ± 2.2</td>
<td>74.6 ± 3.0</td>
<td>7.11 ± 4%</td>
</tr>
<tr>
<td>Altheim 2</td>
<td>12. 5.81</td>
<td>112</td>
<td>-58.0</td>
<td>-8.5</td>
<td>-12.5</td>
<td>55 ( A_{0(cm)} ), 58 ( A_{0(im)} ), 54 ( A_{0(iso)} )</td>
<td>52 ± 4.0</td>
<td>1.5 ± 0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Altheim 2</td>
<td>23. 4.82</td>
<td>113</td>
<td>-55.6</td>
<td>-8.2</td>
<td>-12.4</td>
<td>57 ( A_{0(cm)} ), 57 ( A_{0(im)} ), 54 ( A_{0(iso)} )</td>
<td>48.8 ± 3.4</td>
<td>1.6 ± 0.5</td>
<td>33.4 ± 2.0 ( a ) 0.3 ± 6%</td>
<td></td>
</tr>
<tr>
<td>Blickweller</td>
<td>10. 7.80</td>
<td>76</td>
<td>-56.5</td>
<td>-8.4</td>
<td>-12.9</td>
<td>61 ( A_{0(cm)} ), 58 ( A_{0(im)} ), 55 ( A_{0(iso)} )</td>
<td>37.8 ± 2.0</td>
<td>0.2 ± 0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Blickweller</td>
<td>14. 8.81</td>
<td>77</td>
<td>-57.4</td>
<td>-8.2</td>
<td>-12.6</td>
<td>57 ( A_{0(cm)} ), 56 ( A_{0(im)} ), 52 ( A_{0(iso)} )</td>
<td>31.5 ± 1.7</td>
<td>0.4 ± 0.7</td>
<td>≤ 3.3</td>
<td>0.02 ± 60%</td>
</tr>
<tr>
<td>Blieskastel</td>
<td>10. 7.80</td>
<td>62</td>
<td>-55.6</td>
<td>-8.3</td>
<td>-16.7</td>
<td>67 ( A_{0(cm)} ), 71 ( A_{0(im)} ), 66 ( A_{0(iso)} )</td>
<td>28.1 ± 1.4</td>
<td>0.1 ± 0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Blieskastel</td>
<td>12. 8.81</td>
<td>63</td>
<td>-57.4</td>
<td>-8.1</td>
<td>-16.1</td>
<td>64 ( A_{0(cm)} ), 70 ( A_{0(im)} ), 66 ( A_{0(iso)} )</td>
<td>30.5 ± 2.8</td>
<td>0 ± 0.3</td>
<td>≤ 2.9</td>
<td>0.11 ± 7%</td>
</tr>
</tbody>
</table>

\(^a\) Mean value of three \(^{39}\)Ar measurements: 31.7 ± 3.0; 37.4 ± 3.4; 31.2 ± 2.8.

\(^b\) \( A_{0(im)} \) denotes the correction based on the isotope mixing model, \( A_{0(iso)} \) and \( A_{0(cm)} \) stand for the isotope exchange model and the chemical mixing model, respectively.
in the groundwaters, with the intent of proving the assumption that subsurface-produced $^{39}$Ar can be neglected in this sandstone aquifer.

Table III shows the isotope contents and the initial $^{14}$C concentrations of the groundwaters calculated by means of different correction models. From the measured isotope concentrations, the mean water residence times were calculated on the basis of the piston-flow model and the exponential model (PFM and EM; see, for instance, Ref. [20]). These calculations take into account the different input functions of each isotope. The results are discussed below and are given in Table IV. It has to be emphasized that the applied mixing models and ratios are given as examples from which trends and orders of magnitude can be deduced. Besides variations of the $^3$H input, reasons for the relatively large uncertainties are the measured low $^3$H and $^{85}$Kr concentrations in the waters, which prevent a precise application of the PFM and EM. The interpretation can be improved by considering additional $^{85}$Kr (and $^{39}$Ar) results; however, until now, only a few single results are available.

The $\delta^2$H and $\delta^{18}$O values of all groundwaters (including those from which $^{39}$Ar was determined) follow the relation $\delta^2$H = $8 \cdot \delta^{18}$O + 10‰, which indicates their meteoric origin.

3.3.1. Well Kikkel

From hydrogeology and from the different mean residence times of groundwaters obtained from different isotope concentrations it must be concluded that the water represents a mixing system of young and old water. The young component cannot be of very recent origin because the $^{85}$Kr content corresponds only to 4% of the present atmospheric level and the measured $^3$H content would need a much larger contribution of recent precipitation. This is also evident from the $^3$H/$^{85}$Kr ratios for which recent waters show about 1 TU per dis/min per mL Kr, while in this well 12 TU per dis/min per mL Kr have been measured. Assuming an age of, for instance, 13 years (PFM) and 30 years (EM), respectively, for the young component and an amount of 15% admixture, one can explain the measured $^3$H and $^{85}$Kr activities. The old component, with an amount of about 85%, then can be estimated to have an activity of about 70% modern $^{39}$Ar, which corresponds to a mean, model-independent residence time of about 140 years. This age seems quite high for water from an uncovered well with a relatively small depth, but it is likely that artesian sandstone waters mainly from the Middle Bunter are admixed.

The admixture of the old component implies a slight correction of the $^{14}$C concentration which lies within the error of the $^{14}$C method. Within these limits the measured $^{14}$C concentration is in agreement with the calculated initial $^{14}$C concentration, confirming that the old component also shows a mean residence time of below 2000 years. For this groundwater, all isotope data can be explained consistently by assuming a two-component mixture in the groundwater.
TABLE IV. MEAN RESIDENCE TIMES OF GROUNDWATERS FROM DEEP WELLS DEDUCED BY THE PISTON-FLOW MODEL (PFM) AND THE EXPONENTIAL MODEL (EM)

<table>
<thead>
<tr>
<th>Well</th>
<th>Isotopes</th>
<th>Mean residence times (years)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>EM</td>
<td>PFM</td>
<td></td>
</tr>
<tr>
<td>Kirkel</td>
<td></td>
<td>&lt;2000</td>
<td>&lt;2000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{14}$C</td>
<td>125 ± 35</td>
<td>110 ± 25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{39}$Ar</td>
<td>&gt;60</td>
<td>25 ± 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{85}$Kr</td>
<td>&gt;60</td>
<td>&gt;25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{3}$H</td>
<td>&gt;60</td>
<td>&gt;25</td>
<td></td>
</tr>
<tr>
<td>Altheim 1</td>
<td>$^{14}$C</td>
<td>&lt;2000</td>
<td>&lt;2000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{39}$Ar</td>
<td>130 ± 25</td>
<td>115 ± 20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{85}$Kr</td>
<td>~40</td>
<td>&gt;25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{3}$H</td>
<td>~40</td>
<td>&gt;25</td>
<td></td>
</tr>
<tr>
<td>Altheim 2</td>
<td>$^{14}$C</td>
<td>&lt;2000</td>
<td>&lt;2000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{39}$Ar</td>
<td>770 ± 80</td>
<td>430 ± 30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{85}$Kr</td>
<td>&gt;60</td>
<td>&gt;25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{3}$H</td>
<td>&gt;60</td>
<td>&gt;25</td>
<td></td>
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<tr>
<td>Blickweiler</td>
<td>$^{14}$C</td>
<td>2400–4200</td>
<td>2000–3600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{39}$Ar</td>
<td>&gt;2000</td>
<td>&gt;1200</td>
<td></td>
</tr>
<tr>
<td>Blieskastel</td>
<td>$^{14}$C</td>
<td>8400–12 000</td>
<td>5800–7300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{39}$Ar</td>
<td>&gt;2000</td>
<td>&gt;1200</td>
<td></td>
</tr>
</tbody>
</table>

3.3.2. Wells Altheim 1 and 2

The measured $^{3}$H and $^{85}$Kr activities again stipulate an admixture of a young component. The admixture of present fresh water can be excluded because of the measured $^{3}$H/$^{85}$Kr ratios of 4–5 TU per dis/min per mL Kr in groundwaters of both wells.
The isotopic composition of water from Altheim 1 cannot be explained by assuming water of a single component. A two-component mixture, however, can explain all isotope data: about 30% of young water ($T_{\text{PFM}} = 5$ years; $T_{\text{EM}} = 7$ years) mixed with an old component explains the $^3$H and $^{85}$Kr data.

The $^{39}$Ar activity of the old component is calculated to be about 70% modern Ar. This two-component mixture can be understood from hydrogeology: the borehole collects water which has passed the covering limestone before entering the sandstone, but also groundwater from the Middle Bunter.

Groundwater in Altheim 2 shows a $^3$H/$^{85}$Kr ratio similar to that of Altheim 1, which again suggests an admixture of young but not recent water to an old water component in this well. Because of the deeper casing of the well Altheim 2 compared with Altheim 1, this admixture shows only a 5% fraction of water similar to that which is found in Altheim 1. The remaining 95% of Altheim 2 water then would give a $^{39}$Ar concentration of about 30% modern Ar. The higher age of the old component seems reasonable because the borehole reaches a greater depth in the Middle Bunter (see Fig. 2).

The measured and calculated $^{14}$C values for Altheim 1 and Altheim 2 are not in contradiction to the assumed mixing processes: compared with Kinkel, higher $\delta^{13}$C and lower $A_0$ values show the influence of water whose isotopic composition was influenced while passing the Muschelkalk layers. Within the limits of the method, the corresponding measured and calculated $^{14}$C values indicate that the waters can be expected to be relatively young. The results given in Table III for the measured $^{14}$C contents in groundwater from Altheim 1 seem higher than the calculated $A_0$ values, but this is not a real difference. It can be seen from Table II that the overall uncertainty in calculating $A_0$ can be as high as ± 11 ppm in this area.

3.3.3. Blickweiler and Blieskastel

Both wells show very low $^3$H, $^{85}$Kr and $^{39}$Ar values, which prove that no detectable amount of young water is admixed to the sandstone water. This corresponds to the great drilling depths and effective casings of both wells. The measured low $^{39}$Ar concentration also shows that in these waters the subsurface-produced $^{39}$Ar activity is below 4%. This can be compared with estimated production rates based on the U, Th and K content and on the porosity of the aquifer (see Section 2). Assuming similar conditions in the groundwaters from wells Kinkel and Altheim, subsurface production of $^{39}$Ar can be neglected. The $^{39}$Ar results then correspond only to residence times and mixing ratios of different water components. Depending on the applied model, the corrected $^{14}$C activities give residence times of 2000–4000 years (PFM, EM) for Blickweiler and 5000–12 000 years (PFM, EM) for Blieskastel. However, from the comparable $^3$H and $^{18}$O concentrations of all samples discussed above, ages higher than 10 000 years BP.
seem to be unlikely. Taking into account that the small amounts of CH₄ found in water from Blieskastel affect the calculation of the initial ¹⁴C concentration, the uncertainty of the ¹⁴C age determination in water from this well is relatively high.

4. CONCLUSIONS AND FUTURE WORK

The combined use of ³H, ⁸⁵Kr, ³⁹Ar and ¹⁴C isotope concentrations in this study proved to give valuable information. In young waters where the calculated and measured ¹⁴C concentrations showed no significant difference, only upper limits of groundwater ages could be deduced from ¹⁴C. The range of groundwater ages below about 1000 years, however, could be estimated with ³⁹Ar and additional information was obtained from the ³H/⁸⁵Kr ratios. It turned out to be possible to estimate mixing ratios and to determine mean residence times of mixing components as well. Especially the calculation of ³H/⁸⁵Kr ratios led to the conclusion that the admixed ‘young’ component of a two-component mixing system is an ‘aged’ and not a very recent one.

Therefore, in further hydrological studies, again ³⁹Ar, ⁸⁵Kr, ³H, ¹⁴C and chemical data should be determined in order to obtain quantitative information about mixing processes. For those investigated groundwaters for which ³⁹Ar could give only lower age limits, the ¹⁴C method once more showed its applicability for dating in the range of about 2000–40 000 years B.P.

The present study also shows that isotope results should be discussed in connection with hydrogeological and chemical investigations, which are necessary especially when calculating initial ¹⁴C concentrations and derived ¹⁴C ages. Because of the clear chemical evolution in this area, equivalent results were obtained from calculations of the initial ¹⁴C concentration using different correction models. This agreement is considered to be significant, especially in groundwaters from wells where the measured and calculated ¹⁴C concentrations were in agreement (within the errors of determination and calculation). These ¹⁴C concentrations indicate a groundwater age of below 2000 years, which could be determined quantitatively with ³⁹Ar results. The consistent ³⁹Ar and ¹⁴C age results indicate that the assumptions which had to be made for the ¹⁴C corrections were reasonable. Therefore, additional valuable information for the initial ¹⁴C concentration is obtained from ³⁹Ar determinations.

We were lucky to find an aquifer where, because of deep well casings (the wells are partly artesian) and low U and Th contents, the amount of ³⁹Ar diffusing from the atmosphere into the aquifer as well as the amount of subsurface-produced ³⁹Ar could be neglected. Therefore, all ³⁹Ar activity detected corresponded to the time and mixing history of the groundwater. Expanding the work of investigating the hydrological use of ³⁹Ar, together with the determination of other isotope concentrations, e.g. ³H, ⁸⁵Kr and ¹⁴C, in other aquifer systems, implies further
investigations of the effect of subsurface $^{39}$Ar production. Once we have increased our $^{39}$Ar measuring capacity, these investigations will concentrate on irradiation experiments of core material and on further improvements of the calculation of subsurface isotope production.

Appendix

SUBSURFACE PRODUCTION OF $^{39}$Ar AND OTHER ISOTOPES

In thermal waters from granitic aquifers, $^{39}$Ar concentrations have been found which are several times higher than the $^{39}$Ar concentration of the atmosphere. The reason for this is the effect of subsurface production of $^{39}$Ar by the reaction $^{39}$K(n, p)$^{39}$Ar (see Refs [3, 4]). The examination of the subsurface, neutron-induced production of $^{39}$Ar has begun theoretically and experimentally. As stated in Ref. [21], a variation of stable Ne (and Ar) isotope ratios in gases from minerals and rocks can be correlated with the U and Th concentrations and the concentration of target nuclei in the rock [22-24]. Since information on long-time neutron and alpha radiation can be derived from these ratios, a computer program has been worked out which calculates the neutron- and alpha-induced variation of some isotope abundances per cubic metre of rock and per time interval. The equations for calculating the production rates and equilibrium concentrations of produced isotopes can be found in Refs [3] and [24]. Equilibrium concentrations of radioisotopes, together with variations of stable isotope ratios, have been calculated as a function of the elemental and isotopic composition of sandstone, limestone and granite, as well as their average U, Th and target-nuclei content which was taken from the literature (see Refs [23-25]).

As found out in investigations of the concentrations of subsurface-produced $^{36}$Cl, $^{37}$Ar, $^{39}$Ar, $^{22}$Ne and $^{21}$Ne, the following reactions mainly contribute to the subsurface isotope production (see Refs [21, 22, 26]):

$^{22}$Ne:

$^{19}$F(α, p)$^{22}$Ne; $^{19}$F(α, n)$^{22}$Na $→$ β + $^{22}$Ne

$^{21}$Ne:

$^{18}$O(α, p)$^{21}$F $→$ β + $^{21}$Ne; $^{18}$O(α, n)$^{21}$Ne

$^{37}$Ar, $^{39}$Ar and $^{36}$Cl: $^{40}$Ca(n, α)$^{37}$Ar; $^{39}$K(n, p)$^{39}$Ar; $^{35}$Cl(n, γ)$^{36}$Cl

The reaction $^{34}$S(α, n)$^{37}$Ar gives only 1% of the production rate calculated from the $^{40}$Ca(n, α) reaction for $^{37}$Ar. Similarly, the reaction $^{34}$S(α, p)$^{39}$Cl $→$ β + $^{39}$Ar produces maximally 10% of the total $^{39}$Ar content in normal granite, which is mainly due to the $^{39}$K(n, p)$^{39}$Ar reaction.
Relating subsurface-produced isotope variations to the number of isotopes per cubic metre of aquifer material (corrected for the water and gas content) these isotope concentrations can be expressed in terms of their atmospheric abundance, taken to be 100%.

100% $^{39}$Ar correspond to 0.11 dis/min $^{39}$Ar per litre Ar
and to a ratio of $8 \times 10^{-16}$ $^{39}$Ar/Ar (see Ref. [2])

100% $^{37}$Ar correspond to $2.4 \times 10^{-3}$ dis/min $^{37}$Ar per litre Ar
and to a ratio of $6.5 \times 10^{21}$ $^{37}$Ar/Ar (see Ref. [27])

100% $^{36}$Cl correspond to $2.8 \times 10^{9}$ $^{36}$Cl per gram Cl
and to a ratio of $1.6 \times 10^{13}$ $^{36}$Cl/Cl (see Ref. [27])

Figure A1 compares the calculated $^{37}$Ar, $^{39}$Ar and $^{36}$Cl concentrations as they can be reached in the Cl and Ar content of, for instance, average granite.
If one assumes total diffusion of the produced isotopes from the rock into its pore volume and further that this pore volume is filled with water of normal Ar (and Cl) content, one gets the values shown in Fig.A1. The dot-dashed line indicates the calculated highest isotope concentration which could be reached in this pore water. The equilibrium concentration for $^{36}\text{Cl}$ in pore water is taken from Bentley [24]. Porosity was assumed to be 1% in granite.

The unknown fraction of the subsurface-produced $^{39}\text{Ar}$ isotopes diffusing from the aquifer material into the pore water, the uncertainty of the effective neutron production from ($\alpha$, n) reactions and that arising from the unknown effective neutron energy and from effective cross-sections used for calculations encouraged accelerator experiments in which core material is irradiated with monochromatic neutrons.

In the first experiments, 6 MeV neutrons were used to irradiate Triassic Sandstone where no $^{39}\text{Ar}$ had been found in the aquifer, and to irradiate a granitic core from Wildbad (Black Forest, Federal Republic of Germany) where about 500% modern $^{39}\text{Ar}$ had been measured in groundwater [3]. The diffusion of the produced $^{39}\text{Ar}$ and $^{37}\text{Ar}$ will be examined using the 'stepwise degassing technique' [28]. These experiments are still continuing.

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ENVIRONMENTAL ISOTOPE STUDIES
IN TWO AQUIFER SYSTEMS

A comparison of
groundwater dating methods

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Abstract

ENVIRONMENTAL ISOTOPE STUDIES IN TWO AQUIFER SYSTEMS: A COMPARISON
OF GROUNDWATER DATING METHODS.

The paper presents a summary of results of the study co-ordinated by the IAEA and
initiated to investigate an apparent anomaly between the groundwater residence times
determined by the application of a conventional piston-flow model to 39Ar and 14C data. The
study has also included measurements of hydrochemical data, tritium, stable isotopes of
hydrogen and oxygen, the isotopes 85Kr and 32Si, the inert gases helium, neon, argon, krypton
and xenon, the uranium series nuclides 234U, 226Ra, 222Rn and 238U/238U activity ratios. This
work has been carried out on samples from two aquifers, Blumau, an aquifer of fluvial origin,
in Austria, and the East Midlands Triassic Sandstone in the United Kingdom. Conventional
piston-flow considerations applied to Blumau $^{14}$C and $^{39}$Ar data have resulted in an order-of-magnitude difference between groundwater residence times for the two radionuclides. Hydraulic estimates of the groundwater residence time in the Blumau aquifer are too uncertain to resolve the apparent ambiguity. The East Midlands results, however, are in better agreement. Thus, $^{39}$Ar concentrations above the detection limit were found in three samples derived from boreholes in the confined part of the aquifer but just downgradient from the recharge area which also yielded $^{14}$C levels of 30 pmc or greater. In contrast, in five boreholes the deeper confined groundwater des have both $^{14}$C and $^{39}$Ar concentrations at or around the detection limit and therefore no conclusive comparison is possible. The shift to lighter oxygen and hydrogen isotope composition in deeper groundwater in the East Midlands aquifer has been inferred to be due to palaeoclimatic influences in support of the $^{14}$C data residence time-scale. Similar shifts in the stable oxygen and hydrogen isotopes and inert gases are not present in the Blumau data. Significant amounts of $^3$H and $^{85}$Kr are not present downgradient in the Blumau aquifer and therefore the presence of significant quantities of recent waters is precluded. Significant concentrations of both $^3$H and $^{85}$Kr in downgradient samples from the East Midlands aquifer suggest mixing with recent waters or diffusion of $^{85}$Kr through an aquiclude in some cases. Full comparison of $^3$H and $^{85}$Kr is not possible because the $^3$H data set is incomplete. The concentrations of radiogenic $^4$He are in excess of the estimated values of in-situ production for any reasonable time-scale calculated from U, Th and K abundances in both aquifer matrices. This $^4$He excess has been interpreted to be due to diffusion from adjacent strata. The measured concentrations of U in both aquifers are consistent with observed hydrochemical conditions in both aquifers, but the changes in the $^{234}$U/$^{238}$U activity ratio in both cases follow no regular pattern and are attributed to preferential solution of $^{238}$U. Concentrations of $^{222}$Rn and $^{228}$Ra are uniform in groundwater from both aquifers. Discrepancies between piston-flow age interpretation of $^{14}$C and $^{39}$Ar data have not been resolved satisfactorily in the study of these two aquifers. Groundwater mixing may be an important factor, but quantitative analysis of such mixing is not possible with present data. It has therefore been concluded that more measurements on carefully selected groundwater samples, and further investigations into underground production rates for $^{39}$Ar on one hand and exchange mechanism of $^{14}$C between solution and carbonate on the other, are necessary.

1. Introduction

Environmental isotopes are now almost routinely applied in studies of groundwater resources. Tritium, radiocarbon and stable-isotope ratios of D/H and $^{18}O$/$^{16}O$ have been most widely used, and increasing use is being made of inert gases and uranium series isotopes. Several other radiocisotopes, such as $^{39}$Ar and $^{32}$Si, existing in the water environment have been identified and their data occasionally reported. However, the extremely low levels of radioactivity require processing of large volumes of water, and the high sophistication of measurements needed for these low levels has prevented their broader application.

In general, the levels of environmental isotopes in ground waters have been used to infer times of isolation or confinement. Historically, this method has been generally
referred to as ground-water 'dating' where an 'age' is ascribed to ground water. There is now a greater awareness of the fact that water may have components of different ages and that the residence time is more correctly described by a distribution of times dictated by mixed-flow models such as the exponential or the dispersion model. The interpretation of isotope data by means of a simple piston-flow model without mixing, though still widely used, is an oversimplification.

A previous study (1) in 1978, showing large discrepancies between values of ground-water piston-flow 'age' determined by measurements of $^{14}$C and $^{39}$Ar, caused considerable concern to practising hydrologists and cast some doubt on the value of isotopic studies in water resource evaluations. In order to investigate this apparent anomaly in the light of measurement limitations and ground-water flow models, and to provide comprehensive information on intercomparison of various isotopic methods, the International Atomic Energy Agency organised a coordinated research programme involving seven laboratories during the period 1979 to 1982. Two study areas, the Blumau aquifer in Austria and the East Midlands Triassic Sandstone Aquifer in the UK, were chosen on the basis of assumed well-recognised hydrological conditions and previously determined $^{14}$C contents ranging from modern to activities below detection limit. This paper presents a summary of results of the coordinated study and draws specific conclusions on the use of the various isotope methods in ground-water studies.

2. The Blumau Aquifer

2.1. Hydrogeological background

The confined Blumau aquifer, located in southeastern Austria (Fig. 1), is a part of the Tertiary sedimentary body of the 'Styrian Basin'. The geological strata are defined by a sequence of clays, silts, gravels and sands. The aquifer formation itself has been developed since the early Tertiary in a Pannonian valley by fluvial sedimentation, which later became covered by clay material. Erosion processes during the Quaternary opened this horizon and exposed the aquifer in the South-West.

Former investigations, concerning the flow of the River Feistritz(2) from the crystalline rocks of the Eastern Alps onto the Tertiary deposits, show that in some parts of the valley the sediment permeability would allow some inflow from the river. This happens in the area of Grosswilfersdorf where the recent coarse sediments of the Feistritz valley overlie and are in
FIG. 1. Location of the confined Blumau aquifer in south-eastern Austria.

Hydraulic connection with the Tertiary gravels and sands of the Blumau aquifer.

The aquifer has a northeasterly dip with a gradient of approximately 1% towards the lower Safen valley where it reaches a depth of approximately 60 m in the area of Blumau. There, it is exploited by a number of artesian wells.
Three test boreholes were drilled in order to explore the rather narrow aquifer (Figs 2 and 3). The borehole at Grosswilfersdorf penetrates a thin unconfined shallow aquifer and clay sediments of 11m thickness before entering a gravel horizon between 15 and 21m in depth which forms the aquifer. The underlying clay sediments form an aquiclude below the confined aquifer.

The sequence in the borehole at Jobst shows this aquifer in two very thin sandy layers between 33.4 and 35.2m depth. The small thickness indicates that the borehole is located near the lateral border of the deposit. In the Blumau test borehole, the thickness of the aquifer is approximately 8m and this is overlain by 49m of clay sediments.

Water-level measurements have been carried out to obtain information about the hydraulic connections between the surface
FIG. 3. Vertical cross-section of the three test boreholes specially drilled for the Blumau study, depicting the depth and thickness of the confined aquifer.
water and shallow ground water in the vicinity of Grosswilfersdorf and the deeper confined waters of the aquifer. The results show that the river Feistritz partially recharges the investigated artesian aquifer. The transit time of ground water for this aquifer may be estimated from simple hydraulic considerations assuming piston flow. The cross-section of the aquifer is estimated to be only \(3 \times 10^4 \text{ m}^2\) in the area of Grosswilfersdorf, the permeability \(k\) is estimated to be \(10^{-4}\) to \(10^{-3}\text{m/s}\) (measurements in a nearby aquifer with more coarse sand gave a value of \(3.5 \times 10^{-4} \text{ m/s}\)) and the hydraulic gradient between Grosswilfersdorf and Blumau is 0.03%. Assuming the actual porosity of the aquifer to be about 10%, the estimated transit time of the ground water between Grosswilfersdorf and Blumau ranges from 700 to 7000 years.

2.2. Hydrochemistry

Table 1 shows the analytical results for samples taken during 1981 and 1982. Chemical analyses of samples collected prior to 1981 are considered unreliable and have been excluded. The location of sites is shown in Fig. 2.

Four hydrogeological units are identified in the Blumau area (Fig. 3):

(i) The surface water of the Feistritz river shows the lowest mineralisation of all samples (average 126 mg/L). Its chemical composition is dominated by calcium, bicarbonate and sulphate ions (Table 1).

(ii) Shallow well 7 is in the presumed recharge area. Its hydrochemistry can be assumed to be representative of input to the confined Blumau aquifer. The chemical composition of this water is a result of mixing of the river water, shallow ground water and direct infiltration. The latter is characterised by the relatively high chloride, sulphate and nitrate values resulting from anthropogenic pollution. This three-component mixture provides an explanation for the high degree of undersaturation with respect to calcite and dolomite (see Table 2). The observed variations in the hydrochemical composition can be explained by different recharge and mixing conditions.

(iii) The confined water of the Blumau aquifer is of the calcium-magnesium-bicarbonate type. Chloride and sulphate are minor constituents. The chloride content which is about 6 mg/L at the test borehole at Grosswilfersdorf decreases downgradient in the confined aquifer. The low values at Blumau are believed to be representative of input conditions prior to the activities of man, assuming that chloride has remained conservative in the aquifer.
### Table 1. Chemical Analyses of Surface and Ground Waters (Blumau Study)

Sample localities are shown in Fig. 2. For each site the upper line of data gives the results for samples collected in November 1981 and the lower line gives the results for samples collected in November 1982.

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth (m)</th>
<th>T (°C)</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>Na (mg/L)</th>
<th>K (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Mg (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
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<td>Grosswilerdorf 9 (Feistritz River)</td>
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<td>6.0</td>
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<td></td>
<td>4</td>
<td>2.0</td>
<td>23</td>
<td>4.9</td>
<td>79</td>
<td>4.6</td>
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<td>Shallow Ground Water of the Feistritz Valley</td>
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<td>Confined Ground Waters of Deeper Aquifers</td>
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*n.d. = not determined.
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<th>Site</th>
<th>SI  (Calcite)</th>
<th>SI (Dolomite)</th>
<th>SI (Gypsum)</th>
<th>Ca:Mg:HCO₃</th>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
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<td>Date</td>
<td>$^{14}$C (ppm)</td>
<td>$^{13}$C (‰)</td>
<td>$^{18}$O (‰)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>------------</td>
<td>----------------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>-69.6</td>
</tr>
<tr>
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<td>22.11.82</td>
<td>109.0 ± 6.3</td>
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<td>-68.3</td>
</tr>
<tr>
<td>Grosswilerdorf 7</td>
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<td>-15.8</td>
<td>-61.5</td>
</tr>
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<td>24.11.82</td>
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<td>-60.4</td>
</tr>
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</tr>
<tr>
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<td>17.09.79</td>
<td>47.3 ± 1.2</td>
<td>-13.2</td>
<td>-63.6</td>
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<td>18.09.79</td>
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<tr>
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<td>13.11.81</td>
<td>48.3 ± 1.1</td>
<td>-13.5</td>
<td>-63.0</td>
</tr>
<tr>
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<td>22.11.82</td>
<td>49.8 ± 1.3</td>
<td>-14.0</td>
<td>-63.3</td>
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<tr>
<td></td>
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<td>48.6 ± 1.3</td>
<td>-14.0</td>
<td>-64.0</td>
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<tr>
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<td>-64.7</td>
</tr>
<tr>
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<td>-64.1</td>
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<td>34.0 ± 0.8</td>
<td>-14.1</td>
<td>-65.2</td>
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<tr>
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<td>23.11.82</td>
<td>35.2 ± 1.0</td>
<td>-13.7</td>
<td>-64.1</td>
</tr>
<tr>
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<td>23.11.82</td>
<td>35.3 ± 1.0</td>
<td>-13.7</td>
<td>-63.3</td>
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<tr>
<td>Blumau 15</td>
<td>06.07.79</td>
<td>28.0 ± 0.8</td>
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<td>-64.1</td>
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<tr>
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<td>17.09.79</td>
<td>28.0 ± 1.1</td>
<td>-11.8</td>
<td>-63.1</td>
</tr>
<tr>
<td></td>
<td>13.11.81</td>
<td>28.1 ± 0.6</td>
<td>-11.0</td>
<td>-65.8</td>
</tr>
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<td></td>
<td>24.11.82</td>
<td>27.6 ± 1.0</td>
<td>-12.3</td>
<td>-64.6</td>
</tr>
<tr>
<td>Blumau 14</td>
<td>13.11.81</td>
<td>51.0 ± 2.0</td>
<td>-11.7</td>
<td>-66.2</td>
</tr>
<tr>
<td></td>
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<td>-66.2</td>
</tr>
<tr>
<td>Blumau 11</td>
<td>06.07.79</td>
<td>15.6 ± 0.6</td>
<td>-11.8</td>
<td>-66.8</td>
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<td>17.09.79</td>
<td>15.3 ± 0.6</td>
<td>-11.3</td>
<td>-65.5</td>
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<tr>
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<td>12.11.81</td>
<td>15.9 ± 0.5</td>
<td>-12.1</td>
<td>-66.8</td>
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<td>24.11.82</td>
<td>16.1 ± 0.9</td>
<td>-12.4</td>
<td>-66.6</td>
</tr>
<tr>
<td>Grosswilerdorf 8</td>
<td>12.11.81</td>
<td>2.6 ± 0.3</td>
<td>-10.7</td>
<td>-83.3</td>
</tr>
<tr>
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<td>22.11.82</td>
<td>2.4 ± 0.7</td>
<td>-11.5</td>
<td>-83.5</td>
</tr>
<tr>
<td>Blumau 32</td>
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<td>-75.7</td>
</tr>
<tr>
<td></td>
<td>24.11.82</td>
<td>0.3 ± 0.7</td>
<td>-10.3</td>
<td>-75.5</td>
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</tbody>
</table>
(iv) Grosswilfersdorf 8 and particularly Blumau 32 represent more evolved ground waters in deeper aquifers. The high sodium contents are the result of cation exchange processes with clay materials.

In general, there is only slight hydrochemical variation between 1981 and 1982 in the Blumau aquifer and much of this may be attributed to analytical variance. However, the hydrochemical analyses for Jobst borehole show a significant temporal change which may be due to the sampling in 1982 being preceded by a longer period of pumping during which increasing mineralisation was observed. This borehole is situated on the edge of the aquifer where different mixing regimes may be induced during pumping.

Increases in Ca$^{2+}$ and HCO$_3^-$ between the recharge zone and the boreholes at Grosswilfersdorf and Jobst are indicative of calcite dissolution. The consistently lower values of Ca$^{2+}$ and HCO$_3^-$ downgradient at Blumau do not follow any progressive chemical evolution from present ground water at Jobst and Grosswilfersdorf. However, the Blumau waters are characterised by very low Cl$^-$ and SO$_4^{2-}$ concentrations which suggest that initial conditions for their hydrochemical evolution were different to those for upgradient water. Differences in Na and Mg contents between Blumau 11 and 14/15 demonstrate that inhomogeneities exist. Calculations of saturation indices show that all ground waters sampled in the confined aquifer are at, or close to, equilibrium with respect to calcite and are undersaturated with respect to dolomite and gypsum (Table 2). The molar ratios for calcium, magnesium and bicarbonate suggest that congruent dissolution of low magnesium calcite exerts a dominant influence on the ground-water chemistry.

2.3. Isotopic data for the Blumau aquifer

2.3.1. Carbon isotopes, tritium, D/H and 18O/16O

The interpretation of ground-water ages from $^{14}$C measurements depends on the calculation of the amount of 'dead' carbonate added to solution from the aquifer matrix and of an effective initial value for $^{14}$C concentration. Methods which have been proposed for this calculation have varying degrees of refinement, but are all based on the principle that this 'dilution' of $^{14}$C is accompanied by changes in hydrochemistry and in $^{13}$C/$^{12}$C ratio of dissolved inorganic carbon. The $^{14}$C adjustment models used for data from both the Blumau and the East Midlands aquifer in this study assume that all reactions with carbonate have occurred in a system which is closed to external sources of CO$_2$ and that these reactions are reflected
FIG. 4. Plot of $\delta D$ against $\delta^{18}O$ data obtained in the Blumau study, showing that all the data lie very close to the meteoric line. The solid square represents the annual weighted mean for present precipitation, obtained from samples collected at the Vienna station and included here for comparison.

in shifts in the $\delta^{13}C$ of dissolved inorganic carbon. They also assume that isotopic equilibrium between solution and carbonate minerals is not achieved either on a bulk scale or because of surface exchange reaction on carbonate grains.

The isotope results of samples collected from the Blumau study area during four years are shown in Table 3. The stable isotope compositions of all water samples are close to the meteoric line (Fig. 4). The compositions of samples of the Blumau aquifer are similar to those of contemporary precipitation and show that the Blumau waters are a mixture of shallow and river water. The Feistritz River is draining water
TABLE 4. $^{14}$C PISTON-FLOW AGES CALCULATED ACCORDING TO VARIOUS MODELS
(see text) – (BLUMAU STUDY)

<table>
<thead>
<tr>
<th>Site</th>
<th>$^{14}$C Age (Years)</th>
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</thead>
<tbody>
<tr>
<td>Grosswilfersdorf Test Borehole</td>
<td>Modern (up to 700 years)</td>
</tr>
<tr>
<td>Jobst Test Borehole</td>
<td>2800 - 3800</td>
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<tr>
<td>Blumau 15</td>
<td>4200 - 4800</td>
</tr>
<tr>
<td>Blumau 14</td>
<td>5300 - 5900</td>
</tr>
<tr>
<td>Blumau 11</td>
<td>9100 - 9800</td>
</tr>
<tr>
<td>Grosswilfersdorf 8</td>
<td>24 000</td>
</tr>
<tr>
<td>Blumau 32</td>
<td>&gt;40 000</td>
</tr>
</tbody>
</table>

The following values have been adopted for the calculations:

$\delta^{13}$C (rock) = -2 to +2 $\%_0$; $\delta^{13}$C (CO$_2$) = -25$\%_0$; $\Lambda^{14}$C = 100 pmc.

from a higher altitude as it is more depleted in heavier isotopes than local recharge represented by Grosswilfersdorf shallow aquifer. However, some evaporation of water in the shallow aquifer is also possible which would make it isotopically heavier than the precipitation input. The high tritium content of the river water and shallow aquifer, together with high (110 to 115 pmc) radiocarbon concentrations, confirm that both are very young waters. Waters from Grosswilfersdorf 8 and Blumau 32 are more depleted in $^{18}$O by 1.5 to 2%. This depletion is too great to be attributed to differences in altitude of recharge sources and therefore must correspond to recharge in colder climatic conditions and indicate older water.

The wells in the Blumau aquifer have had constant $^{14}$C concentrations over a period of four years and these decrease along the assumed ground-water flow direction. The occasional presence of small amounts of tritium in a few samples can be explained by contamination with recent water (some boreholes, e.g. Grosswilfersdorf and Jobst, have been pumped only for sampling) or by analytical variation (which is illustrated by duplicate measurements by scintillation counting and gas proportional counting on a Grosswilfersdorf sample from 10/9/1979). The anomalously low $^{14}$C measured for Jobst in 1979 after extensive pumping cannot be satisfactorily explained,
<table>
<thead>
<tr>
<th>Site</th>
<th>39 Ar (1) (% Modern)</th>
<th>39 Ar Mean Residence Time (2) (Years)</th>
<th>85 Kr in Sample (dpm)</th>
<th>02 (4) (% of Extracted Gas)</th>
<th>Air Contamination Estimated from 85 Kr 02 (% of extracted gas)</th>
</tr>
</thead>
<tbody>
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<td>Grossulifersdorf</td>
<td>102.2 ± 4.0</td>
<td>&lt;35 (1.64c)</td>
<td>&lt;35 (1.64c)</td>
<td>0.058 ± 0.014</td>
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<tr>
<td>Test Borehole</td>
<td>100.2 ± 5.1</td>
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<td></td>
</tr>
<tr>
<td>Dobet</td>
<td>54.3 ± 3.0 (5)</td>
<td>340 ± 20</td>
<td>540 ± 30</td>
<td>0.032 ± 0.009</td>
<td>&lt;0.2</td>
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<tr>
<td>Test Borehole</td>
<td>39.5 ± 2.8</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>44.0 ± 3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blunau 11</td>
<td>21.0 ± 2.5 (5)</td>
<td>870 ± 70</td>
<td>&lt;3000</td>
<td>0.027 ± 0.009</td>
<td>&lt;0.2</td>
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<tr>
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<td>9.7 ± 2.3</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>11.8 ± 2.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Samples collected in 1970.

(1) Corrected for contamination by modern air.
(2) Errors given are 2o counting errors.
(3) Corresponding to (a) piston-flow age and (b) exponential model.
(4) Measured by E. Moor, Berne, and P. Bätschi, Würenlingen.
(5) Not used for 'age' calculations; a contamination of the sample by 222Rn or spurious counts during measurements cannot be excluded.
since δ¹³C remained unchanged and a sample was not taken for tritium. However, the ¹⁴C content remained constant at 35 pmC during similar tests in 1982, although tritium results show a decrease with pumping. The probability of mixing in the Jobst borehole, dependent upon pumping conditions, is suggested by the chemical data. The decrease in HCO₃⁻ between Jobst and Blumau is accompanied by an increase in δ¹³C, which is further evidence against these samples representing a progressive chemical evolution and for the Blumau ground waters evolving from different initial conditions for the carbonate system.

Various adjustment models were applied to the ¹⁴C data to infer the radiocarbon piston-flow 'ages': chemical evolution model(3), simple δ¹³C correction(4), 'total carbon' correction(5) and assumption of initial ¹⁴C concentration as measured in the first borehole at Grosswilfersdorf. All correction methods yield very similar ages and the ranges of these are shown in Table 4. The ¹⁴C 'ages' for the ground waters from the deeper aquifers (24 000 to > 40 000 a) are consistent with their lighter isotopic compositions. Variations in δ¹³C for samples from Blumau 32 cannot be explained, although ¹⁴C values are at, or close to, detection limit.

2.3.2. ³⁹Ar and ⁸⁵Kr

The principles of the dating method with the cosmic-ray-produced isotope ³⁹Ar (T₁/₂ = 269 a) are described in ref. 6. From previous measurements, comparing especially ³⁹Ar and ¹⁴C data, it had to be concluded that for some aquifers the results of these two methods disagree if converted to 'piston-flow' or 'exponential-model' ages(1,7). This discrepancy cannot in all cases be explained by assuming mixing of different old water components. The main uncertainties when applying ³⁹Ar to groundwater studies are underground production of this isotope (as measured in several thermal waters from granitic formations) and diffusion of atmospheric air through the aquiclude, especially at or near the recharge area. ⁸⁵Kr is therefore measured in all samples to test for closed-system conditions and to correct the ³⁹Ar results for a possible contamination of the gas samples by modern air during extraction in the field or processing in the laboratory. Although underground production limits the application of ³⁹Ar, samples with ³⁹Ar activities below the present detection limit of about 3% modern have been found in some aquifers. If other samples from these aquifers show measurable ³⁹Ar activities and if for these samples similar conditions regarding an underground-produced ³⁹Ar contribution can be assumed, then information on the time elapsed since equilibrium with the atmosphere can be obtained.
$^{39}$Ar has been measured in replicate in ground-water samples collected in 1979 from three boreholes in the Blumau aquifer (see Table 5). In two cases, the first measurement gave slightly higher values, which may be attributed to small radon contamination or to spurious counts during measurement. The second and third measurements gave consistent results and were used to calculate $^{39}$Ar piston-flow and exponential-model ages. These ages disagree for Jobst and Blumau [11] with those derived from $^{14}$C measurements, although the decreasing trend in flow direction is observed for both isotope results.

All measured $^{85}$Kr activities were close to the detection limit and the errors therefore are quite high. From these low $^{85}$Kr contents, considerable recent water contributions can be excluded, which agrees with the conclusions from the low $^{38}$Kr contents. From both $^{85}$Kr and $^{38}$Kr, contamination of the samples by modern air is estimated to be negligible ($< 1\%$ of the extracted gas).

An $^{39}$Ar activity of around 100% modern and a low $^{85}$Kr content ($< 0.4\%$ of the present atmospheric level) have been measured for Grosswilfersdorf test borehole. Two explanations are possible:

(a) $^{39}$Ar activity could have been increased by a few percent modern by production from cosmic-ray-induced neutrons in shallow subsurface ($< 3$ m) water at Grosswilfersdorf. The measured $^{39}$Ar value would then correspond to an age of less than 45 years, which would be in agreement with the measured low $^{85}$Kr content.

(b) Even without a cosmic-ray-induced activity the $^{39}$Ar and $^{85}$Kr values do not conflict. For this, the input function of $^{85}$Kr has to be taken into account, which shows that around 30 years before sampling (allowed by the $^{39}$Ar result), only about 2% of the present atmospheric value existed[8]. This would have decayed by a factor of 7 during a period of 30 years.

The effect of a diffusive admixture through the 10 m thick aquicluse can be estimated based on the calculations given in ref. 9. Because the concentration gradient of $^{39}$Ar is very low, an $^{39}$Ar diffusive admixture can be neglected. However, for $^{85}$Kr, the inflow concentration has to be considered, depending on the assumed diffusion constant. For values between $1.5 \times 10^{-4}$ and $1 \times 10^{-5}$ cm$^2$/s the reduction factor of the $^{85}$Kr activity relative to the present atmospheric value (taking into account again the time-dependent input function) is 100 or more.

Diffusion of atmospheric $^{39}$Ar through the aquicluse seems unlikely to be the reason for the discrepancy between the $^{39}$Ar
and $^{14}$C mean residence times e.g. in Blumau 11. In addition to the reason stated above, if $^{39}$Ar could diffuse into the aquifer before decaying, one would expect that most of the radiogenic $^4$He would be lost by diffusion and that He contents corresponding to atmospheric levels of solubility would be obtained.

Underground production of $^{39}$Ar is also not considered a likely reason for the discrepancies between $^{14}$C and $^{39}$Ar model ages in the aquifer. As shown in ref. 6, the production rate in the water itself, with dissolved potassium as target, is not sufficiently large. The production rate in the rock material was estimated based on the measured U, Th and K concentrations in rock samples (see Table 6). The calculated value of $8 \times 10^{-3}$ dis/a per cm$^3$ H$_2$O (45% modern) assumes that all produced $^{39}$Ar diffuses without loss owing to decay from the interior of the grains into the pore water. This assumption overestimates the concentrations by several orders of magnitude as is demonstrated by results from the Midlands aquifer or for thermal waters(6). The expected contribution of the underground production is therefore much smaller than the measured activity in Blumau 11.

The following two interpretations of the $^{39}$Ar results can be offered at present:

(a) The waters in Blumau 11 and Jobst can be a mixture of components of different 'ages'; mixing is also supported by the $^4$He results of Blumau 11 and by the fact that both places are near the border of the aquifer; a young component is indicated by the presence of a $^{38}$Si signal which is, however, only slightly above detection limit.

(b) It is possible that the piston-flow or exponential-model ages determined from the $^{39}$Ar results are meaningful. Hydraulic estimations of ground-water 'age' are too uncertain to confirm or refute this.

2.3.3. Radiogenic $^4$He and inert gases

Atmospheric inert gases are dissolved by a ground water owing to equilibration with air at atmospheric pressure in the recharge zone. The amounts of these dissolved gases are determined by their Henry's Law solubility constants, their partial pressures in the atmosphere and the temperature of the recharge zone.

The $^4$He content of a ground water which has been equilibrated with the atmosphere at 10°C is $4.7 \times 10^{-8}$ cm$^3$/cm$^3$ of water. During its movement through the aquifer, such a ground water dissolves further $^4$He which is produced by decay of
<table>
<thead>
<tr>
<th></th>
<th>Blumau aquifer</th>
<th>East Midlands aquifer</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Jobot 2 (39Ar)</td>
<td>Jobot 2 (39Ar)*</td>
<td>Newhall</td>
</tr>
<tr>
<td>U concentration in rock</td>
<td>1.4 ± 0.12</td>
<td>0.43 ± 0.08</td>
<td>2.65</td>
</tr>
<tr>
<td>Th concentration in rock</td>
<td>1.97 ± 0.75</td>
<td>2.15 ± 0.25</td>
<td>12.23</td>
</tr>
<tr>
<td>K concentration in rock</td>
<td>0.24 ± 0.02</td>
<td>0.43 ± 0.035</td>
<td>2.67</td>
</tr>
<tr>
<td>Estimated neutron production rate</td>
<td>2.5</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Assumed porosity</td>
<td>10</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Calculated $^{39}$Ar production rate</td>
<td>$9 \times 10^{-3}$</td>
<td></td>
<td>$8 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Measured lowest $^{39}$Ar activity:
- $2 \times 10^{-3}$ (11% modern)
- $<5 \times 10^{-6}$ (<2.8% modern)

$H_2O$ saturated with modern Ar at 10°C:
- $1.8 \times 10^{-2}$
- $1.8 \times 10^{-2}$

*Measured by U. Krähenbühl, Berne.
†Measured at Bath University.
‡Assuming that all produced $^{39}$Ar atoms reach the pore water before decay.
U and Th and their daughter isotopes. If the 4He is derived solely within the aquifer matrix, and if it is entirely dissolved by the ground water, then the amount produced is related to the radionuclide contents of the aquifer and ground-water residence times(10).

The results obtained from inert gas analyses of waters from the Blumau aquifer are shown in Table 7. The inert-gas data were corrected for excess air in the samples by iterative subtraction of small amounts of the gases in their atmospheric ratios until the best match between solution/atmosphere equilibration temperatures was obtained. Earlier gas analyses of samples collected in glass in 1981 are omitted because the subsequent samples taken in copper tubes have higher inert-gas contents with good reproducibility and therefore suggest leakage from glass.

All of the ground waters from the Blumau district have 4He contents in excess of that dissolved at recharge. In the Blumau aquifer itself, there is some excess radiogenic 4He, increasing to about 20 x 10^{-8} cm^3 STP/cm^3 H_2O at Blumau 14 and Blumau 15. The U and Th contents of the Blumau sediments, determined by γ-ray spectroscopy, are very low (U = 0.4 - 1.4 μg/g, Th = 2.0 μg/g). The residence time required to produce the observed 4He excess is 78 000a (calculated from the 4He growth equation in ref. 10) using values of 2.6 g/cm^3 for density and 0.10 for porosity. This is very much greater than the possible range of ground-water residence times based on hydrological data. The radiogenic helium in the aquifer is therefore probably produced by radioelement decay in the thin confining clay or deeper layers and diffuses from these into the ground water. The 4He content of the ground water would then be a function of the rate of helium diffusion from these deeper strata and the ground-water velocity.

The ground waters from the boreholes into the deeper aquifers (Grosswilfersdorf 8 and Blumau 32) have 4He contents which are much greater than those generally present in the Blumau aquifer itself. These ground waters therefore probably have much longer residence times than those of the Blumau aquifer. It is, however, not possible to estimate ground-water age since there are no available analyses of the radionuclide contents of the formations involved. For average sandstone U and Th contents (3 μg/g U and 10.5 μg/g Th) the residence times calculated from the 4He growth equation(10) would be 58 000a and 400 000a, respectively, for these sources. One ground water in the Blumau aquifer itself (Blumau 11) also has a 4He content which is higher than that generally found in the aquifer. This can be explained if there is some mixing of ground water from
<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Grosswilsdorf 9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.499 ± 0.008</td>
<td>1.66 ± 0.03</td>
<td>0.42</td>
<td>-</td>
</tr>
<tr>
<td>Grosswilsdorf 7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.105 ± 0.006</td>
<td>1.24 ± 0.09</td>
<td>0.62</td>
<td>-</td>
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<tr>
<td>Grosswilsdorf</td>
<td>16.6</td>
<td>2.09</td>
<td>4.27</td>
<td>9.50</td>
<td>1.36</td>
<td>8.2</td>
<td>0.026 ± 0.002</td>
<td>4.90 ± 0.50</td>
<td>2.14</td>
<td>291</td>
</tr>
<tr>
<td>Test Borehole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.014 ± 0.002</td>
<td>5.70 ± 0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jobet</td>
<td>14.3</td>
<td>2.09</td>
<td>4.23</td>
<td>9.92</td>
<td>1.36</td>
<td>8.6</td>
<td>0.019 ± 0.002</td>
<td>8.26 ± 0.97</td>
<td>1.01</td>
<td>266</td>
</tr>
<tr>
<td>Test Borehole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.347 ± 0.012</td>
<td>5.22 ± 0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blumau 15</td>
<td>24.9</td>
<td>2.08</td>
<td>4.01</td>
<td>9.53</td>
<td>1.34</td>
<td>9.0</td>
<td>0.012 ± 0.002</td>
<td>5.60 ± 0.65</td>
<td>0.57</td>
<td>176</td>
</tr>
<tr>
<td>Blumau 16</td>
<td>22.5</td>
<td>2.08</td>
<td>4.12</td>
<td>9.64</td>
<td>1.31</td>
<td>8.2</td>
<td>0.006 ± 0.002</td>
<td>7.60 ± 1.50</td>
<td>0.81</td>
<td>184</td>
</tr>
<tr>
<td>Blumau 11</td>
<td>61.7</td>
<td>2.10</td>
<td>4.06</td>
<td>9.66</td>
<td>1.38</td>
<td>8.4</td>
<td>0.047 ± 0.002</td>
<td>2.79 ± 0.16</td>
<td>0.83</td>
<td>200</td>
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<tr>
<td>Grosswilsdorf 8</td>
<td>126.5</td>
<td>2.18</td>
<td>4.60</td>
<td>10.80</td>
<td>1.58</td>
<td>4.6</td>
<td>0.010 ± 0.002</td>
<td>2.46 ± 0.56</td>
<td>0.93</td>
<td>190</td>
</tr>
<tr>
<td>Blumau 32</td>
<td>1351.7</td>
<td>2.17</td>
<td>4.46</td>
<td>10.95</td>
<td>1.56</td>
<td>4.7</td>
<td>0.015 ± 0.002</td>
<td>6.47 ± 0.82</td>
<td>0.48</td>
<td>240</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>Recharge Temp. (°C)</th>
<th>U content (µg/kg)</th>
<th>234U/238U activity ratio</th>
<th>226Ra content (pCi/kg)</th>
<th>232Th content (pCi/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x 10^-6</td>
<td>x 10^-7</td>
<td>x 10^-7</td>
<td>x 10^-8</td>
<td>x 10^-8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Note:** The inert gas contents, corrected for excess air, are the averages of two or more analyses which agree within ±2%. The precision of 226Ra duplicate determinations is mostly within 10%. 222Rn values are the higher of two determinations selected on the assumption that it represents minimum leakage from the sample. The errors for U content and 234U/238U activity ratios are based on 10 counting errors.
deeper aquifers (similar to Blumau 32) with the Blumau 11 water or, alternatively, by diffusion of $^4$He from deeper strata.

The dissolved neon, argon, krypton and xenon gas contents of the ground waters were used to estimate averages for the temperature at which atmospheric equilibration occurred during the recharge process. These recharge temperatures are between 8.2 and 9.0°C, with associated uncertainties of the average temperatures of less than 1.5°C (1σ) for all of the ground waters from the Blumau aquifer itself. The recharge temperatures (4.6 and 4.7°C respectively) for the deeper aquifers at Grosswilsersdorf 8 and Blumau 32 are significantly lower than those for the Blumau aquifer. This suggests that they were recharged under cooler climatic conditions than those prevailing either at present or during the post-glacial epoch within which the Blumau aquifer has been recharged and that the ground-water age of Grosswilsersdorf 8 and Blumau 32 must therefore be in excess of $10^4$ years. This conclusion is consistent with the depleted values of $\delta^{18}O$ and $\delta^D$ for the water from these deep aquifers.

2.3.4. Uranium isotopes

The ground waters from both the Blumau aquifer and the deep aquifers are oxidising in character. The Eh ranges from +50 to +200mV and traces of dissolved oxygen are generally present. Figure 5 shows that for the bicarbonate contents typical of these ground waters, uranium is stable in solution as $\text{UO}_2^{2+}$ carbonate complexes. The uranium contents of all the ground waters are low (Table 7). This suggests that the dissolved uranium is derived within the aquifer itself and that the small amounts in solution are a consequence of the very low U content of the sediments. The higher U content of the shallow ground water at Grosswilsersdorf 7 suggests that it is a mixture of direct infiltration and input from the river Feistritz. Higher concentrations were measured for Jobst and Blumau 11 in 1981 and these might be indicative of local mixing because both are at the border of the aquifer.

The $^{234}\text{U}/^{238}\text{U}$ activity ratios for the dissolved uranium generally confirm these conclusions. The activity ratio is close to equilibrium in the river water and is only slightly enhanced at Grosswilsersdorf 7. The latter ground water probably derives most of its uranium from the river component and very little by interaction of infiltrating precipitation with the sediments. The activity ratios in the Blumau aquifer are much higher than for the surface or shallow ground waters and are derived by interaction of the ground water with uranium
FIG. 5. $Eh$-$pH$ diagram showing the stability fields of uranyl carbonate complexes in groundwaters of Blumau and East Midlands Triassic sandstone aquifers, with $P_{CO_2} = 0.1$ atm. The dissolved uranium content is $10^6M$. Uraninite boundaries are shown for equilibria with crystalline UO$_2$ (upper boundary) and with amorphous UO$_2$ (lower boundary). The rectangular area shows the range of $Eh$-$pH$ conditions for ground waters in the aquifers studied: the dotted box for Blumau and the cross-hatched box for East Midlands.

in the sediments. The mechanism of $^{234}$U/$^{238}$U activity ratio enhancement may be either an alpha recoil process(11) or may be due to preferential solution of $^{234}$U(12). The possible role of these processes for uranium solution in ground waters has been discussed(13) and the activity ratio changes with time have been determined(14).

The dissolved uranium content of ground waters in the Blumau aquifer is generally of order 0.01 µg/kg. The internal surface area per unit volume of interstitial fluid, $S$, for closely packed gravels of 0.1 cm diameter is 1.70 cm$^2$/cm$^3$. 
The uranium content of the rock surface may be greater than that of the bulk rock matrix if uranium deposition has occurred. Such deposition, however, would be localised in the aquifer and the region of deposition should also have enhanced 222Rn in its ground waters. The 222Rn contents at Grosswilfersdorf and Jobst are somewhat higher than at Blumau 15, 14 and 11, but there is no evidence of a very significant increase in the rock-surface uranium content over that for the matrix. The Blumau gravels from the Jobst borehole have a U content of 1.4 μg/g, and the recoil range of 234mTh in rock matrices is of the order 3 x 10^{-5} cm. With these parameters, it may be shown using equations in ref. 14 that the rate of 234U/238U ratio increase in the aquifer is 6.9 x 10^{-5}/a.

At this rate, the alpha recoil mechanism would require more than 50,000 a to attain a 234U/238U activity ratio of 5, approximating to the values which occur at Grosswilfersdorf, Jobst and Blumau. Even at Grosswilfersdorf 7, in the shallow aquifer and closest to recharge, the model would require an age in excess of 3000 a. These ages are orders of magnitude too large to be compatible with the observed hydrological conditions and it is clear that a recoil model for generation of the enhanced 234U/238U activity ratios is untenable. These enhanced ratios must be the result of preferential solution of 234U within the aquifer and consequently it is not possible to deduce information about ground-water residence time from the uranium isotope chemistry.

2.3.5. Radon and radium

Radon enters solution at the water/rock interface by an alpha-recoil-controlled process assisted by diffusion along microfractures or grain boundaries. The equilibrium 222Rn content is reached after ground-water residence in the aquifer of 20 days or more, and for a given aquifer the spatial variation of the 222Rn content reflects the variability of U content, porosity and relative importance of fracture and interstitial flow(15).

The average 222Rn content of the ground waters from Blumau is 219 ± 46 (1σ) pCi/kg. There is no marked variation either with locality or with depth.

The average 226Ra content of the ground waters is 0.86 ± 0.50 (1σ) pCi/kg. The 226Ra content does not vary significantly from surface waters and young ground waters (Feistritz river and Grosswilfersdorf 9 and 7) to the more evolved ground waters.
### TABLE 8. $^{32}$Si MEASUREMENTS FOR THE BLUMAU AND EAST MIDLANDS STUDIES

<table>
<thead>
<tr>
<th>Site</th>
<th>$\text{SiO}_2$ (mg/L)</th>
<th>$^{32}\text{Si}$ (dph/tonne of water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Blumau aquifer$^{(1)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grosswilferdorf 9</td>
<td>10.2</td>
<td>7.7 ± 0.9$^{(2)}$</td>
</tr>
<tr>
<td>Grosswilferdorf 7</td>
<td>18.0</td>
<td>11.4 ± 0.9</td>
</tr>
<tr>
<td>Grosswilferdorf Test Borehole</td>
<td>29.0</td>
<td>0.2 ± 0.8</td>
</tr>
<tr>
<td>Jobst Test Borehole</td>
<td>30.6</td>
<td>2.1 ± 0.8</td>
</tr>
<tr>
<td>Blumau 15</td>
<td>27.9</td>
<td>1.1 ± 0.9</td>
</tr>
<tr>
<td>Blumau 11</td>
<td>29.0</td>
<td>2.9 ± 1.0</td>
</tr>
<tr>
<td>Grosswilferdorf 8</td>
<td>29.6</td>
<td>0.9 ± 1.1</td>
</tr>
<tr>
<td>Blumau 32</td>
<td>21.3</td>
<td>0.0 ± 1.1</td>
</tr>
<tr>
<td>(b) East Midlands aquifer$^{(1)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Far Baulker 2</td>
<td>7.9</td>
<td>2.6 ± 1.0</td>
</tr>
<tr>
<td>Umpton 3</td>
<td>8.1</td>
<td>2.8 ± 0.9</td>
</tr>
<tr>
<td>Markham Clinton 3</td>
<td>8.1</td>
<td>1.3 ± 1.0</td>
</tr>
<tr>
<td>Grove (Retford) 1</td>
<td>7.7</td>
<td>3.6 ± 1.1</td>
</tr>
<tr>
<td>Gainsborough 3</td>
<td>9.8</td>
<td>0.0 ± 1.0</td>
</tr>
<tr>
<td>South Scarle</td>
<td>10.3</td>
<td>1.6 ± 0.9</td>
</tr>
</tbody>
</table>

$^{(1)}$ Blumau samples collected November 1981; East Midlands samples collected September-October 1980.

$^{(2)}$ Errors quoted are 1σ counting errors.
2.3.6. $^{32}\text{Si}$

$^{32}\text{Si}$ is produced by cosmic-ray-induced spallations of $^{40}\text{Ar}$ in the atmosphere. Its half-life is uncertain and values for $T_{1/2}$ lie in the range $101 \pm 8\text{a}$ to $330 \pm 40\text{a}$, determined by direct measurement and polar ice core studies respectively. $^{32}\text{Si}$ is removed from the atmosphere in the form of silicic acid by precipitation. Decay of $^{32}\text{Si}$ has already been applied to the dating of ice\(^{(16,17)}\). The concentration of silica in polar ice is in the ppb range, whereas the concentrations in ground waters are typically in the range 7–30 mg/L. In contrast to the behaviour in polar ice in which silica remains without exchange, radioactive $^{32}\text{Si}$ entering the soil water undergoes exchange with silica and is diluted\(^{(18)}\). This exchange and loss of $^{32}\text{Si}$ does not allow determination of residence times of ground water unless the rate of loss due to exchange is known. The $^{32}\text{Si}$ results are shown in Table 8. The loss of $^{32}\text{Si}$ activity is demonstrated by data for the Blumau aquifer in which there are high $^{32}\text{Si}$ activities in the two samples of surface water and shallow ground water; all other samples have very low levels of $^{32}\text{Si}$, close to the measurement uncertainties.

3. The East Midlands Triassic Sandstone Aquifer

3.1. Hydrogeological background

The Triassic Sandstone forms a major regional aquifer in the English East Midlands. Ground water is exploited for public supply up to 20 km downgradient in the confined part of the aquifer which dips eastwards at about 2% gradient under confining Triassic mudstones. The sandstones comprise a complex of continental red beds deposited in a major fluvial system extending over several basins in England. In the East Midlands Basin the sandstones have suffered only shallow burial (less than 1 kilometre) and early diagenetic features are preserved, including dolomite cement. The overlying mudstones have a marine origin and contain patches of evaporite minerals. Uplift and denudation occurred in the mid-Tertiary, followed by Pleistocene glacial advance, although the East Midlands was probably ice-free during the last (Weichselian) glaciation at the end of the Pleistocene. Drift deposits occur over about half of the sandstone outcrop. The aquifer unit varies in thickness northwards from 120 metres to 300 metres. The mean intergranular porosity of the sandstone is around 30%. Estimates of hydraulic conductivity from pumping tests give values around 3 m/d, with values occasionally higher in the unconfined aquifer and values down to 0.6 m/d in the deep, confined aquifer. Hydraulic gradients are about 0.4% at outcrop and 0.1% in the confined aquifer, although the regional flow
FIG. 6. Hydrogeological map and cross-section of East Midlands Triassic sandstone aquifer, showing locations of boreholes sampled in this study (modified from Ref.[19]). Solid-line contours represent base of sandstone in metres below sea level; dashed contours represent potentiometric surface of sandstone aquifer, with arrows denoting directions of regional flow. Circle diameters indicate approximate pumping rates in the range of $<10^3 \text{m}^3 \cdot \text{d}^{-1}$ to $>10^6 \text{m}^3 \cdot \text{d}^{-1}$. Segment size indicates percentage penetration of borehole into the Sherwood sandstone aquifer.
pattern is modified locally by pumping around Retford and Newark. Regional ground-water velocities in the confined aquifer calculated from these data according to the Darcy equation are in the range 0.7-4 m/a. No downgradient discharge zones have been identified. Boreholes drilled into the sandstone are not all fully penetrating, particularly in the deeper confined aquifer. The boreholes are generally lined from surface through to the producing sandstone. Submersible pumps are located in this lined section and pumping rates vary from a few litres per second for a private borehole at Rampton up to 20-100 litres per second for the public supply boreholes. Most of these pumping stations have 2 to 4 similar boreholes pumping together or in sequence and at each station one borehole only has been fully sampled. Ten sampling locations were selected to give a representative sequence through the confined aquifer, but only one site was selected in the outcropping aquifer (Far Baulker) (Fig. 6). The hydraulic potential distribution within the aquifer is not at steady state owing to these high abstractions, and the few available rest-water level measurements suggest a falling water level over much of the aquifer.

3.2. Hydrochemistry

The hydrochemistry of this aquifer has been described elsewhere (19). The chemical analyses of samples collected in 1980 agree well with the previous data, although some pH values are lower and some Eh values have risen significantly. Total mineralisation in these samples was all less than 500 mg/L. The chemical evolution of the ground water is dominated by a reaction of minor amounts of carbonate and sulphate minerals in the aquifer matrix. The congruent and incongruent dissolutions of dolomite are the major carbonate reactions. Undersaturation with respect to calcite and dolomite is indicated by the lower pH values, although the earlier data indicate equilibrium in much of the aquifer (19). It is possible that these fluctuations are caused by analytical problems in pH measurement, but actual changes may have occurred in hydrochemical conditions in the aquifer owing to intense pumping over the period between sampling. The redox conditions change as the aquifer becomes confined: Eh falls, dissolved O₂ and NO₃ concentrations fall to zero; however, strongly reducing conditions (negative Eh) are not found in the aquifer. A chronology of ground water in the aquifer based on measurements of tritium, carbon-14, stable oxygen and hydrogen isotopes, and inert gas abundances has been reported (20,18). On this basis the aquifer may be divided into three zones:

(1) A zone with predominantly modern water with significant Δ³H and high Δ¹⁴C (greater than 30 ppm)
### TABLE 9. SUMMARY OF SAMPLING CONDITIONS AND $^3$H, $^{14}$C, $\delta^{13}$C, $\delta^{18}$O AND $\delta$D MEASUREMENTS (EAST MIDLANDS STUDY)

<table>
<thead>
<tr>
<th>Site</th>
<th>Total/cased depth (metres)</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>$E_n$ (millivolts)</th>
<th>Tritium (T.U.)</th>
<th>$^{14}$C (ppm)</th>
<th>$\delta^{13}$C (% PDB)</th>
<th>$\delta^{18}$O (% SMOW)</th>
<th>$\delta$D (% SMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Far Baulkier 2</td>
<td>137/55</td>
<td>10.2</td>
<td>7.7</td>
<td>+410</td>
<td>$^{12.2 \pm 1.0}$ (12 ± 0.4)</td>
<td>58.9</td>
<td>-13.5</td>
<td>-8.5</td>
<td>-50</td>
</tr>
<tr>
<td>Gempton 3</td>
<td>176/52</td>
<td>11.1</td>
<td>7.8</td>
<td>+410</td>
<td>$^{14.0 \pm 0.2}$ (0.4 ± 0.2)</td>
<td>40.6</td>
<td>-13.3</td>
<td>-8.4</td>
<td>-57</td>
</tr>
<tr>
<td>Holme 3</td>
<td>171/76</td>
<td>11.9</td>
<td>7.7</td>
<td>+350</td>
<td>$^{0.5 \pm 0.2}$ (0.5 ± 0.3)</td>
<td>30.9</td>
<td>-10.3</td>
<td>-8.1</td>
<td>-57</td>
</tr>
<tr>
<td>Market Clinton 3</td>
<td>230/60</td>
<td>12.3</td>
<td>7.9</td>
<td>+470</td>
<td>$^{0.5 \pm 0.2}$ (0.5 ± 0.2)</td>
<td>30.4</td>
<td>-12.7</td>
<td>-8.0</td>
<td>-54</td>
</tr>
<tr>
<td>Grove (Refford) 1</td>
<td>335/160</td>
<td>13.3</td>
<td>7.3</td>
<td>+160</td>
<td>18.7</td>
<td>12.3</td>
<td>-8.2</td>
<td>-57</td>
<td>-66</td>
</tr>
<tr>
<td>Rampton</td>
<td>306/183</td>
<td>14.1</td>
<td>7.3</td>
<td>+270</td>
<td>&lt; 0.8</td>
<td>10.2</td>
<td>-9.5</td>
<td>-66</td>
<td>-66</td>
</tr>
<tr>
<td>Newlon 1</td>
<td>381/246</td>
<td>16.9</td>
<td>7.5</td>
<td>+250</td>
<td>1.9</td>
<td>10.6</td>
<td>-9.2</td>
<td>-61</td>
<td>-61</td>
</tr>
<tr>
<td>Newark, Clay Lane 1</td>
<td>366/63</td>
<td>17.6</td>
<td>7.3</td>
<td>+90</td>
<td>$^{3.6 \pm 0.2}$ (3.3 ± 0.2)</td>
<td>&lt; 0.5</td>
<td>8.7</td>
<td>-9.6</td>
<td>-65</td>
</tr>
<tr>
<td>Gainsborough 3</td>
<td>498/290</td>
<td>18.2</td>
<td>7.4</td>
<td>+130</td>
<td>&lt; 1.0</td>
<td>-9.4</td>
<td>-9.2</td>
<td>-64</td>
<td>-64</td>
</tr>
<tr>
<td>South Scarle</td>
<td>354/292</td>
<td>20.9</td>
<td>7.7</td>
<td>+110</td>
<td>&lt; 0.5</td>
<td>-8.8</td>
<td>-9.3</td>
<td>-64</td>
<td>-64</td>
</tr>
</tbody>
</table>

All Samples Collected September - October 1980.

$^3$H values in brackets are for samples collected in 1982.
(ii) Ground water with negligible $^3$H and $^{14}$C between 30 and 15 pmc
(iii) Ground water with $^{14}$C less than 5 pmc and high radiogenic $^4$He content.

The latter two zones are also distinguished by their oxygen and hydrogen compositions and inert gas contents which have been interpreted as reflecting different climatic conditions at the time of recharge of the ground waters. A further feature attributed to palaeoclimate is the remarkably low chloride concentrations in the confined aquifer which are mostly less than 10 mg/l(20). This is also evidence against there being any hydraulic connection with the underlying Carboniferous sequence which is known to contain brines but which is separated from the Triassic aquifer by Permian marls.

Samples of drillcore from the Triassic sandstone have been obtained from two boreholes drilled near to the western edge of the confined aquifer, at Newhall and Gamston (Fig. 6).

3.3. Isotope data for the East Midlands aquifer

3.3.1. Carbon isotopes, tritium, D/H and $^{18}$O/$^{16}$O

Carbon-14 and $\delta^{13}$C measurements on samples collected in 1980 (Table 9) are very similar to the earlier results(20). The apparent temporal fluctuations in pH and equilibrium are not reflected in any changes in carbon isotope data. The hydrochemical evidence for congruent followed by incongruent dissolution of dolomite provides a basis on which the carbon isotope data are adjusted for carbonate reactions. Dissolution experiments using phosphoric acid on drillcore samples have proved the presence of dolomite with $\delta^{13}$C between zero and -4% and $\delta^{18}$O between -0.5 and -4% versus PDB and it is inferred that this dolomite is participating in the dissolution reactions(19). These experiments on core material also show that $^{14}$C has been lost from the ground water to the aquifer rock, assuming that the material analysed was not contaminated by atmospheric carbon. Up to 20 pmc $^{14}$C has been measured in CO$_2$ evolved in the early stages of carbonate dissolution(21). The $\delta^{13}$C of this CO$_2$ was initially low (down to -9%), suggesting that secondary calcite is reacting, and increased towards 0% as reaction progressed(19). The presence of some $^{14}$C is predicted by the incongruent dissolution model, but will influence the validity of the $^{14}$C age derived from this model only if $^{14}$C returns subsequently to the solution. Redissolution of secondary calcite is not permitted by the hydrochemical interpretation of calcite equilibrium persisting throughout the aquifer, although fluctuations of this equilibrium are observed. Adjusted $^{14}$C
TABLE 10. CARBON-14 PISTON-FLOW ‘AGES’ CALculated BY VARIOUS MODELS (EAST MIDLANDS STUDY)

<table>
<thead>
<tr>
<th>Site</th>
<th>Adjusted $^{14}$C ‘Age’ Range (Years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Far Baulker 2</td>
<td>Modern - 2000</td>
</tr>
<tr>
<td>Ompton 3</td>
<td>1500 - 5000</td>
</tr>
<tr>
<td>Halam 3</td>
<td>Modern - 4500</td>
</tr>
<tr>
<td>Markham Clinton 3</td>
<td>3500 - 7000</td>
</tr>
<tr>
<td>Grove (Retford) 1</td>
<td>7000 - 11,000</td>
</tr>
<tr>
<td>Rampton</td>
<td>&gt;30 000</td>
</tr>
<tr>
<td>Newton 1</td>
<td>23 000 - 28 000</td>
</tr>
<tr>
<td>Newark, Clay Lane 1</td>
<td>&gt;29 000</td>
</tr>
<tr>
<td>Gainsborough 3</td>
<td>&gt;25 000</td>
</tr>
<tr>
<td>South Scarle</td>
<td>&gt;30 000</td>
</tr>
</tbody>
</table>

The models used assume the following values: $A^{14}$C = 100 pmc; $\delta^{13}$C (CO$_2$) = -26%; $A^{14}$C (CaCO$_3$) = 0 pmc; $\delta^{13}$C (rock) = 0%; $\delta^{13}$C (DIC) = -18% in the open system; $\delta^{13}$C (DIC) = -13.5% at the end of the congruent dissolution stage; $\epsilon$ (CaCO$_3$ - HCO$_3^-$) $\approx$ +3% $\delta^{13}$C.

'ages' have been calculated according to a chemical and isotopic mass-balance model(3), assuming initial $^{14}$C activity in the open system to be 100 pmc and $\delta^{13}$C (dolomite) to be zero %, also according to incongruent dissolution models(22,23) and a global exchange-mixing model(15). These data are presented in Table 10 and are within the possible ranges of magnitude of those calculated from hydraulic data.

The $\delta^{18}$O and $\delta^D$ results (Table 9) are similar to analyses reported previously for this aquifer(20). They fall into two distinct groups, with samples downgradient of a line between Grove and Rampton having lighter isotopic compositions relative to the upgradient source in the confined aquifer and the recently recharged ground water at outcrop. The lighter
isotopic compositions correlate with low $^{14}$C contents (below 2 ppm) and are interpreted as confirming the presence of significantly older ground water in this part of the aquifer. The palaeoclimatic temperature change implied by these data is in qualitative agreement with the change in the recharge temperature indicated by dissolved inert gas contents (Table 12), although the latter indicate changes in excess of the 1-2°C suggested by the stable-isotope shift.

3.3.2. $^{39}$Ar and $^{85}$Kr

The $^{39}$Ar results given in Table 11 show distinct values above the detection limit of a few percent modern for only three samples. Two samples were measured twice and gave consistent results within statistical limits. The count rates from 6 samples were statistically the same as the count rates from blank samples, which demonstrates the reliability of these results. For these samples, the $^{39}$Ar concentrations are quoted as upper limits in Table 11, applying mostly the 95% confidence level. Somewhat higher levels were used when, for example, the $\chi^2$ test of the measurement intervals was not perfect (e.g. South Scarle).

The measured $^{85}$Kr activities (in dpm) can be converted directly into dpm/cm$^3$ krypton for those samples for which no krypton carrier was added before processing. For Far Baulker, Ompton, Halam, South Scarle and Newark, carrier was added (corresponding to an older separation procedure) and the conversion into dpm/cm$^3$ can only roughly be estimated. Therefore, only the 'carrier-free' activities are precisely comparable with atmospheric levels. (For estimation of possible contamination of the samples by modern air, both procedures can be used).

Considerable $^{85}$Kr activities have been found in the samples collected at or near the recharge area (e.g. Far Baulker, Halam; to a smaller degree for Ompton, Markham). Reasons for this may be young water admixture, gas exchange or diffusion through the aquiclude, or a different pumping system at Halam, Markham and Ompton compared to the other 7 wells. These processes may be identified from the $^{85}$Kr, $^3$H, $^4$He and $O_2$ results. For example, waters from Far Baulker and to a smaller degree Newark show a young water admixture as concluded from the presence of some $^3$H and increased $^{85}$Kr and $O_2$ levels. For Far Baulker, a mean residence time of about 6 years can be estimated from the $^3$H/$^{85}$Kr ratio by application of an exponential model. The $^{85}$Kr content of about 7% of present equilibration concentration (between water and the atmosphere) in the sample from Halam (without significant $^3$H) makes
<table>
<thead>
<tr>
<th>Site</th>
<th>$^{39}$Ar (% modern)</th>
<th>Mean Residence Time (Years)</th>
<th>$^{36}$Ar</th>
<th>dpm in sample</th>
<th>dpm/cm$^3$ Kr</th>
<th>$^{85}$Kr</th>
<th>0$_2$ (%)</th>
<th>Air contamination estimated from $^{85}$Kr (%)</th>
<th>0$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Far Baulker 2</td>
<td>94.3 ± 4.0 (1)</td>
<td>25 ± 20</td>
<td>25 ± 20</td>
<td>1.86 ± 0.04</td>
<td>(4.9)*</td>
<td>28.44 ± 0.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Upton 3</td>
<td>95.2 ± 3.1</td>
<td>220 ± 20</td>
<td>285 ± 20</td>
<td>0.33 ± 0.01</td>
<td>(0.41)*</td>
<td>16.63 ± 0.40</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Halton 3</td>
<td>94.6 ± 3.0</td>
<td>240 ± 20</td>
<td>320 ± 30</td>
<td>1.67 ± 0.03</td>
<td>(2.1)*</td>
<td>26.85 ± 0.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Markham Clinton 3</td>
<td>5.2 ± 1.3(2)</td>
<td>&gt;1000</td>
<td>9.2 ± 2.0(2)</td>
<td>0.056 ± 0.005</td>
<td>0.62 ± 0.06</td>
<td>15.68 ± 0.31</td>
<td>1.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Grove (Wetford) 1</td>
<td>&lt; 4.6 (2)</td>
<td>&gt;1200</td>
<td></td>
<td>0.026 ± 0.007</td>
<td>0.063 ± 0.016</td>
<td>2.22 ± 0.09</td>
<td>0.17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hampton</td>
<td>&lt; 3.3(2)</td>
<td>&gt;1300</td>
<td></td>
<td>0.030 ± 0.004</td>
<td>0.057 ± 0.008</td>
<td>&lt;0.03</td>
<td>0.15</td>
<td>&lt;0.14</td>
<td>&lt;0.14</td>
</tr>
<tr>
<td>Newton 1</td>
<td>&lt; 3.2(2)</td>
<td>&gt;1300</td>
<td></td>
<td>0.030 ± 0.005</td>
<td>0.076 ± 0.012</td>
<td>&lt;0.03</td>
<td>0.20</td>
<td>&lt;0.14</td>
<td>&lt;0.14</td>
</tr>
<tr>
<td>Newark, Clay Lane 1</td>
<td>&lt; 2.6(2)</td>
<td>&gt;1300</td>
<td></td>
<td>0.15 ± 0.02</td>
<td>(0.17)*</td>
<td>0.25 ± 0.02</td>
<td>1.4</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Gainsborough 3</td>
<td>&lt; 3.4(2)</td>
<td>&gt;1300</td>
<td></td>
<td>0.038 ± 0.004</td>
<td>0.080 ± 0.008</td>
<td>&lt;0.03</td>
<td>0.21</td>
<td>&lt;0.14</td>
<td>&lt;0.14</td>
</tr>
<tr>
<td>South Scarie</td>
<td>&lt; 7.2(2)</td>
<td>&gt;1000</td>
<td></td>
<td>0.029 ± 0.009</td>
<td>(0.039)*</td>
<td>&lt;0.03</td>
<td>0.33</td>
<td>&lt;0.14</td>
<td>&lt;0.14</td>
</tr>
<tr>
<td>Modern Air</td>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Samples collected in 1980.

(1) Errors given are 1σ counting errors.
(2) Corrected for contamination by modern air.
(3) Corresponding to (a) piston flow model and (b) exponential model.
(4) Measured by E. Moor, Berne.

*Approximate values for samples which had Kr carrier added in extraction process.
TABLE 12. INERT GAS CONTENTS, DERIVED RECHARGE TEMPERATURES AND RADIOELEMENT CONTENTS OF GROUND WATERS (EAST MIDLANDS STUDY)

<table>
<thead>
<tr>
<th>Site</th>
<th>He x 10^-8</th>
<th>Ne x 10^-7</th>
<th>Ar x 10^-6</th>
<th>Re x 10^-8</th>
<th>Xe x 10^-8</th>
<th>Recharge Temp. (°C)</th>
<th>U content (µg/kg)</th>
<th>234U/238U activity ratio</th>
<th>236Ra content (pCi/kg)</th>
<th>222Rn content (pCi/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of sampling:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Far Baulker 2</td>
<td>10.1</td>
<td>2.08</td>
<td>4.15</td>
<td>9.24</td>
<td>1.36</td>
<td>8.9</td>
<td>0.27 ± 0.01</td>
<td>4.40 ± 0.11</td>
<td>0.40</td>
<td>206</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.26 ± 0.01)</td>
<td>(4.78 ± 0.14)</td>
<td>(0.15)</td>
<td>(203)</td>
</tr>
<tr>
<td>Oatton 3</td>
<td>14.3</td>
<td>2.10</td>
<td>4.27</td>
<td>9.51</td>
<td>1.38</td>
<td>8.1</td>
<td>0.65 ± 0.02</td>
<td>3.36 ± 0.06</td>
<td>0.75</td>
<td>258</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.61 ± 0.02)</td>
<td>(3.42 ± 0.08)</td>
<td>(0.33)</td>
<td>(204)</td>
</tr>
<tr>
<td>Holan 3</td>
<td>11.2</td>
<td>2.08</td>
<td>4.18</td>
<td>9.24</td>
<td>1.35</td>
<td>8.9</td>
<td>1.04 ± 0.02</td>
<td>3.21 ± 0.05</td>
<td>0.44</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.96 ± 0.03)</td>
<td>(3.23 ± 0.03)</td>
<td>(0.39)</td>
<td>(157)</td>
</tr>
<tr>
<td>Markham Clinton 3</td>
<td>12.2</td>
<td>2.10</td>
<td>4.16</td>
<td>9.45</td>
<td>1.41</td>
<td>8.2</td>
<td>3.13 ± 0.02</td>
<td>2.68 ± 0.02</td>
<td>1.18</td>
<td>239</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3.28 ± 0.07)</td>
<td>(2.76 ± 0.03)</td>
<td>(0.69)</td>
<td>(252)</td>
</tr>
<tr>
<td>Grove (Reeford) 1</td>
<td>29.9</td>
<td>2.11</td>
<td>4.38</td>
<td>9.74</td>
<td>1.38</td>
<td>7.4</td>
<td>1.00 ± 0.01</td>
<td>6.68 ± 0.07</td>
<td>0.92</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.90 ± 0.02)</td>
<td>(6.90 ± 0.12)</td>
<td>(0.65)</td>
<td>(139)</td>
</tr>
<tr>
<td>Rampton</td>
<td>81.6</td>
<td>2.22</td>
<td>4.85</td>
<td>11.33</td>
<td>1.73</td>
<td>2.6</td>
<td>0.77 ± 0.01</td>
<td>6.99 ± 0.07</td>
<td>0.56</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.78 ± 0.02)</td>
<td>(6.96 ± 0.12)</td>
<td>(0.37)</td>
<td>(194)</td>
</tr>
<tr>
<td>Newton 1 (Newton 2)</td>
<td>102.6</td>
<td>2.18</td>
<td>4.79</td>
<td>10.76</td>
<td>1.56</td>
<td>4.1</td>
<td>1.14 ± 0.01</td>
<td>5.46 ± 0.06</td>
<td>0.46</td>
<td>293</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1.18 ± 0.02)</td>
<td>(5.53 ± 0.07)</td>
<td>(0.35)</td>
<td>(193)</td>
</tr>
<tr>
<td>Newark, Clay Lane 1</td>
<td>177.7</td>
<td>2.23</td>
<td>5.15</td>
<td>11.34</td>
<td>1.62</td>
<td>2.3</td>
<td>0.55 ± 0.01</td>
<td>6.24 ± 0.18</td>
<td>0.65</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.48 ± 0.01)</td>
<td>(6.33 ± 0.12)</td>
<td>(0.56)</td>
<td>(197)</td>
</tr>
<tr>
<td>Gainsborough 3</td>
<td>199.1</td>
<td>2.19</td>
<td>4.89</td>
<td>10.04</td>
<td>1.55</td>
<td>3.8</td>
<td>0.98 ± 0.01</td>
<td>4.52 ± 0.05</td>
<td>0.99</td>
<td>274</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1.00 ± 0.03)</td>
<td>(4.65 ± 0.09)</td>
<td>(0.35)</td>
<td>(186)</td>
</tr>
<tr>
<td>South Searle</td>
<td>133.7</td>
<td>2.18</td>
<td>4.78</td>
<td>10.83</td>
<td>1.58</td>
<td>4.0</td>
<td>0.83 ± 0.02</td>
<td>4.78 ± 0.10</td>
<td>0.95</td>
<td>316</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.67 ± 0.02)</td>
<td>(4.59 ± 0.10)</td>
<td>(0.68)</td>
<td>(297)</td>
</tr>
</tbody>
</table>

Note: The inert gas contents, corrected for excess air, are the averages of two or more analyses which agree mostly within ±2%. The precision of ²³²³⁰Ra and ²²²Rn determinations is within 10%.

The errors for U content and ²³⁴U/²³⁸U activity ratios are based on counting errors.

Numbers in brackets are results obtained at AERE Harwell.
contamination of the sample by modern air or diffusion of gas through the aquiclue more probable, which to a smaller degree might also be the case for Ompton. For Markham, all processes mentioned above may be considered as reasons for the slightly increased level of $^{85}$Kr (note the low $^{39}$Ar activity). If for Markham the whole $^{85}$Kr activity is attributed to a fresh admixture (water or air) the uncorrected average $^{39}$Ar result is $10.2 \pm 1.6\%$ modern, corresponding to a piston-flow model age of $890 \pm 60\%$. For Grove and the others (with a significantly increased $^{4}$He content) the very small $^{85}$Kr content is probably entirely due to contamination of the samples during collection.

The low $^{39}$Ar results of some samples can be used to estimate the effects of underground production rates in this sandstone aquifer. We assume that the measured $U$, $Th$ and $K$ concentrations in the Newhall and Gamaton boreholes (see Table 7) are similar to those further east in the aquifer and that the observed uniformity of the two boreholes is indicative of the easterly wells. This assumption is supported by the uniform $^{222}$Rn results. From a comparison of the estimated underground production rates (diffusing without decay loss out of the grains) with the lowest measured values we conclude that less than $0.6\%$ of the produced $^{39}$Ar reaches the pore volume. Although this value probably cannot be adopted directly for other aquifers, the order of magnitude is interesting information.

The measured lower limits of $^{39}$Ar mean residence times are credible for 6 of the wells, whereas the piston-flow or exponential model ages calculated for Far Faulker, Ompton and Halam are hard to interpret quantitatively because of the evidence from $^{85}$Kr determinations that some gas diffusion or recent water admixtures occur. The admixture of a very small water component which exchanged gas quite recently cannot be excluded for Markham Clinton.

3.3.3. Radiogenic $^{4}$He and inert gases

The $^{4}$He contents of ground waters from the unconfined part of the aquifer are $< 15 \times 10^{-8}$ cm$^3$STP/cm$^3$H$_2$O, which is somewhat greater than the amount derived from air-equilibration at recharge. The $^{4}$He content of the ground water increases on entering the confined zone and continues to increase as the ground water moves eastwards (Table 12). $^{4}$He contents are up to 7 times greater than was measured previously (10, 20) and this is considered to be due to improved sampling techniques which avoid $^{4}$He losses. The ground-water residence times required to produce the observed amounts of radiogenic $^{4}$He were calculated
for Newton and Newark using the radiocarbon contents of core from the Gamston and Newhall boreholes respectively. In both cases the $^4\text{He}$ generation times are about 10 times the adjusted $^{14}\text{C}$ piston-flow ages (23,000 to 28,000 a and $>29,000$ a respectively). It is evident that $^4\text{He}$ in addition to that generated within the aquifer is required to produce the observed helium within the $^{14}\text{C}$ ages. It is likely that this is produced within the adjacent strata and diffuses into the aquifer from these formations. Without detailed information on radiocarbon distributions within the aquifer and the associated aquicludes, it is impossible to calculate ground-water residence times from $^4\text{He}$ data. Nevertheless, the $^4\text{He}$ content of ground water should generally increase with ground-water age.

The recharge temperatures of the ground waters have been estimated from the amount of dissolved inert gases present (Table 12). The analytical data were corrected for excess air which was present in the samples by iterative subtraction of small amounts of the inert gases in their atmospheric ratios until the best match between solution/atmosphere equilibration temperatures for the various gases was obtained. The inferred recharge temperatures in the east of the confined aquifer, where adjusted $^{14}\text{C}$ ages exceed 20,000 a, are 4-5$^\circ\text{C}$ lower than those in the western part of the confined and unconfined aquifer. The associated uncertainties in the average temperatures quoted are less than 1.5$^\circ\text{C}$ (1σ).

3.3.4. Uranium isotopes

The Eh-pH conditions throughout the aquifer are such that UO$_2$$^{2+}$ carbonate complexes are always stable in solution. The U contents and $^{234}\text{U} / ^{238}\text{U}$ activity ratios were determined for ground waters from the 10 sites selected for this study at two laboratories (Bath and Harwell). The interlaboratory agreement was within 10% or better and repeated measurements after an interval of about one year show that the uranium geochemistry is constant for each site over this timescale (Table 12). The number of sites investigated in this study was too small to reveal any geochemical trends in the aquifer. However, some trends have been revealed in a larger study made in 1977-1980 and these are discussed in ref. 25. Dissolution of dolomite was identified as the major source of U. The $^{234}\text{U} / ^{238}\text{U}$ activity ratio ranges from 3 to 7 on an apparently random basis throughout the aquifer and cannot be correlated with U content of ground water (Figure 7). Consideration of the growth rate of $^{234}\text{U} (14)$ shows that alpha recoil enhancement of the activity ratio cannot occur within the probable ground-water ages throughout the aquifer. The $^{234}\text{U} / ^{238}\text{U}$ activity enhancement must consequently be the result of preferential dissolution of
FIG. 7. $^{234}U$/$^{238}U$ activity ratio plotted against uranium content for ground water from the East Midlands Triassic sandstone. Zone I: ground waters with piston-flow model ages less than a few hundred years; Zone II: ground waters with piston-flow model ages of up to 10 000 years; Zone III: ground waters with piston-flow model ages greater than 16 000 years (from Ref. (25)).

$^{234}U$ relative to $^{238}U$ and the ratio of solution rates of $^{234}U$ and $^{238}U$ varies from 3 to 7 throughout the aquifer. It is concluded that in this situation of active uranium solution accompanying incongruent carbonate solution, activity ratio changes due to $^{234}U$ in growth or decay cannot be used to assess ground-water residence times.

3.3.5. Radon and radium

The $^{222}Rn$ and $^{226}Ra$ results are given in Table 12. The reasons for the differences between some $^{222}Rn$ data from the two laboratories are not obvious and could be due to either leakage from samples or differences in pumping regimes at the times of sampling. The average $^{222}Rn$ content of the East Midlands ground waters is $227 \pm 53$ pCi/kg (see Table 12). This suggests that the aquifer is uniform within 30% with respect to uranium content, porosity and relative importance of fracture/interstitial flow. The two sets of $^{226}Ra$ data show a systematic difference, the causes of which are not understood. The average $^{226}Ra$ content of the ground waters is $0.59 \pm 0.27$ pCi/kg.
3.3.6. $^{32}\text{Si}$

The $^{32}\text{Si}$ content of the youngest ground water (Far Baulker) was found to be at a level which is within the range of analytical results for elsewhere in the aquifer and similar to the estimated errors on individual measurements (Table 8). Therefore, $^{32}\text{Si}$ measurements give no information on ground-water ages in this aquifer.

4. Summary

This study has demonstrated that for the Blumau aquifer an order-of-magnitude difference exists between ground water residence times derived from conventional piston-flow interpretations of $^{14}\text{C}$ and $^{39}\text{Ar}$ data which fall to around 16 pmc (around 9500 a) and 11% modern (around 900 a), respectively, down-gradient at Blumau. Hydraulic estimates of rates of ground-water movement are too uncertain to confirm or refute the estimates from either set of data. Data for the East Midlands aquifer do not show such a contrast: $^{39}\text{Ar}$ above detection limit is only found in three of the upgradient samples which have $^{14}\text{C}$ at levels of 30 pmc or greater. The deeper confined ground waters at five boreholes in the aquifer have both $^{14}\text{C}$ and $^{39}\text{Ar}$ concentrations at or around detection limit, and therefore no conclusive comparison is possible. The hydraulic estimate of ground-water flow velocity is also very uncertain, but suggests residence times somewhat lower than the minimum derived from conventional modelling of $^{14}\text{C}$ data at detection limits (30000-35000 a) for these downgradient samples. Therefore, uncertainty persists in the direct comparison of piston-flow residence times derived from these two dating techniques.

The shift to lighter oxygen and hydrogen isotope compositions for the deep ground water in the East Midlands aquifer is inferred to be due to palaeoclimatic influences and therefore supports the age scale derived from $^{14}\text{C}$ data. Parallel changes in dissolved inert gas concentrations, which are attributed to palaeotemperature changes at recharge, also support this age scale. Similar shifts in stable oxygen and hydrogen isotopes and inert gases are not present in the Blumau aquifer and are not expected within the proposed timescales, although these changes are found in two samples from deeper boreholes and match the much lower $^{14}\text{C}$ concentrations.

Measurements of $^3\text{H}$, $^{85}\text{Kr}$ and $^{4}\text{He}$ are very important qualitative indicators of ground-water age which are particularly applicable in this study to the consideration of samples being mixtures of waters with different residence times or from different sources, e.g. leakage through aquicludes or
mixing within boreholes. The presence of significant quantities of $^{32}$Si in any ground water would clearly indicate a young component, but measured values in both aquifers are of similar magnitude to statistical errors and therefore do not provide conclusive evidence. Significant amounts of $^3$H or $^{85}$Kr are not generally present downgradient in the Blumau aquifer and therefore the presence of considerable amounts of recent (<30 a) water can be excluded. The concentrations of radiogenic $^4$He which are present in the downgradient Blumau aquifer are far in excess of those expected from estimated uranium and thorium abundances in the matrix for any reasonable timescale. They confirm that an additional source of $^4$He in the aquifer is its diffusion from adjacent strata; it is not possible to estimate how much of the excess $^4$He, if any, might be due to mixing of older ground waters. The single sample (Far Baulker) from the outcrop of the East Midlands aquifer shows the highest $^3$H and $^{85}$Kr concentrations, as expected, but some other samples from this aquifer also contain significant concentrations which suggest mixing of recent water (for $^3$H and $^{85}$Kr) or diffusion of gas through the aquiclude (for $^{85}$Kr) in these cases. The presence of $^{85}$Kr (with O$_2$) in samples may also be attributable to air contamination during sampling.

Within these constraints, it seems that significant $^{85}$Kr occurs in four samples from the confined East Midlands aquifer, one of which (Newark) is in the deep aquifer and is accompanied by low but significant $^3$H. Mixing in the borehole seems a probable explanation in this last case. The concentrations of radiogenic $^4$He which are measured in the East Midlands aquifer are far in excess (about 10 times) of those estimated from in-situ production on any reasonable timescale and are interpreted, as in the Blumau aquifer, to be due to diffusive addition from adjacent strata.

The measured concentrations of uranium in both aquifers are consistent with observed hydrochemical conditions. The changes in $^{234}$U/$^{238}$U activity ratios in both cases follow no regular pattern and are attributed to preferential solution of $^{234}$U. Therefore, they offer no information concerning residence time of ground water. Concentrations of $^{222}$Rn for samples from each aquifer are relatively uniform in each case, which suggests that flow mechanisms and U and Th distributions in the vicinity of each sampled borehole are similarly homogeneous. The aquifer uniformity which is inferred from these U and $^{222}$Rn data allows the generalisation of sparse data on U and Th concentrations in the aquifer matrix; these concentrations are necessary for calculations of in-situ production of nuclides including $^{39}$Ar and $^4$He.
5. Conclusions

The observed discrepancies require that the assumptions and models with which the $^{14}$C and $^{39}$Ar data are interpreted should be examined more critically. It must be emphasised that the vastly different half-lives for $^{14}$C and $^{39}$Ar, 5730 a and 269 a, place the most obvious constraint on the widespread comparison of both techniques. The conventional interpretations in terms of piston-flow transit times are clearly too simplistic in most cases, and the exponential model assumes a specific distribution of ground-water flow to give a more realistic estimate of mean residence times for that specific case. Mixtures of waters of different sources which do not show regular distributions of component ages are also possible, for instance in systems with strongly bimodal flow (i.e. fissure and intergranular components) or in leaky aquifers. Discrepancies among environmental isotope data could originate from such mixtures: for example, a mixture of 10% of a recent water with 100% modern $^{39}$Ar and 50 ppm $^{14}$C with 90% of a ground water with 0% of modern $^{39}$Ar and 12 ppm $^{14}$C would give a water with 10% modern $^{39}$Ar and around 15 ppm $^{14}$C. Such irregular mixtures should be resolved by the application of ranges of isotopic and hydrochemical techniques, as has been attempted in this study.

The $^{14}$C interpretations are based on evolution of the dissolved carbonate system of the ground water progressing in such a way that changes in chemistry and in $^{13}$C/$^{12}$C reflect also the maximum extent to which $^{14}$C may have been diluted. Therefore, the models would be in error if exchange reactions with solid carbonate occurred which had no influence on either chemistry or $^{13}$C/$^{12}$C of solution; in such cases, the modelled $^{14}$C ages would always be erroneously high. The chemistry and $^{13}$C/$^{12}$C would remain unchanged only if this reaction took place under conditions of solution-carbonate chemical equilibrium and of bulk or local $^{13}$C/$^{12}$C isotopic equilibrium. Secondary calcite may precipitate in isotopic equilibrium with dissolved bicarbonate during incongruent dissolution of primary carbonate, but redissolution of this calcite should be inhibited if equilibrium conditions persist. Variations in hydrochemical conditions and in computed equilibrium conditions have been measured in time and space in both aquifers, but it is difficult to assess the significance of these in terms of natural rather than analytical variations.

The interpretations of $^{39}$Ar data rely on the relative insignificance of contributions to dissolved $^{39}$Ar from the reaction $^{39}$X(n,p)$^{39}$Ar in the aquifer. Measurements of $^{39}$Ar levels below detection limits in the downgradient ground water in the East Midlands aquifer demonstrate that here the
contribution is very low, less than 1% of total estimated production in the matrix being released to solution. Any contribution to $^{39}$Ar arising from gas diffusion from atmosphere through the aquiclude can also be excluded since this is estimated to be negligible for a 10 m thickness of aquiclude, as it is also for $^{85}$Kr. The accumulation of $^4$He in aquifers also indicates the insignificance of gas diffusion between aquifer and atmosphere. Measurements of $^{39}$Ar need particularly careful investigations to confirm the absence of contamination from sampling and analytical procedures. Simultaneous measurements of $^{85}$Kr and $O_2$ permit the estimation of atmospheric contamination, and the $^{39}$Ar recovery and measurement technique is now considered sufficiently reliable that errors of measurement and contamination are excluded as a basic cause of discrepancy between $^{39}$Ar and $^{14}$C data. However, these studies have also shown that spurious measurements of $^{39}$Ar occur for reasons which are uncertain, as is probably the case for all other isotope and chemical analyses. Analyses of replicate samples are necessary for absolute confidence in data.

Discrepancies between piston-flow age interpretations of $^{39}$Ar and $^{14}$C data are not satisfactorily resolved. Mixing of ground waters may be an important factor. Quantitative analyses of such mixtures using the comprehensive isotope and chemical data are not possible with present data. More measurements on carefully selected ground-water samples, and further investigations of underground production rates for $^{39}$Ar and exchange of $^{14}$C between solution and carbonate are necessary.

Isotope techniques which can give direct information concerning ground-water residence times are measurements of $^2$H, $^{85}$Kr, $^{14}$C and $^{39}$Ar. New techniques looking at $^{36}$Cl and $^{81}$Kr also offer some potential, although problems of interpretation and measurement remain to be resolved. Other techniques which might offer indirect qualitative information include $^{18}$O/$^{16}$O, $^2$H/$^1$H, $^4$He, uranium series isotopes, dissolved inert gases, and $^{32}$Si, but the conclusions of the study are that in many cases this information will be restricted. The quantitative importance and significance of 'age' estimates required for any specific ground-water investigation should be considered very carefully in selecting some or all of these isotopic techniques, and interpretations should reflect all the uncertainties which have been illustrated by this study.

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permission to carry out these investigations and the complete cooperation of their staff in providing sampling facilities. A project of this magnitude cannot be completed without the efforts of many analytical and field staff, too numerous to name, from all the organisations concerned in this study. This effort is gratefully acknowledged. Finally, thanks are expressed to Miss C.J. Soonen of the Geophysical Tracers Group, Harwell, for her untiring efforts in communicating the various drafts to the many organisations involved in this three-year study and in the production of the final text.

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VERIFICATION OF THE PRESENCE OF CARBON-14 IN SECONDARY CARBONATES WITHIN A SANDSTONE AQUIFER AND ITS HYDROLOGICAL IMPLICATIONS

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Abstract

VERIFICATION OF THE PRESENCE OF CARBON-14 IN SECONDARY CARBONATES WITHIN A SANDSTONE AQUIFER AND ITS HYDROLOGICAL IMPLICATIONS.

The estimation of groundwater residence times from $^{14}$C data for dissolved carbonates relies on the use of one of a number of geochemical and physical models to take account of the exchange of carbon, by precipitation and dissolution, between the groundwater and the aquifer rock. Such exchange results in a dilution of the $^{14}$C content of the dissolved carbon by rock carbonate. In this preliminary study, the $^{14}$C content of different fractions of CO₂ evolved by acid dissolution of a rock core from the East Midlands Triassic Sandstone aquifer has been measured using the Harwell small-sample $^{14}$C measurement facility. As much as 20 pmc $^{14}$C has been found on the secondary carbonate phase of the rock and this compares with a $^{14}$C level of 37 pmc measured in groundwater. The measured amount of $^{14}$C present is approximately two orders of magnitude more than that predicted from precipitation, using the Reardon and Fritz geochemical model, indicating that much greater exchange processes could occur, possibly sorption or atomic exchange. The effect of this large 'sink' of $^{14}$C is discussed generally in relation to the estimation of groundwater residence times from $^{14}$C data. It is concluded that further work is required to substantiate the presence and distribution of $^{14}$C on aquifer rocks.

1. INTRODUCTION

The determination of groundwater residence times from measurement of the $^{14}$C content of inorganic carbon in groundwaters relies on correction methods to allow for the relative contributions from biogenic carbon and from carbon of the aquifer matrix. A number of correction methods exist which take account of the chemical and isotopic mass balance [1, 2] and physical exchange [3]. In these
methods the exchange of carbon by precipitation from and dissolution into the groundwater is monitored by measurement of $^{13}\text{C}/^{12}\text{C}$ ratios of the water and host rock, with allowances made for the loss of $^{14}\text{C}$ from the solution during precipitation, but assuming the $^{14}\text{C}$ content of the rock to be zero. This assumption has been questioned because the $^{14}\text{C}$-bearing calcite precipitated onto the surfaces of fissures or pores could be available for redissolution and hence increase the $^{14}\text{C}$ content of the groundwater above the level expected from the dissolution of ‘dead’ carbonate. Until recently, the practical difficulties involved in trying to separate enough secondary calcite precipitate from the rock matrix to enable a $^{14}\text{C}$ measurement have precluded experimental verification of any theory. The advent now, however, of systems which can measure $^{14}\text{C}$ in very small samples, such as high-energy accelerators and small counters, opens up new possibilities for investigating the isotopic composition of fissure surfaces.

This paper describes a preliminary investigation, using the Harwell small-sample $^{14}\text{C}$ measurement facility. This facility has now been successfully operated for routine measurements since November 1981. Basically, it is a multi-counter system employing twelve miniature gas counters of Brookhaven design [4, 5] operated simultaneously, six designated as ‘micro-counters’, which require only about 10 mg of carbon, and six designated as ‘mini-counters’, which need 70 mg of carbon for the measurements. Particular features of the facility are the shielding of the counters in a single, 300 mm long by 300 mm diameter, sodium iodide crystal operating as the anticoincidence guard shield, with data access and quality control checks over the extended counting periods provided by linked micro-computer support [6].

The aim of the investigation was to determine whether $^{14}\text{C}$ is present on the surfaces of grains of rock taken from the East Midlands Triassic Sandstone aquifer at Gamston in the United Kingdom. This aquifer has previously been the subject of isotope hydrology studies [7, 8]. The sandstone contains minor amounts of carbonate, including diagenetic dolomite cements as well as later-stage secondary fresh-water calcite. Earlier work by Edmunds et al. [9] has shown that the $^{13}\text{C}/^{12}\text{C}$ compositions of the various carbonates are clearly different, as observed from measurements of carbon dioxide released following acidification. In the present work, $^{14}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ measurements have been made on samples of rock cores extracted from depths of 38, 69 and 135 m, using the small-counter facility for $^{14}\text{C}$ and mass spectrometry for $^{13}\text{C}/^{12}\text{C}$.

2. GAMSTON BOREHOLE: PETROGRAPHY AND MINERALOGY

The Triassic Sherwood Sandstone in the East Midlands of the United Kingdom was deposited in a fresh-water environment and contains minor amounts (up to 5 wt%) of carbonate minerals in addition to the predominant quartz and feldspar
3. EXPERIMENT DESIGN

The physical problems of trying to distinguish and to separate the various carbonate phases make the method of separation by acid dissolution an attractive proposition. The possibility of obtaining separate analytical data from the dolomite and calcite phases relies on them having different reaction rates when treated with phosphoric acid [9, 10]. It was observed that the $\delta^{13}C$ in the carbon dioxide produced became progressively heavier, as a function of time following the addition of an adequate quantity of acid, changing from about $-7\%o$ to $-1\%o$ PDB after a number of hours reaction time [9], as shown in Fig. 1. These isotopic results indicated $\delta^{13}C$ values for the dolomite fraction of around $-1\%o$, with the secondary calcite being considerably more negative, $-6\%o$ to $-8\%o$. 

FIG. 1. $\delta^{13}C$ as a function of time. CO$_2$ liberated by acidification of a calcite/dolomite cemented sandstone. (After Edmunds et al. [9].)
or lower, depending on the contributions to the earliest aliquots of CO₂ from the different phases.

The procedure adopted for the present investigation was basically the same as that used by Edmunds et al. [9], except that it was not considered practical to attempt to collect specific fractional aliquots using the reaction-time method of discrimination. Instead, specific fractions were achieved by successively adding discrete volumes of acid sufficient to acidify only the fraction required.

The quantity added was based initially on the stated carbonate content of the sandstone (approximately 2 wt%) but was adjusted after one or two initial runs when, by experience, the amount required was better known. In the initial runs, an exact division into three equal fractions was attempted. Following the first ¹⁴C measurements, when no detectable ¹⁴C was observed beyond the first 1/3 fraction, a second round of measurements was attempted to obtain the three earliest 1/9 fractions. This was only possible where the available amounts of material allowed a second acidification attempt. This was followed by an experiment to obtain 1/18 fractions from the 38 m core-rim sample. δ¹³C measurements were made on all samples throughout, including the full set of the nominal 1/18 fraction samples.

Since the samples had originated from rock core obtained some 13 years earlier, efforts were made to investigate whether any results obtained were artefacts of storage. Tests regarding this are discussed in a later section; in the original design of the experiment the main precaution taken was to discard the outer surface (rim) of the core and to treat and measure material from this rim in a separate comparative experiment.
It is probable that, after drilling, the core retained much of its indigenous interstitial solution, which subsequently dried out and precipitated CaCO₃ on the grain surfaces. The $^{14}$C activity of this would obviously contribute to the $^{14}$C measured in these experiments, particularly in the earliest stages of acid reaction. Knowing the approximate alkalinity of the indigenous groundwater (180 mg/L HCO₃) and its present $^{14}$C activity (37 pmc), it can be shown that the maximum amount of carbonate in a 1.5 kg rock sample coming from this source would be about 4 mg carbon equivalent with 37 pmc $^{14}$C. However, if after core collection and before drying out, this interstitial solution exchanged with atmospheric CO₂, then the $^{14}$C content of this 4 mg carbon could be up to 160 pmc, from the excess of $^{14}$C due to thermonuclear testing at the time of drilling. In this case, the contribution to $^{14}$C measured in the acid reaction experiments would be significant, up to 9 pmc $^{14}$C in the total 70 mg of carbon collected as each aliquot of CO₂ from the initial stages of reaction. This possibility must be considered in the interpretation of the experimental results.

4. EXPERIMENTAL PROCEDURE

Samples (1.5 kg) of rock core of 15 cm nominal diameter were crushed and ground to pass a 300 μm sieve. No lower limit of grain size was applied in order that total rock was used in the experiments. The preliminary treatment before acidification consisted of chipping off the outside surface to a depth of approximately 1–2 cm, rough grinding in a pestle and mortar, and sieving. Before addition of the first quantity of acid, the sandstone was thoroughly wetted (enough to obtain a watery slurry to allow mechanical agitation) using demineralized water. This precluded the coincident measurement of $^{18}$O/$^{16}$O but did not affect the $^{13}$C/$^{12}$C and $^{14}$C measurements. The apparatus used for acidification is shown diagrammatically in Fig. 2. With a wetted solution the reaction proceeded immediately and even 30% fractions could be collected in approximately ten minutes. It was also unnecessary to use 100% phosphoric acid; instead, much diluted concentrations (approximately 1M), which are much easier to make and handle, could be used.

After the addition of the calculated quantity of acid, the carbon dioxide being produced was observed by a pressure rise recorded by the pressure transducer (Fig. 2). In the dilute solutions the reaction was quick and within a few minutes no further pressure increase was observed. The pressure was recorded as a relative guide to the fractions obtained, after which the full carbon dioxide produced was frozen into the sample collection vessel. In passing into the collection vessel, the carbon dioxide was dried in a carbon dioxide/acetone trap and, after freezing, the uncondensable residuals above the frozen carbon dioxide were pumped away before removal of the collection vessel from the rig. In this form
TABLE I. $^{14}$C RESULTS, RAW DATA, OF CORE SAMPLE FRACTIONS$^a$

<table>
<thead>
<tr>
<th>Nominal fraction</th>
<th>Depth of core</th>
<th>Weighted mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>38 m</td>
<td>38 m (rim)</td>
</tr>
<tr>
<td>Round 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/18 (first)</td>
<td>-</td>
<td>20.0</td>
</tr>
<tr>
<td>1/18 (second)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Round 2</td>
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<td></td>
</tr>
<tr>
<td>1/9 (first)</td>
<td>12.8</td>
<td>9.3</td>
</tr>
<tr>
<td>1/9 (second)</td>
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<td>8.0</td>
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<tr>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1/3 (second)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Round 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/3 (third)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The results, given as 'per cent modern' (pmc), are expressed relative to 0.95 X NBS oxalic acid standard, consistent with the definitions of Stuiver and Polach [11].

Measurement errors (±1σ) are approximately 0.6—0.7 pmc, with the one exception marked* (38 m, 1/3 fraction) where the sigma was ±2 pmc.

The carbon dioxide was adequately purified for $\delta^{13}$C measurements, but for $^{14}$C counting the standard purification procedure for the small counters was employed [6]. In cases where simultaneous measurements of $\delta^{13}$C and $^{14}$C were required on the same sample, the $\delta^{13}$C measurement was carried out on the same gas, following the $^{14}$C measurement after removal from the counter. The larger of the two sizes of miniature gas counters was utilized. This meant that approximately 120 mL (STP) of carbon dioxide gas was required, a carbon equivalent of approximately 70 mg.

5. RESULTS AND COMMENTS

5.1. Carbon-14

The $^{14}$C results are given in Table I. To simplify their presentation, individual measurement errors (i.e. ±1σ) have been omitted. These were ±0.6 to ±0.7 pmc,
except for the first sample processed (i.e. 38 m depth, first one-third fraction), where, because of a problem in the sample preparation, only ±2 pmc was achieved.

In examining the results, certain observations can be made on the distribution and magnitude of the $^{14}$C levels on the rock. First, there appears to be no significant difference in $^{14}$C levels with depth. Second, all the measurable $^{14}$C occurs in the first 20–30% of total CO$_2$ generated. Finally, the core-rim result is not higher than the within-core result of the comparable fraction.

The most complete set of results was obtained from the rock sample taken at 135 m depth. These results allow the $^{14}$C content to be calculated as a function of the proportion of the total carbonate reacted (Fig. 3). Because of the consistency of the data obtained from the 38 m core rim, the result obtained from the first 1/18 fraction is included in Fig. 3. This curve shows what should be obtained if the aggregated CO$_2$ was analysed as the reaction proceeds. It should be noted that the total carbonate in this case would have a detectable level of approximately 1.5 pmc.
## TABLE II. $^{13}$C/$^{12}$C MEASUREMENTS ON CORE SAMPLE FRACTIONS\(^a\)

<table>
<thead>
<tr>
<th>Nominal fraction</th>
<th>Results of '1/18' samples</th>
<th>Derived '1/3' means</th>
<th>Measured '1/3' results</th>
<th>Derived '1/9' means</th>
<th>Measured '1/9' results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-9.9</td>
<td></td>
<td></td>
<td>-9.75</td>
<td>-8.7</td>
</tr>
<tr>
<td>2</td>
<td>-9.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>18</td>
<td>b</td>
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</table>

\(a\) All results are expressed as $\delta^{13}$C (‰) relative to PDB.

\(b\) Insufficient CO$_2$ available for measurement.

### 5.2. $^{13}$C/$^{12}$C

The $\delta^{13}$C measurements of all CO$_2$ samples are given in Table II and presented diagrammatically in Fig. 4. The $\delta^{13}$C of the dissolved carbonate in the groundwater was measured as $-11.8\%$. Thus the value of $\delta^{13}$C expected in carbonate precipitated from this solution, allowing for fractionation, is about $-9\%$, which is similar to the values of $\delta^{13}$C measured on the aliquots of CO$_2$ from the reaction of acid with the carbonate.
6. SUBSIDIARY EXPERIMENT TO INVESTIGATE POSSIBLE CONTAMINATION

The similarity between the $^{14}C$ levels on the core-rim samples and the within-core samples demonstrates that there is no profile of decreasing contamination with distance into the centre of the material. Such a profile might have been expected if the contaminating source had been the drilling fluid diffusing into the rock matrix. However, with the long storage time of the core material without any special sealing precautions, contamination by exchange with atmospheric CO$_2$ might still have occurred, but its distribution throughout the sample would have been more or less uniform. In this case, measurements of the rim material cannot indicate the occurrence of contamination.

A subsidiary experiment was carried out to investigate the susceptibility of the rock carbonates to exchange carbon with that of the environment during storage. In view of the time of storage, gaseous contamination from atmospheric carbon dioxide was considered the more likely source.

The experiment consisted of exposing three samples of sandstone (ground to less than 300 $\mu$m as before) to carbon dioxide gas which had as large a $\delta^{13}C$
difference from the rock as could be found. This was tank carbon dioxide, which had a δ^{13}C of −33.0%. The procedure consisted of weighing 60 g of the sand into each of the 250 mL flasks (A and B) and one 100 mL flask (C). These were then evacuated and an atmosphere of carbon dioxide from the tank was introduced. In flasks A and C the sand was left dry, but in flask B it was slightly wetted to increase the relative humidity. In the 250 mL flasks it was calculated that the relative numbers of carbon atoms in the solid and gaseous phases were approximately the same, so that it was equally valid to examine the gas or the carbonate solid for possible exchange effects. After one week, carbon dioxide gas was extracted for δ^{13}C measurement, and new gas was put back and left for a further four weeks before measuring again. Finally, the carbonate was acidified and a series of δ^{13}C measurements on approximately 1/18 th fractions made as before. The results are given in Table III.

The results show that no significant change has occurred in the direction of exchange with the gaseous carbon dioxide, giving support to the validity of the core data as representing aquifer conditions. If the exchange of carbon atoms was assumed to be directly proportional to the product of the number of carbon atoms present and the exposure period, the exchange experiment undertaken would be equivalent to exposure times to atmospheric CO₂ (0.03%) of more than 200 years.

7. CARBON-14 ON SECONDARY CALCITE

The existence of ^{14}C on the calcite fraction of the rock is not unexpected. The current geochemical model [9] applied to this aquifer allows for the precipitation of calcite containing ^{14}C and the dissolution of dolomite. However, this model does not allow for the redissolution of calcite containing ^{14}C. This would occur in this aquifer only if the chemical conditions in the aquifer changed.
Redissolution would result in a transfer of \(^{14}\text{C}\) from the rock to the groundwater, a factor not allowed for in correction calculations, resulting in an underestimation of the radiocarbon 'age'.

The presence of relatively large amounts of \(^{14}\text{C}\) on the rock surface raises the question of whether additional processes other than precipitation of calcite might occur. One possibility is exchange of carbon by sorption of the carbonate ion. This is supported by some laboratory sorption studies\(^{12, 13}\) which showed retardation of \(^{14}\text{HCO}_3^-\) in column experiments. Another possibility is atomic exchange between dissolved carbonate and the crystal lattice. In these cases, a retardation of \(^{14}\text{C}\) occurs and the groundwater residence time is overestimated by conventional \(^{14}\text{C}\) interpretation.

To examine the possibility that an additional source of \(^{14}\text{C}\) to the rock over that due to precipitation exists, an assessment of the contribution of \(^{14}\text{C}\) from calcite precipitation has been made from the groundwater chemistry and the observed \(^{14}\text{C}\) values.

The amount of secondary calcite precipitated and its carbon isotopic composition have been estimated from the chemical and isotopic balance model (WATEQF-ISOTOP model 2\(^{11}\)), using hydrochemical data from the aquifer\(^{9}\). The chemical balance suggests that about \(5 \times 10^{-4}\) mol of \(\text{CaCO}_3\) is precipitated from each litre of solution during flow to the deepest point sampled, about 20 km from outcrop. If an average groundwater velocity of 1 m/a is assumed, and if it is also assumed that the calcite is precipitated uniformly throughout the aquifer, then it can be calculated that about \(10^{-5}\) grams of calcite are deposited per gram of total rock in 10 000 years. If the rock is assumed to have 2 \% total carbonate present, then about \(5 \times 10^{-4}\) grams \(\text{CaCO}_3\) are deposited per gram of total carbonate in 10 000 years.

The groundwater present in the aquifer at Gamston has a \(^{14}\text{C}\) content of approximately 37 ppm, which, allowing for isotopic fractionation, would give a precipitated calcite with a \(^{14}\text{C}\) value of approximately 38 ppm. If a uniform deposition of calcite occurred over the last 10 000 years (i.e. about two half-lives of \(^{14}\text{C}\)) the mean level of \(^{14}\text{C}\) would be about 22 ppm. Therefore, using this model, it is estimated that about 0.05\% of the total carbonate present will be calcite with a mean \(^{14}\text{C}\) value of 22 ppm. Clearly, the carbonate of older calcite deposits will have proportionally lower \(^{14}\text{C}\) values.

The dissolution experiments have shown that the first 1/18 fraction (i.e. about 6\%) of total carbonate contains about 20 ppm \(^{14}\text{C}\). As this level of \(^{14}\text{C}\) is associated with about 100 times the amount of carbon estimated to have been precipitated in the last 10 000 years, the total amount of \(^{14}\text{C}\) present in the aquifer matrix is much higher than that expected from precipitation alone. Three possible explanations for this are tentatively proposed:

(a) The drill-core samples used in the dissolution experiments have been contaminated by atmospheric \(^{14}\text{C}\) during storage. Direct contamination by exchange
of CO₂ with solid calcite seems very unlikely on the evidence from the above experiments. The most probable mechanism for contamination would be exchange with interstitial solution before this dried out and at worst could account for half of the measured ¹⁴C.

(b) The active deposition of calcite containing ¹⁴C does not occur uniformly through the aquifer, but it is concentrated in the upgradient part of the aquifer in which Gamston is located and therefore results in a greater rate of secondary calcite precipitation and higher average ¹⁴C concentrations.

(c) The secondary calcite has incorporated ¹⁴C not only during progressive precipitation but also as a result of isotopic exchange between solution and solid surface independently of the predicted sequence of dissolution—precipitation reactions. Complete instantaneous exchange between solution and bulk carbonate would result in the latter having a ¹⁴C value of approximately 38 pmc at Gamston. Any incomplete exchange, for instance with a surface molecular layer, would cause an increase in ¹⁴C level above that predicted here, but with an upper limit of the equilibrium level of 38 pmc.

8. CONCLUSIONS

This study represents a first attempt at measuring the ¹⁴C content of an aquifer rock and its distribution on the different mineralogical phases, by means of small proportional gas counters. Preliminary assessments indicate that maximum possible contamination does not account for all the ¹⁴C measured on the rock. Therefore, it is concluded from these analyses that:

- ¹⁴C is associated with the secondary carbonate fraction of the rock
- the highest value of ¹⁴C measured was 20 pmc associated with approximately 6% of the calcite
- the presence of ¹⁴C is a surface phenomenon and not in bulk isotopic equilibrium with the dissolved carbonate of the surrounding groundwater
- initial estimations, using a geochemical model, indicate that the amount of ¹⁴C present is approximately two orders of magnitude more than that expected from precipitation of calcite from the groundwater.

The existence of such a large sink of ¹⁴C suggests that other mechanisms of exchange exist between ¹⁴C in the groundwater and rock, possibly sorption or atomic exchange. This would have the effect of retarding the movement of the nuclide so that the transit time of ¹⁴C will be greater than that of the water. In this case, the radiocarbon 'age' of the groundwater will be an overestimate of groundwater residence time. Reliable modelling of radiocarbon data must take into account all such exchange processes and may now require substantially more data on ¹⁴C composition of the rock than hitherto.
The preliminary nature of the present work has demonstrated that more comprehensive studies should be carried out on fresh rock samples, treated to minimize the possibility of contamination, using specific samples of the different mineralogical phases of the rock. The current availability of tandem accelerators and small proportional counters for the measurement of $^{14}$C from very small samples now allows the examination of this important element in understanding the behaviour of radiocarbon in groundwater systems.

ACKNOWLEDGEMENTS

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REFERENCES

LABORATORY STUDY ON CARBON ISOTOPE UPTAKE BY CALCITE FROM CARBONATE IN AQUEOUS SOLUTION

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Abstract

LABORATORY STUDY ON CARBON ISOTOPE UPTAKE BY CALCITE FROM CARBONATE IN AQUEOUS SOLUTION.

Laboratory experiments demonstrated that the surface of calcite crystals interacts isotopically with the aqueous carbonate of the solution. A significant absorption loss of $^{13}$C atoms from solution and subsequent permanent ‘fixation’ through recrystallization takes place on crystals with disturbed surface areas and a large number of high-surface-energy sites (because of mechanical treatment). Following absorption, isotope effects are caused by exchange of carbon on the solid surface with carbon in the aqueous phase. For crystals with stable surfaces the absorption process is less important, but $^{13}$C loss does occur through a first-order recrystallization with a reaction constant of about $10^{-8}$ s$^{-1}$. Experiments show that $^{13}$C loss in biogenic calcites occurs at a lower rate than in pure inorganic carbonates. A long-term run with pure calcite demonstrates that $^{13}$C losses from solution continue during the entire experimental period of close to 500 days. The loss rate could not be quantified because it was not possible to correct for surface areas changing with time. Model calculations show that adsorption reactions have no effect on $^{14}$C ‘ages’ of groundwaters, but recrystallization reactions promote strong removal of $^{14}$C atoms from the aqueous carbonate. In natural systems, however, these reactions must proceed at a lower rate than observed in the laboratory. This is possibly due to the fact that only a small portion of the total surface area of available carbonate minerals participates in these reactions.

1. INTRODUCTION

A number of laboratory studies to investigate the carbon isotope exchange processes between aqueous and solid carbonate phases are reported in the literature. Tracers such as $^{14}$C or $^{45}$Ca were used both in flow-through and batch experiments [1–8]. The results obtained by these studies document similar trends but are not...
in complete agreement with respect to reaction half-lives and reaction mechanisms. Furthermore, only in a few studies (e.g. Refs [7, 8]) were chemical equilibria monitored and crystal surfaces characterized: this is probably the most important shortcoming and may explain some of the differences. In addition, the importance of reaction times was not adequately considered.

Recently, Mozeto et al. [9] reported laboratory data on the carbon isotope exchange between aqueous and solid carbonate using $^{13}$C as a tracer. Carbonate chemical equilibria were maintained in all runs and calcites with differently prepared surfaces were used.

This paper presents a summary of the major findings described by Mozeto et al. [9] and discusses new data on exchange reactions with biogenic calcite (coccolithic carbonate) and pure calcite in a long-term run. An attempt is made to assess the significance of these observations for the loss of $^{14}$C from groundwaters.

2. LABORATORY EXPERIMENTS

The experiments of this study were done with calcite-saturated solutions spiked with Na$_2$CO$_3$ (99% $^{13}$C). Spiking was done either before or after pretreatment of calcite crystals of uniform grain size in unspiked but calcite-saturated solutions for varying periods of time. This was done to assess the differential behaviour of thermodynamically stable surfaces (aged crystals) compared with more unstable surfaces (unaged crystals). Two 'types' of calcite crystals were used: clear calcite spar and chemically precipitated calcium carbonate. To obtain aged surfaces, the solution and calcite were kept in contact for several weeks to ensure isotopic and chemical constancy in the solution. This pretreatment resulted in the growth of euhedral calcite crystals. Control runs were carried out without calcite crystals. The data refer to an average laboratory temperature of $23 \pm 3^{\circ}$C measured during the experiments.

The coccolithic carbonate was obtained by disintegrating the 'coccolithic limestone' in deionized water in an ultrasonic bath, sieving through a 25 $\mu$m sieve and decanting the fines. The resulting average grain size was close to 10 $\mu$m. The samples were aged for about 60 days before spiking.

The long-term run utilized aged, pure calcite (average grain size about 50 $\mu$m) which after spiking in a batch was divided into 20 cm$^3$ portions of solution. The calcite/liquid ratio was determined gravimetrically. Each portion was sealed in a break-seal and the individual vessels were sampled at different times.
3. RESULTS AND DISCUSSION

3.1. Short-term experiments with pure calcite

This section describes the results of positive-isotopic-gradient experiments in which the $\delta^{13}C$ values of the solutions were adjusted to be in the range +300 to +1000‰ PDB. These large $\delta^{13}C$ values provided a substantial initial isotopic gradient with respect to calcite crystals (calcite spar, $\delta^{13}C = 1.68 \pm 0.07‰$ PDB, and chemically precipitated calcite, $\delta^{13}C = -38.5‰$ PDB).

Carbon isotope and chemical data (alkalinity) were used to calculate the number of $^{13}C$ atoms lost from solution in the different systems and provided the basis for the quantification of these losses per unit surface area for each crystal type.

All results of these positive-isotopic-gradient runs record a substantial decrease in the $\delta^{13}C$ values of the solution with time (Fig.1). For each 'type' of calcite crystal used, there is initially a short, linear drop (first stage) which later becomes exponential (second stage). The magnitude of the initial $^{13}C$ loss is a function of the length of aging, i.e. the time during which the crystals were in contact with calcite-saturated solution. The more aged the crystals are, the less pronounced and the shorter is the initial linear drop in $^{13}C$ content. The exponential relationships between $\delta^{13}C$ and time (second stage) are then attained in a shorter period. The only exception is the unaged/precipitated calcite run (curve e in Fig.1) the two stages of which cannot be clearly recognized. The existence of these two stages can be interpreted as a first indication that at least two different processes are responsible for the $^{13}C$ losses from solution. The first stage is dominated by a reaction obeying a second-order-rate law with respect to the number of $^{13}C$ atoms lost from solution (Fig.2).

From the slopes it was possible to evaluate an exchange reaction constant for these systems. The values were calculated as $1.6 \times 10^6$ and $1.0 \times 10^6$ cm$^5$/mol·s for aged/crushed and aged/precipitated calcite crystals, respectively (the values are normalized to the surface area of calcite crystals).

The corresponding half-lives for this first-stage reaction were 685 s and 642 s for aged/crushed and aged/precipitated calcite systems, respectively.

The first stage of these experiments is thus characterized by a relatively fast reaction, which could reflect the adsorption of HCO$_3^-$ ions at high-surface-energy sites of calcite crystal surfaces coupled with isotope exchange. Such a mechanism would be in agreement with the observation that surface adsorption reactions in aqueous media are fast phenomena (see, for example, Thilo and Münich [4] and Buddemeir et al. [6] who qualitatively considered adsorption to be an important factor in their experiments).

Adsorption alone is an essentially non-fractionating process and cannot explain the observed $^{13}C$ losses. It is necessary to introduce an isotope exchange
process which follows the adsorption. This is comparable with observations made by Anderson [10] in CO$_2$/calcite exchange experiments.

The $\delta^{13}C$ time relationship for the log-linear (exponential) stage in the systems was also graphically analysed. Straight lines are obtained in graphs of ln $^{13}C$ versus time for the aged/crushed calcite crystals and are presented in Fig.3.

Linear regression analyses of the data shown in Fig.3 yielded a rate constant, normalized to calcite surface areas, of $2.8 \times 10^{-8}$ s$^{-1}$. This indicates that the dominating reaction at the second stage follows a first-order-rate law with respect to the uptake of $^{13}C$ from solution. The reaction's half-life is $2.6 \times 10^7$ s (or about 300 days). An unaged/crushed calcite run yielded results virtually identical with those of aged crystals. These results suggest that losses of $^{13}C$ atoms from the solution during the second-stage reaction proceed via recrystallization of
FIG. 2. Variation of $1/^{13}C$ concentration (normalized to the surface area of calcite used) versus time for the first-stage reaction. $C_{\text{O,fin}}$ is the calculated $^{13}C$ concentration at $t = 0$, taken as the intercept of the regression analyses of second-stage reaction data shown in Fig.1.

calcite on crystal surfaces, whereby carbon isotopes from the solid phase are delivered to the solution through dissolution processes, mixed with the aqueous carbon reservoir and returned through precipitation to the solid phase. This can be described as an isotope exchange process. Such rate constants agree with observations that recrystallization reactions are generally regarded as being slow processes [11, 12].

The number of $^{13}C$ atoms lost from solution during the positive-gradient runs may be related to an equivalent number of molecular layers in calcite crystals and can be evaluated through carbon balances. These 'crusts' on the crystals are assumed to have homogenous $^{13}C$ compositions, and the number of molecular layers involved is determined by the $\delta^{13}C$ solution and the fractionation factor between $\text{HCO}_3^{\text{(aq)}}$ and $\text{CaCO}_3^{\text{(s)}}$ (2.2\% at 25°C [13, 14]). The results of these calculations are listed in Table I and indicate the minimum 'penetration' depth of $^{13}C$ atoms from solution into calcite crystals. It is important to note that the aged crystals acquired only about one molecular layer. This is in agreement with data obtained by Moeller and Sastri [8] who found "not more than one layer" on the basis of $^{44}Ca$ exchange experiments. However, a substantially larger number of layers developed on the unaged crystals. The calculations assume that isotopic
<table>
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<th>Total number of $^{13}$C atoms lost from solution ($\times 10^{16}$) (pos. isot. grad. exp.)</th>
<th>Number of molecular layers in the 'crust'</th>
<th>Thickness of the 'crust' ($10^{-7}$ cm)</th>
<th>Total reaction time (h)</th>
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<td>Unaged/precipitated calcite (curve e in Fig.1)</td>
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equilibrium between these layers and the solution has been established. Should this not be the case, however, should isotopic equilibrium not have been reached, and should isotope gradients exist within the ‘crust’, then the number of molecular layers could be much higher.

It is interesting to note that Mozeto et al. [9] show that the atoms lost from solution during the first stage of the positive runs with aged/crushed calcite can be fully recovered during ‘negative-isotopic-gradient runs’. However, of the $^{13}$C atoms lost during the dominating second stage, only about 25% were recovered, which adds up to about 30% of recovery with respect to the total amount lost. This observation is again in agreement with results obtained by Moeller and Sastri [7] who had a recovery of 60–70% in their experiments during a 50 h run.

The runs with aged/crushed calcite thus show that the process accounting for the loss of $^{13}$C atoms from solution is reversible, as would be expected if adsorption/exchange were dominating the $^{13}$C loss during the first stage of these experiments. On the other hand, the recovery of the $^{13}$C atoms for the unaged calcite runs is less than 2% during negative-gradient experiments, which demonstrates that for the unaged crystals the loss of $^{13}$C atoms during the first stage is essentially non-reversible.

Mozeto et al. [9] also document that in systems with free Mg$^{2+}$ ions (at seawater concentration) a poisoning of the crystal surfaces occurs which retards the recrystallization/isotope exchange processes. Similar observations were previously made by Moeller and Sastri [7]. Mg$^{2+}$ ions are also known to inhibit dissolution and precipitation reactions of calcite [15, 16].

The reaction order proposed here agrees with the results of experimental work done by Wiechers et al. [17] who found that recrystallization of calcite surfaces follows a first-order-rate law with respect to Ca$^{2+}$ and CO$_3^{2-}$ concentrations in the solutions. Their observations also suggest that this is a surface-controlled reaction.
Diffusion of HCO$_3^-$ and CO$_3^{2-}$ ions into calcite particles has been suggested by Thilo and Münich [4] as being responsible for the irreversible losses of $^{14}$C from the solution. The evidence presented here suggests, however, that isotope exchange coupled with calcite recrystallization are the active processes responsible for the change in $^{13}$C (and $^{14}$C) isotopic composition of the solution after a rapid surface adsorption/exchange has come to an end. This process is much faster than solid-state diffusion, which is a slow phenomenon, with coefficients as low as $10^{-33}$ cm$^2$/s [18] for CO$_3^{2-}$ ion diffusion into calcite and as low as $10^{-43}$ cm$^2$/s for diffusion of gaseous CO$_2$ into calcite crystals [19].

3.2. Long-term experiment with pure calcite

A long-term exchange run using pure calcite as a solid phase was designed to obtain information on the long-term validity of the observations made in short-term runs which lasted only 900 hours. The data obtained by Mozeto [20] indicated that additional information about the kinetics of this isotope exchange process may be obtainable in longer runs.

A preliminary interpretation of the results shows that indeed $^{13}$C loss from solution on crystal surfaces occurred throughout the entire experiment which lasted about 500 days. However, one can expect that the surface area of the reacting calcite changes with time and consequently the number of high-surface-energy sites available decreases [9]. Thus a knowledge of the available surface area is essential for the evaluation of the $^{13}$C loss rate during the second-stage reaction. At the time of writing, surface areas of calcite crystals which had reacted for different times were not available and rate normalization had not been performed.

3.3. Short-term experiment with biogenic calcite

In dissolution studies it has been shown that dissolution rates for biogenic carbonates can be significantly smaller than those for pure calcites. Specifically, Keir [21] observed dissolution rates for laboratory-grown coccolith which were about one order of magnitude lower than expected. For this reason, coccolithic limestone from Cretaceous sediments with 0.12% Mg was used in an exchange run.

The results of this run are shown qualitatively in Fig.4. For comparison, a simultaneously performed run with pure calcite is also presented. After a short first-stage reaction, the two samples display quite different behaviour and the slope for the second-stage reaction is significantly lower for the coccolith sample than for normal calcite, reflecting a slower rate of $^{13}$C uptake from solution.

The rate constant, evaluated in a manner similar to the one described for pure calcite, is approximately $9.7 \times 10^{-9}$ s$^{-1}$. This value is lower than those obtained for pure calcites and may substantiate the results obtained for laboratory-grown coccolith. This is an important observation and is of relevance for isotope ex-
change in natural systems where carbonate rocks are often composed of biogenic carbonates. The results may also signify that reaction rate constants obtained from inorganic reactions are not necessarily applicable in natural systems.

3.4. Effect of carbon adsorption and recrystallization on $^{14}$C 'dating' of groundwater

The following discussion is based on results from a shallow groundwater system in Pinawa, Manitoba, Canada, for which abundant hydrogeological, geochemical and isotopic information exists [20, 22]. This sandy aquifer has a porosity of 38% and an average total carbonate mineral content of 14.1%, corresponding to a total surface area of carbonate minerals of $10^6$ cm$^2$ per litre groundwater. The approximate number of exchange sites available on the crystals is $4.1 \times 10^{11}$ cm$^2$/L. Considering this in terms of number of $^{14}$C atoms adsorbed, it can be shown that for all practical purposes and despite the fact that adsorption reactions are fast, the adsorption capacity of calcite crystals is very low. Consequently, the $^{14}$C activity and ultimately the $^{14}$C age of that water will not be measurably affected.
However, the laboratory experiments demonstrate that after achievement of initial $^{14}$C equilibration between crystal surface and water, recrystallization processes will be responsible for further losses. The laboratory-determined rate constant for this reaction is close to $10^{-8}$ s$^{-1}$ and differs little from the rate constant adjusted for the Pinawa situation. Assuming that the entire carbonate surface area is available for exchange and taking an input of 100 pmc for the $^{14}$C activity of the groundwater, only about 75 pmc will remain in the aqueous carbon after one year. This is a very fast loss and does not reflect the field situation. Therefore, if one assumes that only a fraction of the total surface area participates in the process and if a smaller rate constant for biogenic carbonates is taken, the loss will proceed at a slower rate. For the Pinawa situation, either a reduction of the available sites to 5–10% and/or a decrease of the rate constant by somewhat over an order of magnitude would be estimated in order to explain the observed distribution of $^{14}$C in these groundwaters.

5. SUMMARY

The results of positive-isotopic-gradient runs show that exchange reactions between aqueous and solid carbonate crystal surfaces can be described by two processes: (a) an initial, fast adsorption/isotope exchange reaction of HCO$_3^-$ ions onto calcite crystal surfaces, and (b) a subsequent, slow reaction which is the result of a combination of calcite recrystallization/isotope exchange on crystal surfaces. The extent to which both reactions occur is related to the total number of high-surface-energy sites per square centimetre of surface area and is thus a function of aging time.

Calcite recrystallization/isotope exchange was found to be responsible for losses of $^{13}$C atoms from solution during the second stage and followed a first-order-rate law with respect to the $^{13}$C contents in solution, with a rate constant of about $10^{-8}$ s$^{-1}$ and a half-life of about 10$^7$ s.

Negative-isotopic-gradient runs recovered about 30% of the $^{13}$C atoms lost during the second stage in experiments with aged/crushed calcite. On the other hand, less than 2% was recovered in experiments with unaged/crushed and precipitated calcite.

Mg$^{2+}$ ‘poisoning’ runs with aged/precipitated calcite showed a lower slope for the second-stage reaction compared with similar experiments done without magnesium addition.

Results of a positive-isotopic-gradient run using coccolithic carbonate as solid phase yielded a rate constant of $9.7 \times 10^{-9}$ s$^{-1}$. This value is lower than the one for pure calcite and may substantiate dissolution rate data obtained by Keir [21].
The results of a long-term isotopic exchange run using pure calcite show that $^{13}$C losses from solution continue during the 500 days of monitoring. Although normalization of the rate constants was not possible, it cannot be excluded that these rates decrease with time as a function of decreasing surface area during 'aging'. This implies that $^{14}$C 'ages' are not measurably affected by adsorption reactions. However, the effects of recrystallization processes are potentially important.

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UTILISATION DES VARIATIONS NATURELLES D’ABONDANCE ISOTOPIQUE EN $^{15}$N POUR TRACER L’ORIGINE DES POLLUTIONS DES AQUIFÈRES PAR LES NITRATES

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Abstract—Résumé

UTILIZATION OF NATURAL VARIATIONS IN THE ISOTOPIC ABUNDANCE OF $^{15}$N TO TRACE THE SOURCE OF AQUIFER POLLUTION BY NITRATES.

The validity of using the natural isotope nitrogen-15 to trace the source of nitrates contained in aquifers is discussed with reference to experimental devices (lysimeters and experimental plots) and for examples chosen from the Paris area. There are a number of sources of nitrates: (1) industrially synthesized nitrates (fertilizers); (2) nitrates produced by oxidation of organic matter associated with human, agricultural or urban activities; (3) nitrates synthesized in the soil by the decay of organic matter. In the examples studied these sources differ in their $^{15}$N content: (1) fertilizers have a $\delta^{15}$N close to zero (atmospheric nitrogen); (2) the nitrates originating from organic pollution have high $\delta^{15}$N (above 10–12%) and this $^{15}$N enrichment is associated with the volatilization of ammonia during the ammonia stage of mineralization; (3) the isotopic characterization of the nitrates produced by organic matter in the soil is less evident. Initial pedological differences and transformation of organic matter by cultivation determine the change in the isotopic composition of these nitrates. However, except under the special pedological conditions which are pointed out, indirect indications (study of nitrates from non-polluted aquifers) and direct evidence (incubation and study of nitrates in the drainage of lsimeters or of experimental plots without fertilizer application) show that these nitrates have $\delta^{15}$N values close to 7–8%. Citing several examples, the author demonstrates that these three sources are differentiated isotopically. Consideration of the parameters nitrate concentration/isotopic composition reveals simple mixture curves. In the most complicated cases — where there is association with other isotopic ($^{18}$O) or chemical parameters — it is possible qualitatively to trace the sources of nitrogen pollution. Lastly, it is shown that changes caused by microbiological systems in aquifers (for example, denitrification) cannot explain the distribution of the isotopic composition of $\mathrm{NO}_3^-$ in these media.

UTILISATION DES VARIATIONS NATURELLES D’ABONDANCE ISOTOPIQUE EN $^{15}$N POUR TRACER L’ORIGINE DES POLLUTIONS DES AQUIFÈRES PAR LES NITRATES.

La validité du tracé isotopique naturel par l’azote 15 des nitrates contenus dans les aquifères est discutée sur des dispositifs expérimentaux (casus lsimétriques, parcelles expérimentales) et sur des exemples régionaux choisis dans la région parisienne. Les sources de nitrates sont multiples: 1) nitrates de synthèse industrielle (engrais); 2) nitrates provenant de l’oxydation de matières organiques liées à des activités humaines, agricoles ou urbaines;
3) nitrates synthétisés dans le sol par dégradation de la matière organique. Sur les exemples étudiés, ces sources se différencient par leur contenu en $^{15}$N: 1) les engrais ont un $\delta^{15}$N proche de zéro (azote de l'air); 2) les nitrates provenant d'une pollution organique sont caractérisés par des $\delta^{15}$N élevés (supérieurs à 10–12‰) et cet enrichissement en $^{15}$N est lié à la volatilisation de l'ammoniac pendant l'étape ammoniacale de la minéralisation; 3) la caractérisation isotopique des nitrates provenant de la matière organique des sols est moins évidente. Les différences pédologiques initiales et les transformations de la matière organique par la mise en culture interviennent dans le contrôle de la composition isotopique de ces nitrates. Cependant, hormis certaines conditions pédologiques particulières qui sont soulignées, des arguments indirects (étude des nitrates d'aquifères non pollués) et directs (incubations, étude des nitrates au drainage de lysètremes ou de parcelles expérimentales sans apports d'engrais) montrent que ces nitrates ont des $\delta^{15}$N proches de 7 à 8‰. L'étude montre sur plusieurs exemples que ces trois sources sont différenciées isotopiquement. La considération des paramètres concentration en nitrate-composition isotopique permet de mettre en évidence des courbes de mélange simples. Dans les cas les plus complexes, l'association avec d'autres paramètres isotopiques ($^{14}$H) chimiques permet de remonter qualitativement aux sources des pollutions azotées. Enfin, il est montré que des évolution commandées par des systèmes microbiologiques, au sein des aquifères (ex.: dénitrification), ne peuvent expliquer la distribution des compositions isotopiques de NO$_3$ dans ces milieux.

1. INTRODUCTION

Depuis quelques années, l'attention des hydrogéologues, des hygiénistes et des distributeurs d'eau est attirée par la pollution des aquifères par les nitrates. Ainsi, dans certaines régions françaises, la Beauce par exemple, beaucoup d'adductions d'eau potable sont d'excellente qualité pour tous les paramètres chimiques et bactériologiques sauf pour les nitrates qui dépassent la norme de potabilité de 44 mg/L.

Par ailleurs, il est essentiel de savoir si une fraction de l'azote des engrais de synthèse figure parmi les sources de pollution, ce qui représenterait une perte économique, la synthèse de ces engrais étant particulièrement gourmande en énergie. La fixation industrielle de l'azote sous forme combinée (engrais) est sans cesse croissante, doublant environ tous les six ans [1], ce qui entraîne un profond déséquilibre du cycle naturel de l'azote et une menace potentielle pour les teneurs en nitrate dans les eaux.

Kohl et al. [2] furent les premiers à utiliser les variations d'abondance isotopique naturelle en $^{15}$N pour caractériser les sources de nitrate dans les eaux d'un bassin versant agricole. Leur méthode est basée sur l'existence d'une différence de composition isotopique entre les nitrates de synthèse industrielle et ceux provenant de la minéralisation de la matière organique des sols. Les résultats furent critiqués par quelques auteurs [3–5], mais un certain nombre de travaux [6–9] semblent confirmer les observations de Kohl et al.

Le présent travail n'est qu'un résumé des principaux résultats présentés par l'auteur dans une monographie [10]. On y tente de faire le point sur l'appli-
cation de cette technique de traçage isotopique à des milieux naturels, d’en
dégager la portée et d’en souligner les limites.

2. METHODES

L’analyse isotopique de l’azote est conduite selon une méthodologie décrite
par ailleurs [11]. Les compositions isotopiques sont exprimées en unités \( \delta^{15}N \),
relativement à un étalement dont la teneur en \( ^{15}N \) est stable: l’azote atmosphérique [12]:

\[
\delta^{15}N = \left( \frac{^{15}N/^{14}N_{échantillon}}{^{15}N/^{14}N_{étalon}} - 1 \right) \times 1000
\]

La précision sur le \( \delta^{15}N \) est de \( \pm 0.2\% \) pour l’azote des composés minéraux,
et de \( \pm 0.4\% \) pour l’azote organique.

3. ZONE D’ETUDE [10]

Deux régions naturelles ont été étudiées, toutes deux à vocation agricole
essentiellement céréalière:
— au sud de Paris, le plateau de Beauce est une surface structurale tabulaire
composée de terrains tertiaires, essentiellement des calcaires lacustres, au réseau
hydrographique pauvre;
— au sud-est de Paris, la Brie est un plateau tertiaire au réseau hydrographique
dense, fortement drainé.

La fertilisation azotée est voisine, sur blé et maïs, de 150 kg d’azote par
hectare par an.

Les nappes étudiées sont: a) la nappe oligocène, dite de Beauce, une des
plus grandes nappes libres de France; b) celle de l’Eocène Supérieur (calcaires de
Champigny); c) la nappe de la Craie (pour plus de détails, voir [13]). En Beauce,
34 points de captage ont été étudiés, en Brie 19. Certains points ont été analysés
périodiquement, d’autres une seule fois (pour un descriptif détaillé, voir [10]).
En Brie, deux bassins versant ont été étudiés, l’un strictement agricole, le Bassin
de Mélarchez, l’autre mixte, agricole en amont et urbanisé en aval, celui de l’Yerres.

4. RESULTATS ET INTERPRETATION

4.1. Caractérisation isotopique des sources potentielles de nitrate

Sur un bassin versant ou dans une région naturelle du type de ceux présentés
ici, les sources dominantes de nitrates sont: 1) les nitrates, et plus généralement
TABLEAU I. COMPOSITIONS ISOTOPIQUES DE L’AZOTE D’ENGRAIS. VALEURS MOYENNES EXTRAITES DE LA LITTERATURE

<table>
<thead>
<tr>
<th></th>
<th>δ¹⁵N-NH₄⁺</th>
<th>δ¹⁵N-NO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nombre d’analyses</td>
<td>m ± σ</td>
<td>m ± σ</td>
</tr>
<tr>
<td>Présente étude</td>
<td>27</td>
<td>-0,1 ± 1,2</td>
</tr>
<tr>
<td>Freyer et Aly [14]</td>
<td>11</td>
<td>-1,3 ± 1,5</td>
</tr>
<tr>
<td>Shearer [15] et al.</td>
<td>28</td>
<td>-0,5 ± 1,8</td>
</tr>
<tr>
<td>Rennie [16] et al.</td>
<td>4</td>
<td>1,6 ± 1,9</td>
</tr>
<tr>
<td>Aly [9] et al.</td>
<td>?</td>
<td>-2,1 ± 1,1</td>
</tr>
</tbody>
</table>

Note. m: moyenne; σ: écart-type.

l’azote de synthèse industrielle (engrais); 2) les nitrates provenant de l’oxydation de matières organiques liées à des activités humaines, agricoles (fumier, lisier, etc) ou urbaines (effluents domestiques); 3) les nitrates synthétisés dans le sol par les processus microbiaux de minéralisation (puis nitrification) de la matière organique de ces sols.

4.1.1. Composition isotopique de l’azote des engrais

Il est synthétisés à partir de l’azote de l’air. Nous avons mesuré [10] les compositions isotopiques de 27 engrais utilisés dans le Bassin de Paris. On obtient: δ¹⁵N-NH₄⁺ = -0,1 ± 1,2‰, δ¹⁵N-NO₃⁻ = 2,8 ± 2,5‰. Ces valeurs sont très proches de celles de différents auteurs dans divers pays (tableau I). L’azote de synthèse sous forme d’urée présente lui aussi une valeur proche de zéro [9, 10].

Ainsi, l’azote minéral des engrais de synthèse a une composition isotopique proche de celle de l’azote de l’air, en moyenne toujours inférieure à 3‰. En particulier, nous obtenons pour les engrais les plus utilisés, de type ammoniatte, des δ¹⁵N de 0,5 ± 1,0‰ (N-NH₄⁺) et 2,3 ± 0,5‰ (N-NO₃⁻).

4.1.2. Composition isotopique des nitrates provenant d’une pollution organique

Des déchets organiques ayant subi une longue maturation sont le siège d’une importante fermentation ammoniacale. L’ammonium accumulé pourra être l’objet d’une volatilisation partielle sous forme d’ammoniac NH₃, avec un effet isotopique favorisant le départ d’ammoniac enrichi en ¹⁵N. Ainsi, Kretzler [17] observe que
l'ammoniac piégé au-dessus d'une parcelle de sol fraîchement saturé par de l'urine de bœuf présente une composition isotopique très appauvrie en $^{15}$N, voisine de $-20\%$. Un facteur d'enrichissement isotopique à l'équilibre entre ammonium en solution et ammoniac gazeux a été mesuré à $-25\%$ à $25^\circ C$ [10]. Le facteur d'enrichissement isotopique cinétique au cours de la volatilisation est également tel que NH$_3$ volatilisé est appauvri en $^{15}$N, cet effet semblant variable en fonction de la concentration de la solution ammoniacale [18, 10].

Ainsi, le processus de volatilisation partielle de NH$_3$ vers l'atmosphère se traduit par un enrichissement en $^{15}$N de l'ammonium résiduel. Après nitrification totale de cet ammonium, le nitrate apparaîtra sera caractérisé par un $\delta^{15}$N très positif [6–9, 17].

4.1.3. Composition isotopique des nitrates provenant de la minéralisation de la matière organique des sols

Les nitrates dans le sol sont le terme de la séquence de réactions: N organique minéralisable $\rightarrow$ NH$_4^+$ $\rightarrow$ NO$_2^-$ $\rightarrow$ NO$_3^-$. Leur composition isotopique est donc sous contrôle: de la composition isotopique de l'azote minéralisable, des fractionnements isotopiques de chacune des étapes comme de chacun des autres effets isotopiques accompagnant des transformations que peuvent subir les produits intermédiaires (réorganisation de NH$_4^+$ et NO$_3^-$, dénitrification, etc.).

Un tel processus global est très complexe; aussi avons-nous considéré le sol comme une «boîte noire» et suivi le $\delta^{15}$N des nitrates produits naturellement dans des sols pédologiquement représentatifs des régions naturelles étudiées. Nous avons utilisé deux dispositifs expérimentaux, une parcelle drainée et des cas lysimétriques, et réalisé en laboratoire des incubations de sol dans des conditions les plus proches des conditions naturelles.

A. Parcelle expérimentale de Boissy-le-Châtel


Les compositions isotopiques des nitrates pendant ces deux périodes de drainage hivernal sont reportées sur la figure 1. Pour ces deux périodes, les $\delta^{15}$N moyens pondérés par le flux de nitrate sont respectivement de 6,8 et 7,3%. Pendant ces périodes de prélèvement, la quantité d'azote minéral apportée par les eaux de pluie est très nettement inférieure à celle mesurée au drainage et présente un $\delta^{15}$N moyen pondéré radicalement différent: 2,8%. Les nitrates au drainage n'ont donc rien de commun avec ceux de la pluie.
Ainsi, les nitrates biosynthétisés dans le sol de cette parcelle sont caractérisés par des compositions isotopiques voisines de 7‰, très nettement enrichies en $^{15}$N par rapport à l'azote de l'air. De plus (fig. 1), on n'observe pas de corrélation entre le flux en nitrate et le $\delta^{15}$N.

B. Cases lysimétriques

Ces dispositifs de 1,5 m de profondeur ont été installés en 1956 à l'Institut national de la recherche agronomique, à Versailles. Ils sont remplis avec un sous-sol de limon (pour les caractéristiques, voir [10]) dont le $\delta^{15}$N azote total est de 7,4 ± 0,4‰. Trois cases ont été étudiées:
- une case (case 12) où ce sol est maintenu sans couvert végétal et sans apport d'engrais depuis un quart de siècle;
- deux cases sont cultivées, une en maïs (case 15), l'autre en blé (case 24), avec une fertilisation nitrique de 80 unités N à $\delta^{15}$N de 3,0‰.

Le suivi de la composition isotopique des nitrates au drainage de ces cases a été réalisé durant l'hiver 1979–80. La case nue (case 12) permettra de définir une référence géochimique naturelle: les nitrates au drainage proviennent de la seule minéralisation de la matière organique du sol. Les deux autres cases, malgré leur faible taux de fertilisation (80 unités N contre près de 150 en Brie et Beauce), témoigneront de l'influence, sur les nitrates au drainage, de l'azote de synthèse.
FIG. 2. Evolution au cours du temps de la composition de NO$_3^-$ au drainage de cases lysométriques cultivées et fertilisées (15 et 24) et d’une case nue non fertilisée (12).

FIG. 3. Histogramme des valeurs de $\delta^{15}$N-NO$_3^-$ obtenues sur les lysomètres de Versailles (nus ou cultivés). Les flèches donnent les valeurs du $\delta^{15}$N moyen pondéré.

industrielle apporté. Les $\delta^{15}$N moyens, sur la période considérée, pondérés par le flux d’azote, sont respectivement de: +6,4% pour la case 12 (nue), 5,4% pour la case 15 cultivée en maïs, 4,6% pour la case 24 cultivée en blé (figures 2 et 3). On observe ainsi clairement que, sur les cases cultivées, les nitrates présentent une composition isotopique significativement plus basse que celle de la case de référence naturelle dont les nitrates sont très proches isotopiquement de ceux obtenus sur la parcelle de Boissy-le-Châtel (voisins de 7%).

Cette différence de composition isotopique n’est en aucun cas imputable à un effet de fractionnement isotopique au cours de l’assimilation des nitrates par les plantes sur les deux cases cultivées. Nous avons en effet montré [19] que cet effet, sur des plantes à maturité, était nul (pas de fractionnement isotopique entre N-NO$_3^-$ et N organique). Sur des plantes plus jeunes ou poussant
TABLEAU II. TENEUR ET ABONDANCE ISOTOPIQUE DE N-NO₃ APPARU EN 24 SEMAINES D’INCUBATION À 10°C DANS LES HORIZONS Ap DE PROFILS PEDOLOGIQUES DE BEAUCE [10]

<table>
<thead>
<tr>
<th>Profil (horizon Ap)</th>
<th>δ¹⁵N total [Kjeldhal]</th>
<th>N-NO₃ à 24 semaines (ppm)</th>
<th>δ¹⁵N-NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7,0</td>
<td>5,1</td>
<td>8,8</td>
</tr>
<tr>
<td>2</td>
<td>6,4</td>
<td>10,6</td>
<td>6,9</td>
</tr>
<tr>
<td>3</td>
<td>6,9</td>
<td>7,6</td>
<td>8,5</td>
</tr>
<tr>
<td>4</td>
<td>5,8</td>
<td>8,4</td>
<td>12,6</td>
</tr>
<tr>
<td>5</td>
<td>6,0</td>
<td>8,4</td>
<td>6,1</td>
</tr>
</tbody>
</table>

par exemple en conditions limitantes de lumière, on pourrait observer un effet isotopique [20] qui, au contraire, tendrait à enrichir en ¹⁵N le nitrate résiduel non absorbé par la plante dans les cases cultivées: ceci s’oppose à nos observations.

C. Incubation de sols

Des sols cultivés de type limon, prélevés en Beauce, ont été incubés au laboratoire selon une méthode décrite par Müller [21]. Les horizons Ap de ces sols provenant de 5 profils décrits par ailleurs [10] sont placés en allonge, lessivés et maintenus sous une humidité correspondant aux 2/3 de la capacité de rétention, à 10°C pendant 24 semaines. Le δ¹⁵N des nitrates produits est alors mesuré (tableau II). La minéralisation de la matière organique de ces sols produit donc des nitrates très nettement enrichis en ¹⁵N par rapport à l’azote de l’air, les valeurs obtenues étant en bon accord avec celles mesurées au drainage de cases ou parcelles expérimentales (voir ci-dessus).

En conclusion, nous retiendrons que les nitrates naturellement minéralisés dans des sols cultivés de type limon, représentatifs des régions étudiées, présentent des compositions isotopiques toujours plus enrichies en ¹⁵N que celles de l’azote de synthèse industrielle apporté sous forme d’engrais. Ces δ¹⁵N sont voisins de 7%. Ce résultat est à rapprocher des observations de Rennie et al. [16] qui obtiennent sur l’horizon Ap de sols de type chernozem: δ¹⁵N total 8,8 ± 1,1‰, δ¹⁵N-NO₃ (nitrates extraits de sols prélevés au champ) 9,0 ± 3‰, et de celles de Shearer et al. [22] qui obtiennent pour des sols variés une valeur moyenne de 8,5 ± 1,1‰ pour le δ¹⁵N de nitrates produits en incubation. On consultera également Freyer et Aly [8].
Nous observons enfin qu'une fertilisation azotée s'accompagne, sur les cases lysimétriques étudiées, d'un net et significatif appauvrissement en $^{15}$N des nitrates au drainage: la contribution des nitrates des engrais, caractérisés par un $\delta^{15}$N nettement inférieur à celui des nitrates d'origine naturelle, sur les exemples étudiés, est manifeste (figures 2 et 3).

4.2. Principes

Le cas théorique simple du mélange de deux sources d'un même composé chimique de compositions isotopiques différentes où l'une des sources est à flux constant (source A) et l'autre dont la part au mélange M est variable (source B), est résolu sur la figure 4. Il est dit: source A constante homogène, source B variable homogène. On consultera Krouse [23]. Si Q est la concentration ou la masse du composé, $\delta$ sa composition isotopique, il vient:

$$Q_M \times \delta_M = Q_A \times \delta_A + Q_B \times \delta_B; \quad Q_M = Q_A + Q_B$$

d'où $\delta_M = \frac{Q_A (\delta_A - \delta_B)}{Q_M} + \delta_B$
L'évolution de la composition isotopique en fonction du mélange est, dans ce cas, représentée par une hyperbole (fig. 4-I) limitée sur sa branche horizontale et asymptotique à la valeur $\delta_B$.

Si par exemple A est une source de nitrate venue du sol, B la source variable et isotopiquement homogène des engrais, on doit considérer que la source A ne peut être caractérisée par un flux d'émission constant : il va varier en fonction de l'intensité de la minéralisation, elle-même liée, entre autres, aux fluctuations climatiques. Cette source sera donc variable, avec toutefois une gamme de variation très inférieure à celle de B. Le résultat obtenu pour ce cas théorique est représenté sur la figure 4-II. La composition isotopique du mélange en fonction de $Q_M$ couvre donc une aire limitée par les deux branches d'hyperboles correspondant aux valeurs extrêmes de $Q_A$, toutes deux asymptotiques à $\delta_B$.

Une bonne approximation de $\delta_B$ sera donnée par les plus basses valeurs de composition isotopique du mélange, aux plus fortes concentrations (ou flux).

Ce modèle peut s'appliquer à des systèmes naturels de mélange bipolaire : au-delà de deux sources, des paramètres supplémentaires devront être trouvés pour que le système puisse avoir une solution, même qualitative.

4.3. Le cas des eaux de surface

4.3.1. Le bassin de Mélarchez

Situé en Brie, ce petit bassin (6,6 km$^2$), drainé, présente une nappe libre dans les limons. Pour plus de détails on consultera [7] et [10]. Il est à vocation purement agricole, avec prédominance de la grande culture céréalière. L'existence de quelques villages et fermes, notamment à proximité du bief limnigraphique où sont réalisés les prélèvements, permet toutefois de penser que quelques rejets organiques domestiques ou agricoles peuvent atteindre la rivière et contribuer à la pollution azotée de la rivière.

4.3.1.1. Année hydrologique 1971–72

Dans des publications précédentes [7, 10], nous avons montré qu'au cours d'une campagne de prélèvements hebdomadaires (1971–72) on pouvait observer, d'une part, une corrélation positive entre débit liquide et concentration en nitrate, en particulier pendant la période de hautes eaux hivernales et, d'autre part, une liaison entre l'évolution du $\delta^{15}\text{N}$ et celle de la concentration ou des flux de nitrate qui est surtout évidente pendant la période de hautes eaux hivernales où on observe l'abaissement du $\delta^{15}\text{N}$ avec l'augmentation du flux en nitrate. En dehors des périodes de crues, le $\delta^{15}\text{N}$ à l'exutoire est de l'ordre de 7 à 8‰; pendant les crues, le flux en nitrate augmente, et ce $\delta^{15}\text{N}$ s'abaisse vers 4‰. On observe même, pour une crue importante (12/4/1972) qui suit l'application des engrais,
un $\delta^{15}N$ de 1,4‰. Au contraire, pendant l’été, les flux en nitrate sont très bas et on note sporadiquement l’apparition de nitrates à $\delta^{15}N$ élevé, jusqu’à 24‰.

Le calcul du $\delta$ pondéré par le flux en nitrate donne 3,9‰ pour la période hivernale (5/10/1971 au 10/4/1972) et 7,9‰ pour la période d’été et faibles crues d’été. Pour toute la période considérée, ce $\delta$ moyen est de 4,1‰: l’influence des nitrates à bas $\delta^{15}N$ est majeure, celle des nitrates à $\delta^{15}N$ élevé quasiment nulle sur l’année.

4.3.1.2. Crues de février et mars 1977

Il s’agit de l’examen détaillé de périodes de crues hivernales, avec prélèvement horaire (voir détails dans [10]). Les résultats sont reportés sur la figure 5, avec distinction d’une période de montée de crue échantillonnée heure par heure. L’ensemble des points obtenus se place sur une courbe d’évolution dont le meilleur ajustement simple est une hyperbole à branche limitée à $\delta$ 7 à 8‰ et branche asymptotique à $\delta$ 3,8‰. Tout se passe comme si on était en présence d’un mélange simple bipolaire entre une source quasi constante de nitrate à $\delta$ 7 à 8‰.
et une source variable à δ proche de 3,8‰. Ceci a été symbolisé en traçant sur la figure 5 une enveloppe constituée de deux hyperboles asymptotiques à cette valeur de 3,8‰. Durant cette période d'étude, nous avons suivi l'écoulement de drains sous des champs cultivés, par échantillonnage moyen sur 8 ou 24 h. La figure 6 présente les δ$^{15}$N et concentrations N-NO$_3$ au drainage et à l'exutoire du bassin: pendant les crues, quand la concentration nitrique est élevée, on a une identité des nitrates au drainage et dans la rivière, tant en concentration qu'en δ$^{15}$N. Pendant cette période, les flux de nitrates dans la rivière sont contrôlés quantitativement et qualitativement (δ$^{15}$N) par le drainage. Les δ$^{15}$N bas observés dans la rivière correspondent donc à des nitrates apportés par le réseau de drainage, en période de crue.

4.3.1.3. Ensemble des résultats

Sur la figure 7 (diagramme semi-logarithmique, δ$^{15}$N - flux N-NO$_3$ en mg·s$^{-1}$), nous avons reporté l'ensemble de nos résultats concernant les années hydrologiques 1971-72, 1972-73, 1975-76 et les crues de février et mars 1977. On peut décomposer ce diagramme en un premier groupe de points à δ compris entre 8,5 et 3,5‰, avec un point à 1,4‰ (voir ci-dessus) correspondant à des flux de nitrate de 5 à 15 × 10$^3$ mg(N)·s$^{-1}$. Les δ$^{15}$N s'abaissent lorsque ce flux augmente. Un deuxième groupe est caractérisé par des points à δ élevés correspondant à des flux de nitrate très faibles, de 1,5 à 10 mg(N)·s$^{-1}$. Ces résultats sont identiques si on reporte (figure 8) la concentration en nitrate en fonction du δ$^{15}$N.
4.3.1.4. Discussion

La répartition des points dans le premier groupe (δ compris entre 8,5 et 3,5) est proche de celle que donnerait une anamorphose semi-logarithmique de la figure 4-II. On peut ainsi émettre l'hypothèse que l'ensemble de ces points, dans cette configuration, représente le mélange de deux sources d'émission variables et de δ différents. La première source, de δ compris entre 7 et 8,5‰, correspond aux périodes d'étage et trouve, selon nous, son origine dans la minéralisation naturelle de la matière organique des sols cultivés: ces valeurs de δ¹⁵N sont celles trouvées au drainage de la parcelle de Boissy-le-Châtel et de la case lysométrique de Versailles (voir ci-dessus). La deuxième source présente un δ¹⁵N bas, la répartition des points suggérant une valeur asymptotique proche de 3,5‰, sans oublier la valeur exceptionnelle de 1,4‰ en pointe de crue après application des engrais (12/4/1972). Une source évidente d'azote à bas δ¹⁵N est celle des engrais, ce qui nous permet de proposer l'interprétation de ces résultats en terme de mélange d'une source naturelle d'azote et d'une source synthétique, les engrais. Ce point sera discuté plus loin.
La deuxième famille de points se caractérise par des $\delta^{15}N$ élevés, supérieurs à 10‰, qui ne s'observent que pendant les mois d'été, les débits liquides et les flux d'azote étant les plus faibles (voir figures 7 et 8). En terme de bilan annuel la contribution de ces nitrates à $\delta$ élevé est quasi nulle. Il s'agit selon nous de nitrates provenant de l'Oxidation de matières organiques et/ou d'ammoniaque liés à des rejets animaux ou domestiques, ces nitrates étant enrichis en $^{15}N$ par la volatilisation partielle d'ammoniac préalable (voir plus haut). Nous avons en effet suivi la composition d'un écoulement à ciel ouvert, aboutissant dans le bief limnigraphique, en provenance d'une ferme proche. Son débit est très faible et il se caractérise (tableau III) par des concentrations en nitrate relativement élevées, du même ordre de grandeur que la rivière au même instant, mais surtout par un
### TABLEAU III. BASSIN DE MELARCHEZ. PRELEVEMENTS SUR LE BIEF LIMNIGRAPHIQUE (A ET C) MONTRANT L’INFLUENCE D’UN ECOULEMENT DOMESTIQUE (B) SUR LA COMPOSITION ISOTOPIQUE ET CHIMIQUE DE L’EAU

<table>
<thead>
<tr>
<th>Date</th>
<th>N-NO$_3^-$ (mg/L)</th>
<th>$\delta^{15}$N-NO$_3^-$ (%)</th>
<th>K$^+$ (mg/L)</th>
<th>Cl$^-$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bief limnigraphique A) en amont de l’écoulement domestique</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.11.75</td>
<td>10,2</td>
<td>6,4</td>
<td>1,9</td>
<td>31,3</td>
</tr>
<tr>
<td>15.12.75</td>
<td>5,8</td>
<td>5,3</td>
<td>1,5</td>
<td>22,0</td>
</tr>
<tr>
<td>28.01.76</td>
<td>6,9</td>
<td>7,4</td>
<td>1,7</td>
<td>27,8</td>
</tr>
<tr>
<td>25.02.76</td>
<td>8,6</td>
<td>7,5</td>
<td>1,7</td>
<td>26,3</td>
</tr>
<tr>
<td>17.03.76</td>
<td>6,3</td>
<td>7,4</td>
<td>1,6</td>
<td>20,4</td>
</tr>
<tr>
<td>21.04.76</td>
<td>5,7</td>
<td>7,2</td>
<td>1,6</td>
<td>15,6</td>
</tr>
<tr>
<td>Ecoulement domestique B) qui se déverse dans le bief limnigraphique</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.11.75</td>
<td>8,6</td>
<td>10,2</td>
<td>12,0</td>
<td>31,6</td>
</tr>
<tr>
<td>15.12.75</td>
<td>8,9</td>
<td>11,0</td>
<td>9,8</td>
<td>30,9</td>
</tr>
<tr>
<td>28.01.76</td>
<td>6,6</td>
<td>11,5</td>
<td>13,9</td>
<td>29,1</td>
</tr>
<tr>
<td>25.02.76</td>
<td>9,5</td>
<td>10,6</td>
<td>13,7</td>
<td>30,7</td>
</tr>
<tr>
<td>17.03.76</td>
<td>5,6</td>
<td>12,3</td>
<td>18,1</td>
<td>30,2</td>
</tr>
<tr>
<td>21.04.76</td>
<td>6,7</td>
<td>-</td>
<td>26,7</td>
<td>25,4</td>
</tr>
<tr>
<td>Bief limnigraphique C) en aval de l’écoulement domestique</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.11.75</td>
<td>9,3</td>
<td>6,6</td>
<td>2,0</td>
<td>35,0</td>
</tr>
<tr>
<td>15.12.75</td>
<td>3,5</td>
<td>7,6</td>
<td>1,7</td>
<td>22,3</td>
</tr>
<tr>
<td>28.01.76</td>
<td>6,8</td>
<td>7,2</td>
<td>1,9</td>
<td>28,2</td>
</tr>
<tr>
<td>25.02.76</td>
<td>8,6</td>
<td>7,6</td>
<td>2,1</td>
<td>26,7</td>
</tr>
<tr>
<td>17.03.76</td>
<td>5,8</td>
<td>7,9</td>
<td>2,3</td>
<td>22,0</td>
</tr>
<tr>
<td>21.04.76</td>
<td>5,9</td>
<td>7,3</td>
<td>2,0</td>
<td>16,2</td>
</tr>
</tbody>
</table>

$\delta^{15}$N toujours élevé, entre 10,2 et 12,3%. Il s’agit là de prélèvements hivernaux; en été, sous des températures plus élevées, on pourra s’attendre à des volatilisations plus importantes et, partant, des $\delta^{15}$N plus élevés. Cet écoulement se caractérise aussi, comme on pouvait s’y attendre pour des rejets domestiques, par des concentrations en K$^+$ élevées, sans commune mesure avec celles de la rivière. Sur le tableau III, on note que l’influence de cet écoulement domestique sur l’élévation du $\delta^{15}$N et de la teneur en K$^+$ dans la rivière en aval de la confluence est faible: le rapport des débits liquides est largement, en cette période hivernale, en faveur de la rivière. En plein étage estival, on peut par contre estimer que l’influence de tels écoulements domestiques tout au long de la rivière puisse devenir importante et expliquer l’apparition de nitrates à $\delta^{15}$N élevés en été.

L’étude d’un bassin versant proche, fortement urbanisé sur son cours aval et donc susceptible de présenter les traces d’une pollution azotée d’origine organique domestique, va nous permettre de confirmer notre hypothèse.
FIG. 9. Bassin de l’Yerres. Les zones urbanisées sont en noir, les numéros correspondent aux points de prélèvement; les zones de pertes de la rivière sont indiquées en pointillés.

4.3.2. Etude du Bassin de l’Yerres

L’Yerres est un affluent de la Seine sur le plateau de Brie. Elle a déblayé les formations calcaires et argileuses de Brie (Sannoisien-Ludien) et entaillé le calcaire dit de Champigny, fortement karstifié, ce qui établit des échanges entre les eaux superficielles et la nappe du calcaire de Champigny [13], cette dernière étant partiellement alimentée par les eaux de l’Yerres.

Le bassin de l’Yerres, agricole en amont, devient de plus en plus urbanisé vers l’aval (Fig. 9). Une étude du Service régional d’aménagement des eaux (1973) indique que les 30 000 habitants créent une pollution d’environ 4100 kg/jour (somme des matières en suspension et matières oxydables), le rendement des stations d’épuration étant au maximum de 0,55.

Trois profils longitudinaux de la rivière en période de basses eaux ont été réalisés [10]. On constate (fig. 10), pour ces trois campagnes, une augmentation régulière du $\delta^{15}$N-NO$_3$ d’amont en aval de la rivière, une diminution de la concentration en NO$_3$ alors que le flux de NO$_3$ augmente, une augmentation des teneurs en Na$^+$, K$^+$, Cl$^-$, PO$_4^{3-}$ et de la DBO-5,$^1$ corrélée à l’augmentation du $\delta^{15}$N (fig. 11). La DBO étant proportionnelle à la teneur en matières organiques dégradables par voie biologique, l’augmentation de Cl$^-$, K$^+$, Na$^+$, PO$_4^{3-}$ peut être

---

$^1$ DBO-5: Demande biologique en oxygène à cinq jours.
FIG.10. $\delta^{15}$N-NO$_3$ sur trois profils en long de la rivière Yerres. Les points de prélèvements sont situés sur la figure 9.

FIG.11. Rivière Yerres. Relation $\delta^{15}$N-NO$_3$ avec DBO-5, Cl$^-$, PO$_4^{3-}$, K$^+$, Na$^+$. 
l'indice d'une pollution liée à des rejets humains ou animaux (fortes teneurs dans l'urine en particulier), Na⁺ pouvant également être lié à des eaux usées adoucies, les orthophosphates participant également aux formulations des produits détergents.

Tous ces indices, couplés à l'augmentation de la teneur en $^{15}$N des nitrates vers l'aval, conduisent à caractériser une contamination en aval de l'Yerres par des nitrates provenant de l'oxydation de matières organiques liées à des rejets urbains domestiques et enrichis en $^{15}$N par distillation partielle de NH$_3$ au cours de l'étape ammoniacale de l'oxydation. La composante pollution organique se caractérise par des δ supérieurs à 12‰. L'existence des pertes sur le cours de la rivière ne permet pas d'établir un bilan amont-aval significatif.

Cette étude montre que c'est souvent la conjonction de paramètres chimiques et isotopiques qui permet de résoudre des problèmes d'origine : alors que la présence de potassium, chlorures ou phosphates pouvait être attribuée à une contamination organique comme à une fertilisation chimique de type NPK, la composition isotopique du nitrate permet de lever l'ambiguïté.

4.4. **Le cas des eaux souterraines**

Les nappes étudiées en Brie et en Beauce sont, pour l'essentiel, la nappe oligocène dite de Beauce et la nappe de l'Eocène supérieur dite des calcaires de Champaigny [13]. En Beauce, les concentrations en NO$_3^-$ sont très souvent supérieures à 30 mg/L. Sur 30 points étudiés, la médiane atteint 40 mg/L [13]. En Brie, la minéralisation en NO$_3^-$ est moins importante, peu d'ouvrages dépassent 44 mg/L, mais on observe une nette tendance à l'augmentation de ces teneurs depuis une trentaine d'années [13, 10]. Les points étudiés sont soit des forages d'alimentation en eau potable, soit des sources. Leur choix permet d'obtenir un éventail représentatif de l'activité agricole de ces régions en milieu rural et en rase campagne. Certains prélèvements ont toutefois été effectués à proximité d'agglomérations ou dans des situations hydrogéologiques où la nappe est influencée par les eaux de surface (vallée de l'Yerres par exemple).

Une large gamme de concentration en nitrate a été obtenue, avec une attention particulière pour les zones où les nappes ont de faibles teneurs en NO$_3^-$. zones où elles sont naturellement protégées par les assises de surface peu perméable ou prélèvements dans les parties profondes des nappes qui se caractérisent par de faibles minéralisations NO$_3^-$. 

5. **RESULTATS**

Il existe [13, 10] une corrélation positive entre l'activité tritium et la concentration en nitrate, notamment en Beauce: il semble que la minéralisation en nitrate
FIG. 12. Brie-Beauce. Diagramme $\delta^{15}$N – concentration en nitrates en milieu agricole.

soit pour l'essentiel due à l'arrivée dans l'aquifère d'eaux récentes, riches en $^3$H. En Brie et en Beauce, en milieu purement agricole, les résultats obtenus s'ordonnent, dans un diagramme concentration NO$_3$-$\delta^{15}$N-NO$_3^-$, selon une courbe pouvant être interprétée par un mélange de nitrates à $\delta$ proches de 8‰ (points où les nappes sont protégées, ou dans les parties profondes faiblement minéralisées) et de nitrates correspondant à l'asymptote inférieure estimée ici à 2‰ environ (fig. 12). On peut donc penser à un mélange bipolaire: nitrates du sol (faible concentration, $\delta$ proche de 8‰) et nitrates à $\delta$ voisins de 2‰ qui pourraient être les nitrates des engrais (voir tableau I). Ces résultats ne concernent que des points prélevés en ambiance strictement agricole. En Brie, nous avons en outre prélevé des sources ou captages de l'aquifère du calcaire de Champigny dans la vallée de l'Yerres précédemment étudiée, qui sont susceptibles d'être alimentés par les eaux de la rivière par un réseau karstique. Nous avons également suivi deux sources à comportement particulier (Champeaux et Bombon). Sur la figure 13, nous avons reporté l'ensemble des résultats obtenus en Brie: les points particuliers du Val de l'Yerres, de Champeaux et Bombon s'écartent très nettement, dans ce diagramme $\delta^{15}$N – concentration en NO$_3^-$, des points en milieu strictement agricole répartis entre les deux courbes asymptotes définies sur la figure 12: ils présentent des $\delta^{15}$N toujours supérieurs à ceux prévus par l'hypothèse de simple mélange nitrates des sols – nitrates des engrais. Les sources et captages situés dans le Val de l'Yerres (fig. 13) présentent des valeurs regroupées vers 12–13‰, valeurs fréquemment observées
FIG. 13. Nappes de Brie. Diagramme δ^{15}N – concentration NO\textsubscript{3}. Les points Brie et Ozouer-le-Voulgis sont situés dans le Val de l’Yerres.

sur le cours aval de l’Yerres (fig. 10): les relations eaux superficielles – nappe des calcaires de Champigny sont clairement illustrées par le tracage naturel ^{15}N et ceci confirme les observations du Bureau de recherches géologiques et minières [24] qui enregistrent des variations quasi simultanées de certains paramètres chimiques (NO\textsubscript{3}, SO\textsubscript{4}, Na\textsuperscript{+}, Cl\textsuperscript{-}) en aval de la rivière et dans la nappe et constatent l’existence de teneurs élevées en ^{3}H dans la nappe (80–120 UT): les eaux superficielles sont clairement impliquées dans l’augmentation en ^{3}H de la nappe. Ainsi, la source prépondérante des nitrates dans ce secteur de la nappe se trouve dans les pertes de l’Yerres et serait donc, pour l’essentiel, d’origine « organique », liée à une pollution de la rivière par les eaux usées domestiques.
**FIG. 14. Source de Bombon: relation $\delta^{15}$N-concentration en nitrate. Source de Champeaux: relation $\delta^{15}$N-concentration en nitrate et $\delta^{14}$N-$^3$H.**

**TABLEAU IV. TENEURS MOYENNES* (± ECART-TYPE) EN CI, K⁺ ET Na⁺ SUR QUELQUES POINTS DE BRIE**

<table>
<thead>
<tr>
<th>Puits</th>
<th>Cl⁻</th>
<th>K⁺</th>
<th>Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jouy-le-Châtel (Ch)</td>
<td>10,8 ± 5,7</td>
<td>1,1 ± 0,2</td>
<td>5,8 ± 0,4</td>
</tr>
<tr>
<td>Fontenay Trésigny (Br)</td>
<td>23,3 ± 5,5</td>
<td>1,6 ± 0,3</td>
<td>16,2 ± 0,9</td>
</tr>
<tr>
<td>Rosay Vilpré (Br)</td>
<td>44,7 ± 7,0</td>
<td>1,7 ± 0,3</td>
<td>11,3 ± 0,6</td>
</tr>
<tr>
<td>Champeaux (Br)</td>
<td>58,3 ± 10,2</td>
<td>6,3 ± 2,9</td>
<td>17,8 ± 1,6</td>
</tr>
</tbody>
</table>

*a En mg/L.  
*b Les trois premiers puits sont représentatifs de la situation en environnement strictement agricole (fig. 12). Ch: aquifère des calcaires de Champigny; Br: aquifère des calcaires de Brie.

Les sources Champeaux et Bombon seraient, *pro parte*, justiciables d’une interprétation semblable: on constate sur la figure 14 une liaison $\delta^{15}$N – concentration en NO₃ qui suggère un mélange avec des nitrates à δ élevé, nitrates contenus dans des eaux récentes, comme le montre (fig. 14) la relation $^3$H-$\delta^{15}$N à Champeaux. Cette source se caractérise d’autre part par des teneurs en K⁺, Na⁺ et Cl⁻ plus élevées que celles observées dans les sources ou captages en milieu agricole obéissant au modèle de mélange de la figure 12 (tableau IV). De plus, la concentration de ces éléments fluctue en phase avec les teneurs en NO₃, le $\delta^{15}$N-NO₃ et l’activité $^3$H [10]. Les $\delta^{15}$N à Champeaux et Bombon n’atteignent pas les
valeurs élevées du Val de l’Yerres: nous sommes ici clairement en présence d’une double contamination: par des nitrates à bas δ¹⁵N, probablement synthétiques, d’une part, et par des nitrates d’origine organique à δ élevés d’autre part. Selon la part relative de l’une ou l’autre des sources de contamination, les δ résultant peuvent varier dans de sensibles proportions. Ainsi, sur la figure 14, observe-t-on pour la source Bombok, que les valeurs de δ¹⁵N sont plus basses durant les mois de mars et d’avril, période d’application des engrais artificiels.

Des observations semblables ont été faites en Beauce: la figure 15 montre que le captage de Beuvilliers analysé à plusieurs reprises échappe à la répartition hyperbolique de la majorité des points de Beauce, par des δ élevés. Ce captage est situé dans une agglomération où l’absence d’un réseau complet de collecte des eaux usées impose certains rejets dans des puits perdus. À 3 km de Beuvilliers, le captage de Voves va nous servir de référence (tableau V). Beuvilliers apparaît particulièrement chargé en NO₃⁻, Cl⁻, K⁺, Na⁺. Si on calcule la composition isotopique de la charge nitrique qui s’ajoute à Beuvilliers en prenant Voves comme référence, on obtient des valeurs qui oscillent entre 9 et 12‰ [10]. Ces δ élevés associés aux fortes teneurs en Cl⁻, K⁺, Na⁺ conduisent à soupçonner, à Beuvilliers, une contamination azotée d’origine organique domestique. Ceci est confirmé par l’examen des teneurs en boré de quelques captages de Beauce. Cet élément est un excellent traceur des effluents urbains [25, 26]: il est présent dans les lessives, alors que la fourniture en bore par les activités agricoles paraît très faible. La teneur moyenne en bore des aquifères du Bassin de Paris est de 0,020 à 0,030 ppm.
TABLEAU V. COMPARAISON DES PARAMÈTRES CHIMIQUES ET ISOTOPIQUES SUR DEUX CAPTAGES VOISINS EN BEAUCE (MOYENNE DE 9 PRELEVEMENTS SIMULTANÉS)

<table>
<thead>
<tr>
<th>Captage</th>
<th>N-NO₃ (mg/L)</th>
<th>δ¹⁵N-NO₃ (%)</th>
<th>Na⁺ (mg/L)</th>
<th>K⁺ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beauvilliers</td>
<td>25,1 ± 5,6</td>
<td>7,8 ± 0,5</td>
<td>32,6 ± 2,4</td>
<td>41,9 ± 6,0</td>
<td>41,4 ± 7,1</td>
</tr>
<tr>
<td>Voves</td>
<td>7,3 ± 0,8</td>
<td>4,6 ± 0,2</td>
<td>8,6 ± 0,7</td>
<td>1,3 ± 0,3</td>
<td>15,0 ± 6,8</td>
</tr>
</tbody>
</table>

TABLEAU VI. TENEURS EN BORE DE QUELQUES CAPTAGES EN BEAUCE²

<table>
<thead>
<tr>
<th>Captage</th>
<th>Date de prélèvement</th>
<th>Teneur en Bore (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chilleurs-aux-Bois</td>
<td>21/04/1977</td>
<td>0,000</td>
</tr>
<tr>
<td>Girolles</td>
<td>19/01/1977</td>
<td>0,010</td>
</tr>
<tr>
<td>Courcelles</td>
<td>21/04/1977</td>
<td>0,030</td>
</tr>
<tr>
<td>Terminiers</td>
<td>19/01/1977</td>
<td>0,010</td>
</tr>
<tr>
<td>Terminiers</td>
<td>16/03/1977</td>
<td>0,030</td>
</tr>
<tr>
<td>Beauvilliers</td>
<td>16/03/1977</td>
<td>0,130</td>
</tr>
<tr>
<td>Beauvilliers</td>
<td>21/04/1977</td>
<td>0,130</td>
</tr>
</tbody>
</table>

² Les quatre premiers points sont en milieu agricole. Beauvilliers montre une nette influence domestique.

La tableau VI montre que 4 captages en milieu agricole ont des teneurs inférieures à 0,030 ppm alors que Beauvilliers présente une concentration particulièrement élevée. La contamination locale de l’aquifère par des eaux usées urbaines se confirme donc, et s’accompagne de nitrates à δ élevé. Beauvilliers, comme Champeaux et Bombon en Brie, voit donc le mélange de nitrates d’origine naturelle des sols, de nitrates à δ bas probablement synthétiques et de nitrates à δ élevés d’origine organique domestique.
6. DISCUSSION. PORTEE ET LIMITES DE LA METHODE. CONCLUSION.

De cette étude à caractère régional, il ressort que l'on peut caractériser sans ambiguïté des variations de compositions isotopiques des nitrates dans les aquifères, variations que l'on peut essayer d'interpréter en vue de caractériser des sources de pollution.

En milieu agricole, on constate l'existence d'une corrélation de type hyperbolique entre les $\delta^{15}N$ et les concentrations ou flux de nitrates: l'augmentation des teneurs est le fait de nitrates à $\delta^{15}N$ bas, proches de l'azote de l'air, mélangés en proportion croissante avec des nitrates à $\delta^{15}N$ proches de 8.

L'observation fondamentale faite sur les cas lysimétriques de Versailles, où l'on observe que les $\delta^{15}N$ moyens pondérés par le flux en nitrates sont significativement plus faibles sur les cas fertilisés que sur le cas maintenu nu, et le fait que l'azote de l'engrais se caractérise par des $\delta^{15}N$ bas proches de zéro (azote de l'air) nous conduisent à proposer que les nitrates à bas $\delta^{15}N$ responsables des fortes teneurs dans les aquifères pourraient être ceux des engrais. Les nitrates à $\delta$ proche de 7–8% seraient ceux des nitrates apparu naturellement dans les sols cultivés de type limon.

Par contre, les nitrates provenant de l'oxydation de déchets organiques ayant subi une longue maturation avec fermentation ammoniacale et volatilisation de NH$_3$ se caractérisent par des $\delta^{15}N$ élevés (>10‰); ils sont d'autre part accompagnés par un cortège chimique caractéristique (K$^+$, Cl$^-$, B pour les rejets domestiques, etc.).

Ainsi, dans les milieux naturels étudiés, la caractérisation qualitative de l'origine de NO$_3^-$ pourra se faire ainsi: les nitrates d'origine naturelle, en faible concentration, ont des $\delta$ proches de 7‰, les nitrates des engrais ont des $\delta$ proches de N atmosphérique, les nitrates d'origine organique sont les plus enrichis en $^{15}N$. Cependant, les diagrammes $\delta^{15}N$ – concentration ou flux en nitrates ne peuvent, dans l'absolu, résoudre que des mélanges biopaires par l'obtention de courbes de mélange hyperboliques. Des cas plus complexes doivent faire appel à d'autres paramètres, notamment chimiques, comme nous l'avons montré sur nos exemples.

Ce schéma simple ne pouvant être généralisé, nous allons souligner à présent les limites de la méthode.

Sur les sols cultivés de type limon, le $\delta^{15}N$ des nitrates d'origine naturelle se situe vers 7‰. Il peut être mis en évidence que, sur certains types de sols, ces valeurs sont très différentes. De nombreux auteurs [4, 10, 27, 28] ont montré que l'azote total des sols cultivés est plus enrichi en $^{15}N$ que les sols vierges, forestiers notamment. J'ai pu mettre en évidence [10, 28] que, dans les sols, le processus d'humification se traduit par un enrichissement en $^{15}N$ de l'azote total des sols vierges: ainsi, les humus à forte activité biologique, à humification importante (humus de type mull) se caractérisent par un $\delta^{15}N$ élevé à l'opposé des sols à faible activité biologique (humus de type mor ou moder). On comprend ainsi
que la mise en culture, qui s'accompagne d'une stimulation de l'activité biologique, entraîne une élévation du δ¹⁵N de l'azote total.

Ainsi peut-on voir apparaître sous des sols vierges, forestiers par exemple, des nitrates à δ¹⁵N bas, comme cela a été montré sur le site de Bouasle, à l'ouest de Paris [10].

De plus, certains types de sols cultivés peuvent également produire, par minéralisation, des nitrates à δ¹⁵N inférieurs à ceux observés dans cette étude sur des sols de limon cultivés. Nous citerons en particulier les sols de type rendzine sur craie sur lesquels nous avons mesuré [29] des nitrates d'origine naturelle à δ proche de 2–3‰; dans ces sols, le calcaire actif, en enrobant d'une pellicule protectrice la matière organique fraîche, la protège, par séquestration, de la biodégradation microbienne et l'humification est ralentie, ce qui bloque l'enrichissement en ¹⁵N de l'azote total et contribue à l'apparition de nitrates à δ peu élevé [10]. Sur de tels types de sol, le traçage isotopique naturel ¹⁵N ne pourra mettre en évidence la contribution de nitrates d'origine synthétique (engrais) eux aussi à δ¹⁵N bas.

Ainsi, ce traçage ne saurait être généralisé: il est inappllicable dans certaines régions naturelles et nécessite, pour chaque application, la mesure de la référence naturelle. Cependant, sur un grand nombre de sols, la composition isotopique moyenne de l'azote total ou nitrique est élevée, voisine de 6 à 9‰: on consultera [30] et [31]. De plus, nous avons montré [10] qu'au sein d'une même unité pédologique ou d'unités pédologiques voisines, le δ¹⁵N-N total présente de très faibles variations spatiales sur une parcelle de 22 ha (6,0 ± 0,4‰ sur l'azote total, 15 prélèvements); cette observation va dans le même sens que celles de Karamanos et al. [31].

D'autre part, de nombreuses observations [14, 16, 32, 33] montrent que, sur le terrain comme en incubation de laboratoire de longue durée (pour s'affranchir des phénomènes de «flush-effect» [29]), la composition isotopique des nitrates du sol est très proche de celle de l'azote total (ce que nous avions observé sur les cases lysimétriques de Versailles en particulier). Seuls les résultats de Bremner et Tabatabai [4] s'écartent de ce schéma. On trouvera dans Mariotti [10] une présentation synthétique de ces résultats. Ainsi, il semblerait que, pour de nombreux sols d'origines diverses (Illinois, Canada, Bassin Parisien), l'enrichissement isotopique apparent en N organique et N-NO₃ soit proche de zéro. Les cases lysimétriques de Versailles montrent en outre que les fluctuations de δ¹⁵N-NO₃ à 1,5 m de profondeur sont très faibles.

Le traçage isotopique naturel pour la détermination de l'origine des nitrates nécessite: 1) l'existence d'une différence mesurable de δ¹⁵N entre les sources; 2) le maintien de cette différence au cours des transformations subies par l'azote dans son cycle. Pour ce qui concerne la distinction entre nitrate des sols et nitrates des engrais, la différence de composition isotopique existe, au moins pour un certain nombre de sols cultivés mais ne saurait, on vient de le voir, être généralisée.
Le mélange entre ces sources se traduit par la corrélation hyperbolique fréquemment observée: en milieu agricole, la source d‘azote nitrique responsable des concentrations élevées se caractérise par un δ^{15}N bas; les résultats obtenus sur les cases de Versailles permettent de conclure qu’il s‘agit bien de l‘azote de synthèse des engrais.

D’autre part, Feigin et al. [32, 33] et Meints et al. [34] comparent l’estimation de la contribution des engrais au nitrate du sol ou à l‘azote total des plantes obtenue avec la méthode, quantitative, du marquage artificiel par ^{15}N à celle obtenue par le traçage naturel. Les nitrates des sols et les plantes fertilisées avec un engrais (ammoniaical) présentent un δ^{15}N inférieur à celui observé en absence de fertilisation. Il existe une corrélation négative entre le taux d‘application de N(engrais) et le δ^{15}N. Bien sûr, dans tous les cas, l’estimation obtenue avec les abondances naturelles est nettement moins précise qu‘avec l’utilisation de produits enrichis en ^{15}N, et c’est ce que soulignent également Karamanos et Rennie [35] en utilisant les abondances naturelles: « Le calcul du devenir de l‘azote de fumure basé sur le principe de la dilution isotopique a fourni des estimations semi-quantitatives du N engrais trouvé dans les plantes, le sol et le percolat».

Ceci et les observations sur cases nous permettent d‘affirmer que les transformations subies dans le sol par l‘azote des engrais apportés ne masquent pas totalement la différence de δ^{15}N qu‘ils peuvent présenter, par exemple sur les cas évoqués ici, avec les nitrates du sol. Parmi les transformations que peut subir l‘ion nitrate, figure la dénitrification. Gormly et Spalding [36], dans des eaux souterraines du Nebraska, observent une relation δ^{15}N – concentration NO₃⁻ du même type que celle de Brie et de Beauce, qu‘ils interprètent comme une pollution généralisée par des engrais de synthèse à bas δ^{15}N suivie d‘une dénitrification dont l‘effet isotopique normal explique l‘enrichissement en ^{15}N au cours du processus, donc de la baisse des concentrations en NO₃⁻. On consultera également Focht [37]. Nous avons testé cette hypothèse sur nos résultats. Sur le diagramme de la figure 12, nous avons déterminé l‘évolution de ce système soumis à dénitrification à partir des concentrations les plus élevées, avec des valeurs d‘enrichissement isotopique ε [38] variant de −5 à −30‰. La figure 16 montre qu‘il faudrait des effets isotopiques encore plus faibles que ceux correspondant à ε = −5‰ pour expliquer cette répartition des points dans l‘hypothèse dénitrification. Or nos études sur la dénitrification montrent [39] que, dans les conditions naturelles, les valeurs les plus probables se situent vers ε = −20‰. Ce test s‘applique avec les mêmes conclusions à l‘ensemble des résultats publiés: la dénitrification ne saurait expliquer la relation δ^{15}N – concentration NO₃⁻ observée dans le Bassin de Paris, l‘Illinois et le Nebraska.

Cependant les transformations comme la dénitrification que peut subir l‘ion NO₃⁻ sont telles [10] qu‘en aucun cas le traçage isotopique naturel ne pourra fournir d’estimation quantitative des sources de pollution: les indications, dans le meilleur des cas, ne seront que qualitatives.
FIG. 16. Diagramme $\delta^{15}N$-concentration en nitrate pour les eaux souterraines de Brie et de Beauce. On a superposé à ce diagramme l'évolution isotopique théorique que produirait une dénitrification (facteur d'enrichissement isotopique variant de $-5$ à $-30\%$). À l'évidence, la dénitrification ne peut expliquer la répartition des points dans le diagramme.

Si le traçage isotopique semble bien permettre, sur les quelques exemples étudiés, de caractériser localement la cause majeure de contamination des aquifères par les nitrates, il faut se garder d'en généraliser, non seulement les conclusions, mais également l'application a priori. Il est nécessaire de caractériser, avant toute étude, les paramètres isotopiques du mélange : composition isotopique des nitrates naturels, des nitrates introduits dans le cycle, etc. Par ailleurs, l'existence de conditions particulières locales, pouvant entraîner des fractionnements isotopiques susceptibles de masquer le phénomène original, doit être recherchée : par exemple, la dénitrification en milieu anoxique. Enfin, la parfaite connaissance du fonctionnement hydrologique et hydrogéologique du système étudié est également requise et on rappellera l'utilité de certains paramètres apportant des informations sur « l'âge » et le taux de renouvellement de l'eau : $^3H$, $^{14}C$, $^{36}Cl$, $^{32}Si$, $^{22}Na$, etc. Ajoutons que, dès que l'on dépasse deux sources potentielles de contamination, la détermination, même qualitative, de l'origine peut devenir impossible : le traçage isotopique doit s'aider de la mesure d'autres paramètres chimiques : $Cl^{-}$, $Na^{+}$, $K^{+}$, $B$, $^3H$, etc., qui peuvent permettre localement de valider une interprétation.

On aboutit ainsi à un schéma où l'abondance isotopique en $^{15}N$ s'intègre à un dossier analytique général, chimique et isotopique, à des observations et à des
mesures de terrain, pour contribuer à résoudre un problème d'origine : à cet égard, loin d'une panacée, il ne s'agit que d'un paramètre chimique nouveau dont la connaissance peut, en certaines circonstances, se révéler des plus précieuses.

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INTERPRETATION OF ARTIFICIAL AND ENVIRONMENTAL TRACERS IN FISSURED ROCKS WITH A POROUS MATRIX

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Abstract

INTERPRETATION OF ARTIFICIAL AND ENVIRONMENTAL TRACERS IN FISSURED ROCKS WITH A POROUS MATRIX.

Tracer movement in fissured rocks with a porous matrix is considered. Solutions to the transport equation for the piston-flow and dispersion models in the case of instantaneous tracer injection are given. The great number of non-disposable parameters make a correct interpretation of tracer experiments impossible. However, an ordinary dispersion model yields the mean transit time of tracer ($t$), which can be easily related to the mean transit time of water ($t_0$) if the ratio of the matrix porosity ($n_m$) to the fissure porosity is known, namely $t = (1 + n_m/n_f)t_0$. Unfortunately, strong tailing effects make the interpretation difficult to perform for low values of $t_0$ (fast flow and/or short distance). In the case of environmental tracers it is suggested that the lumped-parameter approach may be applied in its present form, but to obtain the water age it is necessary to introduce a correction similar to that for artificial tracer experiments. However, this simple correction applies only if $(\lambda/D_p)^{1/2} L/2 \leq 0.25$ (\lambda is the decay constant, $D_p$ is diffusion in the matrix, L is fissure spacing). In other cases the correction must involve the above-given decay term. Fortunately, this term decreases the correction factor. However, both the fissure spacing (L) and the fissure porosity ($n_f$) are very difficult to evaluate. Thus, in most cases, a tracer experiment will not yield the required information.

1. INTRODUCTION

The aim of this paper is to describe the influence of molecular diffusion in a porous matrix on the interpretation of tracer experiments in fissured rocks. In 1975, Foster [1] pointed out that the anomalously low tritium contents in the Chalk aquifer in the United Kingdom can be explained by diffusion of tritium into the porous matrix during infiltration through the unsaturated zone. Since then, much attention has been paid to solute transport through fissured media with a porous matrix [2–10]. Most of the publications deal with the movement of contaminants and/or the problems of $^{14}$C age determination. An attempt was also made to apply the theoretical plate model developed in gas chromatography to the interpretation of tracer experiments [11, 12]. In the present paper the
attention is focused on the interpretation of artificial tracer experiments as well as on environmental tracers variable in time. The piston-flow and dispersion models for fissures with molecular diffusion in the matrix are considered.

2. PHYSICAL ASSUMPTIONS AND MATHEMATICAL MODEL

A system of identical parallel fissures equally spaced in a porous matrix is considered. The tracer appears at the fissure inlet, having been instantaneously injected into inflowing water, and is transported along the fissures by groundwater flow. The flow rate in fissures is assumed to be fast enough to neglect transport in the axial direction through the porous matrix. The distribution of tracer across the fissure width is assumed to be constant owing to sufficient transverse dispersion and diffusion. Under these assumptions, the following equations for mass balance in fissures and in the matrix can be used:

\[
\frac{\partial c_f}{\partial t} + v \frac{\partial c_f}{\partial x} - D \frac{\partial^2 c_f}{\partial x^2} + \lambda c_f \frac{n_p D_p}{b} \frac{\partial c_p}{\partial y} \bigg|_{y=b} = 0 \tag{1}
\]

\[
\frac{\partial c_p}{\partial t} - D_p \frac{\partial^2 c_p}{\partial y^2} + \lambda c_p = 0 \quad \text{for } b \leq y \leq L/2 \tag{2}
\]

where \(c_f\) and \(c_p\) are the tracer concentrations in water in the fissures and in the matrix, respectively, \(v\) is the mean water velocity in the fissures, \(x\) is the spatial co-ordinate taken in the direction of flow, \(y\) is the spatial co-ordinate perpendicular to the fissure extension, \(t\) is the time variable, \(\lambda\) is the decay constant, \(n_p\) is the matrix porosity, \(D_p\) is the molecular diffusion coefficient in the porous matrix, \(D\) is the dispersion coefficient in the fissures, \(2b\) is the fissure aperture, and \(L\) is the fissure spacing.

Equation (1) describes the convective and dispersive transport in fissures, Eq.(2) the diffusive transport in the matrix in the direction perpendicular to fissures. The following initial and boundary conditions are used to solve these equations for instantaneous injection:

\[
c_f(x,0) = 0 \tag{3a}
\]

\[
c_f(0,t) = A_x \delta(t) \tag{3b}
\]

\[
c_f(\infty,t) = 0 \tag{3c}
\]

\[
c_p(y,x,0) = 0 \tag{4a}
\]
\[ c_p(b, x, t) = c_f(x, t) \] (4b)

\[ \frac{\partial c_p}{\partial y} \left( \frac{L}{2}, x, t \right) = 0 \] (4c)

where \( A_0 = A/(n_f \nu S) \), \( A \) being the injected mass or the activity, \( S \) the cross-section area perpendicular to flow, and \( n_f \) the fissure porosity (\( n_f = 2b/L \)). Solutions to Eqs (1) and (2) for conditions (3) and (4) are given in the Appendix.

3. CONCENTRATION CURVES FOR INSTANTANEOUS INJECTION OF A CONSERVATIVE TRACER

It is shown in the Appendix that, to a good approximation, the mean transit time of a conservative tracer \( \bar{t} \) is related to the mean transit time of water \( t_0 \) by

\[ \bar{t} \approx (1 + n_p/n_f)t_0 = R_p t_0 \] (5)

where \( R_p \) is the retardation factor given as the ratio of the total porosity to the fissure porosity. Equation (5) means that the flow velocity in fissures is not measurable by the tracer method unless the \( n_p/n_f \) ratio is known with sufficient accuracy.

Consider now concentration curves for a piston-flow model (\( D = 0 \) in Eq.(1)). Examples of such curves, computed from Eq.(A.11) (see Appendix), are shown in Fig.1. Computational difficulties encountered at the time of writing this paper prevented us from obtaining curves for flow times of the order of days. In spite of this, several conclusions can be drawn from Fig.1. For low flow and/or large distances, i.e. for high values of \( t_0 = x/v = V_f/Q \) (\( V_f \) is the mobile water volume, i.e. the volume of fissures, and \( Q \) is the volumetric flow rate through the system), the tracer moves as if it moved homogeneously through the total porosity, because the tracer curves have a tendency to become almost symmetrical around the mean value given by Eq.(5). For fast flow and/or short distance, i.e. for low values of \( t_0 = x/v \), the tracer curves are highly asymmetrical. If, in addition, the retardation factor is low \((1 + n_p/n_f < 2)\), the time of maximum concentration is close to \( t_0 \), and this time may, to a rough approximation, serve for estimating \( t_0 \). However, for increasing values of the retardation factor, the tracer curves become more shifted, and the position of \( c_{\text{max}} \) does not correspond to \( t_0 \) even in approximation.

It should be noted that there are six (five) departure parameters in the dispersion model (piston-flow model). These parameters are: \( v \) (or \( t_0 \) for a given \( x \)), \( L \) (or \( n_f \)), \( n_p \) (or \( R_p \)), \( b \), \( D_p \) and \( D \) (or \( D/v = a_L \), or \( D/(vx) = P_e^{-1} \)). These parameters can be reduced to four or three non-disposable parameters by putting
FIG. 1. Examples of concentration curves for the piston-flow model with diffusion, and for the ordinary dispersion model with $\tilde{t} = (1 + n_p/n_p^o) t_o$. 

$$a = n_p \left( D_p \right)^{1/2} / (2b)$$ and $\delta = (L/2 - b)(D_p)^{-1/2}$. Then there are four parameters $(D/(vx), t_o, a, \delta)$ for the dispersion model and three $(t_o, a, \delta)$ for the piston-flow model. The retardation factor can be given as $R_p = 1 + 2a\delta$. A high number of non-disposable (fitting) parameters make the solution to the inverse problem (calibration of the model) rather questionable. It is thus of interest to investigate whether simpler models can supply any information when fitted to the experimental tracer curves.

Here this problem is investigated by comparing the theoretical tracer curves of simple models with those of models more adequately corresponding to the physical situation. In Fig.1, curves 3 to 8 also represent, within the accuracy of the drawn lines, the ordinary dispersion model, introduced in hydrology in Ref.[13] and described in detail in Ref.[14]. This model in the non-normalized form reads

$$c(x,t) = \frac{A x}{n Sv \sqrt{(4\pi Dt)^3}} \exp \left[ - \frac{(x-\nu t)^2}{4Dt} \right] \tag{6}$$

Other ordinary dispersion models can also be used in the cases of low dispersion, as discussed in Ref.[14]. However, it appears that in order to fit the model (6) to the concentration curves of the model (A.11), the mean water velocity ($\nu$) has
to be replaced by the mean tracer velocity, which is obtainable directly from Eq.(5), namely \( \bar{v}_{\text{tracer}} = \bar{v}/R_p \). If Eq.(6) is normalized to obtain dimensionless concentration and time and to reduce the space variable, the following form is obtained after introducing Eq.(5):

\[
\frac{c_t V}{A} = \frac{\sqrt{Pe}}{\sqrt{4\pi(t/\bar{t})^3}} \exp \left[ -\frac{(1-t/\bar{t})^2}{4Pe^{-1} t/\bar{t}} \right]
\]

where \( V \) is the total volume occupied by water (\( V = R_p V_0 \)), and \( Pe^{-1} = D/(\bar{v}x) \) is an apparent dispersion parameter in which the velocity is transferred, using the retardation factor, with \( D \) an apparent dispersion coefficient involving also the dispersion caused by diffusion into the matrix (\( D/v \) is the longitudinal dispersivity, commonly denoted as \( \alpha_L \)). In Figs 1–3, Eq.(7) is used as the ordinary dispersion model. It is clear from Fig.1 that the ordinary dispersion model gives the same concentration curves as model (A.11), except for fast flow (low \( t_0 \) value) and low values of \( R_p \). The same conclusions can be drawn from Figs 2 and 3, where dispersion in the fissures is taken into account (Eq.(A.10)). However, it may be suspected that in cases of high dispersion in fissures, fast flow and low values of \( R_p = (n_f + n_p)/n_f \), the maximum concentration may appear even at times shorter
than \( t_0 \). This suspicion is based on the inspection of concentration curves representing Eq. (6) (see, for instance, Ref. [13]). Computational difficulties connected with oscillations of Eqs. (A.10) and (A.11) prevented us from clarifying this problem.

It should be noted that Eqs. (6), (A.10) and (A.11) as well as Eq. (11) were derived for semi-infinite media. However, assuming that the second boundary (end of a finite system) does not influence the hydrodynamic dispersion in the system, they are also applicable to finite systems.

4. EXPERIMENTAL VERIFICATION

The laboratory experiment of Grisak et al. [3, 4], performed with a fractured clay-loam till, is used here for verifying some ideas presented in the previous section. A till sample, 0.76 m long and 0.65 m in diameter, was placed in a cylindrical drum. Two sets of orthogonal fractures were oriented vertically in the column parallel to the long axis and to the flow direction. The fracture spacing was not well known. According to Ref. [3], an experiment with air bubbles yielded 10 cm spacing in both directions. However, fitting of the tracer curve yielded a
6 cm spacing [3], whereas in Ref. [4] a 4 cm spacing was reported. For a given spacing (L), the fracture aperture (2b) and flow velocity (v) became disposable in that experiment because [3]

\[(2b)^2 = \frac{Q}{S \rho g (dh/dx)} \frac{12 \mu}{L} \]  

\[v = \frac{S \eta}{Q} = 2(2b)S/(LQ) \]  

where Q is the volumetric flow rate through the sample, S is the total cross-sectional area of the sample, \(\mu\) is the dynamic viscosity, \(\rho\) is the fluid density, g is the gravitational acceleration, and \(dh/dx\) is the hydraulic gradient. An additional factor of 2 results from the presence of two sets of fissures.

The following parameters were applied in Ref. [3] and are also used here:
L = 6 cm, 2b = 40 \(\mu\)m, \(v = 29.7 \text{ m} \cdot \text{d}^{-1}\) and \(n_p = 0.35\). From these data, the retardation factor is

\[R_p = 1 + n_p/n_f = 1 + \ln n_p/(4b) = 1 + 0.35 \times 6/(80 \times 10^{-6}) = 264 \]  

and the mean velocity of the tracer is \(\bar{v}_t = v/R_p = 29.7 \text{ m} \cdot \text{d}^{-1}/264 = 0.112 \text{ m} \cdot \text{d}^{-1}\).

In Fig.4, the experimental points represent the passage of chloride anions continuously injected; curve 6 represents the results of a simulation of a numerical solution to Eqs (1) and (2) [3]. The other curves represent the ordinary dispersion model. Because of continuous injection, instead of Eq.(6) its integrated form must be used [14]. This well-known solution reads:

\[c_t/c_0 = \frac{1}{2} \text{erfc} \left( \frac{x - vt}{\sqrt{(4Dt)}} \right) + \frac{1}{2} \exp \left( \frac{vx}{D} \right) \text{erfc} \left( \frac{x + vt}{\sqrt{(4Dt)}} \right) \]  

This equation fits the discussed laboratory data if the velocity is adequately transferred (\(v_t = 0.112 \text{ m} \cdot \text{d}^{-1}\)) and an apparent high dispersivity is selected. It may be worth mentioning that, without knowledge of Eq.(5), Grisak et al. [3] came to the conclusion that no fit of Eq.(11) is possible (see Fig.4, curve 1, for real \(v\), and curve 2 for arbitrary \(v_t\) and a reasonable \(\alpha_L\) value). Curve 5 shows the concentration that would be observed if an instantaneous injection were performed. From the shape of this curve, showing a very long tail, it may be concluded that the mean tracer transit time cannot be determined with good accuracy (see Appendix for the definition of \(\tilde{t}\) and imagine the length of the tail of curve 5 in Fig.4 for \(\tilde{t} = x/\bar{v}_t = 0.76 \text{ m}/0.122 \text{ d} = 6.8 \text{ days}\).

The problem of the interplay of parameters in the dispersion model was quantitatively studied by Kretz [15]. We illustrate this problem by an example: Curve 3 in Fig.4, calculated for arbitrary \(v_t\), gives an equally good fit as curve 4 for which \(v_t\) is calculated with the
Fig. 4. Experimental data and theoretical curves for continuous tracer injection. Curves 1 to 4—ordinary dispersion model for different $\bar{T}$ (4—for $\bar{T} = R_{p}^{2}q$): curve 5 would correspond to curve 4 if the tracer were injected instantaneously; curve 6—simulated for a numerical solution to Eqs (1) and (2). The experimental data and curves 1, 2 and 6 are from Ref. [3].

aid of Eq. (5). This means that in the case of a high apparent dispersion no exact determination of parameters is possible.

5. DISCUSSION OF TRACER EXPERIMENTS IN FISSURED ROCKS

Space limitation and the preliminary stage of this study do not permit of a detailed discussion of the known tracer experiments in fissured rocks. Undoubtedly, all these experiments should be reinterpreted. For instance, the two-well method invented for measuring the effective (mobile water) porosity in fact yields the total accessible porosity following from Eq. (5).

In the case of a low matrix porosity with respect to the fissure porosity (low values of $R_{p}$), a tracer experiment yields approximate flow parameters (e.g., groundwater velocity). In other cases, a tracer experiment is little related to flow parameters and its interpretation in terms of flow parameters is highly questionable.

In the case of a high apparent dispersion, in addition to the interplay of parameters discussed in Section 4, there are practical problems related to the measurement of the tail part of the concentration curve. Most probably, in many field experiments this part was not measurable and in consequence the mean transit time obtained from these experiments represented neither the flow in
fissures nor the apparent flow through the total porosity. Note that a high dispersion may result either from the discussed diffusion effects (then it is an apparent dispersion) or from a wide distribution of the fissure width, as shown in Ref.[7]. Of course, in the case of a high real dispersion the peak concentration does not correspond to the water velocity [13]. In other words, if there is no additional information on the investigated system, the interpreter will not know which model to use.

6. INTERPRETATION OF ENVIRONMENTAL RADIOISOTOPE TRACERS IN A STEADY STATE

Applying the piston-flow model, which for a steady input concentration is a very good approximation in systems with a distant recharge (low values of the apparent dispersion parameter), the radioisotope (e.g. $^{14}$C) age of water is defined from

$$c_f/c_o = \exp(-\lambda t_a) \quad (12)$$

Combining Eq.(12) with the solution to Eqs (1) and (2) for a steady state, we obtain

$$t_s / t_0 = 1 + n_p \cdot \text{gh}(p)/(n_f \cdot p) \quad (13)$$

where $p = (\lambda / D_p)^{1/2} \cdot (L/2 - b)$. For $p \leq 0.25$,

$$t_s / t_0 = 1 + n_p / n_f = R_p \quad (14)$$

whereas for $p \gg 2$,

$$t_s / t_0 = 1 + n_p / (n_f \cdot p) \quad (15)$$

however for $L \to \infty$ (i.e. for a single fissure), $n_p / n_f \to \infty$ and $p \to \infty$, and then

$$t_s / t_0 = 1 + (n_p / b) \sqrt{(D_p / \lambda)} \quad (16)$$

Equation (13) is equivalent to Eq.(7) of Ref.[6], but the form given here is simpler. Equation (16) is equivalent to Eq.(B.5) of Ref.[5]. A graphical presentation of Eq.(13) is given in Fig.5.

It is worth mentioning that if in Eq.(2), $b$ is replaced by the half-thickness of an aquifer ($h/2$) times aquifer porosity ($n$), and if $n_p$ is replaced by the aquitard porosity ($n_a$), we obtain
**FIG. 5.** Relative radioisotope age determined from the piston-flow model for steady-state input (Eq.(13)).

\[ t_a/t_0 = 1 + [2n_a/(hn)]\sqrt{(D_a/\lambda)} \]  

(17)

where \( t_a \) is the radioisotope age (Eq.(12)) in a layered aquifer with a two-side diffusion into porous aquitards, and \( D_a \) is the diffusion coefficient in the aquitard. Equation (17) gives practically the same values of \( t_a/t_0 \) as the more sophisticated Eq.(13) in Ref.[16], which was obtained by taking into account the aquifer dispersivity. If a porous aquitard is on one side of the aquifer, the factor 2 disappears in Eq.(16).

7. **INTERPRETATION OF ENVIRONMENTAL TRACERS VARIABLE IN TIME**

One commonly applied environmental tracer is variable in time, namely tritium, and several other potential tracers, such as \(^{85}\)Kr, freons and tritiogenic \(^{3}\)He, are also variable in time [17, 18]. Usually, the so-called lumped-parameter models are used in the convolution integral which relates the input \( (c_{in}) \) and output \( (c) \) concentrations.
\[
c(t) = \int_{0}^{\infty} c_{in}(t-t') \exp(-\lambda t')g(t') dt'
\]

where \( g(t) \) is the weighting function, also called the exit age distribution of tracer particles which entered the system at a given time \( t = 0 \) [18, 19]. Groundwater systems, contrary to laboratory arrangements and industrial systems, have their entrances (recharge areas) extended in space and thus the physical meaning of the parameters of the weighting function is somewhat different from what it is in a strictly unidimensional case for which Eq.(18) was developed. For instance, if the dispersion model is used for \( g(t) \), then the dispersion parameter is an apparent quantity which practically has no relation to the dispersivity of the system but depends on the relation between the extent of the recharge area and the distance to the measuring point [17, 18]. Thus, it would be quite unrealistic to put as \( g(t) \) the solutions to Eqs (1) and (2), which involve the microscopic phenomena and their relations to the mean velocity and dispersivity in a system of identical fissures. It seems that an exact solution of the problem is not possible at all. To obtain some estimate, consider first the mean transit time of a decaying tracer. Applying the procedure described in the Appendix, the following formula is obtained for the piston-flow model:

\[
\tilde{t}/t_0 = 1 + \frac{n_p(L-2b)}{2b} \left[ \frac{\tgh(p)}{2p} + \frac{1}{2} \cosh^{-2}(p) \right] 
\]

(19)

For \( L \gg 2b \) and \( p \ll 0.25 \), Eq.(19) simplifies to

\[
\tilde{t}/t_0 = 1 + n_p/n_f 
\]

(20)

whereas, for \( p \gg 3 \),

\[
\tilde{t}/t_0 = 1 + (n_p/n_f)/(2p) 
\]

(21)

Figure 6 shows graphs of \( \tilde{t}/t_0 \). In approximation, it may be assumed that the tracer in each flow line is delayed according to Eq.(19). Thus the apparent age, interpreted with the aid of an ordinary lumped-parameter model as applied in Eq.(18), has to be corrected as follows:

\[
t_0(true) = t_0(apparent) / (\tilde{t}/t_0) 
\]

(22)

where \( \tilde{t}/t_0 \) is determined from Fig.6 or directly from Eq.(19). At a first glance, the situation seems to be hopeless because a great number of parameters have to
be known. However, it appears that in many cases the simplified form given by Eq. (20) applies, i.e. for $^{14}$C ($\lambda = 3.83 \times 10^{-12} \text{ s}^{-1}$) and $D_p = 0.5 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ (value found for fractured till in Ref. [3] — see also Fig. 4), $p$ is below 0.25 if $L \leq 1.8 \text{ m}$. Then

$$t_0(\text{true}) = t_0(\text{apparent})/(1 + n_p/n_T) \tag{23}$$

which requires only an estimate of $n_p/n_T$. In the case of tritium ($\lambda = 18 \times 10^{-10} \text{ s}^{-1}$), Eq. (23) applies if $L \leq 0.083 \text{ m}$ for the same $D_p$ as above. In other cases the difference between the true and apparent values will be lower than that indicated by Eq. (23), as can be seen from Fig. 6.

Similar conclusions can be drawn from the dispersion model, for which

$$\frac{T}{t_0} = \text{Eq. (19)} \left[ \frac{1 + 4Pe^{-1} t_0 \lambda}{1 + \frac{n_p (L-2b) tgh(p)}{2 \beta p}} \right]^{1/2} \tag{24}$$

Equation (24) shows that the dispersivity in fissures decreases the retardation, which is in agreement with earlier findings [20]. However, judging from the
experiment described in Section 4, the microdispersivity in fissures is rather low, of the order of centimetres. This means that for experimental situations involving environmental radioisotope problems the dispersion term in Eq.(24) is usually negligible. On the other hand, a high dispersivity in a fissured medium may be observed if the fissure widths are highly distributed [7]. If the fissure widths remain constant along the entire system length, the dispersivity will be proportional to the distance. However, in most groundwater systems, the fissures are of limited length and consequently the dispersivity becomes constant and is usually not greater than a few metres. Thus the dispersion parameter \((D/(vx) = \alpha_f/x)\) becomes very low for large distances and consequently the piston-flow approximation (Eq.(19)) may probably be used instead of Eq.(24).

8. CONCLUSIONS

Solute transport in fissured rocks with a porous matrix is described by multi-parameter models. Thus an unambiguous interpretation of tracer experiments is not possible with the aid of these models. The ordinary dispersion model, applied to long-term experiments, yields an apparent transit time related to total porosity. In short-term experiments, the determination of the mean transit time of tracer is ambiguous because of a high apparent dispersivity and strong tailing effects.

Environmental tracers interpreted with the aid of ordinary lumped-parameter models yield apparent ages greater than the real ages. Under favourable conditions the real age can be found if the ratio of matrix porosity to fissure porosity is known.

The development of mathematical models describing solute movement in fissured media with a porous matrix is the main theoretical achievement of recent years. However, the interpretation of tracer experiments requires further studies.

Appendix

Equations (1) and (2) with initial and boundary conditions (3) and (4) can be solved by applying the Laplace transform, similarly to the solution presented in Ref.[9] for continuous injection. In this way, instead of Eqs (1) and (2), one obtains ordinary differential equations

\[
(p + \lambda) \ddot{c}_f + v \frac{d\dot{c}_f}{dx} = D \frac{d^2 c_f}{dx^2} - \frac{n_p D_p}{b} \frac{d\dot{c}_p}{dy} \bigg|_{y=b} = 0
\]  

(A.1a)
\[(p + \lambda) \ddot{c}_p - D_p \frac{d^2 \ddot{c}_p}{dy^2} = 0 \quad (A.1b)\]

where

\[
\ddot{c}_f = \int_0^\infty e^{-pt} c_f(x,t)dt \quad \ddot{c}_p = \int_0^\infty e^{-pt} c_p(y,x,t)dt
\]

The general solution of Eq.(A.1b) is

\[
\ddot{c}_p = A_1 \exp(r_1 y) + A_2 \exp(r_2 y)
\]

where \(r_{1,2}\) are the square roots of \(p + \lambda - r^2 D_p = 0\), i.e. \(r_{1,2} = \pm [(p + \lambda)/D_p]^{1/2}\). The constants \(A_1\) and \(A_2\) are found by applying conditions (4), which lead to

\[
\ddot{c}_p = \ddot{c}_f \frac{\cosh\left(\{(p + \lambda)/D_p\}^{1/2}(L/2-y)\}}{\cosh\left(\{(p + \lambda)/D_p\}^{1/2}(L/2-b)\}} \quad (A.2)
\]

By finding \(\frac{d\ddot{c}_p}{dy}\bigg|_{y=b}\) and introducing it to (A.1a), one obtains

\[
\frac{d^2 \ddot{c}_f}{dx^2} + \frac{v}{D} \frac{d\ddot{c}_f}{dx} - \ddot{c}_f \left\{ (p + \lambda) + \frac{n_p \sqrt{D_p}}{b} \cdot \sqrt{(p + \lambda)} \right\} \times \tgh \left[ \frac{L/2-b}{\sqrt{D_p}} \sqrt{(p + \lambda)} \right] = 0 \quad (A.3)
\]

The general solution of Eq.(A.3) is similar to the general solution of Eq.(A.1b), where \(r_{1,2}\) are the square roots of

\[
r^2 - \frac{v}{D} r - \frac{1}{D} \left\{ (p + \lambda) + \frac{n_p \sqrt{D_p}}{b} \cdot \sqrt{(p + \lambda)} \right\} \tgh \left[ \frac{L/2-b}{\sqrt{D_p}} \sqrt{(p + \lambda)} \right] = 0
\]

By applying conditions (3) for the determination of constants \(A_1\) and \(A_2\), one obtains

\[
\ddot{c}_f = A_0 \exp \left[ \frac{vx}{2D} \left[ 1 - \left\{ 1 + \frac{4D}{vx} t_0 [(p + \lambda) + (n_p/b) \sqrt{D_p(p + \lambda)}] \right\} \tgh \left[ \{(L/2-b) \sqrt{(p + \lambda)} \sqrt{D_p}\}^{1/2} \right] \right] \quad (A.4)
\]

where \(t_0 = x/v\).
Equation (A.4) is the Laplace transform of the sought tracer distribution in fissures. From this equation the mean transit time of tracer can be found without finding the inverse transform. The mean tracer transit time is defined as

$$\tilde{t}(x) = \int_0^\infty t c_T(x, t) dt = \int_0^\infty c_T(x, t) dt$$  \hspace{1cm} (A.5)$$

which can be transformed to

$$\tilde{t} = \lim_{p \to 0} \left(-\frac{d\tilde{c}_T}{dp}\right) \left/ \lim_{p \to 0} \tilde{c}_T \right.$$  \hspace{1cm} (A.6)$$

By inserting Eq.(A.4) into Eq.(A.6), one obtains for a conservative tracer (i.e. for $\lambda = 0$ in the case of a non-adsorbable substance):

$$\tilde{t} = t_0 [1 + \gamma (L-2b)/2b] \approx t_0 (1 + n_p/n_f)$$  \hspace{1cm} (A.7)$$

where $n_f = 2b/L$ is the fissure porosity. The same formula is obtainable for the piston-flow model, i.e. when $D = 0$ in Eq.(1).

The concentration distribution in the fissures can be calculated from Eq.(A.4) by simplifying it with the aid of the following expressions

$$\exp(-2\Theta) = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp[-\xi^2 - (\Theta/\xi)\xi] d\xi$$

where

$$\Theta = \frac{1}{2} \gamma \left(1 + \beta^2 \left[ p + \sqrt{p} \right. \kappa^{-1} \tanh (\delta \sqrt{p}) \right]^{1/2}$$

$$\gamma = \frac{v x}{2D}, \quad \beta^2 = 4 \frac{D}{v x} t_0, \quad \kappa^{-1} = \frac{n_p \sqrt{D_p}}{b} \quad \text{and} \quad \delta = (L/2 - b)/\sqrt{D_p}$$
After substitutions and rearrangements, Eq.(A.4) takes the form

\[
\frac{\hat{\alpha}_f}{A_0} = \frac{2}{\sqrt{\pi}} \exp(\gamma) \int_0^\infty \exp\left(-\xi^2 - \frac{\gamma^2}{4\xi^2}\right) \cdot \exp[-F(\xi) \tanh(\delta \sqrt{\beta})] \times \exp[-\alpha F(\xi) \beta] d\xi
\]  

(A.8)

where \( F(\xi) = (\gamma \beta)^2 / (4 \xi^2 \kappa) \).

Knowing that

\[
L^{-1}\{\exp[-Y \sqrt{\beta} \tanh(Z \sqrt{\beta})]\} = \frac{1}{\pi} \int_0^\infty e^{\exp(e_R)} \cos(e_t) de
\]  

(A.9)

where

\[
e_R = -\frac{Y e}{2} \left( \frac{\sinh(Z e) - \sin(Z e)}{\cosh(Z e) + \cos(Z e)} \right)
\]

\[
e_t = \frac{e^2 t}{2} - \frac{Y e}{2} \left( \frac{\sinh(Z e) + \sin(Z e)}{\cosh(Z e) + \cos(Z e)} \right)
\]

one finally obtains

\[
\frac{c_f(x,t)}{A_0} = \frac{2}{\pi^{3/2}} \exp\left(\frac{\sqrt{x}}{2D}\right) \int_0^\infty \exp\left[-\xi^2 - \left(\frac{\sqrt{x}}{4D \xi}\right)^2\right] \times \left[ \int_0^\infty e^{\exp(-e_t)} \cos(e_t) de \right] d\xi
\]  

(A.10)

where

\[
w = \frac{1}{2} \left( \frac{\sqrt{x t_0}}{D t} \right)^{1/2}
\]

\[
e_1 = \frac{vx}{8D t_0} \frac{n_p \sqrt{Dp}}{b} \left( \frac{\sinh(\delta e) - \sin(\delta e)}{\xi^2 \cosh(\delta e) + \cos(\delta e)} \right)
\]

\[
e_2 = \frac{e^2}{2} \left( t - \frac{vx t_0}{4D \xi^2} \right) - \frac{vx}{8D t_0} \frac{n_p \sqrt{Dp}}{b} \left( \frac{\sinh(\delta e) + \sin(\delta e)}{\cosh(\delta e) + \cos(\delta e)} \right)
\]
In the case of the piston-flow model, i.e., for $D = 0$ in Eq. (1), the solution reads

$$
\frac{c(x, t)}{A_0} = \frac{1}{\pi} \int_{0}^{\infty} e^{\exp(-e^3)} \cos(e_4) d\epsilon \text{ for } t \gg t_0 \tag{A.11}
$$

where

$$
e_3 = \frac{n_p \sqrt{D_p}}{2b} t_0 e \frac{\sinh(\delta \epsilon) - \sin(\delta \epsilon)}{\cosh(\delta \epsilon) + \cos(\delta \epsilon)}
$$

$$
e_4 = (t - t_0) \frac{e^2}{2} - \frac{n_p \sqrt{D_p}}{2b} t_0 e \frac{\sinh(\delta \epsilon) + \sin(\delta \epsilon)}{\cosh(\delta \epsilon) + \cos(\delta \epsilon)}
$$

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REFLEXIONS SUR LA THEORIE DES TRACEURS: APPLICATIONS EN HYDROLOGIE ISOTOPIQUE

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Abstract–Résumé

CONSIDERATIONS ON THE THEORY OF TRACERS: APPLICATIONS IN ISOTOPE HYDROLOGY.

The theory of tracers is still in the process of development, especially in the area of non-stationary systems. Furthermore, the concepts of theoreticians do not always appear to be well understood by users of tracers, with the result that errors are often found in analyses contained in certain publications or in certain theses for university degrees. The paper points out the relationships between the transfer of water masses and the transfer of the tracer. It can thereby help to avoid the repetition of such errors and promote the development of theory. Under what conditions can two chronological series of values measured at the entry into and at the exit from an aquifer provide information on this system? This problem is considered from the methodological and critical viewpoint with the help of illustrative examples. The chronological series here can be mass flows of a given species (for example, tritium), deviations in relation to a reference (stable isotope versus SMOW) or flow rates of water. The fundamental concepts governing the systems are reviewed: linearity, stationariness and non-stationariness. The paper gives a qualitative example of the conventional interpretation of data on stable isotopes for water in karst hydrology, which clearly defines the problem. By means of a systematic approach the authors determine and critically review the various possible mathematical relationships between concentration, mass fluxes of tracers and, in particular, of stable isotopes in water, and water flow rates. They show under what condition the responses in terms of water flow rate and tracer mass flux can be identical and in what circumstances an aquifer satisfies this condition. The more conventional analytical approach is then discussed.

REFLEXIONS SUR LA THEORIE DES TRACEURS: APPLICATIONS EN HYDROLOGIE ISOTOPIQUE.

La théorie des traceurs est encore en cours de développement, en particulier dans le domaine des systèmes non stationnaires. Il apparaît, par ailleurs, que les concepts des théoriciens ne sont pas toujours bien perçus par les utilisateurs de traceurs; il en résulte souvent des erreurs dans les analyses qui sont présentées dans certaines publications ou dans
certaines thèses. Ce mémoire souligne les relations qui existent entre le transfert des masses d'eau et le transfert du traceur. Il peut ainsi contribuer à éviter la répétition de telles erreurs et participer au développement de la théorie. A quelles conditions deux séries chronologiques de valeurs mesurées à l'entrée et à la sortie d'un aquifère permettent-elles d'obtenir des informations sur ce système? Ce problème est examiné d'un point de vue méthodologique et critique avec des exemples illustratifs. Ainsi, ces séries chronologiques peuvent être des débits de concentration en une espèce donnée (par exemple tritium), des écarts par rapport à une référence (isotope stable vs. SMOW) ou des débits d'eau. On rappelle les concepts élémentaires régissant les systèmes: linéarité, stationnarité et non-stationnarité. Un exemple d'interprétation classique et qualitatif de données relatives aux isotopes stables de l'eau en hydrologie karstique est présenté et permet de préciser le problème posé. En utilisant la méthode d'approche systémique, on établit et on critique les différentes relations mathématiques pouvant exister entre les concentrations, flux massiques de traceurs et, en particulier, d'isotopes stables de l'eau, et débits d'eau. On montre à quelle condition une identité entre la réponse en débit d'eau et en flux massique de traceur peut être obtenue et dans quel cas de figure un aquifère satisfait à cette condition. La méthode plus classique d'approche analytique du problème est ensuite exposée.

1. POSITION DU PROBLÈME

Pour obtenir des informations sur un aquifère, une méthode d'approche globale peut consister à mesurer des grandeurs à l'entrée et à la sortie du système considéré et à chercher des relations entre ces grandeurs.

Les grandeurs mesurées peuvent être:
- les flux d'eau entrant et sortant;
- les concentrations en isotope (oxygène 18, deutérium, tritium ou autres espèces conservatives).

Les relations le plus souvent utilisées sont des produits de convolution supposant des conditions de linéarité entre ces grandeurs.

L'obtention des réponses impulsionnelles permettra alors de caractériser le système: temps moyen de séjour — volume d'eau présent ... etc.

Le problème posé est donc de savoir sous quelles conditions deux séries chronologiques de valeurs, mesurées à l'entrée et à la sortie d'un aquifère, permettent d'obtenir des informations sur ce système.

2. RAPPELS ET REMARQUES LIMINAIRES

Les systèmes physiques peuvent être classés [1–3]:
- en systèmes linéaires et systèmes non linéaires;
- en systèmes stationnaires (invariants) et systèmes non stationnaires (variantes).

Nous précisons ci-dessous les critères sur lesquels sont fondées ces classifications.
2.1. Opérateur linéaire

Un système est linéaire s'il se comporte comme un opérateur linéaire, tel qu'on le définit en mathématique, c'est-à-dire s'il répond aux deux conditions suivantes:

1) Si \( y_1 \) est le signal de sortie correspondant à un signal d'entrée \( x_1 \), alors la réponse à un signal d'entrée \( \lambda x_1 \) est \( \lambda y_1 \), \( \lambda \) étant une constante.

2) Si \( y_1 \) est la réponse à \( x_1 \) et \( y_2 \) est la réponse à \( x_2 \), alors la réponse à \( x_1 + x_2 \) est \( y_1 + y_2 \).

On remarquera, par exemple, qu'une droite \( y = ax + b \) qui ne passe pas par l'origine des coordonnées ne définit pas un opérateur linéaire car la première condition n'est pas satisfaite. Par contre, \( y = ax \) est un opérateur linéaire.

2.2. Système stationnaire

Un système est stationnaire s'il répond à la condition suivante: si \( y(t) \) est la réponse à un signal d'entrée \( x(t) \) agissant à la date \( t \), la réponse à ce même signal différé de \( \tau \), \( x(t - \tau) \), est la réponse initiale différée de la même valeur \( \tau \), \( y(t - \tau) \).

En d'autre termes une translation dans le temps des signaux d'entrée induit une translation identique des signaux de sortie.

2.3. Réponse des systèmes linéaires invariants — Intégrale de convolution

Un système qui ne comporte qu'une seule grandeur d'entrée et une seule grandeur de sortie est dit univariable ou scalaire: s'il possède plusieurs entrées et plusieurs sorties, il est dit multivariable ou vectoriel.

La réponse impulsionnelle \( h(t) \) d'un système scalaire, linéaire ou non linéaire, est sa réponse au signal de Dirac \( \delta^*(t) \), le système étant supposé initialement au repos.

Cette réponse impulsionnelle permet de déterminer la réponse \( y(t) \) d'un système si l'on connaît la fonction \( u(t) \) qui définit les variations du signal d'entrée. Dans le cas des systèmes linéaires invariants, cette réponse est donnée par l'intégrale de convolution:

\[
y(t) = \int_{-\infty}^{+\infty} u(\tau) \cdot h(t - \tau) \, d\tau
\]

que l'on notera:

\[
y(t) = u(t) \ast h(t)
\]

\( t \) étant le temps réel et \( \tau \) une variable auxiliaire représentant un temps.
2.4. Réponse des systèmes linéaires variant — Intégrale de superposition

La réponse \( y(t) \) d'un système linéaire variant à un signal d'entrée \( u(t) \) est donnée par l'intégrale de superposition:

\[
y(t) = \int_{-\infty}^{+\infty} u(\tau) \cdot h(t, \tau) d\tau
\]

que l'on notera:

\[
y(t) = u(t) * h(t, \tau)
\]

Dans ce cas, la réponse impulsionnelle varie avec le temps.

2.5. Transferts conservatifs et non conservatifs

Rappelons que le signal de Dirac a les propriétés suivantes:

\[
\delta^*(t) = 0 \text{ pour } t \neq 0
\]

\[
\int_{-\infty}^{+\infty} \delta^*(t) dt = 1
\]

Si l'on suppose par exemple un écoulement monodimensionnel à débit constant, le transfert d'un traceur entre deux sections de cet écoulement sera définit en relevant la fonction concentration-temps \( C(t) \) dans la section aval consécutive à une injection la plus brève possible du traceur dans la section amont.

Si le transfert du traceur est conservatif entre ces deux sections, la réponse impulsionnelle étant définie par:

\[
h(t) = \frac{C(t)}{\int_{-\infty}^{+\infty} C(t) dt}
\]
on a:
\[
\int_{-\infty}^{+\infty} h(t) \, dt = 1
\]

Si le transfert est *non conservatif*:
\[
\int_{-\infty}^{+\infty} h(t) \, dt \neq 1
\]

### 2.6. Flux massique dans le cas des isotopes stables de l’eau

Les fonctions \( y(t) \) et \( u(t) \) utilisées dans les intégrales de convolution et de superposition sont des *flux massiques*, déterminés par exemple par le produit \( C(t) \cdot Q(t) \) d’une concentration volumique par un débit volumique.

Un problème spécifique aux isotopes stables se pose. Leur teneur ne sont pas en effet exprimées en terme de concentration massique ou volumique, mais par rapport à la teneur isotopique d’un standard de référence selon la définition suivante:

\[
\delta = \left( \frac{R \, \text{éch}}{R \, \text{std}} - 1 \right) \times 1000
\]

Dans cette expression, \( R \) est le rapport entre le nombre d’atomes de l’isotope rare et celui de l’isotope banal; \( R \, \text{éch} \) est relatif à l’échantillon et \( R \, \text{std} \) est relatif au standard.

Dans le cas du standard SMOW et pour l’oxygène 18, ce rapport est:

\( R^{(18O_{\text{SMOW}})} \approx 2 \times 10^{-3} \)

Etant donné la faible abondance des molécules \( H_2 \, ^{18}O \) devant celles de \( H_2 \, ^{16}O \), comme le montre ce rapport, la concentration \( C^{(16O)} \), en mole par litre par exemple, de \( H_2 \, ^{16}O \) peut être considérée égale à celle de l’eau, dans le standard comme dans l’échantillon:

\( C^{(16O)} = 55,55 \, \text{mol/L} \)
Comme il existe dans un litre d'eau autant d'atome-grammes de $^{18}$O que de moles de $H_2^{16}$O:

$$N(18O) = C(18O)$$

On a de même:

$$N(18O) = C(18O)$$

On peut écrire:

$$\delta(18O) = \left[ \frac{C(18O)}{C(18O)_{sach}} - 1 \right] \times 1000$$

$$\delta(18O) = \left| \frac{C(18O)}{55,55} - 2 \times 10^{-3} \right| 0,5 \times 10^{-6}$$

$$C(18O) = 0,111 \left[ 1 + 10^{-3} \delta(18O) \right]$$

Pour le deutérium, la constante est différente puisqu'il y a 2 atomes d'hydrogène pour un d'oxygène; par ailleurs, dans le standard, $N_D/N_H = 158 \times 10^{-6}$.

On obtient:

$$C_D = 0,0173(1 + 10^{-3} \delta_D)$$

La concentration $C_i$ en isotope stable de l'eau d'un échantillon est de la forme:

$$C_i = A(1 + B \delta_i)$$

Cette relation n'est pas linéaire: nous en examinerons plus loin les conséquences.

Cette non-linéarité est d'autant plus marquée que $A$ et $B$ sont petits devant 1.

En conclusion et d'une manière générale, on peut, à partir d'une concentration $C(t)$ et d'une référence $C_o$, définir une relation de la forme:

$$\delta(t) = K \frac{C(t) - C_o}{C_o}$$

où $K$ est une constante.

C'est cette relation que nous utiliserons par la suite.
FIG. 1. Evolution des teneurs en oxygène 18 à l’entrée et à la sortie du système, respectivement dans les eaux des précipitations et dans les eaux à l’extoire.
TABLEAU I. BASSIN DU BAGET: CONCLUSIONS COMPARATIVES SELON DEUX MODES D’EXPLOITATION DES DONNEES

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relation entre les concentrations en oxygène 18</td>
<td>Relation entre les flux massiques en oxygène 18</td>
</tr>
<tr>
<td>L’absence de variations saisonnières des concentrations à la sortie, alors que celles-ci sont importantes à l’entrée, conduit à conclure que:</td>
<td>Les importantes variations saisonnières du flux de sortie, de fréquence identique à celles du flux d’entrée, conduisent à conclure que:</td>
</tr>
<tr>
<td>a) le système est très dispersif;</td>
<td>a) le système est peu dispersif;</td>
</tr>
<tr>
<td>b) les volumes des précipitations d’entrée sont petits par rapport au volume des réserves dans le système</td>
<td>b) les volumes des précipitations d’entrée sont relativement importants par rapport au volume des réserves dans le système.</td>
</tr>
<tr>
<td>La conclusion b) implique un temps de séjour de l’eau très important dans le système</td>
<td>La conclusion b) implique un temps de séjour de l’eau assez court dans le système</td>
</tr>
<tr>
<td>$\bar{t} &gt; 1 \text{ an}$</td>
<td>$\bar{t} &lt; 1 \text{ mois}$</td>
</tr>
</tbody>
</table>

En appliquant alors la relation classique:

Volume du système = Débit moyen × Temps de séjour

$$ V = \bar{Q} \times \bar{t} $$

avec $\bar{t}$ = abscisse du centre de gravité de la réponse impulsionnelle du système,
on obtient, pour un débit moyen annuel de $0,5 \text{ m}^3\text{s}^{-1}$:

$$ V \approx 1,5 \times 10^7 \text{ m}^3 $$

Cette valeur est supérieure de plus d’un ordre de grandeur à celles déterminées par d’autres approches expérimentales.

$$ V \approx 10^8 \text{ m}^3 $$

Cette valeur est en bon accord avec celles déterminées par d’autres approches expérimentales.
TABLEAU I. (suite)

De plus, si l'on compare, pour deux cycles annuels, les valeurs moyennes à l'entrée et à la sortie du système:

\[
\delta_e = \frac{\delta_s}{N} = -8,16\% \\
\delta_e = \frac{\Sigma Q_s - \delta_s}{\Sigma Q_s} = -8,52\%
\]

\[
\delta_e = \frac{\delta_s}{N} = -8,77\% \\
\delta_e = \frac{\Sigma Q_s - \delta_s}{\Sigma Q_s} = -8,38\%
\]

Le déficit de la valeur d'entrée (\(\approx -0,06\%\)) par rapport à la valeur de sortie conduit à un appauvrissement par évapotranspiration des pluies estivales.

Cet appauvrissement est interprété comme l'élimination préférentielle des pluies d'été par évapotranspiration. La réserve superficielle ne serait donc pas un système mélangeur.

Les valeurs sensiblement égales à l'entrée et à la sortie (\(\Delta \approx +0,14\%\)) permettent de conclure que l'évapotranspiration ne minimise pas le flux d'entrée des pluies estivales.

L'évapotranspiration s'effectue dans la réserve superficielle (épikarst) qui se comporte comme un système mélangeur. L'évapotranspiration s'effectue à \(\delta^{18}O\) sensiblement constant.

Dans le cas où le signal de sortie \(\delta^{18}O\) est utilisé pour déterminer l'altitude moyenne du bassin versant considéré,

il faut mesurer ou évaluer l'évapotranspiration car celle-ci a une incidence notable,

il n'est pas tenu compte de l'évapotranspiration, celle-ci n'ayant qu'une très faible incidence sur la valeur de sortie,

cela qui conduit, en considérant une même valeur moyenne de sortie, à déterminer des altitudes moyennes différentes pour un même bassin versant.

3. EXEMPLE D'INTERPRETATION DE RESULTATS EXPERIMENTAUX

Le système karstique expérimental du Baget est étudié depuis plus d'une décennie par Mangin [4], Bakalowicz [5] et Eberentz [6].

Les auteurs disposent d'une chronique des teneurs en oxygène 18 des précipitations et des eaux à l'exutoire (figure 1).
FIG.2. Évolution des teneurs en oxygène 18 à l'entrée et à la sortie du système, pondérées respectivement par les débits des précipitations et les débits à l'exutoire.
4. INTERPRETATION DANS LE CADRE D'UNE APPROCHE «SYSTEME»

4.1. Relations envisageables

L'interprétation qualitative précédente peut être approfondie dans le cadre d'une approche «système». Cette approche «système» sera, au chapitre 6 de ce mémoire, comparée aux méthodes analytiques classiques (équations différentielles, etc.).

Les grandeurs d'entrée et de sortie $C(t)$, $\delta(t)$, $Q(t)$ peuvent être reliées par des opérations de convolution qui peuvent se présenter sous les formes indiquées au tableau II, avec, pour chacune de ces relations:

$$\int_{0}^{\infty} h_i(t) \, dt = 1; \quad i = 1, 2, \ldots, 5$$

A partir de ces cinq relations possibles, on peut alors se poser la question de savoir si les réponses impulsionnelles $h_i(t)$; $(i = 1, 2, 3, 4, 5)$ qui figurent dans ces cinq relations (ou qui pourraient être éventuellement déduites des résultats expérimentaux par déconvolution) sont identiques.

Si oui, on observe alors une redondance entre les informations déductibles des débits et des isotopes; si non, laquelle de ces relations choisir?

4.2. Propriétés de ces relations

Propriété 1: les questions précédentes ne se posent qu'en régime de débit variable.

En effet, en cas de débit constant $Q_{0}(t) = Q_{0}$, les relations $(R_{1})$ et $(R_{2})$ sont identiques ainsi que $(R_{2})$ et $(R_{4})$. 
TABLEAU II. RELATIONS POSSIBLES ENTRE LES GRANDEURS D'ENTREE ET DE SORTIE

Sans pondération par les débits:

\[ C_e(t) = C_e(t) \ast h_2(t) \]  \hspace{1cm} (R_1)

\[ \delta_e(t) = \delta_e(t) \ast h_2(t) \]  \hspace{1cm} (R_2)

Avec pondération par les débits:

\[ C_e(t) \cdot Q_e(t) = [C_e(t) \cdot Q_e(t)] \ast h_2(t) \]  \hspace{1cm} (R_3)

\[ \delta_e(t) \cdot Q_e(t) = [\delta_e(t) \cdot Q_e(t)] \ast h_2(t) \]  \hspace{1cm} (R_4)

Ainsi que

\[ Q_e(t) = Q_e(t) \ast h_2(t) \]  \hspace{1cm} (R_5)

D'autre part, l'acceptation, dans cette hypothèse, de la relation (R_1) conduit également à la validité de la relation (R_2) avec \( h_2(t) = h_1(t) \).

En effet, si l'on a:

\[ C_e(t) = C_e(t) \ast h_1(t) \text{ avec } \int_{0}^{\infty} h_1(t) \, dt = 1 \]

comme \( \delta(t) \) est défini par la relation suivante:

\[ \delta(t) = K \frac{C(t) - C_0}{C_0} \]

on a alors:

\[ \delta_e(t) = \delta_e(t) \ast h_1(t) \]  \hspace{1cm} (R_6)

Pour démontrer cette propriété, il suffit de remplacer les valeurs de \( C_e(t) \) et \( C_6(t) \) dans (R_1) en fonction de \( \delta_6(t) \) et \( \delta_e(t) \) pour obtenir (R_2) avec \( h_2(t) = h_1(t) \).
Propriété 2 : les relations \((R_1)\) et \((R_2)\) en régime de débit variable ne conservent pas les flux.

Dans le cas de débit variable, la relation \((R_1)\) avec

\[
\int_{0}^{\infty} h_1(t) \, dt = 1
\]

ne peut pas être considérée comme valable car cette relation n’est pas conservative.

La transformée de Laplace de \((R_1)\) conduit, en effet, à écrire:

\[
\overline{C_s}(p) = \overline{C_e}(p) \cdot \overline{h_1}(p)
\]

qui, pour \(p = 0\), se réduit à:

\[
\overline{C_s}(0) = \overline{C_e}(0)
\]

car

\[
\overline{h_1}(0) = \int_{0}^{\infty} h_1(t) \, dt = 1
\]

c’est-à-dire:

\[
\int_{0}^{\infty} C_s(t) \, dt = \int_{0}^{\infty} C_e(t) \, dt
\]

La conservation des flux de matière (isotope et débit) impose les relations ci-après:

\[
\int_{0}^{\infty} Q_s(t) \cdot C_s(t) \, dt = \int_{0}^{\infty} Q_e(t) \cdot C_e(t) \, dt
\]

\[
\int_{0}^{\infty} Q_s(t) \, dt = \int_{0}^{\infty} Q_e(t) \, dt
\]
différentes de la relation de conservation des concentrations ci-dessus ne correspondant à aucune réalité physique.

De même, à la suite d'une injection A de traceur à l'instant \( t = u \) dans le débit d'entrée \( Q_e(t = u) \), la concentration entrante est:

\[
C_e(u) = \frac{A}{Q_e(u)} \cdot \delta(u)
\]

La relation (R₁) donne, dans ce cas, une concentration de sortie \( C_s(t) \) égale à:

\[
C_s(t) = \frac{A}{Q_e(u)} \cdot h_1(t)
\]

Le bilan de traceur dans le débit de sortie \( Q_s(t) \) calculé à partir de cette valeur \( C(t) \) déduite de (R₁) est alors:

\[
\int_0^\infty C_s(t) \cdot Q_s(t) \, dt = \int_0^\infty \frac{A}{Q_e(u)} \cdot Q_s(t) \cdot h_1(t) \, dt
\]

La conservation de la quantité de traceur A injecté impose alors la relation:

\[
\int_0^\infty \frac{Q_s(t)}{Q_e(u)} \cdot h_1(t) \, dt = 1 \quad \forall \, t \text{ et } u
\]

Cette condition, compte tenu de la relation:

\[
\int_0^\infty h_1(t) \, dt = 1
\]

impose alors que:

\[
\frac{Q_s(t)}{Q_e(u)} = 1 \quad \forall \, t \text{ et } u
\]

ce qui montre que la relation (R₁) de convolution sur les concentrations ne peut être valable qu'en régime de débit constant.
Si \((R_1)\) ne peut pas, en régime de débit variable, être considéré comme acceptable, il en sera de même de \((R_2)\) qui se déduit de \((R_1)\) par la relation liant d'une manière générale \(C(t)\) et \(\delta(t)\).

Par contre, dans le cadre de cette hypothèse de régime à débit variable, rien n'interdit, a priori, d'admettre les relations du type \((R_3)\), \((R_4)\) et \((R_5)\) et nous étudierons les conséquences de ces choix.

a) **Les relations \((R_3)\), \((R_4)\) et \((R_5)\), en régime de débit variable, conservent les flux:**

Considérons la relation \((R_3)\) concernant les flux isotopiques entrant et sortant \(C_6(t)\cdot Q_6(t)\), \(C_4(t)\cdot Q_4(t)\) et non pas les concentrations comme \((R_1)\).

\[
C_6(t)\cdot Q_6(t) = [(C_6(t)\cdot Q_6(t))]^* h_3(t) \tag{R_3}
\]

La transformée de Laplace de cette relation de convolution, compte tenu de la condition imposée

\[
\int_{0}^{\infty} h_3(t) \, dt = 1
\]

conduit à la relation:

\[
\int_{0}^{\infty} C_6(t)\cdot Q_6(t) \, dt = \int_{0}^{\infty} C_4(t)\cdot Q_4(t) \, dt
\]

traduisant la conservation des flux isotopiques. La conservation des débits d'eau obtenue pour \(C_6(t) = C_4(t) = \) constante est également une conséquence de cette condition.

b) **L'adoption de la relation \((R_3)\) implique la validité de la relation \((R_4)\) avec \(h_3(t) = h_5(t)\).**

En effet, un système alimenté par un flux dont la concentration d'entrée \(C_6(t)\) est constante donnera à l'équilibre une concentration de sortie \(C_4(t) = \) constante. La condition \(C_6(t) = C_4(t) = \) constante, appliquée à la relation \((R_3)\), donne \((R_5)\) relation de convolution sur les débits.

c) **On peut également montrer que l'adoption des relations \((R_3)\) et \((R_4)\) avec \(h_3(t) = h_5(t)\) implique la relation \((R_5)\) avec \(h_3(t) = h_5(t)\).**

On a, en effet, par définition:

\[
\delta(t) = K \frac{C(t) - C_0}{C_0}
\]
(R₄) s’écrit alors [h₃(t) = h₄(t) = h(t)]

\[
\left( K \cdot \frac{C_2(t) - C_0}{C_0} \right) \cdot Q_2(t) = \left( \left( K \cdot \frac{C_2(t) - C_0}{C_0} \right) \cdot Q_2(t) \right) \ast h(t)
\]

ce qui, en tenant compte de (R₃) et après simplification, se réduit à l’expression:

\[
Q_2(t) = Q_2(t) \ast h(t)
\]

expression de la forme (R₄).

d) D’une manière générale, les trois relations (R₃), (R₄) et (R₅) ne peuvent pas être considérées comme indépendantes.

L’adoption de deux d’entre elles R₃ et R₅ avec h₃(t) = h₅(t) implique l’adoption de la troisième avec la même réponse impulsionnelle. Cette situation tient à la relation liant δ(t) et C(t). En effet, δ(t) est une grandeur relative définissant une variation par rapport à une référence C₀. Si le flux de base de concentration C₀ se transmet de la même manière que le flux de concentration C(t), le flux caractérisé par l’écart δ(t) aura alors le même type de transfert et réciproquement.

4.3. Conséquences de ces relations

Dans le cas des isotopes stables par exemple, la concentration en oxygène 18 de l’eau varie très peu au cours du temps (quelques millièmes). Par contre, les variations de débit et les précisions sur ces mesures donnent une nette prépondérance au terme Qt(t) par rapport au terme C(t) (variation de concentration en oxygène 18).

Dans ce cas, pour des raisons pratiques, la relation (R₃) (dans la mesure où elle est applicable) se confond avec une relation du type (R₄): convolution sur les débits. La seule relation utilisable porte alors sur les valeurs de δ(t): écart relatif par rapport à une concentration de référence (SMOW) (relation du type R₄).

Par contre, si C(t) représente les concentrations en tritium, il est possible pratiquement d’utiliser une relation du type (R₃) car ces concentrations en général, dans ce cas, présentent des variations appréciables. Les réponses impulsionnelles qui seraient alors déductibles de ces résultats expérimentaux (opération de déconvolution par exemple), soit h₄(t) et h₅(t), doivent évidemment être identiques car représentatives du mouvement de l’eau à étudier.

En résumé:
- En régime de débit constant, les cinq relations présentées sont cohérentes entre elles et applicables sous réserve que le système soit linéaire vis-à-vis des grandeurs considérées.
— En régime de débit variable, seules les relations (R3), (R4) et (R5) respectant les conditions de conservation sont susceptibles d’être utilisées. Ces relations, dont les dépendances réciproques ont été exposées, supposent évidemment que le système étudié soit linéaire. Les relations liant ces grandeurs sont supposées être du type convolution (réponse impulsionnelle unique déterminable expérimentalement à partir des grandeurs d’entrée et de sortie) et non pas du type superposition (réponses impulsionnelles multiples h(t, u) variant suivant l’instant u d’injection).

4.4. Remarques: conditions d’existence d’une relation de la forme

\[ C_4(t) = C_6(t) * h_6(t) \]

Nous avons précédemment montré qu’en régime de débit variable on ne pouvait pas écrire de relation de superposition entre les concentrations d’entrée et de sortie, avec un noyau h(t) tel que

\[ \int_{-\infty}^{+\infty} h(t) \, dt = 1 \]

Nous allons montrer qu’il est possible de déterminer, à partir des réponses impulsionnelles h(t), des débits Q₆(t) et Q₄(t), un noyau h₆(t) liant les concentrations d’entrée et de sortie par

\[ C_4(t) = C_6(t) * h_6(t) \]

Écrivons (R₃) sous sa forme développée

\[ Q₄(t) \cdot C₄(t) = \int_{0}^{t} Q₆(u) \cdot C₆(u) \cdot h₃(t, u) \, du \]

A une date donnée t₁ nous avons:

\[ C₄(t₁) = \int_{0}^{t₁} C₆(u) \cdot \frac{h₃(t₁, u) \cdot Q₆(u)}{Q₄(t₁)} \, du \]
Définissons:

\[ h_6(t, u) = h_2(t, u) \cdot \frac{Q_6(u)}{Q_3(t)} \]  

(1)

(R3) s’écrit alors:

\[ C_3(t) = C_2(t) \ast h_6(t) \]  

(R4)

Il existe donc entre les concentrations d’entrée et de sortie une relation de superposition dont le noyau est défini par la relation (1).

Au cours du transfert du traceur, seuls les flux massiques sont conservés si le traceur est un traceur idéal; d’une manière générale, les concentrations ne sont pas conservées et:

\[ \int_{-\infty}^{+\infty} h_6(t) \, dt \neq 1 \]

Niemi [7] utilise une approche différente pour établir (R4) et (1). La figure 3 suggère la méthode de détermination de la fonction \( h_6(t) \) à partir des réponses \( h_2(t, u) \), du débit d’entrée et du débit de sortie.

5. RECHERCHE DE CAS REELS OU LES REPONSES IMPULSIONNELLES EN EAU ET EN TRACEUR SONT IDENTIQUES

5.1. Situation générale

Les analyses précédentes, en régime variable, montrent que les opérations de convolution sur les flux d’isotopes impliquent que les débits soient également convouables avec une réponse impulsionnelle identique. Au cas où on n’admettrait pas de telles relations sur les débits (opération linéaire de convolution ou de superposition), on ne pourrait évidemment pas admettre de telles relations sur les flux d’isotopes.

Le problème posé est donc de montrer qu’il existe dans la nature de tels systèmes ayant ces propriétés. Des connaissances sur ces systèmes pourraient ainsi être acquises soit à partir de mesures sur les débits (entrée-sortie) soit à partir de flux isotopiques.

L’écoulement de fluide non compressible dans un tuyau en charge est un cas où une telle condition ne se produirait pas. Les deux réponses impulsionnelles
FIG. 3. Détermination de la fonction $h_e(t, u)$ à partir des fonctions $h_3(t, u)$. 
(en débit et en traceur) sont évidemment différentes. Une impulsion de débit à l'entrée d'un tel système se répercute instantanément à la sortie alors que la réponse impulsionnelle en traceur, représentative de la tranche d'eau traversant la conduite, est différente.

5.2. Application à un aquifère

5.2.1. Réponse impulsionnelle en débit

Soit un aquifère à surface libre et à substratum imperméable alimenté par des pluies \( P(t) \) variables dans le temps. Correction faite de l'évapotranspiration, cet aquifère peut être schématisé par un système alimenté par le débit d'entrée \( Q_e(t) \) proportionnel à \( S \cdot P(t) \) (\( S = \) surface) et dont le débit de sortie en un exutoire unique est \( Q_s(t) \).

Nous allons, d'une manière schématique, rechercher quelle peut être la réponse impulsionnelle de ce système à une pluie unitaire.

Pour cela, nous ferons l'hypothèse simplificatrice que la surface du toit de cette nappe est un plan (aquifère de grande dimension et de perméabilité uniforme) et qu'une pluie unitaire \( dP \) distribuée sur tout le bassin se traduit par une élévation uniforme \( dh \) du plan d'eau (pas de variation du gradient). Dans ces conditions, la variation du débit d'eau \( dQ \) transitant dans une section est alors: \( dQ = K \cdot dh \) où \( K = \) perméabilité \( \times \) gradient.

Si \( \bar{h} \) est la hauteur moyenne du plan d'eau (surface plane), la relation de bilan s'écrit:

\[
S \cdot \frac{d\bar{h}}{dt} = Q_e - Q_s
\]

Dans le cas d'une impulsion unitaire de pluie, on a alors, compte tenu des hypothèses faites, \( dQ_s = K \cdot dh \), et par suite la relation de bilan ci-dessus s'écrit:

\[
\frac{S}{K} \cdot \frac{dQ_s}{dt} = -Q_s
\]

(dimension de \( S/K = \) temps)

C'est-à-dire:

\[
Q_s(t) = Q_0 \cdot \exp \left( -\frac{t}{\alpha} \right)
\]

Avec \( \alpha = \frac{S}{K} \)
Ces hypothèses simplificatrices montrent ainsi que la réponse impulsionnelle d'un tel système est une exponentielle d'argument S/K (S/K = volume/débit indépendamment de la date d'injection).

Quand le débit d'entrée est variable $Q_e(t)$, on obtient alors à partir de l'équation de bilan complète et en tenant compte des hypothèses faites, la relation:

$$Q_s(t) = \int_0^t Q_e(u) \cdot \frac{1}{\alpha} \cdot \exp \left( -\frac{t-u}{\alpha} \right) du$$

Cette relation est une intégrale de convolution entre les débits d'entrée et de sortie avec une réponse impulsionnelle de forme exponentielle.

Ces hypothèses, pour simplificatrices qu'elles soient, ne sont pas toutefois éloignées des réalités. On observe, en effet, expérimentalement, dans le cas de tarissement, des lois de la forme:

$$Q_s(t) = Q_0 \cdot \exp \left( -\frac{t}{b} \right)$$

Or une courbe de tarissement est la réponse d'un système à une fin d'échelon.

Si la courbe de sortie est de forme exponentielle, la réponse impulsionnelle sera alors de forme exponentielle car la dérivée d'un échelon est, en effet, égale à la réponse impulsionnelle (système linéaire) et la dérivée d'une exponentielle est une exponentielle de même argument.

Nous avons ainsi déterminé à partir d’hypothèses simplificatrices la réponse impulsionnelle en débit d’un système aquifère (forme exponentielle) et nous allons ci-après en rechercher la réponse impulsionnelle en tracéur.

5.2.2. Réponse impulsionnelle en tracéur

La réponse impulsionnelle en tracéur est obtenue à partir d'une injection-impulsion de tracéur dans le débit entrant dans le système, c'est-à-dire dans la pluie répartie uniformément sur toute la surface de l'aquifère.

La figure 4 représente les différentes lignes de courant le long desquelles va cheminer l'eau et par suite le tracéur.

D'une manière schématique, et selon la figure 5, on peut considérer le système comme un assemblage de systèmes élémentaires de type piston-dispersion en parallèle, de longueurs $l$ variables ($l$ variant de 0 à L longueur de l’aquifère) et parcourus par des écoulements de vitesses $u$ identiques.
FIG. 4. Lignes de courants dans un aquifère alimenté uniquement par les précipitations.

FIG. 5. Modèle schématique du transfert de traceur.

FIG. 6. Composition des réponses élémentaires en traceur.
La réponse impulsionnelle d'un système élémentaire est

\[ h(t, \ell) = \frac{u}{\sqrt{4\pi Dt}} \exp\left(-\frac{(\ell - ut)^2}{4Dt}\right) \]

avec \( u \) vitesse et \( D \) coefficient de dispersion, et la somme de tels systèmes élémentaires donne la réponse de sortie \( H(t) \)

\[ H(t) = \frac{1}{L} \int_{0}^{L} h(t, \ell) \, d\ell \]

avec \( u \) vitesse et \( D \) coefficient de dispersion variant avec \( \ell \).

Bien que cette schématisation soit purement indicative, cette fonction \( H(t) \) peut toutefois être caractérisée par une décroissance de forme exponentielle (fig. 6).

Cette situation a été observée par d'autres auteurs [8].

La théorie des traceurs montre d'autre part que toute réponse impulsionnelle est caractérisée par l'abscisse de son centre de gravité égale au quotient du volume d'eau contenu dans le système par le débit qui le traverse.

On retrouve ainsi, dans ce cas, une réponse impulsionnelle en traceur de forme voisine de celle obtenue en débit (forme exponentielle d'argument \( \alpha = \text{volume/débit} \)).

Cette schématisation montre ainsi que l'on peut théoriquement espérer dans le cas présent des réponses impulsionnelles en eau et en traceur de forme voisine et caractérisées par un même argument de décroissance.

Des essais sur des modèles physiques de laboratoire (non reproduits dans ce mémoire) ont montré la validité de cette analyse.

Il est possible toutefois que les porosités différentes, auxquelles les phénomènes considérés (drainage — traceur) sont dus, conduisent expérimentalement à des arguments de décroissance quelque peu différents.

6. APPROCHE ANALYTIQUE DU PROBLEME

Il est possible de déterminer les conditions d'application à un processus de l'analyse système présentée au chapitre 2 à partir d'une étude de la forme des équations différentielles qui décrivent ce processus.

Si le fonctionnement d'un système peut être entièrement décrit par une équation différentielle établie entre les signaux \( x(t) \) et \( y(t) \) respectivement observés à l'entrée et à la sortie de ce système et leurs différentes dérivées \( x^1, \)
\( x^2, \ldots, x^m \) et \( y^1, y^2, \ldots, y^n \) et si cette équation est linéaire et à coefficients constants, \( y(t) \) est relié à \( x(t) \) par une intégrale de convolution.

Soit en effet:

\[
\begin{align*}
&\frac{a_n}{dt^n} \frac{d^n y}{dt^n} + a_{n-1} \frac{d^{n-1} y}{dt^{n-1}} + \ldots + a_1 \frac{dy}{dt} + a_0 \cdot y = b_m \frac{dx}{dt^m} + b_{m-1} \frac{d^{m-1} x}{dt^{m-1}} \\
&+ \ldots + b_1 \cdot \frac{dx}{dt} + b_0 \cdot x
\end{align*}
\]

l'équation différentielle d'un système dans laquelle \( a_n, a_{n-1}, \ldots, a_1, a_0 \) et \( b_m, b_{m-1}, b_0 \) sont des coefficients constants. Dans l'espace des transformées, où les images des fonctions \( x(t) \) et \( y(t) \) sont respectivement \( E(p) \) et \( S(p) \), en supposant qu'à l'origine des temps les signaux observés à l'entrée et à la sortie du système et toutes leurs dérivées s'annulent, l'équation précédente s'écrit:

\[
S(p) [a_n \cdot p^n + a_{n-1} \cdot p^{n-1} + \ldots + a_1 \cdot p + a_0] = E(p) [b_m \cdot p^m + b_{m-1} \cdot p^{m-1} + \ldots + b_1 \cdot p + b_0]
\]

Cette expression peut se mettre sous la forme:

\[
S(p) = E(p) \frac{b_m \cdot p^m + \ldots + b_1 \cdot p + b_0}{a_n \cdot p^n + \ldots + a_1 \cdot p + a_0}
\]

La fraction rationnelle du second membre de cette équation est la transformée d'une fonction \( h(t) \) réponse impulsionnelle du système et satisfaisant à l'intégrale de convolution:

\[
y(t) = \int_{-\infty}^{+\infty} h(t - u) \cdot x(u) \, du
\]

Si le fonctionnement d'un système peut être entièrement décrit par une équation différentielle linéaire, mais à coefficients variables, c'est-à-dire une équation semblable à la précédente mais où les paramètres \( a_n, a_{n-1}, \ldots, a_1, a_0, b_m, b_{m-1}, \ldots, b_1, b_0 \), où une partie d'entre eux deviennent des fonctions du temps, les signaux \( x(t) \) et \( y(t) \) observés respectivement à l'entrée et à la sortie de ce système sont reliés par une intégrale de superposition [9].

\[
y(t) = \int_{-\infty}^{+\infty} h(t, u) \cdot x(u) \, du
\]
Enfin, si le fonctionnement d'un système ne peut être décrit que par une équation différentielle non linéaire, c'est-à-dire présentant des produits entre les fonctions $x(t)$, $y(t)$ et leurs dérivées ou des puissances ou des fonctions diverses de ces mêmes termes, il n'est pas possible de relier $y(t)$ et $x(t)$ par une intégrale de convolution ou par une intégrale de superposition.

Un exemple simple de cette impossibilité peut être trouvé dans l'évolution du débit de sortie $y(t)$ d'un réservoir cylindrique vertical présentant un exutoire à sa base et alimenté par un débit d'entrée variable $x(t)$. L'équation différentielle représentant le fonctionnement de ce système s'écrit:

$$y(t) \frac{dy(t)}{dt} + A \cdot y(t) = A \cdot x(t)$$

Dans cette équation, $A$ est une constante liée aux dimensions et à la forme de l'exutoire et à la géométrie du réservoir.

Cette équation différentielle peut être mise sous la forme:

$$y(t) = -A \cdot t + \int \frac{x(u) \cdot dy(u)}{x(u) - y(u)}$$

qui exclut toute relation de convolution ou de superposition entre les fonctions $y(t)$ et $x(t)$.

Toute application des méthodes de l'analyse «système» à des processus décrits par une équation différentielle non linéaire ne peut donc aboutir qu'à l'obtention de résultats erronés. Par contre, il est parfois possible de réaliser des linéarisations locales des équations décrivant de tels systèmes, ce qui autoriserait l'emploi de l'analyse «système» sur des zones restreintes du domaine d'évolution des paramètres conditionnant le processus [10].

7. CONCLUSIONS GENERALES

D'une manière générale et en conclusion, le présent mémoire a été écrit en se fixant deux objectifs:

- réflexion sur l'usage des traceurs en régime de débits variables;
- conséquences et recommandations pratiques.

Après avoir rappelé la notion de linéarité et exposé les relations qui en découlent (intégrale de convolution et de superposition) cette approche «système» a été comparée à l'analyse classique (équations différentielles).
Dans ce cadre et dans le cas de systèmes à débit variable, seuls les flux d'isotopes sont susceptibles d'être liés par de telles relations et non pas les concentrations, contrairement à ce qu'affirment de nombreuses études réalisées.

L'exemple proposé (aqui-fère du Baget) montre qu'il ne s'agit pas de différences subtiles mais de conclusions nettement différentes suivant que l'analyse est conduite sur les flux ou les concentrations.

Ces différents choix conduisent à ce qu'une même relation existe sur les débits d'eau et également sur les valeurs de $\delta(t)$ avec des réponses impulsionnelles identiques. Pour des raisons pratiques, les relations envisagées sont du type convolution (réponse impulsionnelle unique moyenne des différentes réponses impulsionnelles intervenant dans les relations de superposition).

L'exemple proposé concernant un aquifère alimenté par les pluies montre que cette condition d'identité des réponses impulsionnelles (eau-tracer) peut être pratiquement réalisée dans le cas où cette dernière est schématisée par une forme exponentielle.

Ces bases étant posées, la question reste ouverte, d'une part, d'examiner les modes de détermination et éventuellement de combinaison des réponses impulsionnelles dans le cas des systèmes linéaires variant, et, d'autre part, d'évaluer l'incidence des méthodes dites de linéarisation appliquées aux systèmes non linéaires. Elles pourraient, dans certains cas, conduire à une redondance entre les informations fournies par les isotopes et celles qui peuvent être déduites des séries chronologiques des précipitations et des débits.

REFERENCES

ARTIFICIAL ISOTOPE APPLICATIONS

(Session VIII)
Chairman

E. ERIKSSON
Sweden
DISCHARGE MEASUREMENTS
OF THE RIVER RUFUII (TANZANIA)
USING ARTIFICAL TRITIUM

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Abstract

DISCHARGE MEASUREMENTS OF THE RIVER RUFUII (TANZANIA) USING
ARTIFICAL TRITIUM.

The use of chemical or radioactive tracers for measuring stream flow is now the established
method for discharges up to about 200 m$^3$/s. For larger flows and higher suspended load the
chemical tracers and also gamma-emitting radioactive tracers become cumbersome if not
impossible to use when good accuracy is required. Tritiated water proved to be a good and safe
tracer, provided care is taken in handling (no contamination of samples) and the experiments
are adequately planned (good estimation of mixing lengths, water velocity and sampling
duration). The paper describes discharge measurements performed in 1982 and 1983 in the
river Rufuii (Tanzania). Flow rates up to 2000 m$^3$/s have been measured, with estimated errors
varying between 2 and 4%. Because of high river turbulence in the measurement section, good
mixing has been observed over a distance of 7 km (this is much shorter than the distance
recommended by various formulae for calculating the mixing length). The problem of selecting
the mixing length is discussed and recommendations are given for planning future experiments.
Sample contamination as experienced during the first phase of measurements in the river
Rufuii is also treated. It is concluded that, technically and economically, the tritium tracer
method is feasible for calibrating rating curves (water stage/flow relationship) in turbulent
large rivers, also in remote areas.

INTRODUCTION

The use of chemical tracers for measuring stream flow is a well-known
technique for discharges up to 200 m$^3$/s. For larger flows, chemical tracers
become cumbersome and, when the suspended sediment load of the river is high,
these tracers cannot give reliable results since they are lost by adsorption on
sediment particles. In the case of fluorescent tracers, sunlight could also affect
the tracer concentrations. Thus, as indicated in an early assessment of the tracer methods in stream-flow measurements [1], tritiated water is probably the most convenient tracer for large flow rates since: (a) it does not interact with suspended sediment; (b) it is not unduly expensive; (c) it does not pose any serious handling and radiation exposure problems, provided storage, transport and especially injection procedures are adequate; and (d) it can be measured at very low concentrations and at reasonable cost. The successful application of tritium for discharge measurements up to 500 m$^3$/s on the river Tana in Kenya was reported in 1969 [2].

There are, however, some drawbacks in the use of tritiated water in stream-flow measurements: (a) the necessity of having the samples analysed in a laboratory, (b) possible harm to the environment, (c) high probability of contamination of samples when these are not stored and transported properly, and (d) difficulties of communication, and limitation of the injection and sampling locations when the mixing length exceeds several kilometres.

The experiments described in this paper were proposed by the Tanzanian hydrological organization Maji Ubungo in Dar-es-Salaam and the field activities were carried out by Tanzanian hydrologists in co-operation with the authors. The purpose of these experiments was to develop techniques and procedures for routine use of tritiated water for the calibration of the rating curve when the use of current meters is difficult because of flow velocities in excess of 5 m/s. When this is the case, tracer methods could be helpful because high flow velocities in general imply turbulence and thus favourable mixing conditions in the reach where measurements are planned.

DESCRIPTION OF THE RIVER REACH

The Rufiji river is one of the largest rivers in Africa. Its basin (180 000 km$^2$) covers a large portion of Central Tanzania. After collecting all its major tributaries, the river enters the Stiegler Gorge — named after a German explorer — a very narrow gorge barely 100 m wide with vertical cliffs at both banks for about 20 km (Fig. 1). The flow in this reach is very turbulent, even during the low flow season, and can be as high as 8000 m$^3$/s during exceptional floods.

Injection upstream of the water intake was not considered, although contamination of the borehole by tritiated water has a very low probability. For very large flow rates a location a few kilometres upstream of the intake (which is a borehole 50 m away from the river channel) can be chosen without risking adverse effects on the water supply to the Stiegler Gorge Safari Camp. There are two possible sampling locations, as shown in Fig. 1, namely the Kibesa stream gauging station and the Kidai Ferry cross-section. Downstream of Kidai Ferry, the Rufiji river enters an interior delta and splits into a number of tributaries. Thus, if
mixing of the tracer with the river water is not complete at the beginning of the delta, taking samples from tributaries is useless as no further mixing will occur downstream of that point.

MIXING LENGTH

In practice, the selection of injection and sampling points is limited because of several factors, such as contamination of water supplies, access to the sites, and existence of river tributaries and distributaries or diversions from the river. In the past, strong emphasis has been placed on the so-called mixing length formulae. It is easy to demonstrate that such formulae often have very limited use since it is not possible to take into account the large number of factors governing mixing in rivers. These are: presence and frequency of meanders, rapids, waterfalls; hydraulic roughness of the river channel; and channel geometry, i.e. significance of the flood channel with respect to the main channel. Unless these factors are included properly there is no way of developing a sensible and accurate mixing length formula or a mathematical model of the mixing process in a river. The solution to this problem, giving the minimum distance between the injection and sampling locations, is simple experimentation. A few 'blind' experiments will
clearly show the tracer pulse arrival and duration times; also, sampling at both banks or at two sites sufficiently apart on the same bank will determine whether or not tracer mixing with river water is satisfactory. In the case of instantaneous injection, if the tracer concentration time integral at both banks is within 5%, the mixing could be considered satisfactory. The discharge estimate will then be the mean value of the discharges calculated at both banks and the error will still be lower than the errors involved in most measurements made with conventional methods, such as slope/area or area/velocity methods. In the case of continuous injection the same applies to the tracer concentrations at both banks once the plateau of tracer concentration is reached at the sampling site. The minimum good mixing distance depends on the flow rates; the higher the discharge, the longer the mixing length. Thus, if there is good mixing at a location for a given flow rate this will apply a fortiori to lower discharges. It is important that, during the first tracer discharge measurement, mixing is checked for each sampling site; once this is known, there is no need to check the mixing during every discharge measurement.

Perhaps the most important shortcoming of the tritium tracer is the impossibility of measuring its activity at the gauging site. Unsuccessful experiments (due to contamination, due to the wrong sampling schedule or due to incomplete mixing) are identified only after sample measurements in the laboratory.

In the experiments described here, the location for tracer injection has been selected at the water intake; for sampling, Kibesa (7 km downstream) and Kidai Ferry (about 11.5 km downstream) have been selected as the only accessible places on the river bank. Between water intake and Kibesa there is a region of high turbulence due to rapids (Stiegler Gorge) which are favourable for fast tracer mixing. As shown later, the mixing distance of 7 km turned out to be sufficient for flow rates of up to about 1000 m$^3$/s; for a flow rate of 2000 m$^3$/s this distance was apparently too short.

HANDLING OF TRITIATED WATER

Glass ampoules with tritiated water are shipped by the producer in hermetic cans, wrapped in soft plastic material to prevent breaking of the ampoules during transport. It is important that the packages containing tritiated water ampoules are not stored below freezing temperature. The soft material used to wrap tritiated water ampoules may easily be contaminated with tritium. It is recommended to destroy such material by burning it in an open space and to rewrap the ampoules in a soft material to prevent contamination. In no case should tritiated water and the sampling ampoules or bottles be stored or transported together in a closed space, such as a store room, boxes or even a car. The failure of the tritium discharge measurements carried out in 1981 was at least partly due
to inadequate transport methods, which resulted in sample contamination. It is a
good precautionary measure to transport empty or full sampling bottles on the top
or in the front of the car transporting tritiated water, or in a separate car.

Injection of the tritiated water into the river is even more delicate. In past
experiments, the following methods were used: attaching a vial with tritiated
water to a stick and breaking the vial by hitting the stick on a rock and then
washing the tritiated water into the river; or breaking vials containing
tritiated water in a bucket filled with water and then emptying the bucket into
the river. Such methods are not only crude but could also create a radiation
hazard and lead to contamination of personnel and the environment.

In the experiments described in this paper a 2 m long pipe with an inside
diameter slightly larger than the diameter of the tritiated water ampoules and with
small perforations in the closed lower end was used for tracer injection. After
lowering the perforated end of the pipe into the river, a tritiated water ampoule
(or ampoules) was (were) dropped into the pipe and crushed with a piston,
together with another vial containing a concentrated fluorescence solution for
easy observation of the tracer cloud at the injection site.

The amount of injected tritium should be at least 1–2 Ci per 100 m³/s
of the estimated flow rate.

**SAMPLING PROCEDURES**

The sampling procedures are simple, but care must be exercised especially
under difficult field conditions. Obviously, there is no need for sophisticated
equipment such as pumps. Samples can be collected either by grabbing them
directly from the river or, if access is difficult, by using a line and a small heavy
metal cup attached to the end of the line. For the first experiments, sampling
could start at the same time as the injection of the tritiated water and could last
reasonably long to cover the tracer pulse. Analyses of the samples collected
during the first experiments will show the tracer arrival and tracer pulse duration
times for the discharge measured. Shorter times must be assumed for larger
discharges. It is probably reasonable to assume that tracer arrival and tracer
pulse duration times are both inversely proportional to the mean flow velocity
in the reach studied. The mean flow velocity in a given reach can be obtained
by dividing the distance between the injection and sampling sections by the tracer
pulse arrival time.

The sampling frequency is an important factor: the higher the frequency the
less is the estimate error of the time integral of the tracer concentrations in the
river. It appears that for routine discharge measurements there is no need for
more than twenty samples to cover the tracer pulse duration. This means that
about thirty samples must be collected so as to be sure to cover the whole period.
Sampling should be timed using prompting watches for the sampling periods instead of using ordinary watches or chronometers.

Full or empty sampling vials must be carried in proper cases, numbered and protected against water and friction, so that labels and pen marks remain intact. It is known from field work that proper packaging of equipment and water samples before and after the experiments saves a lot of confusion and eliminates sample contamination.

THEORY

The theory of tracer discharge measurements is based on the mass and tracer balance equations. In differential form, the tracer balance equation for any cross-section downstream of the injection point can be written as:

\[ dA = Q(x, t) \cdot C(x, t) \cdot dx \cdot dt \]

where \( dA \) is the amount of tracer crossing the fraction \( dx \) of the cross-section during the time period \( dt \). Integration of this equation with respect to \( x \) and \( t \) yields:

\[ A = \int_{0}^{L} \int_{0}^{T} Q(x, t) \cdot C(x, t) \cdot dx \cdot dt \]

If \( Q \) is not dependent on time and \( C \) is independent of \( x \), the equation simplifies to

\[ A = \int_{0}^{L} Q(x) \cdot dx \cdot \int_{0}^{T} C(t) \cdot dt \]

and finally to

\[ Q = \frac{A}{\int_{0}^{T} C(t) \cdot dt} \quad (1) \]
which gives the river discharge when the value of the tracer concentration integral is constant throughout the cross-section (instantaneous tracer concentrations at different subsections are generally not equal and do not have to be).

A conversion factor \( k \) must be introduced into Eq. (1) when tritium is used and its concentration expressed in TU:

\[
k = 3.193 \times 10^{-9} \text{ ((Ci/m}^3\text{) per TU)}
\]

If the tritium background concentration in the river water must be taken into account, the equation is:

\[
Q = \frac{A}{k \cdot \int_0^T C(t) \cdot dt - C_0 \cdot T}
\]

where \( C_0 \) is the background concentration.

The injected activity corresponds to the product of the amount of tritiated water injected, \( M \) (in grams), and its specific activity, \( A_s \) (in Ci/g).

\[
T
\]

The integral \( \int_0^T C(t) \cdot dt \) can be replaced by the product of the mean sample concentration (\( C \)) and the tracer pulse duration time (\( T \)).

The final equation which is used for calculation is:

\[
Q(\text{m}^3/\text{s}) = \frac{M(\text{g}) \cdot A_s(\text{Ci/g})}{3.193 \times 10^{-9}\text{((Ci/m}^3\text{) per TU)} \cdot (C - C_0)(\text{TU}) \cdot T(\text{s})}
\]

The mean tritium concentration in the tracer pulse is calculated from the data of individual samples which are contained in the tracer pulse duration time \( T \).

If the background concentration is not negligible compared with the tritium pulse concentrations, then the background concentration must be taken into account. Usually, the tracer pulse duration time \( T \) is related to the tracer arrival time \( t_a \) so that the tracer pulse duration time is one to two times the tracer arrival time.

The specific activity, \( A_s \), of the tritiated water is, in general, not known with sufficient accuracy; therefore, a small amount (e.g. 0.1 g) of an aliquot is usually requested from the producer of the tritiated water. This sample of aliquot is then carefully diluted in the laboratory (great care must be taken in order to avoid any contamination) and measured for accurate calculation of \( A_s \).
EXPERIMENTS

A total of six experiments were made to study the adequacy of the injection and sampling procedures, tracer mixing conditions, time of arrival of the tracer pulse and tracer pulse duration, and the logistics problems created by the lack of roads and tracks and by rainy weather.

In the beginning (first two experiments), because of lack of radiocommunication between the injection and sampling points, water sample collection at the downstream station (Kidai Ferry) lasted for too short a period. Figure 2 shows, as an example, the tracer curves from experiment 2. Later, good radiocommunication was established, which resulted in proper timing of sample collection. Figures 3 and 4 show tracer curves for experiments 3 and 4. Table I summarizes the results of experiments performed in 1982 and of two experiments made in spring 1983 by the Tanzanian team. Table II shows the values of tracer arrival time and tracer pulse duration.

The samples were measured by direct liquid scintillation counting using TRICARB 3255 and an Insta-gel cocktail. The accuracy of tritium determination in water samples was ±15 TU (1 σ), resulting in a determination error of the tracer integral of about 2%. The error in determining the injected activity was estimated to be 1.5 – 2%. Thus the error of flow-rate measurement could be about 2.5 – 3.0%, assuming good tracer mixing.
FIG. 3. Experiment 3 of 20 May 1982.

FIG. 4. Experiment 4 of 21 May 1982.
<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Date</th>
<th>Amount of Uptake (Ci)</th>
<th>Flow rate from rating curve (m³/s)</th>
<th>Flow rate measured (m³/s)</th>
<th>Kibrisa</th>
<th>Kilim</th>
<th>Left bank</th>
<th>Right bank</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>82-4-16</td>
<td>7.41</td>
<td>about 750</td>
<td>85.2</td>
<td>85.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>82-4-17</td>
<td>7.41</td>
<td>about 670</td>
<td>not sampled</td>
<td>1048</td>
<td>1002</td>
<td>995</td>
<td>1021</td>
</tr>
<tr>
<td>3</td>
<td>82-5-20</td>
<td>8.73</td>
<td>about 1000</td>
<td>not sampled</td>
<td>946</td>
<td>1936</td>
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<td>not sampled</td>
</tr>
<tr>
<td>4</td>
<td>82-5-21</td>
<td>12.46</td>
<td>about 950</td>
<td>946</td>
<td>946</td>
<td>1936</td>
<td>2045</td>
<td>1936</td>
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<tr>
<td>5</td>
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<td>about 1500</td>
<td>822</td>
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<td>83-4-22</td>
<td>8.22</td>
<td></td>
<td></td>
<td>822</td>
<td>822</td>
<td>822</td>
<td>822</td>
</tr>
<tr>
<td>Exp. No.</td>
<td>Flow rate (m³/s)</td>
<td>Kibesa</td>
<td>Kidai Ferry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Arrival time (min)</td>
<td>Pulse duration (min)</td>
<td>Arrival time (min)</td>
<td>Pulse duration (min)</td>
<td>Arrival time (min)</td>
<td>Pulse duration (min)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>~800</td>
<td>–</td>
<td>–</td>
<td>140</td>
<td>–</td>
<td>170</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>852</td>
<td>60</td>
<td>90</td>
<td>150</td>
<td>–</td>
<td>170</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1025</td>
<td>–</td>
<td>–</td>
<td>125</td>
<td>170</td>
<td>140</td>
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<td></td>
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<tr>
<td>4</td>
<td>1021</td>
<td>60</td>
<td>90</td>
<td>130</td>
<td>170</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>~1500 (?)</td>
<td>45</td>
<td>100</td>
<td>–</td>
<td>–</td>
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<tr>
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<td>45</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
</tbody>
</table>
DISCUSSION OF RESULTS

Because of the short sampling time the first experiment did not give an opportunity to estimate the discharge. However, the results clearly indicated the tracer arrival time and to some extent the arrival of the tracer peak at Kidai Ferry. The second experiment, which was made without knowing the results of the first one, covered the whole tracer pulse at Kibesa station. The calculated discharge was 852 m$^3$/s, compared with 666 m$^3$/s obtained from the rating curve for the same gauge height. This discrepancy is probably due to the change of the water stage/discharge relationship because of shifting of the low-flow controls at the reach studied, and not to incomplete tracer mixing, because later experiments showed that mixing at Kibesa station was satisfactory for larger discharges (about 1000 m$^3$/s).

The tracer pulse at Kidai Ferry proved to be covered only partially, but again information was obtained on tracer arrival and tracer peak arrival times, which helped to estimate the discharge in later experiments by increasing the duration of the sampling time.

The measurements of the samples collected during the third experiment, which were made after the results of the first two experiments were known, indicated that the tracer pulse at Kidai Ferry was completely covered. The calculated discharge was 1002 m$^3$/s for the right bank and 1048 m$^3$/s for the left bank, with a mean value of 1025 m$^3$/s and an error of 2.5%. This result compares favourably with the value of 993 m$^3$/s obtained from the rating curve for the same gauge height.

The fourth experiment was made one day after experiment 3. Because of an accidental failure of the electronic watch used at the right bank at Kidai Ferry the tracer curve constructed for this bank did not give reliable results. The discharge calculated using the concentrations of the samples collected at the left bank was 995 m$^3$/s. The estimate of the discharge from the samples collected at the right bank of Kibesa station was 1048 m$^3$/s. For the same gauge height the rating curve indicated a discharge of 940 m$^3$/s. These results should be considered satisfactory, in view of the following: The rating curve was developed using discharge data obtained from a rather turbulent river section over several years; the data may therefore not have been accurate enough for using them when the tritium measurements were made. Also, the mean gauge heights and the discharge were rated without considering the rise and fall of the water stage. It is well known that river discharge is higher during rising stages than during falling stages.

The mixing conditions at Kibesa station can be assumed to be satisfactory for discharges up to 1000 m$^3$/s. The last two experiments, for which high-flow-rate samples were collected only at Kibesa, show that tracer mixing at Kibesa is probably not sufficient for a flow rate of 1500 m$^3$/s because sampling at the bank opposite to that where injection was made systematically yielded higher discharge estimates.
CONCLUSIONS

The experiments, carried out by Tanzanian hydrologists in co-operation with IAEA experts in the field and in the laboratory, showed that tritiated water can be used by hydrological organizations in special cases of river discharge measurements for very high discharges in turbulent rivers. The tracer handling methods described in this paper are simple and adequate for such measurements. Mixing conditions, and tracer arrival and tracer pulse times have to be determined by experimentation rather than using formulae. Problems are related to logistics such as transport, access roads and travel in remote areas. The experiments showed, for example, that the use of a sturdy boat would eliminate many problems encountered in land transportation, such as flat tires, being stuck in ravines and in deep mud, and being unable to reach sampling stations on time.

Further experiments with low and high flow rates (above 1000 m$^3$/s) are necessary for checking the validity of the rating curve for present channel conditions. Obviously, Kidai Ferry must be used for sampling at higher flow rates, in spite of the difficult accessibility of this location, and the river must be sampled at both banks to check the mixing conditions at high discharges. If this is not done, there is no sound way of interpreting the results of the last two experiments.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the young hydrological staff of Maji Ubungo and to all technicians, drivers and gauge observers of the Maji Ubungo hydrological organization of Tanzania who performed the experiments under difficult field and weather conditions with dedication.

REFERENCES


TRACER AND MODEL STUDIES OF A RIVER AND AN ESTUARY

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Abstract

TRACER AND MODEL STUDIES OF A RIVER AND AN ESTUARY.

Radioisotope tracers and mathematical models are used to study transport properties and water quality in the Kymi river and in its estuary in southern Finland. The research area — 200 km² estuary and 75 km river section — is extensively loaded with industrial and municipal waste waters. Detailed information on dispersion and transport dynamics is gained by four independent tracer studies with 82Br. The results of one study are employed to fix model parameters while the other studies test model validity. In addition to tracer results, direct current recordings and water quality observations are compared with the model results. The river model computes the transport and dispersion of waste releases along the river section. It is used in the analysis of accidental releases which may result in drastic environmental effects. The estuary model computes water flow, transport and dispersion of waste components, as well as water quality distributions under the desired conditions as a function of location and time. Its results now serve as the basis for water quality planning and future management in the area. In general, the combined use of tracer and model techniques seems to be the most adequate approach towards solving the practical prediction problems. The model greatly improves the interpretation and significance of the tracer results while the tracer studies attach the model to reality.

1. INTRODUCTION

Reliable estimates of the effects of management alternatives are needed for proper planning of water use and protection needs. This is emphasized by the limited economic possibilities, the high degree of exploitation of water resources and the opposite forms of water use, e.g. water supply and waste water release. For management purposes the role of each pollution source must be determined separately.

Tracer studies are very appropriate for analyses of this kind [1, 2]. They are capable of determining the contribution of any specific source under prevailing flow conditions and of predicting the effects of changes in the discharge point and the discharge rate. In contrast, changes in the flow conditions — for instance as a result of dams, embankments or dredging — call for model description; these changes cannot be simulated by tracer studies alone [3].
FIG. 1. The research area in south-eastern Finland.

### TABLE I. WASTE LOADS OF THE KOTKA ESTUARY IN 1982

<table>
<thead>
<tr>
<th>Source</th>
<th>Water flow (m³/s)</th>
<th>BOD₇ᵃ</th>
<th>Total-Pᵇ (g/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kymi river</td>
<td>150–230</td>
<td>40</td>
<td>360</td>
</tr>
<tr>
<td>Pulp and paper industry</td>
<td>3</td>
<td>30</td>
<td>52</td>
</tr>
<tr>
<td>Other industry</td>
<td>0.02</td>
<td>2.5</td>
<td>1.4</td>
</tr>
<tr>
<td>City of Kotka</td>
<td>0.25</td>
<td>0.3</td>
<td>20</td>
</tr>
</tbody>
</table>

ᵃ Biological oxygen demand in 7 days.
ᵇ Total phosphorus.
In addition to flow conditions and bottom topography, the weather conditions and discharges can be freely selected in a model. This will improve the analysis of tracer results in unsteady situations and render the tracer studies significant under any weather conditions. On the other hand, models considerably benefit from the tracer results, in that detailed information regarding model parameters can be obtained and a rigorous comparison for model validity is possible.

Against this background, it is obvious that tracer and model studies do not replace each other but can support each other in many ways. In the present case study, radioisotope tracers are used because of their easy and sensitive detection, and mathematical models because of their flexibility and relative cheapness.

2. RESEARCH AREA AND PROBLEMS

The research area consists of a 75 km river section and an estuary of 200 km².

In the river studies, principal attention is paid to the most eastern fork of the Kymi river (Fig. 1) which discharges outside of the city of Kotka. The mean flow in the uniform upstream part of the river amounts to 280 m³/s, with an average variation of from 170 m³/s in winter or late summer to 410 m³/s in spring. The flow is controlled by several hydropower plants and in the most eastern fork it is almost constantly 95 m³/s. The average width of the river section is 180 m and its average depth is 4.7 m, with a mean flow rate.

The estuary area (Fig. 1), 14 km by 14 km, has a mean depth of 10.5 m and a maximum depth of 33 m. Its water surface amounts to 105 km².

Both the estuary and the river are extensively loaded with industrial and municipal waste waters (Table 1). For the purpose of regional water quality protection, the District Water Office of Kymi plans better ways of waste water discharge and treatment in the area. The river tracer and model studies aim at explaining the transport properties at different flow rates. The estuary studies aim at predicting the changes in the flow field and water quality distribution with different management alternatives. In addition to the tracer and model studies, water quality observations (twice a year) and water current measurements (at three points in the area) are available [4]. The river waste loads on the estuary are obtained from a separate one-dimensional water quality model not treated here [5].

3. TRACER STUDIES

3.1. Tracer method

The radioactive tracer $^{82}\text{Br}$ (half-life 36 h) is pumped into the river as a KBr solution at a hydropower plant where the concrete structures give protection
TABLE II. CHARACTERISTICS OF TRACER RELEASES

<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>Activity (GBq)</th>
<th>Duration (min)</th>
<th>Location (km)</th>
<th>River flow (m³/s)</th>
<th>Study area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15 Sep. 1980</td>
<td>75</td>
<td>10</td>
<td>42</td>
<td>290</td>
<td>River</td>
</tr>
<tr>
<td>2</td>
<td>16 Sep. 1980</td>
<td>75</td>
<td>10</td>
<td>74</td>
<td>290</td>
<td>River</td>
</tr>
<tr>
<td>3</td>
<td>8 July 1981</td>
<td>520</td>
<td>6</td>
<td>74</td>
<td>470</td>
<td>River</td>
</tr>
<tr>
<td>4</td>
<td>1 March 1982</td>
<td>520</td>
<td>14</td>
<td>5</td>
<td>(350)</td>
<td>Estuary</td>
</tr>
</tbody>
</table>

*a Distance from the river mouth.

against direct radiation and where the initial mixing is enhanced by high water turbulence. Thereafter, the transport and dilution of the tracer are measured (see Refs [1, 2])

- automatically at fixed locations
- by submerging the detector at different depths at the points of interest for short counting periods
- (in the summer) by hauling the detector at a fixed depth across the tracer cloud.

In the measurements, NaI(Tl) scintillation detectors (usually 1 in by 1 in, NEA) are used, together with a special portable analyser and recorder called TRACER¹. The ratio between count rate and concentration is about 0.6 counts/s per kBq/m³ (20 counts/s per μCi/m³) and the background radiation in water is about 0.3 counts/s.

3.2. Use of tracer results

The transport properties in the river were studied with three different tracer releases (Table II). Detailed information on local dynamics was gained in each of the experiments. The results of the third study were used to fix the model parameters, while the other two studies tested the model validity.

The transport in the estuary was studied with a similar release at the most eastern river fork. With its flow rate of 95 m³/s, the tracer was carried to the estuary in 7 – 8 hours. The results were used to test the assumptions on the vertical flow structure, the dispersion dynamics and the model validity in the area.

¹ Manufactured by Outokumpu Oy Co., Finland.
4. RIVER MODEL

4.1. River transport model

The river section is subdivided into 23 segments, with relatively constant properties in each of them. Their length varies from 0.7 to 10.2 km, their width from 40 to 500 m and the depth from 1.6 to 7.7 m. The flow distribution at bifurcations is determined by rating curves, which also indicate the changes in water depth at different flow rates.

The flow and dispersion within each segment are assumed to be constant; this enables an analytical solution of the impulse response:

\[
g_i(t) = \frac{Pe}{\sqrt{4\pi t \cdot \tau}} \exp\left[-\frac{Pe}{4\tau} (\tau - t)^2\right]
\]

(1)

where \( t \) is time, \( \tau = V_i/Q_i \), \( Pe = Q_i \cdot \Delta s_i^2/(V_i \cdot D_i) \) is the Peclet number, \( Q_i \) is water flow through segment \( i \), \( V_i \) is water volume in segment \( i \), and \( \Delta s_i \) is length of segment \( i \) (\( i = 1, 2, \ldots, 23 \)).

Within each segment the longitudinal dispersion coefficient \( D_i \) is assumed to be proportional to the flow velocity \( u_i \) and the depth \( H_i \) [6]:

\[
D_i = \delta \cdot u_i \cdot H_i
\]

(2)

The transport of an arbitrary input pulse \( C_{i-1}(t) \) through segment \( i \) is then determined by its convolution integral with the impulse response \( g_i \)

\[
C_i(t) = \sum_{j=1}^{n} C_{i-1}(t - (j - \frac{1}{2}) \Delta t) \cdot g_i((j - \frac{1}{2}) \Delta t) \cdot \Delta t
\]

(3)

where \( \Delta t \) is the time step of the numerical solution, \( t = (n - \frac{1}{2}) \cdot \Delta t \) is time, and \( C_i(t) \) is concentration at time \( t \) at the end of segment \( i \).

The analytical solution is started at the point of injection \( i = i_0 \). Thereafter, the concentrations \( C_{i_0+1}, C_{i_0+2}, \ldots \) up to the river mouth \( C_{23} \) are computed. The accuracy of the input data is maintained, since the numerical dispersion is totally eliminated by the analytical solution of the impulse response (1).

4.2. River model computations

The time step is selected so as to equal the period of tracer injection (Table II), viz. \( \Delta t = 0.1 \) and 0.17 hours. The proportionality \( \delta = 20 \) is suggested by the
FIG. 2. Model calibration (a) and validation (b, c) in the Kymi river: measured (solid line) and model (broken line) tracer responses at different locations (distance from injection indicated above the lines).
results of the third tracer study (Fig. 2(a)). The other tracer studies with different flow rates confirm the model validity (Fig. 2(b, c)).

After validation, the river model is used to determine the waste concentrations from releases of different duration from different locations and at different flow rates. The results have been of use, for instance, in specifying the amount and origin of accidental waste releases which have resulted in fish deaths.

5. ESTUARY MODEL

5.1. Flow-field model

In the estuary the research area is subdivided into equidistant rectangular grids (Fig. 3) with grid spacing $\Delta x = \Delta y = 720$ m and dimensions 19 by 19 squares. The depth of each grid square is taken from a map, and the water motion and the surface elevation in each square are determined by means of the flow model [7]. This takes into account winds, river flows, boundary flows and their balance with accelerative and frictional forces (Reynold’s equation of motion) as well as the imperishability of water (the continuity equation).

The vertical stratification in the estuary is measured as being relatively constant. Within $2 - 3$ km from the river mouths, fresh water is observed from the surface to the bottom; along the next two kilometres, strong vertical mixing takes place, and outside this area a surface layer of $5$ m is typically observed. The waste waters move mainly in the surface layer and therefore the model deals only with this. The surface-layer flow is increased by vertical mixing by a factor of 2.2 as compared with river discharge. Simultaneously, the friction between the water layers is increased from $0.3$ mm/s to $17$ mm/s at six specific grid squares ($n = 15, 14, 13; m = 5, 9$; the grid index $n$ increases from the open sea to the coast and the index $m$ increases from west to east).

The time-step of the flow-field solution is $\Delta t = 20$ s, the horizontal eddy viscosity $\nu = 10$ m$^2$/s, the wind friction in the summer $\lambda = 1.6 \times 10^{-6}$, and non-linear advective terms are taken into consideration.

The currents observed are adequately explained by river flow and winds in the summer but not by sea-level variations. Consequently, the latter are excluded from the model applications, and the currents in the model area boundary are extrapolated from those generated at the interior of the model area.

5.2. Water quality and transport model

Changes in the water quality components are also determined in the grid of Fig. 3. The major part of the waste waters is mixed into a layer of $3$ m. Because of the vertical velocity profile, this layer moves about 1.65 times as fast as the
FIG. 3. Model flow field in the Kotka estuary surface layer (0–5 m), winter 1982. Comparison with observations (circled) at straits A, B and C.

5 m surface layer simulated with the flow model. In addition to discharge and advective motion, the waste waters are mixed by turbulence and shear effects. These are described by means of the dispersion coefficient $D = 0.7 \text{ m}^2/\text{s}$.

River and waste waters and their effects on the water quality are simulated in the model, taking into consideration a radioisotope tracer ($^{82}\text{Br}$), electric
conductivity, sodium-lignosulphonate (NaLS), biological oxygen demand (BOD),
oxogen (O₂) and total phosphorus (tot-P). Their changes and reactions during
tracer transport are computed by the water quality model [4, 8]. Within the
temperature range T_ref = 2 – 18°C (winter/summer), the most important para-
ters varied as follows: BOD decay rate k₁ = 0.01 – 0.3 d⁻¹, BOD settling rate
k₂ = 0.01 – 0.3 m/d, NaLS decay rate k₃ = 0.015 – 0.05 (mg/L)⁻¹·d⁻¹, phosphorus
settling rate k₄ = 0.1 – 0.3 m·d⁻¹·(mg/L)⁻¹, aeration coefficient k₅ = 0 (ice
cover) to 0.086 m/d and saturation content of oxygen O_sat = 13.8 – 9.4 mg/L.

The time-step for dispersion and water quality reactions is Δt_d = 45 min.
Discharge and advective motion are simulated with their own time-step Δtₚ \leq Δt_d.
Its value is determined by the stability conditions of explicit upwind algorithm.
It changes with changes in the flow field induced by weather conditions, which
are observed every three hours. As large a time-step as possible is used in order
to reduce the numerical dispersion and to minimize the computation costs.

On the open-sea boundaries the exponential extrapolation from the interior
and the external background concentration are weighted as 0.8 : 0.2.

5.3. Comparison with observations

Both horizontal and vertical tracer distribution during the experiment (No. 4 in
Table II) is relatively similar to the corresponding model results. However, the
observations manifest more irregularities than the model. This is easy to understand,
since in reality the tracer transport is subject to short-term fluctuations, sharp
wedges of flow, casual eddies and rapid variations in the weather, while in the
model an assumed constant surface layer (3 – 5 m), grid square averaging (720 m
by 720 m), finite time-stepping (about 10 – 45 min) and three-hourly weather
periods (constant conditions below the ice cover) smooth out many of the irregu-
larities.

This is clearly shown by the tracer responses (Fig. 4) which were continuously
measured at the automatic counting stations close to the location of the recording
current meters (Fig. 3). Particularly in straits A and C a strong back and forth
motion considerably increased the response. In strait B the flow was more stable
and the observation and model results were almost identical. Integration of the
model responses results in dilution ratios for continuous discharge under average
flow conditions: 0.9 at point A, 0.4 at B and 0.2 at C – in agreement with the
conductivity observations. Half of the river water is conveyed through strait B
and half through strait A.

In 1977, 1980 and 1982 the water quality in the estuary was observed once
in the winter and once in the summer. The results of 1980 were used to fix
the model parameters, whereupon the model validity was tested with the results
of 1977 and 1982. As an example, the agreement between the measured and the
model values for oxygen and sodium-lignosulphonate content is shown in Fig. 5.
FIG. 4. Measured (solid line) and model (broken line) tracer responses at straits A, B and C (Fig. 3) in the estuary.

5.4. Estuary predictions

The water quality in the estuary can be improved, for instance, by decreasing the waste loads, by changing the location and timing of waste releases, and by changing the flow conditions by means of dams, embankments, dredging or pumping. The BOD load can be reduced to 20% of the present level by biological treatment of the industrial waste waters. With the present technology, this may increase the phosphorus load while the NaLS releases remain unchanged. Important recreation and fishing areas in the eastern part of the estuary can be protected in the winter by a dam in strait A. In the summer a small opening for shipping must be left there.
FIG. 5. Measured (dark column) and model (open column) oxygen ($O_2$) and sodium-lignosulphonate (NaLS) content in the estuary surface layer (0–3 m) in winter 1982.

The river flow is a considerable source of loading of the estuary, but it also dilutes the waste releases into the estuary. Therefore, predictions are made for two different river flow rates, 120 m$^3$/s and 300 m$^3$/s. The low-flow situation appears to be the more critical. Figure 6 gives a comparison between some alternatives in the winter. The distribution of industrial waste waters — indicated by sodium-lignosulphonate (Fig. 6(b)) — is considerably changed by the closure of strait A. Oxygen concentrations (Fig. 6(a)), however, show that the decreased load is compensated by the decreased dilution and water exchange in the eastern areas near the coast.

A host of similar comparisons serve now as the basis for water quality planning and future management in the area. In summer, the phosphorus concentrations are also of importance, and several time-dependent wind situations are considered.

6. CONCLUSIONS

The combined use of radioisotope tracers and mathematical models has proved to be very successful in studies of surface water transport and water quality. Both methods as such are useful tools for the solution of practical prediction problems,
FIG. 6. Model oxygen ($O_2$) and sodium-ignosulphonate ($NaLS$) content in the estuary surface layer (0–3 m) with different management alternatives (winter, river flow rate 120 m$^3$/s).

but their special merits can best be utilized when close co-ordination between them is established.

It is characteristic of tracer techniques that they truly indicate real situations. They take into account all the processes occurring in reality. Mathematical models, however, describe only those processes which are intentionally included therein. It is advisable to make the model as simple as possible, without damaging its prediction ability. The tracer results are of assistance in the selection of the model structure needed. Furthermore, the resolution of a numerical model is limited by grid spacing and time-step. Small-scale and short-term effects are described by model parameters which can be estimated from tracer results. Finally, the tracer results are the most sensitive data for testing the validity of a transport model, since, for instance, water quality data are the result of long-term data accumulation, smoothing out local and temporal differences.

Model applications, however, are not limited to the existing weather conditions, to the existing bottom topography, or to the tracers available or their detection sensitivities. Any factors and properties important in reality can be included in a mathematical model. Changes in flow conditions and bottom geometry are predicted by the flow-field model. The external model conditions, such as the
weather, can be freely selected. They can also be time-dependent, thus superseding
the assumption of a steady state which considerably limits the analysis of tracer
results [3]. Finally, the repetition of model 'experiments' under different weather
conditions, with changed load or with alternative loading points is usually very
cheap.

The insight into reality can still be supplemented by the results of other field
observations, like direct current recordings and water quality sampling.

In conclusion, the main contribution of tracer studies lies in

- the selection of the model structure
- the estimation of the model parameters
- the detailed test for model validity.

The task of mathematical models includes

- the explanation of the tracer results (also under unsteady conditions)
- the generalization of the tracer results so that they apply to the desired weather
and flow conditions
- the generalization of the tracer results so that they apply to the desired
quantities directly indicating the water quality and the usability of water
- the prediction of the effects of planned changes in load, discharge point,
bottom geometry, etc.

The mathematical model can also include direct economic and social indicators
and optimization procedures.

The next step in the co-ordination of tracer and model studies may be
their simultaneous use, i.e. location and timing of field observations according
to a real-time simulation of a tracer experiment. If the costs of field work can
thus be reduced, the demand for tracer studies will certainly be stimulated.

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SORPTION METHOD FOR LEAKAGE LOCALIZATION IN WATER RESERVOIRS OF HYDROTECHNICAL PLANTS

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Abstract

SORPTION METHOD FOR LEAKAGE LOCALIZATION IN WATER RESERVOIRS OF HYDROTECHNICAL PLANTS.

Two technical variants of the radiotracer sorption method for leakage localization in large water reservoirs have been developed. The first version is usually applied for checking the tightness of the reservoir bottom, the second for localizing leakages through screens of dams and embankments. The method described consists of the application of radiotracer possessing good sorptive characteristics with respect to typical materials, such as soil, concrete and asphalt/concrete. The method and apparatus proposed have been applied successfully for bottom leakage localization in a large water reservoir in Przeczyce, for checking the tightness of the expansion joints of the concrete dam elements in Wisła-Czarne, and for checking the effectiveness of reconstruction work carried out on the asphalt/concrete screen of the upper reservoir of the hydroelectric power plant in Żarnowiec.

INTRODUCTION

Water may escape from hydroengineering systems through leaks in certain parts. This has become a serious problem for large water reservoirs of hydroelectric power plants with regard to safety and economics.

Engineering activities undertaken for sealing up a dam, reservoir bottom or embankment should always be preceded by a careful localization of leaks and an estimate of their dimensions. The investigations following maintenance and reconstruction should, in turn, enable an estimate of the effectiveness of such activities by assessing the tightness of the water storage system.

Makowski [1] and Guizerix et al. [2] describe two basic variants of the radiotracer method of leakage localization in large water reservoirs. The first variant consists of investigating the distribution of the tracer cloud activity over the bottom. In the second method, the radioactive tracer is introduced into the

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FIG. 1. Scheme of the tracer cloud and distribution of radioactivity adsorbed on the reservoir bottom.
water and then permanently adsorbed onto the surface of the investigated material at the leakage place.

We have developed the sorption method in our Department during the last few years. In our opinion, this method has some remarkable advantages compared with the tracer cloud investigation. The advantages are as follows:

(a) Possibility of direct measurement of the radioactivity adsorbed by the material around the leak. This enables a more precise determination of the leakage position and the sorptive surface area, and becomes particularly important when testing the tightness of dam screens.

(b) Facility of distinguishing leaking places from places of increased filtration through the bed material.

(c) Possibility of delayed measurements with respect to the time of dosing (for instance on the next day, when $^{198}$Au is used as a tracer).

Figure 1 shows the principle of the method. Radioactive tracer is introduced in the form of a cloud at a constant distance from the bottom and can be adsorbed permanently onto the material of the examined bottom surface, dam screen, etc. The vertical component of the water velocity towards the leak causes the tracer to travel from the cloud and to be adsorbed at the leaking place. Radioactive stains thus formed in the examined region are then localized by means of a specially designed detecting device which is drawn along the bed.

A number of radioisotopes have been examined under laboratory conditions. The best sorption characteristics with respect to typical materials, such as sand, crushed stone aggregate, concrete or asphalt/concrete, were found for the following radionuclides:

- Indium-113m obtained from a $^{113}$Sn/$^{113m}$In high-activity generator, in the form of an aqueous solution of InCl$_3$
- Gold-198 in the form of a colloidal gold or chloroauric acid solution.

An activity of ~10 MBq was sufficient for 1 m length of the investigated section.

The method has been worked out in two different technical variants. The first aims at localizing leakages through bottoms of large water reservoirs, the second is used for checking the tightness of dam screens, embankments and other hydro-engineering constructions.

LOCALIZATION OF LEAKAGES THROUGH THE BOTTOM OF A WATER RESERVOIR

Bottom leakages of reservoirs were localized in different regions of the impounding reservoir in Przeczyce (Silesia district). Portions of active $^{113m}$In were injected at certain points of the reservoir, along a cross-section marked by
lines of buoys. The injection device was placed on the specially designed 'sledge' shown in Fig.2.

The initial dimensions of the tracer cloud during a single travel of the sledge were 300 m × 4 m. After a certain time interval (approximately 1 hour for $^{113m}\text{In}$, having a half-life of 100 min), a sledge carrying the measuring gear was towed along the dosing line. The measuring apparatus (Fig.3) consisted of four scintillation detectors connected with a counter/recorder field system placed on a hauling boat.
The positions of the sledge were marked by buoys visible on the surface. Two theodolites placed on the top of the dam were precisely aimed at a buoy by means of telescopic viewfinders provided with cross-hairs. This was done continuously during the whole measurement cycle. A permanent radiocontact was maintained between the crew of the boat and the position-checking staff. When an activity peak appeared on the recorder, a signal was given from the boat and the position of the boat was carefully recorded by taking the theodolite reading of the intersection angle.

Figure 4 shows examples of 'radioactivity spectra' of the bottom surface. Distinct, sharp activity peaks undoubtedly indicated leakage places. Wide, weakly marked maxima of the curve indicate increased filtration through large areas of the bottom surface.
LOCALIZATION OF LEAKAGES THROUGH EMBANKMENTS AND DAM SCREENS

Investigations of such defects were carried out in Wisła-Czarne in order to detect leakages through a certain part of the dam, and in the Żarnowiec hydroelectric power plant in order to localize leakages in the screen of the upper reservoir after reconstruction work.

In these experiments, $^{113m}$In and $^{198}$Au radiotracers were used. The dosing device and the measuring apparatus, similar to those shown in Figs 2 and 3, were placed on trolleys and towed along the screen surface with a distance-marked rope reeling off a winding drum. In Wisła-Czarne the trolleys travelled along subsequent expansion joints of the dam screen; in Żarnowiec the trolleys were towed along profiles marked every two metres. Examples of the radioactivity curves recorded are shown in Figs 5 and 6.
FIG. 6. Examples of radioactivity distribution along measuring profiles (Żarnowiec hydro-electric power plant).
FIG. 7. Map of leakages for a part of the bottom of the artificial water reservoir in Żarnowiec.

The measuring device was towed at a constant velocity along the profiles. On the activity diagram plotted by the recorder, points were marked at every two metres subsequent to the starting point. Such a procedure allowed leakages to be localized with approximately ±10 cm accuracy. The 'activity spectra' obtained were then normalized relative to the background pulse rate, according to the function

$$\frac{N - N_0}{N_1 - N_0} = f(1)$$
where N is the recorded bottom activity at a given point of the profile examined, N₀ is the background pulse rate recorded under water before introducing the radiotracer, N₁ is the background pulse rate in the examined profile during the experiment, coming from the tracer dispersed in the water, and l is the distance from the starting point of detection.

The presentation of the results allows the relative intensity of all detected leakages to be compared. On the basis of the results obtained, a map of the leakages occurring in the examined region can be drawn, also taking into account their relative intensities (Fig. 7). The amplitude of the recorded activity peaks is related to the leakage intensity. In this way it is possible to quantitatively estimate the observed phenomena.

So far, a method of quantitative determination of leakage intensity has not been developed. It is certain that the development and adoption of such a method would be advantageous in hydroengineering practice, since it would provide additional data for assessing the security of hydroengineering objects.

Recently, a physical model for simulating leakages of known intensity has been designed. We hope that systematic model experiments will soon permit the relation between the leakage intensity and the recorded peak amplitude of the tracer activity to be obtained. The mathematical relationship obtained on the basis of such experiments should enable a quantitative interpretation of the field experiment results.

REFERENCES


MÉTHODES DE TRAÇAGE RADIOACTIF POUR MESURER DE TRES FAIBLES VITESSES DE FILTRATION DANS UN FORAGE PROFOND ET POUR DETERMINER LA FISSURATION DE LA ROCHE

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Abstract—Résumé

MÉTHODES DE TRAÇAGE RADIOACTIF POUR MESURER DE TRES FAIBLES VITESSES DE FILTRATION DANS UN FORAGE PROFOND ET POUR DETERMINER LA FISSURATION DE LA ROCHE.

Deux méthodes d'investigation par radiotraceurs artificiels sont décrites. La première permet de réaliser des mesures de très faibles vitesses horizontales de filtration dans un forage très profond (1000 m) et de faible diamètre (10 cm). Elle exploite les variations de masse, dans le temps, d'un traceur injecté dans le forage. La seconde permet de déterminer le degré de fissuration de la roche en place dans un massif rocheux à partir d'un forage de faible diamètre. Elle exploite l'information fournie par un radiotraceur fixé sur une résine échangeuse d'ions qui est retenue dans les fissures.

RADIOACTIVE TRACER METHODS AS APPLIED TO THE MEASUREMENT OF VERY LOW FILTRATION RATES IN DEEP BOREHOLES AND TO THE DETERMINATION OF FISSURING IN ROCKS.

Two methods of investigation using artificial radioactive tracers are described. The first method can be applied for measuring very low horizontal filtration rates in very deep boreholes (1000 m) of small diameter (10 cm). It makes use of the variations in time in the mass of a tracer injected into the borehole. By the second method it is possible to determine the degree of fissuring in a rock mass in situ through a small-diameter borehole on the basis of the data yielded by a radioactive tracer fixed in an ion-exchange resin, which remains in the fissures.

1. INTRODUCTION

Deux méthodes d'investigation en milieu souterrain, aisément mises en œuvre à grande profondeur à partir d'un forage unique et de faible diamètre, ont été développées par la Section d'application des traceurs (SAT) du Centre
d'études nucléaires de Grenoble en collaboration avec le Professeur Tazioli de l'Université d'Ancône (Italie).

Toutes deux utilisent un radiotracer. L'une permet de mesurer de très faibles vitesses horizontales apparentes même en présence de courants verticaux, l'autre permet d'identifier et de localiser avec précision les fissures d'une roche en place, même si elles sont étroites, et d'évaluer leur ouverture et leur extension en profondeur.

2. METHODE DE MESURE DES VITESSES HORIZONTALES DE FILTRATION UTILISABLE DANS UN FORAGE PROFOND

2.1. Rappels sur les méthodes classiques de mesure des vitesses horizontales de filtration d'une nappe

La mesure par radiotracer des vitesses horizontales de filtration des nappes à partir d'un forage équipé d'un tube crénéné s'est particulièrement développée au cours des années 1960, avec la réalisation de nombreux appareils (rhéomètres) qui nécessitaient la délimitation d'une «chambre de mesure» dans le forage, au droit de la portion étudiée [1–3].

Dans les années 1970, appelés à effectuer des mesures à grande profondeur, et pour pallier les inconvénients inhérents à ce confinement, certains expérimentateurs ont réalisé des mesures relatives des vitesses horizontales de filtration rencontrées sur tout ou partie de la hauteur noyée d'un forage en supprimant l'aménagement d'une «chambre de mesure» [4].

Au début des années 1980, pour répondre à une demande croissante de mesures à grande profondeur, le Service d'application des traceurs a conçu et expérimenté une méthode de détermination des vitesses horizontales de filtration permettant d'atteindre de très faibles vitesses dans des forages très profonds. Cette méthode ne présente pas les inconvénients des procédés précédents tout en reposant sur le même principe de base qui consiste à observer la disparition progressive d'un traceur entraîné par l'écoulement de la nappe.

2.1.1. Mesure de la vitesse horizontale de filtration dans une chambre de mesure

2.1.1.1. Principe de la mesure

Le procédé consiste à enregistrer la fonction concentration-temps $C(t)$ de disparition du traceur injecté dans une «chambre de mesure» délimitée par deux obturateurs généralement pneumatiques. Lorsque l'eau contenue dans cette chambre est constamment homogénéisée, la fonction observée de disparition
progressive du traceur présente, après une période transitoire, une allure exponentielle dont l'argument est déterminé soit graphiquement par tracé sur un diagramme semi-logarithmique, soit par régression linéaire à partir des valeurs logarithmiques des concentrations (figure 1).

La vitesse de filtration est alors donnée par la relation

\[ V_f = \frac{\pi R^2}{2e} \cdot \frac{1}{\Delta t} \cdot \frac{\ln \frac{C(t_0)}{C(t)}}{\ln \frac{C(t_0)}{C(t)}} \]  

où:
R: rayon du forage
\( e \): coefficient caractérisant la largeur de l'écoulement intercepté par le forage \( (0 < e < 2) \)
\( \Delta t \): temps écoulé entre \( t_0 \) et \( t \): \( \Delta t = t - t_0 \)
\( C(t_0) \): concentration origine prise au temps \( t_0 \) sur la partie exponentielle de la courbe
\( C(t) \): une concentration plus faible prise au temps \( t \) sur la même courbe.

Lorsque le traceur utilisé est un élément radioactif, la mesure ne donne pas directement des concentrations mais des taux de comptage \( N(t_0) \) et \( N(t) \) qui leur sont proportionnels. Le coefficient de proportionnalité, qui dépend de l'étalonnage de la sonde de détection, demeure constant durant tout l'essai et disparait donc du rapport \( \frac{C(t_0)}{C(t)} \).
2.1.1.2. Inconvénients de ce procédé

La mesure peut être influencée par de nombreux petits effets parasites décrits par Moser [2]. Il convient de citer:
– les effets de l’agitation qui contribue à accélérer la sortie du traceur de la chambre de mesure;
– l’accroissement de la vitesse horizontale de l’eau au niveau de la chambre de mesure, provoqué par la présence des deux obturateurs qui resserrent les filets d’écoulement;
– la présence de courants verticaux qui s’établissent à l’extérieur du tube créné, soit naturellement, soit par le fait des courants de densité ou de convection thermique dans les forages profonds.

Outre l’alimentation électrique du détecteur, de l’injecteur et du dispositif d’homogénéisation, ce procédé nécessite une commande pneumatique des obturateurs qui l’alourdit notablement lorsque le forage atteint 50 ou 100 m et le rend pratiquement inutilisable lorsqu’il dépasse 200 m.

2.1.2. Mesure de la vitesse horizontale de filtration sans chambre de mesure (mesures relatives)

2.1.2.1. Principe de la mesure

Le procédé consiste à injecter un radiotraceur d’une manière homogène, sur toute la hauteur noyée du forage, à l’aide d’un injecteur continu remonté à vitesse constante.

La fonction taux de comptage — hauteur est ensuite enregistrée au cours de plusieurs explorations successives réalisées aux temps t₀, t₁, t₂, ..., tₙ.

Ces explorations sont effectuées avec un détecteur nucléaire déplacé sur toute la hauteur de la zone marquée du forage à une vitesse constante assez lente pour ne pas perturber la distribution du traceur.

La méthode de calcul précédente est alors appliquée à la variation, en fonction du temps, du taux de comptage observé à une cote donnée [4].

La répétition de ce calcul à différentes cotes permet d’obtenir un profil vertical des vitesses horizontales sur toute la hauteur noyée du forage (figure 2).

2.1.2.2. Inconvénients de ce procédé

Ce procédé devient rapidement inutilisable lorsque le nuage de traceur subit un déplacement vertical. Ce déplacement peut être causé:
– par l’étalonnage vertical du nuage à la suite de l’entraînement du traceur par le passage de la sonde et de son câble porteur au fur et à mesure des explorations;
FIG. 2. Mesures relatives des vitesses horizontales de filtration.

— par la présence de courants verticaux dus par exemple à des mouvements convectifs de l'eau ou au court-circuit provoqué par le forage entre deux nappes circulant à des niveaux différents.
La méthode de mesure que nous présentons élimine ces inconvénients.

2.2. Mesure des faibles vitesses horizontales de filtration à grande profondeur

La méthode mise au point par la Section d'application des traceurs de Grenoble, en collaboration avec le Professeur Tazioli, permet de mesurer de très faibles vitesses horizontales de filtration dans des forages de grande profondeur et d'un diamètre de l'ordre de 7 cm. Sa mise en œuvre est simple bien que nécessitant un matériel adapté.

2.2.1. Principe de la mesure

La méthode proposée ne change pas fondamentalement le principe et le mode de calcul de la vitesse horizontale de filtration. Sa particularité réside dans l'acquisition d'un rapport de masse similaire au rapport $C(t_0)/C(t)$ de la relation (1), c'est-à-dire l'évaluation du volume d'eau renouvelé dans le forage en cours de mesure.
L'absence d'obturateurs n'empêchant pas une déformation verticale du nuage de traceur, l'information est donnée par la diminution, en fonction du temps, de la quantité de radioactivité injectée dans le forage. Cette quantité
est proportionnelle à l'intégrale de la fonction taux de comptage — hauteur que l'on enregistre lors d'une exploration du forage avec un détecteur nucléaire.

A la suite d'une injection de traceur, une série d'exploration du nuage marqué permet d'enregistrer les fonctions taux de comptage — hauteur à des dates \( t_0, t_1, t_2, \ldots, t_n \) successives. Après correction de la décroissance nucléaire du traceur et du bruit de fond naturel, l'intégrale de ces fonctions suit statistiquement une loi exponentielle décroissante dont l'argument permet de calculer les valeurs \( A(t_0) \) et \( A(t) \) de la relation (1) modifiée comme suit:

\[
Vf = \frac{\pi R}{2e} \cdot \frac{1}{\Delta t} \cdot \ln \left( \frac{A(t_0)}{A(t)} \right)
\]

Dans cette relation:

\[
\begin{aligned}
A(t_0) &= K \int_{H_1}^{H_2} \left[ N(h,t_0) - b(h,0) \right] dh \\
A(t) &= K \int_{H_1}^{H_2} \left[ N(h,t) - b(h,t) \right] dh
\end{aligned}
\]

\( A(t_0) \) est la quantité de radioactivité présente dans le forage au temps \( t_0 \).
Cette valeur est proportionnelle à l'intégrale de la différence entre la fonction taux de comptage — hauteur \( N(h,t_0) \) enregistrée au temps \( t_0 \) et la fonction taux de comptage — hauteur \( b(h,0) \) du bruit de fond enregistrée initialement.

Les deux fonctions sont définies entre les cotes minimale et maximale, \( H_1 \) et \( H_2 \), encadrant largement les cotes extrêmes atteintes entre le début et la fin de l'expérimentation. \( K \) est le coefficient d'étalonnage de la sonde de détection. Il permet de transformer les taux de comptage en quantité de radioactivité; il s'élime dans le quotient \( A(t_0)/A(t) \).

\[
\begin{aligned}
H_2
A(t) &= K \int_{H_1}^{H_2} \left[ N(h,t) - b(h,t) \right] dh
\end{aligned}
\]

De même, \( A(t) \) est la quantité de radioactivité présente dans le forage au temps \( t \). Cette valeur est proportionnelle à l'intégrale de la différence entre la fonction taux de comptage — hauteur enregistrée au temps \( t \), corrigée de la décroissance nucléaire subie par le radiotracer pendant le temps \( \Delta t = t - t_0 \) et la fonction taux de comptage — hauteur \( b(h,t) \) du bruit de fond à la date \( t \).

Généralement, le bruit de fond ne varie pas et \( b(h,0) = b(h,1) \). Cependant, une correction peut être envisagée si une évolution progressive a été remarquée lors des explorations préliminaires.
2.2.2. *Avantages de la méthode*

Dans la méthode proposée, toutes les contraintes mécaniques et les effets parasites inhérents aux procédés précédents sont éliminés.

Les déplacements verticaux de la sonde de mesure sont généralement suffisants pour assurer l'homogénéisation radiale du traceur dans les faibles diamètres de forage rencontrés à grande profondeur.

En l'absence de courant vertical, un étalement vertical du nuage de traceur est observé. Cet étalement provoqué par les passages répétés de la sonde de mesure et par la dispersion naturelle ou convective de l'eau ne perturbe pas la mesure de la vitesse horizontale de filtration. Toutefois, cet élargissement du nuage augmente la hauteur sur laquelle est calculée cette vitesse (figure 3).

En présence d'un courant vertical modéré, la vitesse horizontale de filtration n'est pas perturbée si la durée d'une exploration du nuage de traceur demeure faible devant son déplacement vertical.

Une même injection permet alors de mesurer simultanément les deux vitesses. La vitesse verticale est alors calculée en suivant l'évolution dans le temps du centre de gravité des fonctions taux de comptage — hauteur enregistrées pour la détermination de la vitesse horizontale (figure 4).

Lorsque la vitesse verticale rencontre dans le forage devient supérieure à environ mille fois celle de l'écoulement horizontal de filtration, cette dernière devient impossible à mesurer. La méthode peut alors être utilisée pour mesurer la vitesse verticale.

2.2.3. *Appareillage nécessaire à la mesure*

Dans ce procédé, l'injection du traceur et le suivi de l'évolution du nuage marqué sont réalisés à l'aide de deux outils solides ou non d'un même câble: l'injecteur et la sonde de mesure.

2.2.3.1. Injection du traceur

L'injecteur est un appareil constitué d'un réservoir de traceur radioactif dont le contenu peut être injecté en une seule fois ou par petites fractions au moyen d'un dispositif de commande installé en surface.

Lorsque l'appareil est remonté avec une vitesse constante, il est possible de réaliser une injection linéaire ou un chapelet de petites injections successives sur une hauteur déterminée.

2.2.3.2. Détection du traceur

Le détecteur est une sonde de détection nucléaire associée à un ictomètre et un enregistreur. La vitesse de défilement de ce dernier est asservie à la vitesse de déroulement du câble porteur de la sonde.
FIG. 3. Détérmination de la vitesse horizontale de filtration moyenne entre \( H_1 \) et \( H_2 \) en présence d'une vitesse verticale nulle. 

A: Évolution de la fonction taux de comptage – hauteur en fonction du temps. 
B: Évolution de l'intégrale des fonctions taux de comptage – hauteur en fonction du temps.
FIG. 4. Détermination de la vitesse horizontale de filtration moyenne et de la vitesse verticale. 
A: Evolution de la fonction taux de comptage – hauteur en fonction du temps.
B: Evolution de l'intégrale des fonctions taux de comptage – hauteur en fonction du temps.
C: Evolution des centres de gravité en fonction du temps (vitesses verticales).
Lorsque l’injecteur et le détecteur sont solidaires du même câble porteur, l’injecteur est placé à environ 1 mètre sous le détecteur. La sonde de détection est alors protégée par un blindage de plomb de telle sorte qu’elle ne puisse être influencée par le traceur contenu dans le réservoir de l’injecteur.

Comme cela a été dit précédemment, l’exploration de la zone marquée du forage avec la sonde de détection provoque une homogénéisation radiale généralement suffisante pour les besoins de la mesure.

2.2.4. Tactique expérimentale de mesure

Sur le terrain, le mode opératoire suit la séquence ci-dessous :
– Enregistrement à plusieurs reprises du taux de comptage naturel correspondant au bruit de fond \( b(h,0) \) sur toute la hauteur noyée du forage.
– Injection continue ou discontinue du traceur à la profondeur choisie.
– Enregistrement des fonctions taux de comptage – hauteur \( N(h,t) \) aux temps \( t_0, t_1, t_2, \ldots, t_n \) des \( n \) explorations successives. Le taux de comptage définissant \( N(h,t) \) et la cote \( h \) du détecteur nucléaire sont enregistrés simultanément; la durée d’une exploration est toujours faible devant l’intervalle de temps séparant deux explorations successives, la totalité d’une exploration peut donc être affectée de la date atteinte lorsqu’elle est à moitié réalisée.

L’exploitation des résultats consiste alors à effectuer les opérations suivantes :
– Retrancher le bruit de fond \( b(h,t) \) correspondant aux fonctions taux de comptage – hauteur, \( N(h,t) \) enregistrées.
– Procéder à la correction de la décroissance du signal due à la période du radiotracer.
– Calculer l’intégrale de la fonction résultante et observer son évolution afin de déterminer la vitesse horizontale moyenne sur la hauteur délimitée par les deux extrémités haut et bas \( (H_2 \text{ et } H_1) \) du nuage radioactif lors de la dernière exploration (figure 3). Si le nuage subit une translation verticale durant l’essai, la vitesse moyenne obtenue concerne en fait la zone du forage comprise entre les cotes extrêmes atteintes par les extrémités opposées du nuage entre la première et la dernière exploration.
– Mesurer l’évolution de la cote du centre de gravité des fonctions taux de comptage – hauteur pour calculer la vitesse verticale (figure 4).

2.2.5. Gammes de mesure et précision de la méthode

Des calculs théoriques sur les vitesses horizontales parasites, engendrées par la diffusion et la convection thermiques, laissaient penser que la vitesse minimale mesurable serait de l’ordre du centimètre par jour. L’erreur de mesure demeurerait difficile à préciser. Les expériences présentées dans le chapitre suivant montrent qu’il est possible de mesurer une vitesse nulle à ± 0,5 cm par jour, cette précision étant donnée à 2 écarts-types près.
La vitesse horizontale maximale mesurable par cette méthode dépend principalement du temps de séjour du traceur dans le forage, par rapport à la durée d’une exploration.

2.3. Expérimentation dans un forage profond

Le procédé a été expérimenté en France, sur un forage de 1000 m de profondeur percé dans le granite.

2.3.1. Injections

Quatre injections séparées chacune d’un intervalle de temps de deux jours ont été réalisées successivement aux cotes –950 m; –810 m; –455 m et –305 m. Chacune de ces injections a comporté l’émission instantanée de 10 ml d’une solution aqueuse contenant 50 μCi d’iode 131.

L’injecteur utilisé a été conçu par le Professeur Tazioli [4]. Il est du type seringue déclenchée par un messager.

2.3.2. Explorations

Les explorations des nuages de traceur ont été effectuées soit à la descente, soit à la remontée de la sonde de détection. Celle-ci se déplaçait à la vitesse de 3 m/min. Au début des marquages, la sonde était mise en attente à proximité du nuage observé après chaque exploration.

Cette tactique présente l’avantage de gagner du temps, de laisser la sonde de détection à la température du milieu et d’éviter l’élargissement du nuage par un déplacement inutile de la sonde et de son câble porteur.

Ensuite, la nécessité d’explorer successivement 2, 3 puis 4 nuages de traceur, dans un temps restreint, a accéléré la dispersion verticale des nuages de traceur.

2.3.3. Résultats des mesures

Les courbes taux de comptage – hauteur, enregistrées lors des explorations, demeurent symétriques par rapport à la cote d’injection (figure 5). Cette disposition indique l’absence de courant vertical.

Après les corrections habituelles de sensibilité de mesure, de décroissance radioactive et de bruit de fond, les valeurs des intégrales des courbes taux de comptage – hauteur en fonction du temps ont été portées sur un diagramme semi-logarithmique. Un calcul utilisant la méthode de régression des moindres carrés a permis de déterminer le coefficient angulaire de la droite correspondante.
FIG. 5. Reproduction superposée des enregistrements des explorations du nuage de traceur injecté à -305 m aux temps $T = 2 \text{h}$ et $T = 10 \text{h}$ (vitesse d’exploration: 3 m/min).
FIG. 6. Valeurs des vitesses horizontales de filtration calculées avec leurs marges d’erreur à ± 2 écarts-types.

A partir de ce coefficient angulaire et de son écart-type, il est possible de calculer la vitesse horizontale moyenne de filtration à ± 2 écarts-types près pour la zone située autour de la cote d’injection.

Les résultats obtenus sont les suivants:

• à −950 m (de 0 h à 35 h), Vf = + 0,059 cm · d⁻¹ ± 0,32 cm · d⁻¹;
• à −810 m (de 0 h à 50 h), Vf = − 0,0086 cm · d⁻¹ ± 0,05 cm · d⁻¹;
• à −810 m (de 50 h à 130 h), Vf = + 0,0415 cm · d⁻¹ ± 0,22 cm · d⁻¹;
• à −455 m (de 0 h à 100 h), Vf = + 0,0093 cm · d⁻¹ ± 0,17 cm · d⁻¹;
• à −305 m (de 0 h à 50 h), Vf = − 0,16 cm · d⁻¹ ± 0,08 cm · d⁻¹.

Ils sont reportés sur le graphique de la figure 6.

Une vitesse négative n’ayant aucune signification dans le mode de mesure, ainsi que le montre la figure 6, les vitesses horizontales de filtration calculées sont égales à 0 cm par jour ± 0,5 cm par jour. Cette dernière marge d’erreur étant définie à 2 écarts-types près.

Les nuages de traceur s’étaient lors de la dernière exploration sur les gammes de hauteurs ci-dessous:
- pour l’injection à −950 m: 46 m;
- pour l’injection à −810 m: 79 m;
– pour l’injection à – 455 m: 83 m;
– pour l’injection à – 305 m: 78 m.

Les valeurs des vitesses de filtration obtenues sont donc des valeurs moyennes calculées sur ces portions du forage.

3. EVALUATION DE LA FISSURATION D’UN MASSIF ROCHEUX

3.1. Position du problème

Le degré de fissuration naturelle de l’enrochem ent recouvrant ou constituant un gisement minier ou un site destiné au stockage de déchets est l’un des paramètres importants à déterminer.

Les techniques classiques d’estimation de ce degré de fissuration consistent généralement à examiner des échantillons de roches (carottes) prélevés à partir d’un forage de reconnaissance. Cette façon de procéder, malgré toutes les précautions prises lors de la réalisation du forage, ne permet pas d’obtenir une parfaite représentativité de l’enrochem ent en place. En effet, non seulement les échantillons prélevés ne demeurent pas dans les conditions initiales de contraintes mécaniques mais ils sont généralement fracturés accidentellement lors de leur prélèvement.

L’étude proposée vise à mettre au point un procédé permettant d’évaluer la fissuration naturelle d’une roche en place, par injection d’un radionucléide suivie d’une diagraphie gammamétrique, à partir d’un forage de faible diamètre.

3.2. Méthodologie

3.2.1. Principe de la méthode proposée

Un radionucléide en solution dans l’eau est injecté sous pression dans un forage de faible diamètre réalisé dans la roche en place.

Sous l’effet de la pression, la solution radioactive pénètre dans les fissures interceptées par le forage.

Après remise à la pression normale et récupération du volume résiduel de solution radioactive, une décontamination soignée des parois du forage est effectuée par rinçage à l’eau.

Il est alors procédé à une exploration du forage au moyen d’un détecteur de rayonnements nucléaires. Le passage de celui-ci devant une fissure ayant retenu une fraction de la solution radioactive se manifeste par un accroissement du taux de détection.

Le signal résultant de l’exploration du forage se traduit par une courbe continue qui traduit l’intégration du taux de détection; ce dernier présente un pic chaque fois que le détecteur passe devant l’un de ces fissure.
3.2.2. Contraintes expérimentales

La mise en œuvre du procédé proposé fait apparaître trois difficultés majeures:

a) La mise en pression de la solution marquée dans le forage provoquera un élargissement des fissures ouvertes et, éventuellement, une ouverture des fissures fermées. Au retour à la pression normale, ces fissures se refermeront plus ou moins en évacuant tout ou partie de la solution marquée qu'elles contenaient. Toutes les fissures ne contenant pas nécessairement un dépôt argileux susceptible d'adsorber, au moins partiellement, le radiotracer, certaines d'entre elles se refermeront en expulsant la totalité de la solution marquée. Leur repérage sera alors impossible.

b) Sur toute la longueur d'un forage, même s'il n'a que quelques mètres, il existe toujours un risque d'intercepter une fissure de grande extension en communiquant avec un réseau débitant et susceptible d'évacuer un important volume de solution marquée. Il serait alors impossible, à moins d'utiliser des volumes très importants, de mettre en pression la solution marquée pour que celle-ci pénètre dans les fissures plus fines ou de moindre extension. Par ailleurs, la solution marquée devant être suffisamment concentrée pour que même les fissures de faibles dimensions retiennent une masse de radiotracer permettant de les localiser lors de la diagraphie, cela conduirait à mettre en œuvre des quantités de radiotracer très importantes, voire rédhibitoires.

c) Si, dans une partie du forage, les fissures interceptées sont très peu distantes entre elles, il existe un risque de ne pouvoir séparer les signaux émanant chacune. La courbe traduisant l'évolution du taux de détection en fonction du déplacement du détecteur ne présenterait alors probablement qu'un seul pic, plus ou moins étalé. Ce phénomène sera d'autant plus marqué que l'énergie du rayonnement du radiotracer utilisé sera élevée. Ce rayonnement traversera en effet de plus importantes épaisseurs de roche, non seulement dans le plan de fissuration, mais également obliquement. A ce propos, il convient de remarquer que pour simplifier le problème, nous postulons que les plans de fissuration sont peu inclinés sur l'axe du forage. Une forte inclinaison de ces plans restreindrait encore le pouvoir séparateur du procédé.

Il paraît cependant nécessaire d'utiliser un radiotracer émettant un rayonnement d'énergie suffisante pour traverser une épaisseur de roche d'une dizaine de centimètres afin que les parties profondes des fissures contribuent largement au signal observé par le détecteur. S'il n'en était pas ainsi, et que seules les lèvres des fissures qui interceptent le forage émettent un rayonnement observable, il y aurait un grand risque que la présence des fissures soit masquée par la contamination résiduelle qui affectera nécessairement les parois du forage (bruit de fond).
3.2.3. Solutions proposées

3.2.3.1. Fixation du radiotracer sur une résine échangeuse d’ions

Idéalement, après injection sous pression de la solution marquée, le radiotracer utilisé devrait être entièrement retenu dans le volume des fissures et pas du tout à la surface des parois du forage.

La solution proposée consiste à réaliser une suspension dans l’eau d’une résine échangeuse d’ions sur laquelle un radiotracer est fixé de façon irréversible. Si la résine utilisée est de granulométrie assez faible, la suspension injectée sous pression dans le forage pénètre même les plus fines fissures de la roche. Au retour à la pression normale dans le forage, les grains de résine restent en partie piégés dans les fissures au moment où celles-ci commencent à se refermer. Ensuite, un rinçage énergique du forage permet d’éliminer la plus grande partie des grains de résine déposés sur les parois.

3.2.3.2. Injection par tronçon entre deux packers

Nous avons admis d’effectuer l’exploration en plusieurs étapes réalisées en série en injectant le traceur dans un volume constitué par le forage et délimité par deux packers.

Cette disposition permet de travailler avec une chambre d’injection de longueur réduite (environ un mètre); le volume de suspension à injecter est ainsi plus faible et en grande partie récupéré au retour à la pression normale puis réutilisé après déplacement de la chambre d’injection.

Des déplacements successifs permettent l’injection de la suspension marquée sur la quasi-totalité de la profondeur du forage (sauf la longueur des packers au voisinage du fond et de la surface).

3.2.3.3. Blindage du détecteur

Ce dispositif, présenté à la figure 7, a pour but d’améliorer le pouvoir séparateur du détecteur.

Sur la face avant du détecteur, un revêtement de plomb de 4 cm d’épaisseur assure une protection importante avec une atténuation d’un facteur 8 environ pour un rayonnement d’énergie 1,6 MeV.

Le blindage latéral est composé de deux tubes mobiles de plomb. Ces deux tubes peuvent être rapprochés ou éloignés à volonté, de façon à laisser apparaître un intervalle circulaire de largeur réglable au droit de la partie sensible du détecteur. L’épaisseur de ces tubes de plomb est de 1,7 cm et atténue d’un facteur 2,5 un rayonnement d’énergie 1,6 MeV.

La largeur de l’intervalles de collimation, définissant le pouvoir de résolution de l’appareil, peut être ajustée à une valeur optimale. Cette valeur est fixée
FIG. 7. Représentation schématique du blindage et de la collimation du détecteur à scintillation.

FIG. 8. Evolution du taux de détection de part et d'autre d'une source ponctuelle de lanthane 140.

par la nécessité de recevoir sur le détecteur une quantité suffisante de rayonnement pour que la précision statistique de la mesure demeure satisfaisante compte tenu du temps d'observation.

La figure 8 présente la courbe traduisant le pouvoir séparateur du détecteur pour un intervalle de collimation de 1 cm et montre que le rendement de détection varie d'au moins un facteur 2,5 pour une translation de 5 cm de part et d'autre du plan de collimation.
3.3. Mise en œuvre

3.3.1. Choix du radiotraceur

Le lanthane 140 (140La) a été retenu en raison des principales propriétés suivantes. Tout d'abord, ce radioélément est un émetteur gamma de grande énergie (1,6 MeV). Un tel rayonnement est très pénétrant puisqu'en effet il n'est atténué que d'un facteur 3,5 après traversée de 10 cm de roche. Il est donc possible de le détecter au travers de quelques dizaines de centimètres. Ensuite, la période radioactive du 140La est de 40 h. Cette durée, suffisante pour une mise en œuvre lors d'un essai d'une semaine, est cependant assez modeste pour n'entraîner, par décroissance naturelle, qu'une contamination très momentanée du site expérimental. Enfin, le 140La est un élément de la famille des terres rares (électropositif et réducteur) et se fixe de façon quasi irréversible sur une résine cationique en ne s'échangeant pratiquement pas avec les carbonates de la roche en raison de sa valence élevée 3. Il en résulte une faible contamination superficielle dans le forage après rinçage.

3.3.2. Choix de la résine échangeuse d'ions

Celle-ci devant former une suspension homogène et stable dans l'eau, nous avons utilisé la plus fine résine cationique disponible sur le marché. Sa courbe granulométrique s'étend de 3 à 60 µm. Les grains d'un diamètre supérieur à 40 µm, susceptibles de sédimerter rapidement, ont été éliminés par elutriation.

Les essais en laboratoire ont montré qu'une suspension dans l'eau à 50 g·L\(^{-1}\) d'une telle résine fixait sur la phase solide, et de façon quasi irréversible après un temps de contact de 10 min, plus de 95% de nitrate de lanthane (La(NO\(_3\))\(_3\)) initialement en solution à la concentration de 0,5 g·L\(^{-1}\).

3.3.3. Dispositif d'injection

Ce dispositif, schématiquement présenté à la figure 9, a été conçu et réalisé spécialement pour cette étude.

Entièrement manœuvrable à distance, il permet de réaliser en toute sécurité les diverses phases nécessaires à la mise en œuvre du radioélément, à savoir:
- dessertissage de la cartouche en aluminium de transport dans laquelle le 140La (La(NO\(_3\))\(_3\)) est contenu sous forme de poudre;
- mise en solution avec agitateur magnétique dans un volume de 60 mL d'eau (solution mère);
- fractionnement de la solution mère et transfert des doses successives dans le réservoir de 18 L contenant la suspension de résine;
- homogénéisation de la suspension de résine pendant la phase d'adsorption du 140La sur les grains;
FIG. 9. Représentation schématique du dispositif expérimental.

- aspiration de la suspension marquée et refoulement sous pression réglable à l'aide d'un surpresseur pneumatique (type Pétrometalic 1/13 de 0 à 80 bar);
- injection sous pression dans le forage entre deux packers distants d'un mètre après gonflage (canne d'injection à tuyaux dilatables, type Bimbar, Pétrometalic);
- reprise, après remise à la pression normale, du volume de suspension marquée contenu dans la chambre d'injection; cette suspension est directement récupérable par pompage;
- récupération, après dégonflage des packers, du volume résiduel de suspension non récupéré lors du pompage précédent;
- contrôle permanent des volumes de suspension mis en œuvre (injectés et récupérés) par capteur de pression;
FIG. 10. Exploration gamma-métrique dans le forage (A) et comparaison des résultats des différentes méthodes (B).

— rinçage à l'eau de l'ensemble du dispositif et du forage;
— récupération et stockage des effluents contaminés.

Pour ces différentes phases, les manœuvres nécessaires sont effectuées à distance:
— soit à l'aide de pinces de manipulation à tête orientable de 3 m de long:
  • transfert de la cartouche en aluminium depuis le container de transport (plomb épaisseur 10 cm) jusqu'au mandrin de la dessertisseuse;
  • transvasement, après dessertissage, dans le flacon de mise en solution;
  • remise de la cartouche en aluminium dans le container de transport;
soit à l'aide de cannes de 4 m de long spécialement adaptées pour
les différentes manoeuvres:
- positionnement, serrage et desserrage du mandrin de la dessertisseuse;
- positionnement du dispositif de fractionnement;
- ouverture et fermeture des différentes vannes;
soit par commande électrique basse tension (12 V) pour les différents organes rotatifs:
- dessertisseuse;
- agitateur magnétique pour la solution mère;
- micropompe de fractionnement et de transfert de la solution mère;
- agitateur pour la suspension marquée;
- pompe péristaltique pour la récupération de la suspension résiduelle dans
le forage;
soit par commande pneumatique à l'aide de bouteilles d'azote comprimé:
- gonflage des packers de la canne d'injection;
- ajustement et maintien de la pression d'injection de la suspension marquée.

3.3.4. Résultats expérimentaux

Deux campagnes d'essais ont été réalisées sur deux sites expérimentaux
à partir de forages implantés spécialement dans des galeries de mines.
La figure 10 présente, à titre d'exemple, l'interprétation d'une exploration
gamamétrique et compare ces résultats à ceux obtenus par des méthodes plus
classiques.
Par carottage, on constate que le nombre des fissures recensées est très
important (certaines, qui n'existaient pas dans la roche en place ont pu être
produites lors de l'extraction de l'échantillon). L'exploration endoscopique,
par contre, ne permet de recenser que les fissures très ouvertes et ne permet
d'accéder qu'à de faibles profondeurs (6 à 8 m).

4. CONCLUSION

A partir d'un forage et avec l'aide d'un radiotracer approprié, les deux
métodes décrites apportent de nouvelles possibilités de mesure des vitesses
d'écoulement de l'eau et de la fracturation de la roche en place dans un
aquiètre profond. Les campagnes d'essais réalisées sur le terrain en ont montré
la validité.

A) La première méthode permet de mesurer des vitesses horizontales de
filtration très faibles, voire nulles, avec une précision de ± 0,5 cm/d à deux
écart-types près. La mesure peut être faite en présence de courants verticaux
assez importants dont les vitesses sont alors évaluées au cours de la même opéra-
tion. Cette méthode ne présente pas les inconvénients des anciens procédés.
mais nécessite un matériel adapté aux mesures à grande profondeur. Il faut noter que la vitesse horizontale de filtration ainsi calculée est une vitesse moyenne; celle-ci est déterminée sur la hauteur de l’aquifère définie par les deux limites opposées du nuage de traceur entre la première et la dernière explorations.

B) La seconde méthode permet de détecter et de localiser sur place les fissures de la roche avec une bonne précision. La forme et l’amplitude des pics d’activité observés et la connaissance des volumes de suspension marquée introduits dans la roche permettent d’estimer comparativement la largeur et l’extension latérale des fissures. Bien que l’expérimentation décrite ait été effectuée à faible profondeur, cette méthode est parfaitement applicable dans des forages très profonds pour lesquels les problèmes technologiques ont tous été résolus au cours de l’étude.

REFERENCES


UTILISATION DES JUAGES NUCLEAIRES
DE DENSITE POUR ETUDIER ET MESURER
AU LABORATOIRE ET IN SITU
LA FORMATION ET LA CONCENTRATION
DES DEPOTS DE VASE

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Abstract—Résumé

USE OF NUCLEAR DENSITY GAUGES FOR STUDYING AND MEASURING SILT
DEPOSIT FORMATION AND CONCENTRATION IN THE LABORATORY AND IN SITU.

The settling of cohesive sediments in the still waters of engineering installations, such
as navigational channels, harbour basins, dams, etc., involves costly maintenance work. It is
necessary to know the behaviour of this type of material under water in order to perform such
work efficiently. The physical state and the resuspension of these sediments by water currents
depend basically on their density. The latter varies in space and time and is a function of the
mineralogical composition of the sediments. Non-destructive techniques causing the least
possible disturbance are called for to measure and study patterns of change in the vertical con-
centration profiles in sediment deposits. For this purpose, two nuclear density gauges have
been designed and constructed: (1) a photon-transmission gauge, which is used in the laboratory
to observe the formation and variation of deposits in settling columns as a function of para-
meters, such as initial concentration of the deposit, sediment height, time, etc.; (2) a photon-
scattering gauge, which is used in the field for measuring the density of the sediment deposit
in the mud bed. It supplements the data of echo-sounders which only measure the depth of
the upper level of mud and the hard bottom, if any. From the density profile it is possible,
by means of integration, to estimate the total accumulated masses of sediment and to deter-
mine the maximum navigable depth. These instruments have a range from 50 to 800 g·L⁻¹,
with an accuracy of ±10 ·L⁻¹, depending on the mode of operation. The data obtained are
useful for improved monitoring of the navigability of the channels and better management of
dredging sites and reservoirs.
UTILISATION DE JANGES NUCLEAIRES DE DENSITE POUR ETUDIER ET MESURER AU LABORATOIRE ET IN SITU LA FORMATION ET LA CONCENTRATION DES DEPOTS DE VASE.

La décantation des sédiments cohésifs dans les eaux calmes des ouvrages de génie civil (chenaux de navigation, bassins portuaires, retenues de barrage, etc.) entraîne de coûteux travaux d'entretien. Pour les effectuer avec efficacité, il est nécessaire de connaître le comportement sous l'eau de ce type de matériau. Or, l'état physique et la remise en suspension par les courants des dépôts de ces sédiments dépendent essentiellement de leur densité. Celle-ci varie dans l'espace et le temps et dépend de la composition minéralogique des sédiments. Pour mesurer et étudier l'évolution des profils verticaux de concentration dans les dépôts de sédiments, il est nécessaire de faire appel à des procédés non destructifs et aussi peu perturbants que possible. Pour cela, deux jauge nucléaires de densité ont été étudiées et réalisées. 1) Une jauge à transmission de photons, utilisée au laboratoire pour observer la formation et l'évolution des dépôts dans des colonnes de décantation en fonction de paramètres tels que la concentration initiale du dépôt, la hauteur du culot, le temps, etc. 2) Une jauge à diffusion de photons, employée sur le terrain pour mesurer, au sein de la couche de vase fluide, la densité du dépôt sédimentaire, complétant ainsi les indications des écho-sondeurs qui mesurent uniquement les couches du sol de vase fluide ou sur le fond dur. Le profil de densité permet par intégration d'estimer les masses totales de sédiment accumulées et de définir la profondeur limite de navigabilité. Ces appareils fonctionnent dans la gamme 50 à 600 g L⁻¹ avec une précision de ±10 g L⁻¹ suivant les modes d'utilisation. Les informations obtenues servent à assurer une meilleure surveillance de la navigabilité dans les chenaux et à améliorer la gestion des chantiers de dragage et des retenues de barrage.

1. INTRODUCTION

L'envasement des baies, des estuaires, des chenaux de navigation, des bassins portuaires et des retenues de barrage est un problème permanent qui, ces dernières années, est devenu préoccupant. Les dragages pour maintenir les profondeurs et, ainsi, assurer le passage des navires portent sur des dizaines de millions de mètres cubes de matériaux par an et par pays, avec un coût de 1 à 5 dollars des États-Unis par mètre cube. Les vidanges de barrages pour lutter contre le comblement des lacs réservoirs sont des techniques nocives pour le milieu naturel, en raison de la nature des matériaux remaniés généralement porteurs de polluants urbains et industriels qui, de plus, risquent de colmater les lits des fleuves.

Par conséquent, ces méthodes de lutte contre l'envasement doivent être utilisées avec efficacité et discernement, donc en connaissant aussi bien que possible les paramètres qui régissent le comportement sous l'eau de ces sédiments très fins (inférieurs à 0,04 mm). L'un des paramètres essentiels est la concentration $T_s$ en matière sèche, appelée également turbidité (exprimée en gramme de matière sèche par litre d'échantillon). On utilise également la masse volumique $\rho$ [1].

A partir du mélange liquide/solide (exprimé en g L⁻¹) de cette concentration, intégrée dans les trois dimensions, on peut déduire la masse totale des sédiments.
en place à draguer, mais aussi la rigidité initiale $\xi_y$ (exprimée en N·m$^{-2}$):

$$\xi_y = K T^n_s$$

avec K et n comme constantes fonction du type de sédiment.

Cette rigidité initiale $\xi_y$ est elle-même liée à la vitesse critique de remise en suspension $U_x$ (m/s) des sédiments cohésifs [1] par les courants, selon une formule empirique telle que:

$$U_x = 0,017 \frac{\xi_y^{0.25}}{\xi_y}$$

Les deux paramètres de cette formule peuvent être légèrement différents selon le degré de compaction du dépôt, c’est-à-dire de son âge.

La mesure de $T_s$ et de $\xi_y$ conduit à une estimation des masses sédimentaires à draguer et à la détermination des conditions hydrauliques qui permettent de les évacuer.

Or, en raison de la composition de ce type de sédiment (colloïdes, matières organiques, argiles, sables fins), tous en proportions variables, et de l’influence du milieu aquéreux, dont la salinité peut évoluer dans l’espace et le temps (cas des estuaires), il est indispensable de mesurer la distribution verticale des concentrations sédimentaires et d’étudier très soigneusement ses variations en fonction de la hauteur (gradient vertical de concentration) et du temps (âge des dépôts) [1].

De telles déterminations doivent être faites au laboratoire et in situ en utilisant des procédés non destructifs et non perturbants: les jauges nucléaires sont, dans ce cas, des instruments de choix.

2. QUELQUES CONSIDE RATIONS SUR LES JAUAGES NUCLEAIRES DE TURBIDITE

Malgré de nombreuses études ou réalisations diverses, les jauges nucléaires de turbidité n’ont pas connu, jusqu’à maintenant, le développement que l’on pouvait espérer en raison de leur intérêt manifeste. A ceci, on peut trouver plusieurs raisons:

A) Conçus par des spécialistes compétents en radioactivité et des hommes de laboratoire, ces dispositifs ne répondaient pas toujours exactement aux besoins des sédimentologues et, de plus, ils étaient souvent mécaniquement mal adaptés ou trop fragiles pour être utilisés durablement sur le terrain.

B) L’instabilité électronique de certains composants de la chaîne de mesure provoquait des dérives du signal, supérieures à celles induites par les variations du paramètre à mesurer.
C) La mauvaise information des utilisateurs, souvent peu compétents en radioactivité, conduisait à une mise en œuvre inadaptée de la méthode et de l’instrument ou à des interprétations erronées des résultats.

D) La livraison d’appareils sans les moyens pour en assurer l’entretien et le dépannage condamnait à court terme le matériel à l’immobilisation, souvent définitive, en particulier dans les pays en développement.

E) La crainte de la radioactivité, même sous forme de sources scellées et protégées, pouvait restreindre l’emploi de ces appareils.

Or, les travaux réalisés et publiés au cours de la dernière décennie [2–6] permettent de partir de bases théoriques et conceptuelles solides.

Aussi, afin de remédier à cette situation, le Service d’application des radio-éléments du Commissariat à l’énergie atomique a entrepris de réaliser des jauge nucléaires de turbidité sur des bases nouvelles:

A) En créant une association étroite et permanente entre utilisateurs (laboratoires d’hydraulique, bureaux d’études, ingénieurs hydrographes, sédimentologistes) et les spécialistes de la radioactivité, ce qui permet de définir les problèmes et d’affiner les solutions par une concertation permanente.

B) En effectuant une optimisation portant à la fois sur la physique de l’interaction photons γ–matière, sur l’adaptation des configurations source – blindage – détecteur dans le domaine de densité à contrôler, sur la réalisation des corps de sonde (lests, centrage des masses, profil hydrodynamique), sur le choix des composants (cristal, photomultiplicateur, électronique associée à la sonde) et, surtout, sur de très nombreux essais systématiques de prototypes tant en laboratoire que sur différents sites.

C) En mettant en œuvre des sources radioactives scellées agrées (tmatière sous forme spéciale) particulièrement fiables et, de plus, en utilisant des activités aussi faibles que possible compte tenu des mesures à réaliser.

D) En utilisant aussi souvent que possible la micro-informatique afin, d’une part, de convertir les données nucléaires en grandeurs physiques utilisables par l’exploitant, et, d’autre part, d’automatiser le pilotage de l’outil.

Nous en donnons ici deux exemples.

3. MESURE EN LABORATOIRE DU GRADIENT VERTICAL DE LA CONCENTRATION DES DEPÔTS DE VASE

Les sédiments très fins se compactent progressivement en perdant leur eau interstitielle, et ainsi passent d’un état fluide à un état plastique, puis solide.

On observe [1] que la concentration moyenne d’un dépôt à une profondeur donnée varie comme le logarithme du temps et qu’il existe entre la surface et le fond un gradient de concentration.
Selon l'origine minéralogique du sédiment, ce gradient est différent; aussi est-il étudié au laboratoire en fonction de différents paramètres: concentration initiale de la suspension, hauteur du dépôt, temps, etc., dans des colonnes de 8, 10 ou 12 cm de diamètre et dont la hauteur peut atteindre 3 m. Pour réaliser rapidement ces mesures non destructives, une jauge à transmission a été réalisée (figures 1–4).

L'auscultation verticale de l'échantillon est obtenue par le déplacement à vitesse constante (5 mm/s) de l'ensemble source-détecteur.

Selon la nature des échantillons à mesurer et le diamètre des tubes, on utilise de faibles activités (0,5 à 5 mCi) de sources d'américium 241 ou de baryum 133.

Le premier de ces radionucléides, grâce à ses photons γ de 60 keV, assure la meilleure sensibilité de mesure avec une précision de 3% dans la gamme 50 à 500 g·L⁻¹. L'autre radioélément est utilisé lorsque les échantillons à mesurer contiennent des éléments ayant des numéros atomiques élevés (Fe, Zn, Pb).

Le détecteur (scintillateur NaI (Tl); Φ: 38 mm; h: 25 mm) et l'électronique de mesure sont de qualité océanographique afin de garantir robustesse, étanchéité et fiabilité.

Les mesures en continu sont sorties, soit sur enregistreur Analogique, soit sur imprimante.

L'étalonnage du dispositif est effectué avec des échantillons sédimentaires de concentration connue et ayant la même origine que ceux à étudier. Des éprouvettes de matériaux composites solides sont utilisées pour contrôler périodiquement la stabilité de l'ensemble de mesure.

Les résultats obtenus au cours de ces études servent à calculer la vitesse critique d'entraînement des matériaux par les courants. C'est ainsi que l'on peut estimer le débit liquide minimum à employer pour transporter, par le seul jeu des courants créés par une vidange de barrage, le maximum de sédiment en aval d'un barrage [7]. En s'écartant trop fortement de ces conditions, on risque, soit d'utiliser inutilement de l'eau sans entraîner de sédiment, soit au contraire de provoquer un colmatage important du lit de la rivière.

4. **MESURE IN SITU DU GRADIENT VERTICAL DE LA CONCENTRATION DES DEPOTS DE VASE**

Dans les chenaux de navigation et les bassins portuaires, le maintien des profondeurs pour assurer le passage des navires est indispensable. Or, dans les zones envasées, il est particulièrement difficile de situer avec précision l'interface eau-fond, car, en fonction de la profondeur, l'eau devient de plus en plus chargée en matière solide. La hauteur d'eau mesurée par échosondeur est imprécise et dépend de la fréquence utilisée. Aussi, par sécurité, des travaux de dragage coûteux et souvent inutiles sont effectués alors que la navigation est possible. Pour
FIG. 1. Jauge de tassement de sédiments à transmission de photons γ.
FIG. 2. Schéma de l'installation et de l'appareillage de mesure pour l'étude de la variation de la concentration dans un dépôt sédimentaire de vase en cours de tassement.

FIG. 3. Absorption des rayons γ en fonction de la densité de la vase.
FIG. 4. Exemples de gradients de concentration pour différents dépôts de vase ou limons.
éviter ce gaspillage et mieux gérer les opérations de dragage, il est nécessaire de localiser directement in situ le toit de vase au-dessous duquel, la navigation étant dangereuse, il est indispensable d’extraire les sédiments.

La détermination du profil de concentration de la vase déposée, dans la gamme de 50 à 800 g·L⁻¹, est obtenue par une jauge nucléaire à diffusion de photons gamma contenant une source d’activité comprise entre 0,1 et 1 mCi de césium 137. Le principe et la réalisation du dispositif sont résumés par les figures 5 et 6.

Les photons émis par la source diffusent dans le milieu biphasique eau-sédiment dans lequel plonge la sonde [6]. Le signal R (taux de comptage) recueilli par le détecteur à scintillation est lié à la masse volumique ρ du milieu par une relation linéaire empirique de la forme:

\[ R = R_0 (1 + a\rho) \]

\( R_0 \) est mesuré dans l’eau claire et un paramètre, a, qui dépend en particulier de la distance source–détecteur, est déterminé au laboratoire par étalonnage en immergeant la sonde dans des solutions de silicate de sodium de densité connue.
Ce produit liquide est utilisé pour simuler des dépôts sédimentaires difficiles à manipuler en grands volumes homogènes.

Le volume sédimentaire concerné par la mesure est sensiblement un cylindre d’axe vertical coïncidant avec celui de la sonde dont la hauteur est de 10 cm et le diamètre de 60 cm. La précision est de ±10 g·L⁻¹ avec des temps de mesure de 10 s.

La hauteur d’eau est mesurée par l’intermédiaire d’un capteur de pression disposé dans la sonde. Un câble électro-porteur (longueur: 50 à 100 m; diamètre: 4,6 mm; résistance à la traction: 1200 daN) et un treuil électrique à contacts tournants complètent le dispositif. La sonde (longueur: 1000 mm; diamètre: 54 mm; poids: 20 kg), pénètre par gravité dans les dépôts de vase (2 à 4 m). La mesure d’un profil de concentration est obtenue en moins de 2 min.

Un micro-ordinateur (APPLE II) assure le déroulement du treuil: vitesse d’exploration rapide dans l’eau claire, vitesse d’exploration lente dans les dépôts de vase, montée, descente, etc. Il assure également le traitement des données.
leur mise en forme, la visualisation sur écran, le stockage des résultats sur disque souple et leur impression (fig. 7).

Ce dispositif est progressivement mis en service dans les ports soumis à des envasements prononcés.

On doit remarquer que ce type de jauge nucléaire peut être installé dans les puits de dragage, après certains aménagements matériels, pour estimer la vitesse de remplissage des puits et les quantités de matériaux dragués par les dragues aspiratrices en marche [6].
5. CONCLUSIONS

La gestion des masses d'eau et des masses sédimentaires contenues dans les ouvrages de génie civil (chenaux de navigation, bassins portuaires, retenues de barrages) et les estuaires est devenue une nécessité économique en raison du volume et du coût des travaux de dragage.

L'un des paramètres essentiels à cette gestion est la concentration des sédiments déposés. Cette concentration, variable dans l'espace et le temps, doit être mesurée au laboratoire et/ou in situ au moyen de dispositifs rapides et non perturbants en raison de la nature physico-chimique de ces matériaux.

Les jauge nucléaires décrites ici sont des outils performants et bien adaptés pour répondre avec une précision suffisante (± 10 g·L⁻¹) dans la gamme des concentrations à mesurer (50 à 800 g·L⁻¹). Elles sont le résultat des études approfondies faites au cours de la dernière décennie dans plusieurs pays et ouvrent l'ère de l'utilisation systématique de cette technique nucléaire dans le domaine du génie civil maritime et fluvial.

REFERENCES

DETERMINACION DEL TRANSPORTE DE FONDO EN EL ALTO RIO LERMA MEDIANTE IRIDIO 192

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Abstract–Resumen

DETERMINATION OF RIVER-BED TRANSPORT WITH IRIDIUM-192 IN THE UPPER REACHES OF THE RIVER LERMA.

The upper reaches of the river Lerma discharge at an average rate of 29 m³/s into the Solís barrage, which is one of the largest in the Mexican high plateau. This barrage covers an area of 10³ ha and is subject to problems of sedimentation, which result in an estimated reduction in useful volume of about 4.8 X 10⁶ m³ per year. Its hydraulic characteristics are those of a torrential river; during the rainy season, almost instantaneous variations in its flow rate of 15 m³/s to 70 m³/s are recorded, and during some hours the flow rate even reaches 100 m³/s to 300 m³/s. Since radioactive tracers have proved very useful in studying river-bed transport in this type of river, one kilogramme of glasses labelled with 0.685 Ci of ¹⁹²Ir was used to determine the quantity of solid material carried by the river to the Solís barrage. The grain size of the tracer injected (0.84–1.10 mm) was determined from a mathematical model for size distribution of the river-bed sediment. The experiment lasted 232 days and covered the whole floodwater period (June to October). A unit solid flow rate of 2.25 ± 0.66 t/m²·d was estimated on the basis of the spatial integration of the tracer. For the purpose of comparison, various semi-empirical formulae (Einstein, Meyer Peter-Müller, Schoklitsch, Kalinske, and others) were used to calculate river-bed transport. Agreement was found between some of these results and those obtained using the radiotracer.

DETERMINACION DEL TRANSPORTE DE FONDO EN EL ALTO RIO LERMA MEDIANTE IRIDIO 192.

El alto río Lerma descarga un caudal medio de 29 m³/s en la presa Solís, una de las más importantes del altiplano mexicano. Este presa riega una superficie de 10³ ha y presenta problemas de azolvamiento, esterlándose pérdidas en su volumen útil del orden de 4.8 X 10⁶ m³ por año. Por sus características hidráulicas el río es de tipo torrential; durante la estación de lluvias se registran variaciones en su caudal de 15 m³/s a 70 m³/s casi instantáneamente, presentándose inclusivo gastos que alcanzan de 100 m³/s a 300 m³/s durante algunas horas. Dado que los trazadores radiactivos han demostrado una gran utilidad para estudiar el transporte de fondo en este tipo de ríos, se utilizó un kilogramo de vidrios activados con 0,685 Ci de iridio 192 para determinar la cantidad de material sólido que arrastra esta corriente hacia la presa Solís. El intervalo granulométrico del trazador inyectado (0.84 mm a 1.10 mm) se determinó del modelo matemático de la distribución de tamaños de los sedimentos del lecho.
La fase experimental tuvo una duración de 232 días y cubrió totalmente el período de avenidas (junio a octubre). A través de la integración espacial del trazador se estimó un gasto sólido unitario de 2,25 ± 0,66 t/m·d. Como forma de comparación se aplicaron diversas fórmulas semiempíricas (Einstein, Meyer Peter-Müller, Schokitsch, Kalinske, etc.) para calcular el transporte, encontrándose concordancia entre algunos de sus resultados y los obtenidos con el radiotrazador.

1. **INTRODUCCION**

La evaluación de los materiales sólidos transportados por las corrientes fluviales es de suma importancia para las ramas de la ingeniería vinculadas con la planeación, mantenimiento y manejo de obras de infraestructura hidráulica.

El conocer los volúmenes de tales materiales permite, por ejemplo, estimar los cambios que puede sufrir un río tanto en su configuración como en sus características hidráulicas y, por tanto, prever dónde va a existir depósito, transporte o erosión de material sólido, lo que lleva a predecir y controlar el azolamiento de lagos y presas.

El caudal de una corriente fluvial está integrado por el correspondiente de agua y, en menor cuantía, por el material sólido que lleva conjuntamente, ya sea en suspensión o en forma de carga de fondo.

La cantidad de los materiales transportados en suspensión se determina satisfactoriamente mediante el muestreo directo de la corriente en casi cualquier tipo de río. La evaluación de los volúmenes de sólidos arrastrados en el fondo implica un problema muy diferente al de sólidos en suspensión, ya que las mediciones puntuales pueden ser influidas por características de tipo local que ponen en duda la representatividad de los valores, además de involucrar problemas de aplicación práctica, como en el caso de las trampas de sedimentos. Las estimaciones de los acarreos se basan, por lo general, en modelos semiempíricos cuyas predicciones difieren ampliamente entre sí. Un estudio a fondo del transporte de sedimentos hace necesaria la medición directa del proceso, ya que es el único medio para analizar la validez y el rango de aplicación de las teorías y para proporcionar los datos para el ajuste de los modelos semiempíricos, todo esto adaptado a las características particulares del río o de la cuenca en estudio, en donde pueden influir factores locales tales como la geología o la capacidad de la cuenca para generar los sedimentos.

Con el propósito de disponer de un método experimental para estudiar esta segunda forma de transporte, se recurrió a los trazadores radiactivos, dado que han demostrado una alternativa de gran utilidad para describir el comportamiento de los cauces aluviales [1, 2]. Con este fin se utilizaron vidrios activados con iridio 192 para estimar la cantidad de materiales sólidos que el alto río Lerma transporta por arrastre hacia la presa Solís (Fig.1).
2. **AREA DE ESTUDIO**

La cuenca aportadora de la presa Solís tiene un área de 2328 km², de los cuales 1608 km² corresponden a la subcuenca del alto río Lerma y los restantes 720 km² a la subcuenca del río Tigre (Fig. 1).

La presa riega anualmente una superficie de $10^5$ ha y presenta problemas de azolvamiento, estimándose pérdidas en su volumen útil del orden de $4,8 \times 10^6$ m$^3$ por año.

El 92% de los escurrimientos captados por el vaso provienen del río Lerma, por lo que la mayor cantidad de sedimento la aporta esta corriente.
El río Lerma tiene un gasto medio de 29 m³/s y presenta características torrenciales durante la estación de lluvias (junio a octubre), registrándose variaciones en su caudal de 15 m³/s a 70 m³/s en intervalos de tiempo menores a ocho horas. Incluso se pueden producir gastos que alcanzan de 100 m³/s a 300 m³/s durante algunas horas [3].

El estudio del transporte de fondo con el radiotrazador se llevó a cabo en un tramo de río localizado aproximadamente a 10 km aguas arriba de la presa (Fig.1).

3. EL METODO DE LOS TRAZADORES RADIATIVOS

El arrastre de fondo asociado a una corriente fluvial se define, en forma clásica, como el flujo de masa que atraviesa una superficie unitaria en la unidad de tiempo. De esta manera el gasto sólido unitario \( g_b \) queda expresado como:

\[
\dot{g}_b = \rho_s \cdot V_m \cdot E
\]  

(1)

Los parámetros determinantes del transporte son por tanto el espesor, \( E \), de la capa de fondo y la velocidad, \( V_m \), con la cual se mueve en el cauce; \( \rho_s \) es la densidad global del sedimento natural.

El empleo de un trazador radiactivo permite describir el comportamiento dinámico del lecho durante largos períodos de tiempo. La evolución de la nube radiactiva que forman los granos del trazador, bajo las condiciones hidráulicas que influyen en el fenómeno, determina cuantitativamente los parámetros \( E \) y \( V_m \). El método utilizado en el presente estudio para estimar tales parámetros es el que desarrollaron Courtois y Saizay [4], recurriendo a un balance entre las actividades inyectada y recuperada.

Cuando se inyecta una actividad, \( A \), de trazador radiactivo en un lecho arenoso, por ser éste un medio absorbente, se cumple que a mayor enterramiento de los granos radiactivos, menor es la tasa de conteo que se recibe en un reactor de radiación. Este efecto implica una relación entre el espesor de la cama móvil y la tasa de conteo.

En un punto \( x \) de la superficie del lecho habrá una tasa de conteo \( n \) producida por el trazador, la cual estará dada por:

\[
n = \int_0^{e_x} f(z) \cdot c(z) \, dz
\]

(2)

En esta expresión, \( e_x \) representa el espesor de la capa de sedimento en el punto \( x \); \( f(z) \) es la función que determina la respuesta del detector para una actividad
unitaria distribuida uniformemente sobre una superficie unitaria a la profundidad \( z \), y \( c(x) \) es la actividad por unidad de volumen a la profundidad \( z \).

La tasa de conteo total \( N \), integrada sobre toda la nube radiactiva, estará dada por la ecuación siguiente:

\[
N = \int_{x} n \cdot ds \tag{3}
\]

Expresando la Ec.(3) en forma múltiple, se representa la realidad física de las detecciones de campo:

\[
N = \int_{x_1}^{x_2} \int_{y_1}^{y_2} n(x, y) \, dx \, dy = \int_{x_1}^{x_2} \left[ \int_{y_1}^{y_2} n(x, y) \, dy \right] \, dx \tag{4}
\]

La detección del trazador en el cauce se realiza dinámicamente mediante rastreos transversales a la dirección del flujo. El conteo \( N_i \) integrado en cada rastreo es función del tiempo \([5]\) y se representa analíticamente de la siguiente manera:

\[
N_i = \int_{0}^{t} F(t) \, dt = \int_{0}^{t} f(y(t)) \, dt = \int_{0}^{t} f(x_0, a+vt) \, dt \tag{5}
\]

en esta ecuación \( y(t) = a + vt \), donde a es una constante, y \( v \) es la velocidad de desplazamiento del detector sobre la superficie del lecho.

Si la velocidad del detector se mantiene constante en cada recorrido, el conteo correspondiente a cada rastreo \( N_i \) se representa como:

\[
\int_{0}^{t} F(t) \, dt = \frac{1}{v} \int_{y_1}^{y_2} f(x_0, y) \, dy \tag{6}
\]

Sustituyendo este resultado en la Ec.(4), se puede representar la forma como se determina la tasa de conteo \( N \) sobre el lecho del río:

\[
N = \int_{x_1}^{x_2} \left[ v \int_{0}^{t} F(t) \, dt \right] \, dx \tag{7}
\]
Por otro lado, la Ec.(3) puede reescribirse analíticamente de la manera siguiente:

\[ N = \int \int f(x) c(x,y,z) \, dx \, dy \, dz \]  

(8)

Esta ecuación fue resuelta por Courtois y Sazay [4] recurriendo a una función \( \Gamma(z) \) para representar la actividad existente en toda la nube radiactiva dentro de una capa de espesor \( dz \) a la profundidad \( z \). Así el valor de \( N \) se expresa como:

\[ N = \int f(z) \, \Gamma(z) \, dz \]  

(9)

Experimentalmente se encuentra que la función \( f(z) \) varía exponencialmente según la forma \( f(z) = f_0 \, e^{-\alpha z} \), siendo \( \alpha \) un coeficiente característico del sedimento natural, del radisótopo utilizado y de la geometría empleada durante la detección.

La ecuación del balance del radiotrazador que relaciona las actividades inyectada y recuperada con el espesor del transporte es:

\[ \frac{\alpha N}{\beta f_0 A} \, E = 1 - e^{-\alpha E} \]  

(10)

En la expresión, \( \beta \) es un coeficiente que depende de E y varía según la forma de la función \( \Gamma(z) \); el valor de \( N \) se obtiene de la ecuación (7).

La velocidad media del transporte \( Vm \) se determina experimentalmente a través del desplazamiento del centro de gravedad del trazador en función del tiempo: \( \Delta x_g / \Delta t \). El espesor E se obtiene mediante la solución gráfica o por aproximaciones sucesivas de la Ec.(10).

4. DESARROLLO DEL METODO

4.1. Modelo granulométrico

Para introducir en el medio un trazador radiactivo se requiere que éste sea hidrodinámicamente idéntico al sedimento natural, y su representatividad para describir el comportamiento dinámico del lecho depende del tamaño de las partículas que lo forman.
El análisis de los diámetros de los granos del lecho permite, además de definir el tamaño del trazador, conocer algunas de sus propiedades colectivas, tales como: porcentajes de gravas, arenas y finos; diámetros representativo y medio; etc.

El modelo matemático de la distribución de tamaños de los materiales del lecho se determinó a través de un análisis por mallas, de muestras de sedimento de diversas secciones del cauce, colectadas bajo las condiciones hidráulicas prevalentes. El ajuste teórico a la curva granulométrica fue de tipo log-normal (Fig. 2).

Este modelo permite seleccionar el intervalo granulométrico representativo del trazador y estimar los diámetros que se emplean en las fórmulas convencionales de la hidráulica para calcular el transporte de fondo.

De acuerdo con la distribución granulométrica, el cauce del río se clasificó como de tipo aluvial con sedimento de granulometría extendida [6]. Su diámetro mediano ($D_{50}$) resultó de 1,033 mm y su diámetro medio ($D_m$) de 1,935 mm.

4.2. Características del trazador

Cuando los materiales que forman el lecho de un río presentan una granulometría extendida, diversos autores (Shields, Straub, Zeller, Engelund, etc.) consideran que el diámetro representativo del fondo es el que corresponde a $D_{50}$ del modelo granulométrico [7].
FIG. 3. Diagramas de transporte del iridio 192 en el cauce del río Lerma: la gráfica de la configuración 10 se extiende a 1026 m.
De acuerdo con este criterio, se eligió un diámetro de grano para el trazador comprendido entre 0,84 mm y 1,10 mm, intervalo que corresponde a los tamaños acotados por los valores $D_{43}$ y $D_{43}$ del modelo granulométrico (Fig.2). Por otro lado, el emplear una distribución limitada y bien conocida simplifica la interpretación de los resultados debido a la proporcionalidad entre el diámetro y la actividad de cada grano [8].

La cantidad de trazador inyectada fue de un kilogramo de vidrios activados con 0,685 Ci de iridio 192 ($T_{1/2} = 74,2$ días, $E_{γ} = 0,34$ MeV). Los vidrios activados contienen una pequeña cantidad de elemento radiactivo (0,3%) distribuida uniformemente en su volumen, y su densidad es de 2,70 ± 0,5 g/cm³.

Debido a que el río no presenta un régimen estable, la representatividad del intervalo granulométrico del trazador se verificó recurriendo a un análisis estadístico de los datos hidrométricos históricos (período 1971–1980) de la estación El Gigante, localizada a 5 km aguas arriba del tramo estudiado [3]. Se encontró que el gasto más probable está comprendido en el intervalo de 23,0 m³/s a 26,0 m³/s, el gasto medio es de 29,1 m³/s y los gastos máximo y mínimo son de 366,5 m³/s y 2,0 m³/s respectivamente. Esta información, junto con las características hidráulicas del río donde se efectuó la inmersión y el modelo granulométrico, permitieron aplicar el criterio de Gessler, en la forma adimensional propuesta por Cruickshank y García [9, 10], para determinar la probabilidad que tendría de moverse el trazador. Para el gasto más probable esta resultó del 94%.

4.3. Inmersión del trazador

La inmersión del trazador se realizó en una sección del río previamente determinada sobre una carta topográfica del cauce, aproximadamente a 10 km aguas arriba de la presa Solís (Fig.1). La inmersión se realizó en forma puntual e instantánea sobre el lecho, mediante un inyector mecánico operado remotamente desde la superficie.

4.4. Detección y localización

A partir del instante en que se libera el trazador, las fuerzas tractivas ejercidas por la corriente lo integran gradualmente en el lecho. Cuando alcanza un comportamiento dinámicamente similar al sedimento natural, proporciona información representativa del desplazamiento y del espesor del transporte.

El rastreo del trazador se realizó con un detector de centelleo ($θ = 1,5$ pulg, $h = 1$ pulg) a velocidad constante, sobre trayectorias perpendiculares a la dirección de la corriente (transectos). Simultáneamente a la detección se construyeron diagramas de distribución del trazador, mediante el vaciado de los datos de campo sobre una carta topográfica del cauce, para rediseñar el rastreo.
<table>
<thead>
<tr>
<th>Fecha</th>
<th>25-3-81</th>
<th>26-3-81</th>
<th>28-3-81</th>
<th>31-3-81</th>
<th>3-4-81</th>
<th>8-4-81</th>
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<td>10</td>
</tr>
<tr>
<td>Tiempo transcurrido (d)</td>
<td>Inmersión</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td>9</td>
<td>14</td>
<td>45</td>
<td>50</td>
<td>106</td>
<td>232</td>
</tr>
<tr>
<td>Tiempo entre dos mediciones (d)</td>
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<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>31</td>
<td>5</td>
<td>56</td>
<td>126</td>
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<tr>
<td>Actividad recuperada (%)</td>
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<td>37,12</td>
<td>93,95</td>
<td>100,0</td>
<td>97,24</td>
<td>80,93</td>
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<td>45,19</td>
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<tr>
<td>Dist. recorrida por el C G (m)</td>
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<td>69,0</td>
<td>116,6</td>
<td>150,6</td>
<td>195,0</td>
<td>294,0</td>
<td>349,0</td>
<td>547,0</td>
<td>655,0</td>
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<tr>
<td>Dist. entre dos mediciones (m)</td>
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<td>198,0</td>
<td>103,0</td>
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<tr>
<td>Vel. media Vm del C G (m/d)</td>
<td>28,0</td>
<td>23,0</td>
<td>19,43</td>
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<td>6,98</td>
<td>5,16</td>
<td>2,82</td>
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<td>3,2</td>
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<td>0,82</td>
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<td>Espesor del transporte E (cm)</td>
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<td>-</td>
<td>-</td>
<td>0,6</td>
<td>3,7</td>
<td>11,7</td>
<td>11,2</td>
<td>16,5</td>
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<tr>
<td>Gasto sólido gb (t/m · d)</td>
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<td>2,02</td>
<td>2,07</td>
<td>2,25</td>
<td>(0,41)</td>
<td>(0,60)</td>
<td>(0,61)</td>
<td>(0,67)</td>
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</table>

\(^a\) La actividad del trazador ha decaído a 60 mCi y puede no ser representativa del transporte.
y no dejar secciones sin determinar, ya que las áreas de alta concentración requieren una densidad mayor de transectos que aquellas donde la radiación es relativamente inferior.

Los valores de las detecciones periódicas, correspondientes a los 232 días que duró la campaña de observaciones, permitieron elaborar diez configuraciones del trazador. Estos valores ya corregidos por decaimiento, radiación de fondo y transformados mediante la Ec.(6), aparecen graficados en función de la distancia al punto de inyección en la Fig.3. Dichas gráficas se denominan diagramas de transporte y describen el estado de movimiento que guarda el trazador en el momento de realizar la detección.

4.5. Calibración de instrumental

El instrumental de detección utilizado se calibró en el laboratorio, simulando las condiciones hidráulicas y geométricas bajo las cuales se realizó el rastreo de campo. Los valores de los coeficientes de la función de calibración \( f = f_0 e^{-\alpha z} \) para el radisótopo utilizado, el tipo de sedimento y la geometría adoptada resultaron ser \( f_0 = 23.4 \) (cuentas/s)(\( \mu \)Ci/m\(^2\))\(^{-1} \) y \( \alpha = 0.155 \) cm\(^{-1} \).

5. PRESENTACION DE RESULTADOS

5.1. Actividad recuperada

Los diagramas de transporte del trazador (Fig.3) permiten deducir directamente los parámetros que caracterizan el transporte de fondo resultante, bajo los efectos hidrodinámicos presentados durante la temporada de observaciones. Estos diagramas representan la distribución del trazador en función de la distancia al punto de inmersión, y permiten calcular la tasa de conteo \( N \) expresada por la Ec.(7), mediante la integración del área bajo la curva, así como determinar la posición del centro de gravedad de la nube radiactiva.

Los porcentajes de actividad recuperada en función del tiempo están indicados en el Cuadro I. Cada porcentaje se determinó comparando las actividades inyectada \( A \) y recuperada \( N/f_0 \), mediante la relación \((N/f_0 A) \times 100\).

5.2. Espesor del transporte

El espesor del transporte, \( E \), se determinó haciendo las siguientes suposiciones: a) la diferencia entre las actividades inyectada y recuperada se debió exclusivamente al enterramiento del trazador, y b) el valor de \( \beta \) varía de acuerdo con una distribución de la forma \( \Gamma(z) = \Gamma_0 (1 - Z^2/E^2) \). Los espesores obtenidos al resolver la Ec.(9) para las configuraciones 5, 6, 7, 8 y 9 se indican en el Cuadro I.
5.3. Velocidad media del transporte

La distancia efectiva recorrida por la nube radiactiva desde el punto de inmersión está caracterizada por el centro de gravedad (CG) de los diagramas de transporte. La posición de este punto se localiza normalizando al 100% el área bajo la curva de los diagramas de transporte y graficando los porcentajes acumulados en función de la distancia al punto de inmersión (Fig.4). Estas gráficas se denominan diagramas de transporte acumulado y permiten analizar la distribución de los porcentajes del trazador en el lecho. El punto correspondiente al 50% de la actividad recuperada indica el desplazamiento $\Delta x_g$ del centro de gravedad en el intervalo de tiempo $\Delta t$ (Fig.4). La velocidad media del transporte queda entonces determinada por la relación $V_m = \Delta x_g / \Delta t$. Los resultados están indicados en el Cuadro I.

5.4. Gasto sólido unitario

El gasto sólido unitario $g_b$ se calculó de acuerdo con la Ec.(1) asignando al sedimento una densidad igual a 2,65 g/cm³ (véase el Cuadro I).
CUADRO II. CARACTERISTICAS HIDRAULICAS DEL RIO LERMA

<table>
<thead>
<tr>
<th>Gasto líquido (m³/s)</th>
<th>Velocidad media de la corriente (m/s)</th>
<th>Radio hidráulico (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22,7 ± 5,4</td>
<td>0,75 ± 0,18</td>
<td>0,92 ± 0,17</td>
</tr>
<tr>
<td>24,5ᵃ</td>
<td>0,77</td>
<td>1,17</td>
</tr>
<tr>
<td>29,1ᵇ</td>
<td>0,82</td>
<td>1,26</td>
</tr>
</tbody>
</table>

ᵃ Valor más probable. ᵇ Valor medio histórico.

6. METODOS CONVENCIONALES

Dentro de los métodos convencionales de la hidráulica fluvial, se cuenta con un número muy extenso de fórmulas semiempíricas para determinar el transporte de fondo en cauces aluviales. En su gran mayoría se han desarrollado a partir de evidencias experimentales, obtenidas en canales de laboratorio rectos y de poca profundidad y, en algunos casos, con flujos estacionarios y granulometrías uniformes [11]. Las fórmulas, por lo general, son muy sensibles a cambios en las características del flujo, por lo que pequeños errores en las mediciones introducen un gran error en el cálculo del transporte. Por este hecho, su extrapolación a cauces naturales es dudosa y los resultados obtenidos varían notablemente entre sí [12].

Como un método de comparación de los resultados obtenidos con el radiotrazador, se emplearon algunas de las fórmulas que han mostrado mayor aplicabilidad al caso de corrientes con características parecidas a las del alto río Lerma [13, 14].

Los parámetros hidráulicos del alto río Lerma, correspondientes a la temporada que duró el experimento, se determinaron en forma rutinaria en una estación hidrométrica instalada temporalmente sobre una sección representativa del tramo estudiado. Con la información de los perfiles de velocidad y los tirantes de la corriente se calcularon los gastos por el método de áreas-velocidades para calibrar una curva de elevaciones-gastos. La curva permitió determinar, mediante extrapolación, las características hidráulicas del cauce para los gastos medio y más probable, obtenidos del análisis estadístico de la información hidrométrica histórica.

En el Cuadro II se muestran algunas de las características hidráulicas correspondientes al gasto medio registrado durante la temporada que duró el experimento y a los gastos históricos más probable y medio respectivamente.
<table>
<thead>
<tr>
<th>Gasto líquido (m³/s)</th>
<th>Straub, Zeller</th>
<th>Kalinske</th>
<th>Barekyan</th>
<th>Scholliersch</th>
<th>Engelund</th>
<th>Meyer-Peter-Müller</th>
<th>Einstein</th>
</tr>
</thead>
<tbody>
<tr>
<td>22,7</td>
<td>122,77</td>
<td>5,19</td>
<td>2,56</td>
<td>3,11</td>
<td>14,26</td>
<td>3,49</td>
<td>1,95</td>
</tr>
<tr>
<td>24,5^a</td>
<td>141,75</td>
<td>5,23</td>
<td>3,25</td>
<td>3,50</td>
<td>17,12</td>
<td>3,98</td>
<td>2,76</td>
</tr>
<tr>
<td>29,1^b</td>
<td>165,08</td>
<td>5,51</td>
<td>4,15</td>
<td>3,98</td>
<td>20,82</td>
<td>4,67</td>
<td>3,70</td>
</tr>
</tbody>
</table>

^a Valor más probable.

^b Valor medio histórico.
Adicionalmente, se realizó un muestreo intesivo del sedimento, y del análisis granulométrico de las muestras se encontró que, durante la temporada, el diámetro mediano del cauce fue de 0,847 mm. Este diámetro está comprendido en el intervalo granulométrico del trazador, lo cual verifica su representatividad.

Empleando la pendiente del cauce (0,00084) y los diámetros dados por el modelo granulométrico del sedimento en las fórmulas semiempíricas, se obtuvieron, para el gasto líquido medio registrado durante el experimento y los gastos líquidos más probable y medio históricos, los gastos sólidos que se muestran en el Cuadro III.

7. ANALISIS DE RESULTADOS

Los resultados del presente estudio permiten analizar, con cierto detalle, las diversas etapas de movimiento del trazador en el cauce del río. Los valores correspondientes a las primeras configuraciones indican que a partir del momento de la inmersión, el trazador se dispersa superficialmente sobre el lecho hasta alcanzar, en la cuarta configuración, una distribución en la que se recupera el 100% de la actividad inyectada. Los porcentajes de actividad de las tres primeras configuraciones son menores al 100%, debido a que durante este período la actividad se encuentra concentrada en áreas relativamente pequeñas, ocasionando la saturación del equipo de detección. Los valores de las configuraciones subsecuentes (5 a 10) indican que el trazador se integra paulatinamente en el lecho. Este proceso se hace evidente por la forma en que decrécen, a
medida que pasa el tiempo, tanto la actividad como la velocidad media del centro de gravedad de la nube y por el incremento gradual en el enterramiento del trazador. Para ilustrar este efecto, en la Fig. 5 se han graficado la velocidad media y el espesor del transporte en función del tiempo transcurrido.

Los resultados de la última configuración (9–11–81) no se tomaron en cuenta para calcular el gasto sólido, debido a la baja actividad recuperada (11%). Este porcentaje podría deberse a las avenidas presentadas durante la última semana del mes de julio de 1981, en que se registraron gastos cercanos a 150 m³/s, lo cual pudo ocasionar pérdidas significativas por suspensión del trazador. También debe tomarse en cuenta que la actividad original ha disminuido por decaimiento radiactivo a 60 mCi y, dada la alta dispersión del trazador, podría ya no ser representativa del fenómeno.

Por tanto, se considera que los valores más representativos del transporte son los de la novena configuración (9–7–81); con estos datos se obtiene que el gasto sólido unitario transportado por el río durante la parte experimental ha sido de 2,25 ± 0,67 t/m·d.

En el Cuadro III se puede observar que el valor de este gasto comparado con los resultados de los métodos semiempiricos es ligeramente inferior al de las fórmulas de Schoklitsch y Meyer Peter-Müller. Los resultados de las fórmulas de Einstein y Barekyan caen en el intervalo del valor obtenido con el trazador. Los resultados correspondientes a las fórmulas de Engelund y Straub-Zeller son significativamente mayores debido a que el primero de ellos se recomienda para granulometrías uniformes y el segundo para rangos de partículas con diámetros menores a 0,5 mm [15].

8. CONCLUSIONES

El método de los trazadores radiactivos ha permitido estimar el transporte de la capa de fondo en el alto río Lerma; su valor para el período observado resultó de 2,25 ± 0,67 t/m·d.

Los gastos sólidos calculados a través de las fórmulas semiempíricas muestran cierta concordancia con los resultados del trazador, particularmente los de las fórmulas de Barckyán y Einstein.

Es evidente que el método ofrece amplias perspectivas para estudiar el movimiento de la capa de fondo en cauces naturales, especialmente si las características hidráulicas de la corriente no son estacionarias. Las mediciones que se obtienen con el trazador son la resultante de todos los procesos hidrodinámicos que influyen en el fenómeno; por tanto, medir los parámetros que caracterizan el transporte de fondo bajo las condiciones particulares de cada río y de su cuenca aportadora contribuirá ampliamente en la planeación, manejo y conservación de las obras hidráulicas del país.
REFERENCIAS

EXAMEN DE LA STABILITÉ D'UNE PLAGE ARTIFICIELLE ET DU TRANSPORT DES SEDIMENTS FINS EN SUSPENSION A L'AIDE DE TRACEURS RADIOACTIFS†

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Abstract–Résumé

A STUDY OF THE STABILITY OF AN ARTIFICIAL BEACH AND OF THE TRANSPORT OF FINE SEDIMENTS IN SUSPENSION USING RADIOACTIVE TRACERS.

The paper describes two applications of radioactive tracers in dynamic sedimentology in the light of experiments carried out in Singapore, between 1981 and 1982, along the new beaches reclaimed from the sea. The first part deals with the properties of transfer of a silt sediment suspension by the west tide. The tracer used was $^{198}$Au-labelled silt. Successive determinations were made of the trajectory, average velocity, variation in time of the vertical and horizontal dispersion, and dilution and settling of sediments released into the sea by point and instantaneous injection, after which the data were extrapolated to continuous release. The second part is devoted to a study of the stability of the artificial beaches forming the new coastline, using for the purpose $^{192}$Ir-labelled glass tracer of the same grain size as the sediments in situ. The results are presented in the form of isoactivity curves and transport diagrams. They can be used to determine the axis and average velocity of transport and the dispersion parameters (dimensions of the patch, change in the centre of gravity and quartiles). The thickness and rate of bed-load transport are then calculated by the 'method of count-rate balance'. Each part has a section on 'methodology', in which the tracer technique is reviewed (principle, labelling, release and detection) and a section where the results are analysed. The study has shown the hazards of beach pollution and the silting-up of harbour installations through the discharge of sediments into the sea as well as the hazard of erosion at the edges of the new coastline by the north-east and south-west monsoons.

EXAMEN DE LA STABILITÉ D'UNE PLAGE ARTIFICIELLE ET DU TRANSPORT DES SEDIMENTS FINS EN SUSPENSION A L'AIDE DE TRACEURS RADIOACTIFS.

Ce mémoire rend compte de deux applications des traceurs radioactifs en sédimentologie dynamique, à la suite des expériences effectuées à Singapour, au cours des années 1981–82, le

† Cette étude a été réalisée à Singapour avec l’assistance de l’IAEA (projet SIN/8/008).

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long des nouveaux rivages gagnés sur la mer. La première partie est consacrée à l'étude des propriétés de transfert d'une suspension des sédiments silteux par marée d'ouest. Le traceur utilisé est de la vase à l'or 198. On détermine successivement la trajectoire, la vitesse moyenne, l'évolution dans le temps de la dispersion verticale et horizontale, la dilution et la décantation des sédiments immergés en mer de façon ponctuelle et instantanée, puis on extrapole au cas d'un rejet continu. Dans la deuxième partie, on étudie la stabilité des plages artificielles qui constituent la nouvelle ligne de côte, en utilisant comme traceur du verre à l'iridium 192 ayant la même granulométrie que les sédiments en place. Les résultats sont présentés sous la forme de courbes isoclines et de diagrammes de transport. Ils permettent de déterminer l'axe et la vitesse moyenne de transport et les paramètres dispersifs (dimensions de la tache, évolution du centre de gravité et des quartiles). Puis, par application de la méthode du bilan des taux de comptage, on calcule l'épaisseur de transport et le débit de charriage. Chaque partie comporte un chapitre «métodologie» où on rappelle la technique des traceurs (principe, marquage, immersion, détection), et un chapitre où on analyse les résultats. Cette étude a permis de mettre en évidence, d'une part les risques de pollution des plages et d'envasement des installations portuaires dus au rejet de sédiments en mer, et, d'autre part, le risque d'érosion des extrémités de la nouvelle ligne de côte par les moussons de nord-est et de sud-ouest.

INTRODUCTION

Pour poursuivre son extension, la République de Singapour doit gagner de nouveaux terrains sur la mer en déversant des matériaux à proximité du rivage, dans la zone des petits fonds. L'aéroport international de Changi a été construit de cette façon, sur un site d'environ 660 hectares formant des plages artificielles de 8 km de long. De même, 15 millions de m³ de sédiments provenant de la zone de Loyang et Tampines sont actuellement rejetés à 750 m du rivage, et le terrain ainsi déblayé doit servir à l'agrandissement de la ville (fig. 1).

Ces travaux posent deux problèmes:

- l'augmentation de la turbidité du milieu par la fraction silteuse rejetée (sédiments de diamètre inférieur à 40 microns) dont le transfert et le dépôt risquent de polluer les plages avoisinantes et de provoquer l'envasement des ouvrages portuaires (fig. 1);
- la stabilité des nouveaux rivages.

Afin de prévoir les effets de ces travaux sur l'environnement, des expériences mettant en œuvre des techniques de traceurs radioactifs se sont déroulées in situ, pour étudier:

- d'une part, les propriétés de transfert et décantation d'une suspension de sédiments silteux soumis à l'action des courants et de la turbulence marine;
- d'autre part, les mouvements sédimentaires sur les plages et les petits fonds sous l'action des courants et des vagues en période de mousson.

Ces techniques, les seules à permettre le suivi des sédiments rejetés dans des conditions choisies et connues, et donc de déterminer leur évolution et leur devenir.
sous l'effet des différentes actions hydrodynamiques agissantes, sont complémentaires des méthodes classiques telles que la mesure de la courantologie locale. Elles faisaient toutes deux partie d'un vaste programme de protection du littoral.

Ce mémoire rend compte des méthodes mises en œuvre et des principaux résultats obtenus lors des expériences de traceurs.

1. **ETUDE DES PROPRIETES DE TRANSFERT D'UNE SUSPENSION DE SEDIMENTS SILTEUX AU MOYEN DE TRACEURS RADIOACTIFS AU LARGE DE SINGAPOUR.**

Le problème de pollution des aménagements balnéaires et d'envasement des installations portuaires, se posant essentiellement par marée d'ouest, les expériences eurent lieu au cours d'une telle marée. On en trouvera l'exposé détaillé dans [1]. En ce qui concerne la méthodologie et le principe d'analyse des résultats, on pourra également consulter [2], ou sa remise à jour [3]. En voici les grandes lignes:
FIG. 2. Principe de marquage et immersion du traceur (vase à l'or 198).

FIG. 3. Schéma de l'équipement des bateaux chargés de la détection.
1.1. Méthodologie

La méthodologie comprend le marquage, l'immersion du traceur et sa détection.

1.1.1. Marquage et immersion

Afin de déterminer les propriétés de transfert d'une suspension de sédiments silex de l'étalonnage progressif est dû essentiellement aux gradients de vitesse et à la turbulence, un échantillon de 5 L de vase à 200 g/L provenant du site à étudier est marqué avec 9 Cl d'198 Au (période 64 heures, énergie γ de 410 keV), puis immergé ponctuellement à 1 m sous la surface, après dilution à 18 g/L.
D'une durée d'environ 1 min, le rejet peut donc être considéré comme instantané et ponctuel dans l'étude du champ lointain.

Le marquage a lieu sur le site, en même temps que l'immersion (fig. 2).
Le principe de fixation de l'or sur les particules de vase est basé sur les propriétés réductrices de celles-ci, et a fait l'objet d'une étude détaillée en laboratoire [4].
En particulier, on a montré que les propriétés hydrodynamiques de la vase naturelle ne sont pas affectées par le marquage, tant que la concentration en 198 Au ne dépasse pas 250 mg/kg de sédiment sec. Cette condition est toujours respectée au cours des expériences.

1.1.2. Détection

La détection en continu dans l'espace et dans le temps, avec des détecteurs de radioactivité placés à des profondeurs données (1 et 5 m pour une hauteur d'eau de 12 m environ), est assurée dès la fin du rejet par deux bateaux à moteur autres que celui chargé de l'immersion, et qui effectuent des traversées successives du nuage dans le sens transversal et longitudinal, pendant environ 3 h 1/2.

Leur équipement comprend notamment (fig. 3):

- 2 sondes à scintillation NaI (TI) 1 1/2"-1" dont la sensibilité pour l'or 198 est de 12 coups s⁻¹/µCi m⁻³;
- 2 icômètres (IPP4) dont le seuil est réglé à 50 keV;
- 2 échelles de comptage;
- des enregistreurs numérique et graphique.

En outre, un système de radio-localisation et une carte du site au 1/5000e permettent le positionnement minute par minute (fig. 4). Ceci est indispensable pour le bon déroulement de l'expérience.
FIG.5. Exemple de profils transversaux d'activité (Singapour, 22 juin 1982). L'échelle verticale (coup/s) varie d'un enregistrement à l'autre.
1.2. Analyse des résultats

Les relevés d’activité (fig. 5) obtenus au cours de l’exploration du nuage permettent de déterminer les paramètres suivants:
— trajectoire du centre de gravité des sédiments;
— vitesse moyenne de transport;
— dispersion verticale et horizontale,
— dilution du rejet
— décantation des particules, s’il y a lieu.
La méthode, illustrée par les figures 4 à 9, est résumée ci-après.

La trajectoire du centre de gravité est définie par les maxima trouvés au cours de la détection transversale (fig. 4). La vitesse moyenne est obtenue en portant sur un graphique la distance des maxima d’activités au point d’immersion en fonction du temps. Pour des courants de marée pouvant être considérés comme établis, ces points peuvent être calés par une droite dont la pente représente la vitesse moyenne de transport (fig. 6). A noter que la trajectoire et la vitesse moyenne de transport obtenues par cette méthode sont, dans le cas présent, tout à fait comparables à celles trouvées à partir du suivi des flotteurs.

Si on compare les relevés d’activité obtenus à 1 et 5 m de profondeur (fig. 5), on peut conclure à une forte tendance d’homogénéisation des profils verticaux de concentration par le milieu.

La dispersion horizontale peut être caractérisée par l’évolution dans le temps (ou dans l’espace) des écarts-type longitudinal et transversal, σ_x et σ_y (fig. 8). Ceux-ci sont obtenus en ajustant les relevés d’activité mesurés à différents instants par une loi de régression gaussienne, le seul paramètre étant l’écart-type (fig. 7).

La dilution, ou évolution dans le temps du maximum d’activité R_{max}, peut être déterminée en portant sur un graphique les maxima mesurés au cours de l’exploration de la tache, en fonction du temps. L’enveloppe de tous ces points représente la courbe de dilution (fig. 9).

Enfin, une estimation de la décantation peut être faite à partir d’un bilan des particules en suspension, en utilisant les lois de dispersion et de dilution précédentes.

Dans le cas présent, nous trouvons:

\[ R_{max} \approx 1/\sigma_x \cdot \sigma_y \]

Or, selon la théorie de diffusion gaussienne, cette relation, jointe à l’homogénéité des profils verticaux d’activité, implique l’absence de décantation, ce qui est d’ailleurs confirmé par le bilan.

Suite du texte p. 783.
Relevé des maxima d'activité:
- 8 juin 82
- 22 juin 82

*FIG. 6. Détermination de la vitesse moyenne de transport.*
FIG.7. Ajustement des profils d'activité par une loi gaussienne (22 juin 1982; détection transversale à z = 5 m de profondeur).

--- : relevé expérimental; ○ : représentation discrète du relevé expérimental; ——— : ajustement par une loi gaussienne $R = R_{\text{max}} \exp^{-t^2/2\sigma_w^2}$;

$a: VR = \frac{\Sigma (\Delta R)^2}{\Sigma R^2}$ = variance résiduelle.
FIG.8. Evolution de l'écart-type transversal $\sigma_y$ en fonction de la distance au point d'immersion.
FIG. 9. Délai d'évolution du maximum d'activité en fonction du temps.
1.3. Extrapolation au cas d’un rejet continu par marée d’ouest.
Consequences du rejet sur l’environnement

Associés à des mesures eulériennes de vitesse de courant et au suivi de flotteurs, les résultats obtenus par l’analyse précédente ont été extrapolés au cas réel d’un rejet continu des sédiments. Ils ont permis de mettre en évidence les points suivants (fig. 10):

a) Par marée d’ouest, les sédiments en suspension sont transportés parallèlement à la côte, à la vitesse \( U = 0,40 \) à \( 0,45 \) m/s, et atteignent donc l’entrée du port et son chenal environ 9 heures après leur introduction dans le milieu.

b) Les profils verticaux de concentration deviennent rapidement homogènes sous l’action de la turbulence et de la gravité ; ils peuvent être considérés comme tels 30 min après leur immersion.

c) Exprimé en fonction de la distance \( x = U \cdot t \) au point de rejet, l’écart type transversal \( \sigma_y \) peut s’écrire:

\[
\sigma_y = 4,17 \times 10^{-4} (U \cdot t)^{1.48}
\]

avec \( \sigma_y \) et \( U \cdot t \) en m.

Ceci implique que les sédiments atteignent la proximité des plages environ 4h 1/2 après avoir été rejetés.

d) Pour un rejet continu de sédiments fins, à raison de \( q \) kg/s dans un milieu de profondeur \( H \) constante (dans le cas présent \( H \approx 12 \) m), la dilution du panache est alors donnée par l’expression classique:

\[
\bar{C}_{\text{max}} = q/\sqrt{2\pi H \cdot U \cdot \sigma_y}
\]

avec, dans le système MKSA, \( \bar{C}_{\text{max}} \) en kg/m\(^3\) ou g/L, et le débit \( q \) de sédiments silteux en kg/s.

e) Dans les conditions de cette étude, la turbulence du milieu semble suffisante pour contrebalancer les effets de la gravité sur les particules solides et, dans ce cas, la décantation n’est pas mesurable. Elle aura essentiellement lieu au cours de la renverse de marée car, alors, les vitesses décroissent jusqu’à s’annuler. Par conséquent, il n’est pas exclu qu’une fraction des sédiments rejetés, qui n’a pas été évaluée à partir de ces expériences, puisse se déposer dans les installations portuaires. Ce point a été vérifié postérieurement par des sondages.

2. EXAMEN DE LA STABILITÉ D’UNE PLAGE ARTIFICIELLE EN UTILISANT DES TRACEURS RADIOACTIFS

Cette étude a fait l’objet d’un rapport [5]. Sa durée exceptionnelle, près de 10 mois, a permis d’observer l’effet des moussons de N-E et de S-O sur les
FIG. 10. Trajectoire, vitesse moyenne de transport, dispersion et dilution d'un rejet continu de sédiments silteux au cours d'une marée d'ouest.
transports sédimentaires le long de la nouvelle ligne de côte où se trouve actuelle-ment l’aéroport de Changi.

Les points d’immersion sont indiqués sur la figure 1. P1 et P2 sont sur la ligne de côte; P3 et P4 dans la zone des petits fonds (environ 2 m de profondeur) et P5 sur un banc de sable à −7 m.

Outre les mesures effectuées au moyen de traceurs radioactifs, les paramètres suivants on été relevés dans la zone d’étude:
− granulométrie des sédiments en place,
− courants de marée,
− houles,
− vents en vitesse et direction.

2.1. Méthodologie

La méthodologie comprend successivement:
− le choix du traceur (granulométrie, isotope radioactif, masse et activité à immerger),
− le marquage,
− la mise en œuvre, soit l’immersion et la détection.
Tous ces points ont été analysés dans [3] et [7].

2.1.1. Choix du traceur et marquage

Les particules marquées doivent être représentatives du sédiment naturel.
En particulier, elles doivent avoir la même granulométrie ainsi que des propriétés physico-chimiques et un comportement hydrodynamique semblables.

Dans le cas du transport par charriage en des zones sableuses, les expériences doivent durer plusieurs mois. On utilise alors du verre à l’iridium 192 (période 74 jours, spectre γ complexe d’énergie 296 à 885 keV) broyé, puis tamisé aux dimensions du sédiment naturel prélevé sur le site (fig. 11).

Pour des raisons de commodité d’interprétation des résultats, on restreint volontairement l’intervalle granulométrique en éliminant la fraction trop fine, susceptible d’être remise en suspension et de ne plus être détectée, et la fraction la plus grossière qui reste sur place et ne participe pas au transport.

La masse et l’activité immergées dépendent de la dispersion et de la profondeur d’enfouissement dans le milieu, de la taille des grains et de la méthode de détection. Ainsi, la détection point par point nécessite 10 fois plus de grains que la détection dynamique [6].

Pour des raisons de manipulation, de sécurité et de représentativité (bon mélange et incorporation au milieu), la masse et l’activité doivent être minimales.
**FIG. 11.** Courbes granulométriques des sédiments prélevés sur l'estran (A) et en mer (B).
Mais, pour des raisons de représentativité également, elles doivent être suffisantes pour que le nombre de particules marquées vues par le détecteur soit significatif du point de vue statistique, de même que le signal aux limites de la tache vis-à-vis du bruit de fond.

Dans le cas présent, on a utilisé 500 g de verre et 1 Ci d'iridium 192, le verre étant activé par réaction (n, γ) dans un réacteur nucléaire.

2.1.2. Immersion et détection

La figure 12 montre le schéma du dispositif de mise en place du traceur sur l'estran et celui de l'appareil d'immersion en mer. Sur l'estran, le traceur est recouvert d'une fine couche de sable mouillé, afin d'éviter sa dispersion par le vent et les premières vagues. En mer, pour la détection sur le fond, le principe et l'appareillage sont pratiquement les mêmes que dans le cas d'une suspension décrit dans la première partie. Cependant, on ne dispose que d'un seul bateau qui tractive un traineau portant le détecteur de radioactivité (fig. 3).

Sur la plage, les détections sont effectuées à marée basse. Un opérateur tire le chariot porte-sonde et relève les valeurs lues sur un intégrateur IPP4 en prenant la moyenne sur un pas de 5 m à 10 m ou plus, suivant la distance au point d'immersion. Un piquetage mis en place au préalable permet le positionnement.

Sur l'estran, 2 × 12 détections ont été réalisées sur ce principe aux points P1 et P2; puis 3 × 7 détections en mer aux points P3, P4 et P5, entre les mois de mars et décembre 1981.

2.2. Présentation et analyse des résultats

Les taux de comptage obtenus au cours des explorations successives de la tache peuvent être présentés de trois manières différentes et complémentaires:
- courbes isocactives (fig. 13),
- diagramme de transport (fig. 13 et 14),
- diagramme de transport cumulé (fig. 15).

Sur les diagrammes de transport, on porte en ordonnée le taux de comptage total mesuré suivant les transversales perpendiculaires à l'axe de transport, et en abscisse leur distance au point d'immersion. Les diagrammes cumulés sont la représentation intégrale des diagrammes de transport.

Suite du texte p. 793.

1 partie fixe
2 partie mobile
3 goulotte de sécurité
FIG. 13. Courbes isoactives et diagrammes de transport, Changi, Point 3 (Cps: coups par seconde).
POINT 1

Immersion en O le 3/3/81

6^e détection le 25/5/81
11^e détection le 28/10/81

Centres de gravité: $x_{G_6} = -28\ m$
$x_{G_{11}} = -100\ m$

Dispersion: $G_6 = 35\ m$
$G_{11} = 156\ m$

FIG. 14. Diagramme de transport.
FIG.15. Diagramme de transport cumulé.
### TABLEAU I. PRINCIPAUX RESULTATS OBTENUS SUR L'ESTRAN

<table>
<thead>
<tr>
<th>POINT 1</th>
<th>POINT 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chronologie de la Détection</td>
<td>Déplacement du centre de gravité</td>
</tr>
<tr>
<td>date (1981)</td>
<td>nbre de jours cumulés</td>
</tr>
<tr>
<td>3/3</td>
<td>immersion</td>
</tr>
<tr>
<td>5/3</td>
<td>2</td>
</tr>
<tr>
<td>13/3</td>
<td>10</td>
</tr>
<tr>
<td>19/3</td>
<td>16</td>
</tr>
<tr>
<td>1/4</td>
<td>29</td>
</tr>
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</tr>
<tr>
<td>24/6</td>
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</tr>
<tr>
<td>24/7</td>
<td>135</td>
</tr>
<tr>
<td>21/8</td>
<td>163</td>
</tr>
<tr>
<td>19/9</td>
<td>192</td>
</tr>
<tr>
<td>28/10</td>
<td>231</td>
</tr>
<tr>
<td>9/12</td>
<td>273</td>
</tr>
</tbody>
</table>

<sup>a</sup> Méthode du bilan des taux de comptage.

<sup>b</sup> Carottes.
L'analyse de ces courbes permet d'en déduire des informations d'ordre qualitatif ou semi-qualitatif, telles que:
- l'axe principal de transport,
- la vitesse du centre de gravité,
- les paramètres dispersifs et l'étendue de la tache,
- l'influence de la morphologie du terrain sur le transport et la dispersion des sédiments,
- l'action des courants, des marées et de la houle,
- la remise en suspension et le recouvrement.

La méthode permettant de quantifier le transport et de déterminer l'enfouissement des sédiments qui participent au mouvement est due à [6]. Elle est basée sur le fait que, pour une activité donnée, le taux de comptage total N de la tache radioactive est une fonction décroissante de l'épaisseur d'enfouissement E des grains:

\[ N = f_0 \cdot \frac{\beta}{\alpha} \left(1 - \exp\left(-\alpha E\right)\right) \cdot \frac{A}{E} \]

où
- N s'obtient directement par intégration du diagramme de transport;
- A est l'activité totale immergée;
- \( \beta \) est un paramètre qui dépend des profils verticaux de concentration du traceur, et qui est proche de 1,15 pour les épaisseurs de transport rencontrées usuellement;
- et enfin, \( f_0 \) et \( \alpha \) sont des constantes d'étalonnage des détecteurs, dont la loi de réponse en fonction de la profondeur z s'écrit:

\[ f = f_0 \cdot \exp(-\alpha z) \]

Comme la vitesse moyenne peut être déterminée à partir des diagrammes de transport (fig. 14), on en déduit le débit massique de sédiments sur une largeur \( L_T \):

\[ Q = \rho \cdot L_T \cdot V_m \cdot E \]

où
- \( \rho \) est la masse volumique des sédiments charriés;
- \( V_m \) est leur vitesse moyenne sur l'épaisseur de transport E.

La méthode suppose que:
- la totalité de l'activité immergée est détectée; en particulier, il n'y a ni remise en suspension, ni recouvrement, ni migration des sédiments au-delà des limites de la zone explorée;
- l'épaisseur et la vitesse moyenne de transport sont les mêmes partout et, par conséquent, le débit de charriage est le même dans toute tranche de largeur unité du lit.
Le tableau I résume les principaux résultats obtenus sur l’estran par cette méthode. On remarquera que les épaisseurs de transport calculées sont très voisines de celles mesurées à partir de carottes. Par ailleurs, on peut en tirer les conclusions suivantes:

a) Sur l’estran (fig. 16), les transports sédimentaires s’effectuent parallèlement à la côte sans grands échanges avec la mer. Le mouvement est orienté alternativement vers le S-S-O et le N-N-E, sous l’action des deux moussons.

b) La mousson de S-O se fait sentir sensiblement de la même façon sur tout l’estran, tandis que l’action de la mousson de N-E est plus importante lorsqu’on se déplace vers le sud.

c) Au point 1, la mousson de S-O a une capacité de transport supérieure à celle de N-E. Par suite, environ 730 t/an de sédiments sont entraînés vers le N-E.

d) Au point 2, au sud-ouest de la plage, il y a compensation entre les effets des moussons. Mais les sédiments expulsés en mer par la mousson de N-E (≈ 950 t/an) ne sont pas capables de revenir. Les extrémités de la nouvelle ligne de côte sont donc érodées par les moussons.


3. CONCLUSIONS

Les techniques de traceurs radioactifs ont vu le jour et se sont perfectionnées au cours des dernières décennies, avec le rôle de plus en plus important joué par les sédiments dans les problèmes de pollution.
Associées aux mesures classiques de courantologie et météorologie locales, ces techniques de mesure in situ constituent à l'heure actuelle un outil précieux lorsqu'on s'intéresse au comportement et au devenir des sédiments fins, que ce soit en mer à la suite de rejets à proximité d'ouvrages portuaires et de zônes balnéaires, ou en rivières et barrages lors des manoeuvres de chasse.

A Singapour, les problèmes posés par l'important remaniement des sédiments dans le cadre du programme d'élargissement de la côte ont été mis en évidence à la suite d'une longue campagne de mesures par tracers radioactifs. Ces problèmes sont de deux natures:

- en mer, ils impliquent la pollution des plages et le colmatage des installations portuaires dû à l'augmentation de la turbidité du milieu;
- sur le rivage, ils tiennent au danger d'érosion aux extrémités de la nouvelle ligne de côte sous l'action des moussons N-E et S-O.

REFERENCES


Un modèle numérique de dispersion et une carte du champ des vitesses ont été établis. Pour vérifier ce modèle numérique, trois campagnes de mesure ont été effectuées.

1) Les méthodes du puits unique utilisant $^{82}$Br comme traceur radioactif ont été appliquées à différentes profondeurs dans douze puits pour la détermination du champ des vitesses dans cette partie de l’aquifère du Bruxellien.

2) Les méthodes des puits multiples ont été appliquées au puits émetteur S42 par:
   a) traçage au KCl: le traceur a été recueilli après quelques heures dans 3 puits récepteurs concentriques localisés à 1,50 m de l’émetteur;

---

1 Les mesures ont été réalisées par l’Institut de radiohydrométrie de Neuherberg dans le cadre du projet IAEA-1645/RB.
FIG. 1. Vitesse moyenne de filtration et direction d’écoulement de la nappe au droit du lac de Louvain-la-Neuve (puits S42).

Les vitesses de filtration et les directions de l’écoulement qui résultent du modèle numérique et celles déterminées par les 3 campagnes de mesure sont comparées entre elles. Un exemple de comparaison est illustré par la figure 1 dans le cas du puits S42 où les trois méthodes concordent bien pour la vitesse mais non pour la direction.

L’analyse des résultats des trois méthodes montre que:
- le modèle numérique permet seulement d’approcher le comportement de l’aquifère;
- la technique du puits unique utilisée décrit ponctuellement les hétérogénéités de l’aquifère;
- les deux techniques des puits multiples reflètent le même comportement de l’écoulement souterrain dans une zone de l’aquifère. La méthode des puits multiples semble dès lors être celle à utiliser dans les études de vulnérabilité et de détermination des zones de protection des puits de pompage.
ISOTOPIC ANALYSES OF GROUNDWATER
FROM THE RAPAKIVI GRANITE,
SOUTHERN FINLAND,
FOR RADIOACTIVE WASTE MANAGEMENT

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Espoo, Finland

Groundwaters were investigated in the vicinity of the Loviisa nuclear power plant, on the island of Hästholmen, the aim being the assessment of the age and origin of groundwater in the Hästholmen rapakivi granite (see Table I).

The groundwaters were sampled during 1980–83 in boreholes, from a depth of about 200 m, at the most fractured levels in the bedrock, using a 3.5 m long packer-sampler. In addition to radiocarbon dating, $^3$H, $\delta^{13}$C and $\delta^{18}$O were measured, chemical analyses made, and microfossils analysed. The groundwater of Hästholmen consists of two chemically different groundwater zones: shallow fresh water and deep saline water. The salinity of the latter is nearly double that of coastal deep-sea water. The saline water resembles in many respects present-day sea water, but there are some differences regarding inter-element relationships.

The shallow groundwaters show high tritium contents, contrary to what would be expected from the radiocarbon activity. The deep groundwaters have low tritium contents and radiocarbon activities. Both recent and fragmentary microfossils were found even in the deepest groundwater samples. It is concluded that the deep saline groundwater in Hästholmen consists of a mixture of waters of different ages and origins. It is partly more than 10 000 years old (inter-glacial or preglacial) and partly it is relict sea water from the time of the Litorina stage of the Baltic Sea.
<table>
<thead>
<tr>
<th>Lab. No.</th>
<th>Drill hole/depth (m)</th>
<th>Sampling date</th>
<th>$^{14}$C-activity (% modern)</th>
<th>$\delta^{13}$CPDB (%)</th>
<th>Cl$^-$ (mg/L)</th>
<th>$^3$H (TU)</th>
<th>$\delta^{18}$O (%)</th>
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<tbody>
<tr>
<td>Su-954</td>
<td>Y1/50.4–53.9</td>
<td>6.10.80</td>
<td>39.66 ± 0.59</td>
<td>−18.0</td>
<td>11.5</td>
<td>38</td>
<td>−11.33</td>
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<tr>
<td>Su-1113</td>
<td>Y1/50.4–53.9</td>
<td>27.5.82</td>
<td>43.45 ± 0.51</td>
<td>−19.0</td>
<td>24.4</td>
<td>11.4 ± 1.2</td>
<td>−8.8</td>
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<tr>
<td>Su-953</td>
<td>Y1/81.2–84.7</td>
<td>1.10.80</td>
<td>26.00 ± 0.57</td>
<td>−13.9</td>
<td>3500</td>
<td>24</td>
<td>−7.9</td>
</tr>
<tr>
<td>Su-952</td>
<td>Y1/174.7–178.2</td>
<td>29.9.80</td>
<td>17.72 ± 0.45</td>
<td>−14.0</td>
<td>5139</td>
<td>6.5 ± 0.7</td>
<td>−8.83</td>
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<td>Su-1114</td>
<td>Y1/174.7–178.2</td>
<td>1.6.82</td>
<td>13.94 ± 0.53</td>
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<td>4759</td>
<td>&lt;1.2</td>
<td>−11.33</td>
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<tr>
<td>Su-1219</td>
<td>Y1/174.7–178.2</td>
<td>18.3.83</td>
<td>20.67 ± 0.42</td>
<td>−12.6</td>
<td>5070</td>
<td>10 ± 3</td>
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<td>Su-984</td>
<td>Y2/75.9–79.4</td>
<td>23.11.80</td>
<td>22.41 ± 0.34</td>
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<td>11.4 ± 1.3</td>
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<td>Su-985</td>
<td>Y2/145.7–149.2</td>
<td>3.12.80</td>
<td>18.77 ± 0.32</td>
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<td>5075</td>
<td>3.2 ± 1.2</td>
<td>−10.4</td>
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<td>Su-1033</td>
<td>Y5/56.0–59.5</td>
<td>23.7.81</td>
<td>58.58 ± 0.81</td>
<td>−19.5</td>
<td>20</td>
<td>55.1 ± 1.9</td>
<td>−11.09</td>
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<tr>
<td>Su-1120</td>
<td>Y5/56.0–59.5</td>
<td>29.6.82</td>
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<tr>
<td>Su-1218</td>
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<td>27.3.83</td>
<td>66.78 ± 0.51</td>
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<td>13.9</td>
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</tr>
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<td>Su-1034</td>
<td>Y5/153.0–156.5</td>
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<td>12.94 ± 0.23</td>
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<td>Su-1121</td>
<td>Y5/153.0–156.5</td>
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<td>5022</td>
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<td>17.79 ± 0.50</td>
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<td>7.2 ± 1.1</td>
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<tr>
<td>Su-1118</td>
<td>Y11/158.0–161.5</td>
<td>17.6.82</td>
<td>19.91 ± 0.23</td>
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<td>5126</td>
<td>&lt;2.0</td>
<td>−7.94</td>
</tr>
</tbody>
</table>

**Sea water**

$140.10 \pm 1.14 \quad -0.75 \quad \approx 60 \quad -0.44 \quad -8.17$
$^{18}$O/$^{16}$O AND $^2$H/$^1$H RELATIONSHIP BETWEEN RAINFALL AND INFILTRATION WATER IN THE ENGLISH CHALK

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Detailed studies of the isotopic variations in rainfall and unsaturated-zone water have been carried out at a research site on arable land in eastern England in order to investigate the mechanisms of water movement. The results also have implications for the interpretation of thermonuclear tritium profiles and the transport of pollutants such as nitrate towards the water table. The isotopic composition of rainfall has been monitored over several years during which four cored profiles of the soil and unsaturated chalk have been taken. Water has been extracted from this drill core at 20 cm intervals by centrifugation. An undisturbed lysimeter on grassland, 5 m deep, has also permitted natural drainage water to be sampled periodically. Two further profiles on permanent grassland permit comparisons for the effects of land use and lithology. Duplicated profiles generally show impressive similarity.

The stable-isotope composition of unsaturated-zone interstitial water is virtually uniform below about 4 m depth. Drainage from the lysimeter is mostly homogeneous isotopically and chemically, although there is a rapid hydraulic response to rainfall; infrequent departures from uniformity may represent unusual infiltration events. Above 4 m, the profiles show light isotopic compositions at intermediate depth and marked enrichment of heavy isotopes in the top few tens of centimetres, except in one case in which the opposite occurs. The isotopically heavy water in the top zone shows very little evidence of evaporative modification and is predominantly from unmodified rainfall. The scale of variations and the isotopic balance at this site suggest that the penetration depth by infiltrating rainfall varies greatly with time and season. The presence of a zone of mixing, extending several metres down from the surface, does not permit a 'piston-displacement' mechanism to be applied. Below this zone of mixing, however, the diffusive interchange of water held in fissures and pore spaces with different sizes and hydraulic conductivities ensures an approach to isotopic homogeneity.
The results of this study suggest that infiltration below permanent grassland at this site is about 5% \( \delta^2 \)H lighter than infiltration below adjacent arable land. There are insufficient data to give a valid comparison between these compositions and the average for rainfall, though it is observed tentatively that both infiltration below grassland and saturated-zone water have isotopic compositions closer to the composition of average rainfall (1979–82) than to that of infiltration below arable land.

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INTERRELATIONS BETWEEN RIVER WATER AND GROUNDWATER IN WATER SUPPLY AREAS USING ENVIRONMENTAL ISOTOPES

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In many densely populated regions the groundwater resources can no longer meet the demand for drinking water. As a result, many water catchment areas using bank filtration water are being installed near rivers. In special cases the groundwater supplies from such catchment areas can be increased by artificially induced infiltration of river water. In three case studies the infiltration rates and flow parameters of the bank storage in relation to the extracted groundwater are determined using environmental isotopes in combination with the usual hydrological methods.

(1) The water supply area of about 2 km\(^2\) is situated in the confluence area of two rivers. The aquifer consists of sandy gravel layers of a thickness of 6–8 m. The \(^18\)O data from pumping and observation wells enabled the quantitative calculation of the relative proportions of infiltrated river water and their spatial distribution. The proportions of water in the pumping wells from each of the rivers were determined as a function of time, using the isotope curves for the pumping wells and for both rivers. Proportions of between
50 and 100% of specific river water have been found in the different pumping wells, with an estimated accuracy of ±5%. Correlation with results of pumping tests led to a localization of the infiltration areas.

(2) The second case concerns a water catchment area on an approximately 0.3 km² large river island. The changing $^{18}$O content of the river water is well suited for the determination of the water infiltrated into the tapping wells and its flow velocities. Assisted by the large number of observation wells, it was possible to draw a detailed map of the proportions of river water in the groundwater (40–100%) and to determine flow velocities of between 2 and 15 metres per day. The results obtained by isotope measurements were supported and confirmed by dye tracer tests and measurements of electrical conductivity.

(3) In the case of an artificial groundwater enrichment by injected river water the amount and transit time of infiltrated groundwater were estimated by means of $^2$H data. Using a simple mixing equation, a proportion of 90 ± 5% of artificially infiltrated water in relation to the autochthonous groundwater was calculated for a pumping well. Utilizing hydrological models together with the annual isotope variation, the mean transit time was determined to be between two and four months.

IAEA-SM-270/35P

$^{18}$O/$^{16}$O RATIO
AS A TOOL IN STUDIES
OF WATER MOVEMENT
IN THE SOIL

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The measurement of the $^{18}$O/$^{16}$O ratio is a tool in studies of water movement in the soil column and its way down to the groundwater. Water is a tracer of low cost, which is available in large amounts. Water of a slightly depleted or enriched $^{18}$O/$^{16}$O ratio should be used. For the practical application of the method the fractionation of isotopes at the soil surface must be known. Under the climatic conditions of Jülich, no fractionation is observed between the mean $\delta$-values of precipitation, soil water and groundwater. Especially at the soil surface no enrichment of $^{18}$O was observed, except under extremely dry conditions.
The annual minimum of the $^{18}$O/$^{16}$O ratio in spring can be used as a natural tracer of the water movement in the soil. The $^{18}$O/$^{16}$O ratios of air water vapour (observed daily since 1981) and local precipitation (monthly means since 1974) are close to the equilibrium liquid/gas phase. These equilibrium conditions are responsible for the lack of $^{18}$O enrichment at the soil surface.

A first experimental study was made with a grass-covered lysimeter which had been filled with 'parabraunerde' (loess type) and left in the field for two years. At the beginning of the observation period an amount of 7 L/m$^2$ $^{18}$O-enriched water (+60‰, artificially enriched by distillation) was applied to the surface. Two days later the same amount of water of normal local isotopic content (−7.6‰) was added. Cores were taken regularly. It was found that the label moved down the soil column very quickly. In the plant water the higher $\delta^{18}$O values were immediately apparent. On the next day the plant water rapidly went down to a lower $\delta$-value, this being the result of the mean isotopic composition in soil water and in air water vapour. The distribution of $^{18}$O in the soil depends on the root activity. The transport of water in the roots lowers the amount of tracer and contributes to the mixing process within the soil column. Tracer studies must take into account the effect of vertical water transport by the roots, which is upwards. The water in the plant xylem has the mean isotopic composition of the root zone in the soil.

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DEUTERIUM IN TREES
AS AN INDICATOR FOR ISOTOPIC COMPOSITION OF PRECIPITATION WATER IN THE SCOTTISH HIGHLANDS

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The relation between deuterium content in precipitation ($\delta D_p$) and tree cellulose ($\delta D_C$) was examined for a mountainous area in north-east Scotland, especially the Cairngorms mountains.

Method. The deuterium/hydrogen ratios were measured in nitrated cellulose of pine trees (Pinus sylvestris L.) on a north-facing slope of the Cairngorms mountains between 300 and 800 m. Several samples of environmental water were taken at different dates.
Results. The δD-values for the trees are plotted against altitude in Fig.1.
If the ● and ▲ data are eliminated, a linear regression of $\delta D_t = -0.14 \, m + 0.02$ is obtained. The linear correlation coefficient $r$ is $-0.96$. The aberrant data coincide with extremely windy sites (▲) or more sheltered sites (●).

The following D/H measurements of environmental water were performed:

<table>
<thead>
<tr>
<th>Date</th>
<th>River Alt Mor, 440 m$^a$</th>
<th>Loch Morlich, 318 m$^b$</th>
<th>Soil water, 480 m$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 May 1983</td>
<td>$-67.4%\circ$</td>
<td>$-62.1%\circ$</td>
<td></td>
</tr>
<tr>
<td>10 July 1983</td>
<td>$-65.1%\circ$</td>
<td>$-59.5%\circ$</td>
<td></td>
</tr>
<tr>
<td>1 Sep. 1981</td>
<td>$-61.7%\circ$</td>
<td>$-53.2%\circ$</td>
<td>$-57.8%\circ$ (n = 3)</td>
</tr>
</tbody>
</table>

$^a$ Catchment area of the river extends up to 1200 m.
$^b$ This lake is fed by the Alt Mor and overflows into the river Luineag.
$^c$ Water extracted from peat soil at 20 cm depth.

Although it is difficult to calculate from these results the absolute fractionation between deuterium in precipitation and deuterium in cellulose, it is possible to estimate its relationship. Taking into account the maximum reported decrease
of $\delta D_p$ (precipitation) with altitude, i.e. $-4\%$ per 100 m, and our value of $\delta D_c$ (cellulose nitrate) of $-14\%$ per 100 m, we obtain a slope of 3.50 $\%$
$\delta D_c/\delta D_p$ instead of the 0.91 $\%$ of Epstein’s linear regression (YAPP, C.J., EPSTEIN, S., Geochim. Cosmochim. Acta 46 (1982) 955) obtained from trees growing throughout the North American continent.

Conclusions. These results indicate that in mountainous areas the isotopic composition of precipitation is not necessarily the primary factor controlling the D/H ratio in tree cellulose. The high slope in Fig.1 can be explained by the increase of the relative humidity with altitude in this area, effecting a decrease in deuterium content of the leaf water and thus of $\delta D_c$. Aberrant results can be attributed to a wind effect, modifying the local relative humidity.

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ORIGINE ET ALIMENTATION DES NAPPE DE LA BORDURE NORD-EST DU BASSIN DES ILLEMMENDEN (NIGER): APPORT DES TECHNIQUES ISOTOPIQUES

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Pour répondre aux besoins du complexe industriel et de la ville d’Arlit implantés en pleine zone désertique à 850 km au nord-est de Niamey, 10 millions de mètres cubes d’eau sont extraits annuellement des nappes souterraines locales. Dans cette région où les précipitations ne sont que de 40 mm par an en moyenne, et l’évaporation (Piche) de 4.5 mètres, l’origine d’une éventuelle recharge actuelle des nappes contenues dans les formations sédimentaires de la plaine de l’Irhazer ne peut être recherchée que dans leurs relations avec le massif cristallin de l’Afir qui, plus à l’est, bénéficie d’une pluviosité de l’ordre de 120 mm par an.
L'étude, effectuée sur la base de l'analyse \((^{18}\text{O}, D, {^{13}}\text{C}, {^{14}}\text{C}, T)\) de 59 échantillons collectés au cours de trois campagnes, a permis de mettre en évidence une nette différenciation isotopique des nappes dont on trouvera sur la figure 1 les principales caractéristiques. 

A) Dans l’Air, dont le sommet dépasse 2000 m, les nappes des plaines alluviales (koris) 1 présentent une teneur en oxygène 18 variant de \(-1 \delta \approx -4,2\delta\) (\(^\circ\) vs SMOW) suivant l’altitude moyenne de la zone de recharge. L’absence de signe d’évaporation dans la relation \(D/^{18}\text{O}\) témoigne d’une infiltration rapide des pluies dans les sables grossiers des koris qui alimentent ensuite le système de fracturation du massif 2.

B) Dans la plaines, d’une altitude moyenne de 400 m, la composition isotopique des aiguifères paléozoïques démontre une origine différente des eaux:

- L’aiguifère de Guezouman (C2), dont la profondeur à Arlit est d’environ 150 m, montre les plus faibles teneurs en oxygène 18 (moyenne \(-8,07 \delta\circ\), \(\sigma = 0,37\)), teneurs caractéristiques des eaux profondes de la partie occidentale du Sahara. Sur le flanc est du synclinal d’Arlit, où la formation affleur (14, sur la figure), l’activité relativement élevée en carbone 14 (31%) suggère une contribution locale à l’alimentation 3.

- L’aiguifère de Tarat (C3), entre 40 et 150 m de profondeur, a des teneurs comprises entre \(-7,66\) et \(-6,02\). Sa recharge principale estimée par les teneurs en carbone 14 se serait effectuée entre 30 000 et 10 000 ans, épisode terminé par la destruction du tapis végétal pouvant être à l’origine des nitrates dont la concentration atteint 100 mg/L dans certains forages.

C) Les formations mésozoïques (Continental Intercalaire), qui affleurent plus au sud le long de la bordure occidentale de l’Air jusqu’à Agadès, renferment la nappe du Tchoua (T) \((^{18}\text{O} \text{compris entre} -8,2 \text{et} 5,4, {^{14}}\text{C de} 8 \text{à} 45\%); ces données témoignent d’une recharge actuelle mélangeé à de l’eau ancienne d’origine profonde.

Sur l’ensemble de la zone d’investigation, la recharge actuelle, quand elle existe, s’effectue à l’affleurement au contact des aiguifères quaternaires, dans les lits des koris eux-mêmes alimentés, d’une part, par les crues irrégulières descendant de l’Air (12 sur la figure: \(\delta^{18}\text{O} = -2,01\)), d’autre part par la circulation de fissures du massif (11 sur la figure: \(\delta^{18}\text{O} = -4,24\)).

En outre, l’étude isotopique a mis clairement en évidence le rôle des accidents tectoniques:

Le long de la flexure Arlit-Inourarem d’orientation N-S: 4
- alimentation des grès d’Agadès par les aiguifères confinés du Tarat, et de Guezouman à Inourarem:
- alimentation du Tarat par l’aiguifère du Guezouman (4 sur la figure: \(\delta^{18}\text{O} = -8,1\) 16: \(\delta^{18}\text{O} = -8,36\)).

Le long de la flexure de Madaouela: 5
- alimentation des alluvions quaternaires par les eaux de Tarat (13 sur la figure: \(\delta^{18}\text{O} = -7\)) à Madaouela.
RESPONSE OF (FRESHWATER) LAKE KINNERET AND THE (SALINE) DEAD SEA TO CHANGING ATMOSPHERIC TRITIUM LEVELS

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Lake Kinneret and the Dead Sea, both situated in the Jordan Rift Valley, are exposed to similar atmospheric conditions and the Jordan river connects them. The characteristic parameters of the two lakes are summarized below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lake Kinneret (monomictic, throughflow)</th>
<th>Dead Sea (meromictic, terminal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area</td>
<td>168 km²</td>
<td>950 km²</td>
</tr>
<tr>
<td>Watershed</td>
<td>2730 km²</td>
<td>43 000 km²</td>
</tr>
<tr>
<td>Maximum depth</td>
<td>43 m</td>
<td>320 m</td>
</tr>
<tr>
<td>Volume</td>
<td>4 km³</td>
<td>146 km³</td>
</tr>
<tr>
<td>Evaporation</td>
<td>1.8 m/a</td>
<td>1.5 m/a</td>
</tr>
<tr>
<td>Salinity</td>
<td>0.65 g/kg</td>
<td>276 g/kg</td>
</tr>
<tr>
<td>Surface temperature</td>
<td>15–28°C</td>
<td>19–34°C</td>
</tr>
</tbody>
</table>

Lake Kinneret is monomictic, with an annual turnover every winter. By contrast, the Dead Sea has been meromictic during the last two centuries. However, the permanent stratification was gradually destroyed in the 1970s, leading to a complete overturn in 1979 (ASSAF, G., NISSENBAUM, A., in Desertic Terminal Lakes, Utah State University Press (1977) 61).

The inflow and outflow of Lake Kinneret are monitored accurately. For the Dead Sea these parameters are unknown; therefore, the evaporation rate, estimated by conventional methods, has a large uncertainty (about 15%). Because of the high salinity of the Dead Sea its evaporation rate is lower than that of the freshwater Lake Kinneret, although the environmental conditions are similar for both.

Tritium released into the atmosphere by thermonuclear testing appeared at the same level over both lakes. Figure 1 shows the response of their surface waters to the atmospheric tritium levels. The general picture is similar, but the
FIG. 1. Measured tritium concentrations in surface waters of Lake Kinneret (●) and the Dead Sea (○) between 1960 and 1983.

Details depend on the limnological characteristics of each lake. Thus, the tritium levels in the surface waters of Lake Kinneret rose faster and higher than those of the Dead Sea because of the shorter residence time of water in Lake Kinneret (5.2 years, compared with 18 years in the upper layers of the Dead Sea). Between 1964 and 1975, concurrent with the decrease in atmospheric tritium levels, molecular transfer through the surfaces of the lakes played an important role in diluting the surface tritium concentrations in both lakes. However, after 1975, as the salinity of the top layers of the Dead Sea was increasing rapidly, mixing with deeper, tritium-free layers occurred. The effect of this destratification process is reflected in the accelerated decrease in surface tritium levels in the Dead Sea between 1975 and 1979.

A model was set up for each lake to describe the variations of the tritium inventory and the surface water concentration. The model used the available bathymetric and hydrological data, and the available tritium data for the lakes and the various inputs. In the Lake Kinneret model the free parameter was the atmospheric tritium levels in the summer, which is always without rain. In the early 1960s, the levels were found to be higher than those for the rainy season, because of the high tritium input into the atmosphere. Thereafter, as the tritium input into the atmosphere declined, this relation gradually changed, probably owing to the diluting effect of the Mediterranean Sea.
In the Dead Sea model the free parameter was the evaporation rate. The output of the Lake Kinneret model, i.e. the atmospheric tritium levels in the summer, completed the data set of tritium inputs into the Dead Sea. It turned out that the sensitivity of the model to the free parameter was very high so that the evaporation rate could be determined with a precision of 5%, which is better than that obtained by conventional hydrological balance methods.

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SHORT-TIME VARIATION OF OXYGEN-18 AND ELECTRICAL CONDUCTIVITY IN FOUR SWEDISH RIVERS

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The variations of oxygen-18 in four Swedish rivers are presented as monthly values for the period 1978–1982 and as daily values during the snow-melt period of 1980. Also included are the variation of electrical conductivity for the latter period as well as river discharges. There are obvious seasonal patterns in the oxygen-18 variations. The northern rivers show fairly constant oxygen-18 values, except for a marked decrease at snow melt in May. The southern rivers display more sinusoidal variations, with a minimum in spring and a maximum in late summer and autumn. This difference is partly due to different runoff regimes. In the north, all winter precipitation is accumulated as snow and does not affect runoff until snow melt. In the south, there are quite substantial autumn and winter rains in addition to a less pronounced spring flood. Other factors influencing the oxygen-18 variations are the catchment area and its physiographical characteristics, the number of lakes and the climate. These govern the ratio of groundwater contribution to direct runoff, response time, damping and heavy-isotope enrichment by evaporation.

The short-time variations show that the decrease of oxygen-18 in spring is an immediate response to the increasing discharge.

The electrical conductivity varies in a similar way, with low values during the spring flood and high values when the discharge is smaller.
INVESTIGATION INTO THE APPLICATION OF STABLE ISOTOPES IN HYDROLOGICAL STUDIES IN THE UNITED KINGDOM

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In the United Kingdom, hydrological studies have in general neglected the use of stable isotopes as natural tracers, possibly because without the extremes of climate and/or relief found elsewhere, successful application is less certain. Such assumptions, however, have apparently not been supported by systematic investigations, and the purpose of the work reported here is to attempt to obtain methodical information by studying $^{18}$O/$^{16}$O isotope relationships between natural waters in a selected area. Malham in North Yorkshire, an area of horizontal karstified limestone, was chosen because of its short throughput times, the presence of a significant altitudinal range (185–645 m O.D.) and the availability of information from previous conventional hydrological studies.

The nature of the $\delta^{18}$OSMOW input signal and its correlation with surface waters have been examined over short and extended time-scales (up to 2½ years). On a monthly basis, the values are seen to follow a definable structure with some seasonal trends, normally within the range $-4\%_o$ to $-10\%_o$. Examinations of weekly and within-storm sample measurements, however, reveal a wide range of values (at least $12\%_o$), the details of which cannot be observed in a single month’s rainfall collection.

An average isotope depletion rate of $0.11\%_o$ per 100 m is discernible in summer months, although at other times the altitude effect appears erratic.

On recharge, a rapid smoothing of the $\delta^{18}$OSMOW input signal appears to occur, shown by a subdued and variable response in surface waters, which exhibit an average base-flow value of approximately $-7.8\%_o$. Unexpectedly, the most well-defined seasonal signal is found in the lake (Malham Tarn) which is fed by streams from the upper catchment, although only a weak correlation is found between the $\delta^{18}$OSMOW values in these waters and in the previous month’s
rainfall ($r = 0.36$). The naturally labelled lake water is clearly identified in lower-altitude springs, to which it is known to contribute. The definition of the signal is assumed to be due to evaporation, despite the lack of seasonal temperature extremes in the area.

It is concluded that, although for many applications the use of stable isotopes is inevitably limited in the United Kingdom, the nature of the seasonal signal in the lake suggests an important application for studies of leakage from, or interconnections with, surface storage systems.

IAEA-SM-270/76P

APPORTS DES ANALYSES ISOTOPIQUES
A LA CONNAISSANCE DU COMPORTEMENT HYDROGEOLOGIQUE DES ROCHES FISSUREES

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Des prélèvements d’eau dans les roches fracturées et fissurées du socle cristallin ou cristallophyllien ont été effectués sous des climats très différents aux émergences de sources, dans des forages ou dans des galeries creusées à grande profondeur dans le massif du Hoggar en Algérie, dans le plateau Mossi en Haute-Volta et dans les massifs cristallins externes des Alpes françaises (Chaine de Belledonne et Massif du Rissiou).

Des analyses des teneurs en tritium, oxygène 18 et deutérium ont été réalisées sur ces eaux qui ont toutes pour caractéristique de présenter une faible minéralisation à l’exception de très rares venues hydrothermales.
On constate tout d’abord de très grandes variations des teneurs en tritium des eaux, d’un point à l’autre dans une même zone d’étude pourtant homogène du point de vue géologique, ou d’une fracture aquifère à une autre située à quelques mètres seulement dans la même galerie lors du percement de celle-ci.

 Certaines fractures permettent la circulation très rapide, souvent avec de forts débits, d’eaux dont les teneurs en tritium sont identiques à celles des pluies et qui sont donc récentes alors qu’à quelques mètres les eaux ne se renouvellent pratiquement pas et sont des eaux quasiment sans tritium et donc anciennes. Ces faits s’observent tant au-dessus du niveau de base géographique des circulations aquifères comme dans les Alpes françaises qu’au dessous de ce niveau de base comme c’est le cas dans les régions d’Afrique étudiées.

 Les teneurs en oxygène 18 et en deutérium confirment par ailleurs qu’il existe des infiltrations rapides donnant des eaux souterraines ayant les mêmes caractéristiques isotopiques que celles des précipitations et d’autres infiltrations beaucoup plus lentes correspondant à des eaux des précipitations. Elles sont soit de type océanique, comme dans les Alpes françaises ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$) soit de type nettement différent comme au Hoggar où la relation devient $\delta^2\text{H} = 6 \delta^{18}\text{O} + 2$.

 On peut ainsi montrer que l’alimentation tant des altérités en pays tropical que des remplissages alluviaux des lits des oueds provient dans bien des cas de mouvements ascendants des eaux depuis le substratum cristallin alimenté depuis les zones d’affleurement mais que parfois, selon les saisons, il y a inversion du sens des échanges entre couverture et substratum.

 D’une manière générale, l’étude de la répartition des isotopes de l’environnement dans les eaux souterraines rencontrées dans les roches fissurées montre que ces formations, qui peuvent donner lieu à des circulations aquifères à des profondeurs supérieures à 100 mètres dans le socle du bouclier africain et à 1000 mètres dans les Alpes françaises, ont un comportement hydrogéologique extrêmement hétérogène qu’il est important de connaître tant pour l’exploitation des eaux souterraines que pour la réalisation de grands travaux souterrains, mais aussi sur un plan plus théorique, pour la compréhension des phénomènes d’infiltration et l’hydrothermalisme.
ETUDE ISOTOPIQUE DE LA REGION DU HORST DE NDIASS
Son intérêt pour la détermination des conditions d’alimentation en eau de la ville de Dakar (Sénégal)

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L’accroissement démographique accéléré de la ville de Dakar, capitale du Sénégal, créant une augmentation des besoins tant en eaux industrielles qu’en eaux de consommation, a entraîné l’exploitation intensive des ressources en eaux souterraines, d’autant que la presqu’île du Cap-Vert ne dispose ni de cours d’eau permanent, ni de site de barrage proche.

Plus de dix ans après une étude exploratoire menée conjointement par l’OMS et l’AIEA, de nouveaux travaux isotopiques sur les eaux souterraines de la région du horst de Ndiass permettent de préciser les conditions actuelles de recharge des aquifères captés ainsi que les limites de cette exploitation.

Le horst de Ndiass est un large dôme circonscrit (altitude maximum: 105 m) d’axe nord-sud. Sa bordure est tronquée par des falaises côtières. Vers le nord, il s’empoîne sous la dépression du lac Tanma. Il est constitué de formations maestrichtiennes subaffleurentes, sableuses et grése-calcaires, masquées le plus souvent par des formations latéritiques et par des recouvrements sableux quaternaires.

A l’est du horst, un système de failles nord-sud met en contact les formations maestrichtiennes avec les dépôts paléocènes, calcaires marneux et calcaires zoogènes (profondément karstifiés). Ce Paléocène, souvent recouvert par des sables quaternaires plus ou moins argileux qui combinent parfois un réseau hydrographique fossile, s’énnoie progressivement sous des dépôts marneux éocènes. Hydrogéologiquement, on distingue la nappe superficielle phréatique sur Maestrichtien ou sur Paléocène, la nappe profonde maestrichtienne ainsi que la nappe des calcaires paléocènes partiellement libre dans sa partie ouest.

* Actuellement: Centre de recherches géodynamiques, Thonon-les-Bains, France.
Trente-cinq échantillons correspondant à ces différents aquifères ont été analysés chimiquement (éléments majeurs et fluor) et isotopiquement: $^{14}$C, $^{13}$C, $^{18}$O, $^3$H et $^3$H (fig.1).

Les résultats ont été comparés à ceux de 1970 et confrontés aux données isotopiques des précipitations régionales.

Les informations obtenues sont les suivantes:

1) La nappe superficielle montre une hétérogénéité qui se traduit par des zones contenant des eaux pauvres en tritium et des zones où l'on peut trouver jusqu'à 20 UT.

2) L'utilisation d'un modèle de mélange (Hubert, 1970) montre que, pour la nappe superficielle, moins de 2% en moyenne des précipitations annuelles participe à la recharge, ce qui correspond à une lame d'eau inférieure à 12 mm.

3) La recharge de la nappe superficielle provient directement de la percolation des pluies locales ($^{18}$O = $-5,5\%$).

4) Les zones de recharge récente (activité élevée en $^{14}$C) de la nappe profonde sont bien localisées dans l'espace. L'évolution des activités varie conformément aux axes d'écoulement déterminés par la piézométrie.

5) Les datations sur les nappes profondes montrent des eaux subactuelles (1000 ans) à très anciennes (30 000 ans). L'exploitation intensive des forages profonds semble rajeunir les eaux en faisant appel à des aquifères plus superficiels.

6) La faille de Thiès séparant le horst du compartiment non soulevé joue le rôle d'une barrière étanche ou très faiblement perméable dans sa partie nord.
(âge différent de part et d'autre de la faille qui met pourtant en contact deux faciès perméables). Ce phénomène n’est pas décelable dans la partie sud.

7) La nappe paléocènes, soutenue par la artésienne dans la partie sud-est du horst montre en outre une stratification isotopique en $^{14}\text{C}$.

8) La nappe paléocène, soutenue par la nappe maestrichtienne en charge, montre très localement des réalimentations au niveau des vallées fossiles et des dépressions de type karstique.

Il s’avère donc que l’alimentation de la ville de Dakar s’effectue actuellement en grande partie à partir de la nappe profonde à recharge négligeable. Ceci s’est traduit en 10 ans par un rabattement de 5 à 10 m et par un début d’invasion marine dans les eaux souterraines sur la côte sud-est. Ceci va nécessiter dans le futur proche la recherche de nouvelles zones d’exploitation dans des régions plus éloignées des côtes, pour éviter de dégrader le potentiel existant.

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OXYGEN AND SULPHUR ISOTOPE RATIOS IN SULPHATE FROM ATMOSPHERIC PRECIPITATIONS

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Observations of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of the sulphate dissolved in rain and snow were carried out in 1979. These data, combined with the $\delta^{18}\text{O}$ and pH values of water, and the $\text{SO}_4^{2-}$ and $\text{Cl}^{-}$ concentrations, provided information on the way of $\text{SO}_4^{2-}$ formation in the atmosphere: (1) High and variable sulphate concentrations (from 1 to 19.3 mg/L) and low $\text{Cl}^{-}$ content (below 3 mg/L in most cases) point to continental derivation of the sulphate. (2) Nearly constant values of $\delta^{34}\text{S}$ (+3.7‰) represent an average isotopic composition of numerous $\text{SO}_4$ emitters distributed over a large area. (3) The $\delta^{18}\text{O}$ value of the sulphate is significantly correlated with that of water ($r = 0.62$, $n = 32$).

The following regression line has been derived from the collected data:

$$\delta^{18}\text{O}_{\text{sulphate}} = 16.0 \pm 0.9 + (0.38 \pm 0.07) \delta^{18}\text{O}_{\text{water}}$$
The slope and intercept of this line depend on the season. In winter, the values approach 1/4 and 14, respectively, for slope and intercept, which confirms the industrial origin of $\text{SO}_3^-$, with an initial $\delta^{18}O$ value of $+23\%$ and the incorporation of one atom of oxygen from water into $\text{SO}_4^{2-}$. Higher values of the slope and intercept must be due to partial oxygen isotope exchange between water and $\text{SO}_2/\text{SO}_3$.

IAEA-SM-270/96P

ORIGIN OF GROUNDWATERS IN THE UPPER SILESIAN COAL BASIN ACCORDING TO STABLE-ISOTOPE COMPOSITION

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Geological background. The total area of the Upper Silesian Coal Basin is 7500 km$^2$. The Carboniferous coal-bearing deposits (8200 m thick) are covered by permeable Mesozoic and Quaternary rocks in the northern and eastern parts. In the southern part, these deposits are covered by Tertiary clayey impermeable formations (up to 1000 m thick). Two hydrological regions can thus be distinguished (I and II). The contemporary recharge areas for the Carboniferous aquifers are mainly located in region I. The drainage of these aquifers is mainly by coal mines, as a result of water pumping (down to 600 m).

The hydrological problem. For reasons of safety and economy, it is essential to estimate the potential inflow of water into the mines and to establish its condition (static or dynamic). Therefore, the origin of groundwaters within the whole basin must be known. The traditional hydrochemical and hydrodynamical methods do not solve the problem, but the environmental isotope techniques represent a new approach.
FIG. 1. Relations of $\delta D$ and $\delta^{18}O$ for mining waters in the Upper Silesian Coal Basin.

FIG. 2. $\delta D$ values of mining waters versus depth.

Results. 133 water samples were collected from different mines and boreholes, from the Tertiary, Triassic and Carboniferous aquifers. The $\delta^{18}O$ and $\delta D$ values of all samples were measured in the laboratories of the IAEA and the Institute of Physics and Nuclear Techniques of the Academy of Mining and Metallurgy. The water chemistry was determined in the laboratories of the Geological Institute, Upper Silesian Branch, at Sosnowiec, and the Geological Enterprise at Katowice.
The tritium content of some of these samples was determined at depths of down to 300 m (region I) and down to 400 m (region II); $^{14}$C was determined at depths of down to 400 m (region I) and down to 260 m (region II). The $\delta^{18}$O values vary from $-11.6\%$ to $+0.3\%$ and the $\delta$D values vary from $-72.9\%$ to $-1.2\%$ (Fig. 1). The TDS values vary from 0.14 g/L to 215 g/L, with a simultaneous differentiation in chemical composition.

Conclusions

(a) Both chemistry and isotopic composition permit three groups of waters to be distinguished: infiltration waters (1), mixed infiltration and relict waters (2), and relict (synsedimentary) waters (3). Figure 2 shows their vertical range.

(b) First group: HCO$_3$-SO$_4$-Ca-Mg waters, TDS = 10 g/L, $\delta^{18}$O = $-12.1\%$ to $-8.8\%$, $\delta$D = $-77.1\%$ to $-62.0\%$, tritium = (5 ± 2) TU to (18 ± 2) TU, observed only down to 300 m. Carbon-14 was detected in this group down to 400 m (11.1 ± 1.3%). It can be concluded that the aquifer recharge took place in Holocene and Pleistocene.

(c) Second group: Mainly Cl-SO$_4$-Na or Cl-Na-Ca waters. TDS = 14–230 g/L, $\delta^{18}$O = $-8.8\%$ to $-1.0\%$, $\delta$D = $-62.0\%$ to $-15.0\%$. Mixed waters of groups (1) and (3) with older relict waters. There is no correlation between the stable-isotope content and total mineralization, probably because relict waters were squeezed out from Tertiary sediments which had different initial mineralization.

(d) Third group: Cl-Na waters, TDS = 32–52 g/L, $^{14}$C free; the isotope composition corresponds to SMOW. These waters have to be considered as synsedimentary/Tertiary waters.

(e) Waters from region II show a depletion of heavy isotopes down to 600 m (Fig. 2). This indicates the presence of mixing processes forced by the mining activity.
IAEA-SM-270/100P

CARBON DIOXIDE CONTENT AND
ISOTOPIC COMPOSITION OF
GAS IN THE UNSATURATED ZONE
AS AN INDEX OF GEOCHEMICAL ACTIVITY
IN RECLAIMED MINERAL LANDS,
ALBERTA, CANADA

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The results of a study of gases in the unsaturated zone suggest that the partial pressures of CO₂ (PCO₂) in the natural, undisturbed settings are relatively stable or increasing slightly over time, and that the values range between 0.03 and 3.5 mol%. The PCO₂ levels in one mine (Vesta) are similar to the natural levels (0.1–4.0 mol%) while the CO₂ levels in the other mine (Diplomat) reached a maximum of 23 mol% and varied significantly during the course of the one-year monitoring period. Values of PCO₂ generally increased with respect to depth in the unsaturated zone. Higher-than-normal levels of CO₂ in the unsaturated zone were attributed to the land disturbance and were believed to be indicative of non-equilibrium geochemical conditions.

The values of δ¹³C/¹²C of CO₂ from the Vesta and Diplomat mines (−17 to −19‰ and −11 to −12‰, respectively) were sufficiently different that a dual source of CO₂ was deduced. The first source was organic carbon, which was reflected by the values of δ¹³C/¹²C of CO₂ from the natural, unmined settings (−21 to −17‰). The second source consisted of marine carbonates, hydrolysed by sulphuric acid produced during pyrite oxidation (≈0‰). The samples from the two mines represent mixtures of CO₂ from both sources.

There was an excellent correlation between the values of PCO₂ actually measured and those calculated on the basis of an equilibrium chemical model (WATEQF) from the chemical composition of groundwater. The maximum value of PCO₂ for the Diplomat mine samples was about two times that of the Vesta mine (6.0 versus 3.0 mol%), in keeping with the range of PCO₂ actually measured through gas sampling.
TRACER TRANSPORT MODELLING
FOR THE UNSATURATED ZONE
Effect of anion exclusion and immobile water

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The tracer injection method (BLUME, H.P., ZIMMERMANN, U., MUNNICH, K.O., in Isotope and Radiation Techniques in Soil Physics and Irrigation Studies (Proc. Symp. Istanbul, 1967), IAEA, Vienna (1967) 315) for the evaluation of mass flow of moisture in the unsaturated zone is based on the 'piston-flow' model. The assumptions inherent in this concept are that the dynamic behaviour of the tracer is similar to the behaviour of the moisture in transport and that there is no 'immobile' component of soil moisture.

Our studies indicate that the above assumptions can be verified by a suitable mathematical simulation of the experimental data. The multi-cell mixing model and the advection-diffusion model have been used to simulate the laboratory and field tracer profiles obtained by us (RADHAKRISHNAN NAIR, A., PENDHARKAR, A.S., NAVADA, S.V., RAO, S.M., in Isotope Hydrology 1978 (Proc. Symp. Neuherberg, 1978), Vol.2, IAEA, Vienna (1979) 803) and other authors.

Adopting the iterative approach for the multi-cell model to suit the specific conditions of the tracer injection method, we formulate the tracer profile as follows:

\[ C_n^N = \frac{(N + n - 2)!}{(N - 1)! \cdot (n - 1)!} \cdot \frac{t^{n-1} \cdot W^N}{(1 + W)^N + n - 1} \]

where \( C_n^N \) is the tracer concentration in the nth cell after N iterations,
\( C_0 \) is the initial tracer concentration in the first cell,
\( I \) is the recharge pulse per iteration and
\( W \) is the moisture volume in each cell.

Both the iterative approach as given above and Bear's analytical solution (BEAR, J., Dynamics of Fluids in Porous Media, Elsevier, New York (1972) 586) for the multi-cell model have been used to verify the 'piston-flow' concept of moisture transport as well as the integrity of the tracer used. Tracer profiles
FIG. 1. Field tracer profiles in clayey soil (Wagoda).

FIG. 2. Breakthrough curves for a clayey soil from a laboratory column experiment.
obtained with tritiated water in some clayey soils (Figs 1, 2) could be simulated using the total measured moisture content, but the moisture content had to be considerably reduced to simulate the profiles obtained with $K_3^{60}\text{Co(CN)}_6$ under similar soil conditions. Two conclusions can be drawn: (1) the total measured moisture participated in the transport, and (2) the hexacyanocobaltate ion underwent strong anion exclusion. The model simulation revealed that the $(\text{Co(CN)}_6)^{3-}$ moved ahead of tritium because of anion exclusion and that there was no retardation of tritium due to exchange with ‘immobile’ water.

The one-dimensional advection-diffusion model has also been applied to the profiles referred to above, using the measured values of mean transport velocities. It is seen that the effective diffusion coefficient for $(\text{Co(CN)}_6)^{3-}$ is larger (nearly twice as large in some cases) than the coefficient for HTO. This may be explained as being caused by reduction in the diffusion cross-section for the cobaltate ion due to anion exclusion.

Tracer profiles have been simulated using the modified advection-diffusion model and taking into account the mobile and immobile components of soil moisture in order to look for deviations from the ‘piston-flow’ concept of the soil moisture transport. No significant presence of immobile water could be seen in either profile.

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ИЗОТОПНЫЙ СОСТАВ ЛЕДНИКОВ ЕВРАЗИЙСКОЙ АРКТИКИ КАК ИСТОЧНИК ПАЛЕОКЛИМАТИЧЕСКОЙ ИНФОРМАЦИИ

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Изотопно-кислородные профили по горным ледникам Центральной Европы показывают, что несмотря на перекопирование талых и дождевых вод первичный изотопный состав снегового покрова претерпевает только незначительные изменения [1].

Нами была сделана попытка использовать вариации изотопного состава кислорода талых ледников Евразийской Арктики для палеоклиматических реконструкций. Исследования проводились на архипелагах Шпицберген и Северная Земля.

Долговременными наблюдениями на Шпицбергене было установлено, что несмотря на слабую корреляцию при разовых осадках существует надежная связь между среднемесячными величинами $\delta^{18}$О в атмосферных осадках и температурой. Наши результаты и данные по станциям МАГАТЭ/BMO [2] показывают, что в районе Северной
Атлантические амплитуды вариаций δ18O в осадках и корреляция между δ18O и температурой увеличиваются в восточном и северо-восточном направлениях от южной ложбины. Анализ вариаций δ18O в атмосферных осадках на архипелаге Шпицберген также указывает на существенное влияние направления влагонесущих воздушных масс на характер взаимосвязи между изотопным составом осадков и температурой. По-видимому, это связано с изменением доли водяного пара локального происхождения в процессе формирования осадков.

Для уточнения степени сохранения первичной информации в теплых ледниках мы провели исследования на ледниках с разными типами питания на Шпицбергене и Северной Земле. Влиянием δ18O в ледниковом керне, сформированном в нынешнем столетии на ледоразделе Гренфюрд–Фриттойф (о. Западный Шпицберген) сопоставлялись со среднегодовыми температурами за это время. Изотопно-киссаторный профиль удовлетворительно согласуется с температурной кривой. На плато Ломоносова (о. Западный Шпицберген) и на куполе Вавилова (Северная Земля) проводились детальные исследования δ18O в шурфах и кернах. Установлено, что несмотря на инфильтрацию талых и дождевых вод, сезонные вариации δ18O в снегово-фирновых толщах сохраняются удовлетворительно.

ЛИТЕРАТУРА


IAEA-SM-270/13P

ISOTOPIC COMPOSITION OF $\delta^{34}$S(SO$_4$)
IN RAIN WATER OVER ISRAEL

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Since 1974, more than 100 rain samples from Israel have been analysed for $\delta^{34}$S(SO$_4$) and chemical composition. The data have been compared with the available $\delta^{18}$O(H$_2$O) values reported by Gat and Dansgaard (GAT, J.R., DANSGAARD, W., J. Hydrol. 16 (1972) 177) and by Levin et al. (LEVIN, M., GAT, J.R., ISSAR, A., in Arid Zone Hydrology (Proc. Adv. Group Mtg. Vienna, 1978), IAEA, Vienna (1980) 3).
The physiography of the region comprises the following units, stretching roughly in a north-south direction: (a) the Mediterranean Coastal Plain, (b) the central mountainous backbone, (c) the Jordan Rift Valley, and (d) the Golan Heights (forming the northern extension of the highlands east of the Jordan Rift).

The isotopic and chemical results point to a 'isotopic stratification' of the sulphur load of the air masses reaching Israel from the Mediterranean, in agreement with the preliminary model assumption (Wakshal, E., Nielsen, H., Earth Planet. Sci. Lett. 61 (1982) 272). It is suggested that sea-water spray droplets with a $\delta^{34}S$ value of $+20\%$ dominate the lower air mass while sulphate of biogenic origin with $\delta^{34}S$ of about zero prevails within the upper air mass. Thus, although the isotopes of sulphur (sulphate) and oxygen (water) reflect two different pathways of fractionation, their mutual distribution within the studied rain water could be correlated, in accordance with a local altitude effect. Therefore, the isotopic composition of $^{34}S$ and $^{18}O$ in rain water between the Mediterranean Coastal Plain and the Upper Galilee and Golan Heights follows the empirical equation

$$\delta^{34}S(SO_4) = 3.7 \delta^{18}O(H_2O) + 27$$

It is believed that our samples from northern Israel were not contaminated significantly by anthropogenic input of sulphur, whereas rain water in the vicinity of major cities may frequently indicate this source of pollution. Other dominant factors controlling the isotopic composition of $\delta^{34}S(SO_4)$ in rain water during the observation period are the intensity of wind storms over the land and the Mediterranean Sea, and aeolian dust from the Negev and African deserts. The most prominent enrichment of $\delta^{34}S$ as compared with the average local isotopic value was recorded during February 1975, when an approximate increase of $\Delta \delta^{34}S$ of $2\%$ took place over all sampling sites. Snow samples have been analysed in three cases, two at Mt. Hermon and one at Jerusalem. The measured isotopic value of these samples is heavier by $\approx 1.5\%$ than the appropriate mean rain-water composition.
Environmental isotope techniques ($^3$H, $^2$H or $^{18}$O) can contribute to making the runoff and storage behaviour of Alpine catchment areas more transparent by means of runoff component separations and mean residence time calculations.

Runoff components were separated for the following single events: snow melt, snow melt plus rain, and storm. The direct component was defined as having the isotope content of the actual input. Snow-melt events were found to yield the most reliable results, provided snow lysimeters are available (HERRMANN, A., MARTINEC, J., STICHLER, W., in Proc. Mtg. Modelling of Snow Cover Runoff, Crel, Hannover (1979) 288). This is mainly due to the isotopically fluctuating but always light inputs from snow-cover outflows compared with the stable-isotope contents of the pre-event waters or the indirect component. Direct runoff proportions can reach 30% during snow-melt events and 50% during storms. Subsurface water is, therefore, considered to play a dominant role in peak discharge formation. During the main ablation season in glaciated areas the dominant role can be attributed to the ice melt-water component, which is free of tritium. In this special case, more than two components were separated. Additionally, a quick and a delayed snow/firm melt-water component were discriminated by stable isotopes, and the mineralized groundwater fraction was determined by measurements of the electrical conductivity (BEHRENS, H., et al., in Isotope Hydrology 1978 (Proc. Symp. Neuherberg, 1978), Vol.2, IAEA, Vienna (1979) 829.

Annual data of the stable-isotope output allow distinct runoff seasons to be distinguished which have positive or negative deviations from the isotopic
mean and are of different length. A comparison with the isotopical input curves of the respective time intervals permits the calculation of seasonal direct runoff proportions of between 30 and 50%. This confirms the results from the single-event analyses.

The mean residence times $T_r$ of the subsurface reservoirs were derived from comparisons of the $^3$H and $^2$H or $^{18}$O input and output functions, the specific hydrological models and the model age distributions applied. $T_r$ varies between 1.5 and 4 years in the studied areas, the results from stable-isotope and $^3$H data being in good agreement (MAŁOSZEWSKI, P., RAUERT, W., STICHLER, W., HERRMANN, A., J. Hydrol. 66 (1983)). By introducing hydrological data, such as mean and minimum stream flow, it was possible to discriminate between two separate sub-reservoirs with different $T_r$ values, i.e. 0.1–1 year and 4–7 years.

The combination of hydrological and isotopical investigation methods enables a new insight into the water balances of the studied catchment areas. For example, the infiltration rates amount to about 50% of the precipitation depths, allowing for an evaporation loss of 25%. The subsurface storage volumes are of the order of $10^8$ times the discharge, with $T_r$ of 2.5 years. Assuming effective porosities of 20%, the calculated mean aquifer thickness is of the order of 10–15 times the precipitation depths.

IAEA-SM-270/33P

**KRYPTON-85 FOR GROUNDWATER DATING**

*Measurement, models, applications*

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The use of environmental $^{85}$Kr in isotope hydrology is necessary in view of the decreasing $^3$H concentrations in mixing systems. Krypton-85 is an ideal tracer: its amount still increases, it has virtually no sinks outside of radioactive decay and it has no remarkable seasonal variations. The atmospheric $^{85}$Kr concentration in the southern hemisphere is only 10–20% lower than that in the north, an important fact, as the $^3$H content in the south is only one tenth of that in the north (RÓŻAŃSKI, K., Environ. Int. 2 (1979) 139).
The measurement of $^{85}$Kr in water is done in three steps: vacuum gas extraction of 200–600 L water in one hour; separation of 10–20 μL krypton from a 6–8 L gas sample by chemical and gas-chromatographic treatment; and measurement of the $^{85}$Kr activity in a low-volume spherical proportional counter (background 0.03 counts/min, counting efficiency 80%).

Up to now, all $^{85}$Kr measurements (20 samples) turned out to be necessary for precise $^3$H, $^{14}$C and $^{39}$Ar interpretation. Through the combined use of $^{85}$Kr and $^3$H the fraction and mean residence time of a young water component, mixed with an older $^3$H-free component, could be calculated. Because of the small seasonal variations of $^{85}$Kr, in some cases the main recharge time during one year could be determined. In addition to clarifying ambiguous values of mean residence times calculated from $^3$H data and compared with $^{85}$Kr, the different input/output functions of $^3$H and $^{85}$Kr have been used to select the most appropriate flow model (piston flow, dispersion, exponential). Furthermore, environmental $^{85}$Kr has been successfully used in the unsaturated soil zone for evaluating diffusion and seepage velocity. The theoretical calculations confirm the experience that diffusion is not a limiting factor for the application of $^{85}$Kr in isotope hydrology (SALVAMOSER, J., thesis, University of Munich, 1982).

IAEA-SM-270/43P

ENVIRONMENTAL ISOTOPE-AIDED STUDIES ON RIVER WATER AND GROUNDWATER INTERACTION IN THE REGION OF SEOUL

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Recently, river water pollution in Korea has caused serious problems with regard to crop production, drinking water contamination, and so on. Therefore, it is of prime importance to protect water resources from pollutants.
A preliminary study of the isotope hydrology of the Han river valley is presented. This investigation is part of a project the overall aim of which is to relate the levels of heavy metal ions to the dynamics of the groundwater movement, in order to establish whether there is any evidence for the deterioration of groundwater quality associated with the release of industrial effluents, and, if this is the case, to determine the migration pathways. Evidence is presented that the water recharge mechanism is principally determined by the degree of urbanization. In the metropolitan area of Seoul, river recharge dominates, which is probably due to the combined effects of reduced infiltration and increased pumping. In the inter-urban region, the major source of recharge is local precipitation. During the spring sampling period when the river levels were low, evidence was obtained for appreciable groundwater infiltration in the vicinity of the upstream transection.

An environmental isotope survey of the groundwater from the shallow alluvial and the underlying crystalline rock aquifer of the Han river valley has been undertaken. The analysis of the data produced the following results: (i) confirmation of the hypothesis that the groundwater of the metropolitan area is recharged from the river, whereas that from the non-urbanized region of the valley is replenished by infiltrating precipitation; and (ii) verification of recharge of the crystalline rock aquifers by groundwater from the overlying alluvium.

A small, well-defined region of water with very low tritium levels in both the alluvium and the underlying crystalline rock was found close to the coast. The explanation of the low tritium levels is that this region was not formed by sea-water intrusion but by meteoric water recharged at a remote location in pre-nuclear times.

Stable-isotope evidence confirmed that recharge to the karst areas occurs at a significantly higher elevation than recharge to the alluvial aquifer. An analysis of the tritium levels of samples collected during one year suggests that the residence time of groundwater is probably not more than a few months.

There is no evidence for a correlation between the zinc content of the groundwater and the location, depth, isotopic content or electrical conductivity of the groundwater. The magnesium and cadmium levels were generally too low for a systematic study.
The Crocodile River in the Transvaal, South Africa, forms part of an extensive irrigation scheme which serves farmers along more than 100 km of the river course. Occasional accidental releases of crop-damaging pollutants from an industrial area situated upstream of the river have resulted in the establishment of a monitoring station to warn farmers against the presence of excessive levels of pollutants in the river. Effective implementation of the system required information about transit times and dilution characteristics. These were consequently determined by means of a radioactive tracer study.

The experimental work involved the release of 20-50 GBq of $^{82}$Br into the river at two positions and the monitoring of downstream irrigation channels. Samples were collected and counted on a NaI(Tl) detector, and the required information was obtained from the analysis of the resulting tracer response curves.

Mean transit times were calculated directly from the weighted means of the response curves. Estimates of the degree of mixing were made in terms of a dimensionless Peclet number, using a mathematical flow model and a non-linear regression technique. The results showed that a single value of the Peclet number could be used to predict downstream concentrations by means of the flow model to an accuracy of 25% in widely varying situations. This accuracy was considered sufficient for the intended purpose of these predictions.

Finally, a semi-empirical relation between transit time and river flow rate was established, which made the prediction of downstream pollutant behaviour possible in terms of the transit time, the time taken by a pollutant to pass a specific point and the expected maximum concentration.
EMPLEO DE LOS ISOTOPOS 
$^{82}$Br Y $^3$H PARA EL ESTUDIO 
DINAMICO UNIDIMENSIONAL DE ESTUARIOS

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Se describe aquí la metodología seguida por los autores en el estudio dinámico de dos estuarios de unos 20 km de longitud, situados en la costa atlántica de Andalucía (España): el del Tinto-Odiel y el del Guadalete.

Se ha desarrollado un modelo matemático unidimensional de dispersión y transporte basado en la división de cada estuario en un conjunto de compartimentos (alrededor de 100) con propiedades diferentes, y en el empleo de una matriz de reparto $R_{ij}$ constituida por los porcentajes del contenido de trazador del compartimento $i$ que en el ciclo de marea siguiente se encontrarán en los compartimentos $j$, superponiendo después los resultados. Se trata, pues de un modelo intermareal.

El modelo se calibró en cuanto a coeficientes de dispersión con experiencias a base de $^{82}$Br, y en cuanto a coeficientes de transporte con experiencias de $^3$H.

Las primeras se llevaron a cabo inyectando pastillas de bromuro potásico en una sección durante una pleamar (o una bajamar) y midiendo la distribución longitudinal de actividades cada vez que transcurriera un semiciclo de marea hasta que éstas se hacían parecidas a las del fondo. Estas experiencias se repitieron varias veces con inyecciones en distintos puntos a lo largo de cada estuario, incluyendo una en pleamar cerca de la desembocadura para investigar el porcentaje de trazador que, una vez salido al mar, volvía al estuario.

Las experiencias con $^3$H consistieron en inyectar una cierta cantidad de éste a una distancia de la desembocadura aproximadamente igual a los 4/5 de la longitud total y medir sus concentraciones en unas 10 estaciones donde periódicamente se tomaban muestras (coincidiendo siempre con pleamar o bajamar) que, tras ser concentradas electrofícticamente, se median con un espectrómetro de centelleo líquido.
TECHNIQUES USED IN ISOTOPE HYDROLOGY STUDIES AT CHALK RIVER

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Techniques in use at Chalk River for studying the hydrology of existing and potential waste management sites include: (a) devices to scan radioactivity in situ and to obtain samples or to inject tracers into groundwater systems; and (b) isotope measurements to follow dispersion, to differentiate between surface water and groundwater, and to obtain information on the age of the groundwater.

Groundwater discharge into a lake bed is measured by a 'seepage meter' consisting of the end of a steel drum which is embedded in a lake bed and vented to a plastic bag which inflates with the incoming water. Groundwater flow near the shoreline of a lake has been studied using several arrangements for injecting tracers in a uniform plane and collecting samples in the flow path. For sampling in a shallow borehole in rock, a string of simple inflatable packers with sampling intervals is constructed from readily available materials.

Dispersion in a sand aquifer has been studied using $^{131}$I tracer; this has been monitored over 20 m of travel by gamma-scanning an array of dry PVC pipes in the flow system. This enabled detailed observation of tracer flow without the labour of discrete sample analysis and with no disturbance due to withdrawal of water from the flow system. Results from grain-size analysis and hydraulic conductivity measurements indicated the aquifer to be homogeneous, but the in-situ scanning technique revealed three layers of different velocity. Within discrete layers, observed and calculated breakthrough curves yielded surprisingly low dispersivities ($\approx 1$ cm), in agreement with laboratory measurements.

Measurements of environmental $^3$H, $^{14}$C, uranium isotopes and deuterium are being used to characterize groundwater discharging from bedrock and to estimate its age. Detectable tritium is taken as an indication of the presence of recent surface-water input, either residual drill fluid or leakage from the surface. Carbon-14 is measured by CO$_2$ absorption in an amine-type liquid scintillation cocktail when sufficient sample is available. The accelerator mass-spectrometry technique has been used for measuring samples of a few milligrams, e.g. from groundwater carbonate of 0.5 L samples taken in down-hole samplers or from fracture-coating calcites.
APPLICATION DE L'IDENTIFICATION DE L'ORIGINE DES NITRATES PAR TRAÇAGE ISOTOPIQUE AU CHAMP CAPTANT D'AUBERGENVILLE (FRANCE)

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La Société lyonnaise des eaux et de l'éclairage (SLEE) exploite, dans la vallée de la Seine en aval de Paris, deux usines de production d'eau potable très importantes dans le dispositif d'alimentation en eau de l'agglomération parisienne: ces sont les usines du Pecq-Croissy et d'Aubergenville. L'usine élevatoire d'Aubergenville dessert les communes situées en rive gauche de la Seine, de part et d'autre d'une adduction qui va d'Aubergenville jusqu'aux réservoirs de la ville de Paris situés à Saint-Cloud. Elle alimente en partie la ville de Paris et fournit aussi de l'eau aux ouvrages de la Compagnie des eaux de Baulieu situés au Mont Valérien.

Cette usine d'Aubergenville refoule l'eau prélevée dans la craie sénonienne sous les alluvions de la Seine au moyen d'une vingtaine de puits répartis sur un territoire de 15 km² environ dans la plaine alluviale. Le débit pompé est en moyenne de 100 000 m³ par jour et peut être porté à 150 000. La nappe aquifère est libre et en équilibre avec le niveau du fleuve. La dépression du niveau de la nappe par les pompages crée un appel d'eau à partir de la Seine et cette réalimentation induite a conduit la SLEE à réaliser un traitement complet de l'eau avant refoulement, traitement identique à un traitement d'eau de surface. Il existe également par ailleurs un dispositif d'alimentation artificielle par bassins pour pallier aux inconvénients d'une pollution de la Seine. La nappe souterraine est donc vulnérable à la pollution, celle du fleuve, mais aussi celle créée par l'urbanisation et l'industrialisation de cette région. Au nombre des problèmes posés au distributeur d'eau par la pollution des eaux souterraines figure celui des nitrates.
C'est dans le but d'identifier l'origine des nitrates dans les eaux souterraines que la SLEE a entrepris en 1982, avec le concours de l'Agence du Bassin Seine-Normandie, une étude en collaboration avec le Laboratoire de géologie dynamique de l'Université Pierre et Marie Curie de Paris. L'autre objectif principal de l'étude sera de prévoir l'évolution de la teneur en nitrates de la nappe. Les premiers résultats ont été acquis au moyen du traçage isotopique utilisant les abondances naturelles de l'azote 15.

IAEA-SM-270/89P

RELATIONS ENTRE LA TENEUR EN CARBONE 14, EN HELIUM 4 ET EN SELS DISSOUS
DANS LES EAUX D'UNE NAPPE CAPTIVE
Conséquence pour l'évaluation de l'activité originelle en $^{14}C$ du carbone dissous

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Des mesures de la teneur en $^{14}C$, en $^4$He et en sels dissous (conductivité) ont été effectuées (tableau 1) dans des forages artésiens de la nappe captive du Bazois (France, département de la Nièvre).

Trois prélèvements, situés dans un même environnement géochimique, montrent (fig.1) qu'il existe une étroite corrélation entre les trois paramètres mesurés.

L'augmentation du temps de séjour de l'eau dans l'aquifère, qui se traduit par une décroissance de la teneur en $^{14}C$, correspond de façon proportionnelle à un enrichissement de la teneur en $^4$He et en sels dissous.

La pente des droites de corrélation dépend du contexte géologique et hydrogéologique régional (fig.1).

Ces corrélations, notamment entre $^4$He et $^{14}C$, peuvent être mises à profit pour déterminer l'activité originelle ($A_o$) en $^{14}C$ du carbone dissous.

En effet, il suffit de savoir que la teneur originelle en $^4$He est pratiquement constante et de l'ordre de 45 pp 10$, ce qui correspond à la teneur en hélium d'une eau atmosphérique en équilibre avec l'hélium atmosphérique dans les conditions normales de température et de pression, pour en déduire la teneur originelle en $^{14}C$ correspondante de l'eau de la nappe étudiée.
**TABLEAU 1. CONDUCTIVITÉ, TENEUR EN \(^{4}\text{He}\), ACTIVITÉ EN \(^{14}\text{C}\) DANS LES EAUX D'UNE NAPPE CAPTIVE**

<table>
<thead>
<tr>
<th>Numéro de sondage et situation</th>
<th>Conductivité (mS/m)</th>
<th>(^{4}\text{He}) (ppm v/v)</th>
<th>(^{14}\text{C}) (%)</th>
<th>Age ((A_0 = 43%)) (années)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Amont</td>
<td>43</td>
<td>62</td>
<td>29,8 ± 1</td>
<td>2945</td>
</tr>
<tr>
<td>2. Intermédiaire</td>
<td>75</td>
<td>170</td>
<td>15,1 ± 0,9</td>
<td>8406</td>
</tr>
<tr>
<td>3. Aval</td>
<td>122</td>
<td>367</td>
<td>4,6 ± 0,6</td>
<td>17 955</td>
</tr>
</tbody>
</table>

**Remarques:** Ces trois échantillons ne contiennent pas de tritium. Le calcul de l'âge est effectué par l'intermédiaire de la formule suivante:

\[
t = 8033 \cdot \frac{A_0}{A_t}
\]

avec \(t\) en années, \(\ln\) = logarithme népérien, \(A_0 = \text{activité originelle en }^{14}\text{C}\), \(A_t = \text{activité actuelle en }^{14}\text{C}\).

Pour l'hélium, les résultats sont exprimés en proportions volumiques.

---

**FIG. 1. Relations entre la teneur en \(^{14}\text{C}\), la teneur en \(^{4}\text{He}\) et la conductivité.**
Cette méthode devrait être d'autant plus fiable que:
- l'hélium est un gaz inerte, qui n'intervient par conséquent dans aucune réaction chimique,
- les teneurs en hélium observées dans les nappes captives sont généralement très supérieures à la teneur en hélium originelle, de sorte qu'il faudrait faire une très forte erreur sur la teneur en hélium originelle pour que cela ait une conséquence faîcheuse sur le calcul de A0.

Dans le cas de la nappe captive du Bazois, cette méthode conduit à une estimation de l'activité originelle A0 du 14C de l'ordre de 43% et à une conductivité originelle de l'ordre de 32 mS/m: ces résultats sont parfaitement admissibles.

IAEA-SM-270/94P

SEASONAL VARIATIONS
IN CHEMISTRY AND 13C/12C RATIOS
OF CARBONATE-DISSOLVING WATERS

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Significant variations in pH, molality of HCO3\(^-\) and 13C/12C ratios of total dissolved inorganic carbon have been observed in samples taken at 24 points in the period January to May 1977. The sampling area is part of the southwestern Lublin Upland in which Cretaceous and Tertiary bedrock limestone is overlain by Pleistocene aeolian rock and/or Holocene alluvia.

The observed values of mHCO3\(^-\) and 13C/12C plotted versus pH show small and multi-directional variations in winter/early spring and a generally increasing trend in late spring. The observed variations are for a period in which the limestone aquifer was fed by water which penetrated the soil under different conditions. In late spring the feeding of the aquifer came to an end and the trends observed approached the evolution lines theoretically predicted by Deines et al. (DEINES, P., LANGMUIR, D., HARMON, R.S., Geochim. Cosmochim. Acta 38 (1974) 1147). Applying a theoretical model, the δ\(^{13}\)C of the soil-generated CO2 is estimated as −21 to −25‰ and the partial pressure of CO2 as 10\(^{-1.0}\) to 10\(^{-1.6}\) atm.
ИЗУЧЕНИЕ ВАРИАЦИЙ $\delta D$ И $\delta^{18}O$ ПОДЗЕМНЫХ ВОД ТАШКЕНТСКОГО ГЕОДИНАМИЧЕСКОГО ПОЛИГОНА

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В последние годы гидрогеохимические исследования существенно расширили возможности поиска предвестников и предсказания землетрясений [1]. Настоящая работа посвящена изучению стабильных изотопов термоминеральных вод Ташкентского геодинамического полигона с целью выявления вариаций $\delta D$ и $\delta^{18}O$ в периоды сейсмической активности на полигоне.

Под наблюдением находятся 28 термоминеральных скважин Приташкентского артезианского бассейна, расположенных в направлении с северо-востока на юго-запад от областей питания бассейна и охватывающих полосу территории геодинамического полигона длиной около 100 км и шириной около 25 км. Изучаемые воды приурочены к отложениям меловой системы. Глубина вскрытия водоносных горизонтов - 1300-2400 м. Воды верхнего мела - пресные (0,5-1,5 т/н), щелочные (pH = 7-8,5), гидрокарбонатно-натриевые, с повышенным содержанием сульфатов, реже хлоридов. Воды нижнего мела - солоноватые (~ 16 т/н), хлоридно-натриевые. Скважины - самоизливающиеся, с температурой на устье 40-60°C.

Измерения $\delta D$ и $\delta^{18}O$ выполнялись на масс-спектротрече MAT-250 ($\sigma_{D} = \pm 0,03\%$). Водород для анализа получался при реакции примерно 10 мл воды с ураном при t = 700°C. Точность определения $\delta D$ составила $\pm (0,3-1,0\%)$, а в случае $\delta^{18}O$, с использованием методики уравновешивания CO2 с H2O, $\sigma_{D} = \pm 0,04\%$. Все экспериментальные значения рассчитывались в промилле по отношению к стандарту V-SMOW.

Исследованиями установлено, что изотопный состав изучаемых вод изменяется при проявлении сейсмичности на полигоне. На рис.1 представлены вариации $\delta D$ и $\delta^{18}O$ в воде скважины 9 (Улуебек), которые наблюдались в период землетрясений с M = 5,3, происшедших 11 декабря 1980 г. на Ташкентском геодинамическом полигоне.

Стрелками указан временной ход измеренных значений $\delta D$ и $\delta^{18}O$. Часть результатов мы уже сообщали [2, 3], здесь же представлены данные, охватывающие период наблюдений с сентября 1979 г. по ноябрь 1982 г. Изотопный сдвиг не объясняется только подтоком в исследуемый водоносный пласт "другой воды". Окончательно, в данном случае проявили себя воды дегидратации, а также не последнюю роль сыграл изотопный обмен воды с углекислым газом, концентрация которого в воде скважины 9 непосредственно перед землетрясением увеличилась на 250% [3]. На рис.1 пунктирной стрелкой соединены значения $\delta D$ и $\delta^{18}O$, полученные, соответственно, в 1982 и 1979 годах.
Дальнейшие наблюдения на полигоне покажут, являются ли величины 1982 г. фоновыми значениями, и тогда можно будет считать, что с ними в 1979 г. начались вариации изотопных характеристик воды скважины 9 в связи с подготовкой очага землетрясения.

Начиная с мая 1981 г. и по настоящее время, на полигоне проводятся наблюдения за δD и δ18O воды скважины 18 (Ленин-Юги), из которой отбираются одновременно пробы H2O из двух водоносных горизонтов — нижнего (Сг1) и верхнего (Сг2) мела. Воды этих горизонтов сильно отличаются как на геохимическом, так и на изотопном уровне. Оценки, произведенные с помощью изотопного метода [3], подтвердили весьма слабую связь между Сг1 и Сг2. Экспериментальные наблюдения показали, что характер вариаций δ18O в водах горизонтов различен. Воды нижнего мела в отдельные периоды времени повышают содержание кислорода-18, что обусловливает возможную связь этого горизонта с нижележащими водосодержающими толщами. Дальнейшие режимные наблюдения за поведением стабильных изотопов вод этих горизонтов, в случае проявления сейсмичности на полигоне, конечно, несомненно помогут полнее интерпретировать природу гидрогеосейсмологического предвестника.

**ЛИТЕРАТУРА**


POSTER PRESENTATIONS

IAEA-SM-270/110P

ISOPOE HYDROLOGY
OF THE SHALLOW GROUNDWATERS
OF THE WESTERN DESERT

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The Nubian aquifer of Egypt and the northern Sudan (Fig. 1) is part of one of the largest sandstone aquifer systems in the world. The origin and direction of flow of its waters has been disputed for more than half a century. Early models suggested that vast amounts of water in this system fell as rain and infiltrated thousands of years ago under a much more pluvial climatic regime, and that they have remained essentially stagnant and unrecharged ever since. Another early model maintains that the system is actually being recharged in the tropical and sub-Saharan regions of Chad and the Sudan, and that water slowly flows north-eastward toward the Egyptian oases and the lower Nile.

In the 1920s, Ball proposed that the piezometric surface of the aquifer followed the regional slope of the land surface, and that the minor oases or 'birs' in the desert, as well as the major oases such as Kharga and Dahkla, occur in topographic depressions where the surfaces intersect. Radiocarbon analyses of deep waters in the major oases have shown that they have been in the subsurface for times of the order of 10,000 to 20,000 years. Although most of this area lies between the zero-isohyets, some more recent models propose that there is currently enough recharge during occasional rains in the desert to maintain the hydraulic gradient observed.

During the field seasons of 1979 and 1982, our study involved sampling 17 sources of shallow groundwater for isotopic analyses, in an attempt to determine their origin. The results are presented in Table I. Deuterium and oxygen-18 results for these sites showed that most of the waters have not been subject to an appreciable heavy-isotope enrichment by evaporation from compositions expected in local meteoric waters. After modeling corrections for isotopic dilution by the dissolution of mineral carbonates, the majority of samples were shown to have radiocarbon contents which can be reconciled only with the presence of $^{14}$C from nuclear weapons tests. One of the sites
FIG. 1. Plan of the Nubian aquifer.
<table>
<thead>
<tr>
<th>Location</th>
<th>Age</th>
<th>Comments</th>
<th>Discharge</th>
<th>Depth to water (m)</th>
<th>pH</th>
<th>$\delta^2$H versus SMOW (%)</th>
<th>$\delta^{18}$O versus SMOW (%)</th>
<th>$^3$H (TU)</th>
<th>$^{14}$C (pmc)</th>
<th>$^{13}$C versus PDB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bir Ayed</td>
<td>modern</td>
<td>perched?</td>
<td>bailed</td>
<td>0.60</td>
<td>0.65</td>
<td>9.1</td>
<td>-7.9</td>
<td>13.1 ± 0.7</td>
<td>80.4 ± 10</td>
<td>-12.3</td>
</tr>
<tr>
<td>Bir Nakhilai</td>
<td>mixed</td>
<td>-</td>
<td>bailed</td>
<td>0.30</td>
<td>0.60</td>
<td>7.5</td>
<td>-8.4</td>
<td>16.4 ± 0.8</td>
<td>38.1 ± 0.5</td>
<td>-4.0</td>
</tr>
<tr>
<td>Bir Oyo</td>
<td>modern</td>
<td>-</td>
<td>bailed</td>
<td>1.3</td>
<td>2.0</td>
<td>9.2</td>
<td>-66</td>
<td>-4.6</td>
<td>-107.2 ± 0.9</td>
<td>-2.3</td>
</tr>
<tr>
<td>Bir Sahara</td>
<td>modern</td>
<td>-</td>
<td>bailed only</td>
<td>17.0</td>
<td>37.5</td>
<td>8.1</td>
<td>-7.8</td>
<td>27.1 ± 0.8</td>
<td>112.2 ± 0.8</td>
<td>-0.9</td>
</tr>
<tr>
<td>El Qasr</td>
<td>old</td>
<td>Nubian</td>
<td>~0.5 m³/min</td>
<td>?</td>
<td>800</td>
<td>6.8</td>
<td>-9.5</td>
<td>-</td>
<td>2.6 ± 1.3</td>
<td>-10.3</td>
</tr>
<tr>
<td>GPC # 1</td>
<td>modern</td>
<td>-</td>
<td>bailed only</td>
<td>11.6</td>
<td>107</td>
<td>8.5</td>
<td>-78</td>
<td>21.3 ± 1.1</td>
<td>97.7 ± 1.3</td>
<td>-14.5</td>
</tr>
<tr>
<td>GPC # 2</td>
<td>modern</td>
<td>-</td>
<td>bailed only</td>
<td>36.4</td>
<td>114</td>
<td>8.9</td>
<td>-76</td>
<td>19.5 ± 1.0</td>
<td>11.7 ± 0.5</td>
<td>-9.3</td>
</tr>
<tr>
<td>GPC PZ 1/1</td>
<td>old</td>
<td>used</td>
<td>~0.2 m³/min</td>
<td>27.0</td>
<td>100</td>
<td>6.9</td>
<td>-84</td>
<td>-9.8</td>
<td>8.85 ± 0.6</td>
<td>-6.1</td>
</tr>
<tr>
<td>GPC PZ 3/2</td>
<td>-</td>
<td>-</td>
<td>bailed</td>
<td>37.5</td>
<td>255</td>
<td>7.6</td>
<td>-89</td>
<td>-10.0</td>
<td>64.6 ± 1.0</td>
<td>-8.9</td>
</tr>
<tr>
<td>Hussein</td>
<td>-</td>
<td>fault?</td>
<td>bailed</td>
<td>0.85</td>
<td>2.0</td>
<td>8.1</td>
<td>-9.4</td>
<td>-</td>
<td>49.6 ± 1.0</td>
<td>-9.4</td>
</tr>
<tr>
<td>Kiseiba</td>
<td>-</td>
<td>fault</td>
<td>bailed</td>
<td>1.5</td>
<td>1.7</td>
<td>7.9</td>
<td>-6.2</td>
<td>-</td>
<td>45.6 ± 2.0</td>
<td>-12.8</td>
</tr>
<tr>
<td>Laqiya Arbaia</td>
<td>modern?</td>
<td>-</td>
<td>bailed</td>
<td>0.4</td>
<td>1.0</td>
<td>7.3</td>
<td>-8.9</td>
<td>16.2 ± 0.9</td>
<td>78.0 ± 1.0</td>
<td>-12.8</td>
</tr>
<tr>
<td>Laqiya Umran</td>
<td>mixed</td>
<td>seep</td>
<td>bailed</td>
<td>0.25</td>
<td>0.25</td>
<td>8.1</td>
<td>-9.2</td>
<td>22.7 ± 1.1</td>
<td>20.1 ± 1.0</td>
<td>-11.8</td>
</tr>
<tr>
<td>Merga Lake</td>
<td>modern</td>
<td>spring?</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.8</td>
<td>-28</td>
<td>+3.2</td>
<td>129.5 ± 1.6</td>
<td>-1.2</td>
</tr>
<tr>
<td>Merga Well</td>
<td>modern</td>
<td>-</td>
<td>bailed</td>
<td>0.65</td>
<td>1.10</td>
<td>8.5</td>
<td>-82</td>
<td>-9.2</td>
<td>84.4 ± 0.8</td>
<td>-10.3</td>
</tr>
<tr>
<td>Selima</td>
<td>mixed?</td>
<td>-</td>
<td>bailed</td>
<td>0.5</td>
<td>2.0</td>
<td>7.6</td>
<td>-8.4</td>
<td>15.3 ± 0.9</td>
<td>65.6 ± 1.0</td>
<td>-4.4</td>
</tr>
<tr>
<td>Tarfawi West</td>
<td>modern</td>
<td>-</td>
<td>bailed</td>
<td>0.7</td>
<td>0.9</td>
<td>7.8</td>
<td>-3.9</td>
<td>2.95 ± 1.1</td>
<td>96.5 ± 1.0</td>
<td>-10.3</td>
</tr>
</tbody>
</table>
where anthropogenic radiocarbon (112.2 ± 0.8 pmc) was detected is more than 10 km from Bir Tarfawi West, the nearest 'bir', and was sampled from a shallow borehole which penetrates more than 10 metres of unsaturated zone. Water at the 'bir' itself and in nearby boreholes was found to contain appreciable amounts of anthropogenic radiocarbon (>96 pmc). Similar high radiocarbon concentrations (84–130 pmc) have been detected in shallow groundwaters associated with the small lake at Merga in the Sudan. These findings indicate that appreciable recharge, probably from very rare, rapidly infiltrating cloud-bursts, has occurred in the last 20 years at locations having the topographic depressions and shallow water tables associated with the 'bir'. Some elevated tritium levels in these waters support this hypothesis. Further, some wells showed essentially no tritium when sampled in 1978; however, significant amounts of tritium found in 1979 indicate the first recharge since the beginning of the nuclear age.

Although these data from shallow water samples are insufficient to conclude that active recharge of the Nubian aquifer is currently taking place, it is clear that infrequent precipitation events in this zone of 'no rain' contribute to the local groundwater. This groundwater may be perched, mounded on a stagnant or slowly flowing system in the Nubian aquifer, or it may recharge the regional aquifer system at points where the aquifer is near the surface.

IAEA-SM-270/111P

CALCULO DEL COEFICIENTE DE DISPERSION Y ECUACIONES REPRESENTATIVAS DE LAS CURVAS DE PASO EN EL RIO BOGOTA

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INTRODUCCION

Dentro de los programas de aplicación de técnicas isotópicas en hidrología, el Instituto de Asuntos Nucleares (IAN) realizó los estudios tendientes a la determinación de tiempos de tránsito en el río Bogotá, con el objeto de optimizar los usos de este recurso hídrico y energético.
FIG. 1. Coeficiente de difusión en la zona alta del río Bogotá.

METODO DE TRABAJO

Para la determinación de los tiempos de tránsito se empleó como radiotrazador $^{82}$Br en forma de bromuro de amonio, el cual se obtuvo en el reactor IAN R1. Se utilizaron detectores de NaI acoplados a escalímetros y registradores donde se obtuvieron las curvas de paso.

Este trabajo se llevó a cabo en dos etapas. La primera etapa se efectuó con caudales bajos en la zona alta del río que comprende desde el municipio de Villapinzón hasta Alicachín. La segunda etapa se realizó con caudales altos desde Villapinzón hasta Alicachín y posteriormente hasta el puente Salsipuedes, antes de la desembocadura en el río Magdalena.

Las inyecciones del trazador en todos los casos se realizaron en el centro del río y se siguieron los requisitos de mínima distancia de mezcla para el trazador.

RESULTADOS

Se obtuvieron alrededor de setenta curvas de paso con las cuales se calcularon los tiempos de tránsito para diferentes caudales y en diversas condiciones del río.
Se calcularon velocidades medias empleando estos tiempos, y las distancias entre las estaciones se hallaron por levantamientos topográficos o directamente de los mapas.

Con las curvas de paso, los tiempos de tránsito, ancho del río, profundidad, distancia entre estaciones, etc., y empleando la fórmula de Hull que se aplica a caudales y ríos se calcularon los coeficientes de dispersión.

En la Figura 1 se puede apreciar claramente como es la relación D/Qv para el río Bogotá.

Paralelamente a estos cálculos de dispersión se encontró una ecuación que se ajustará a las curvas de paso y diera cuenta de su evolución temporal y que incluyera parámetros físicos del río tales como la sección transversal y la distancia (Figura 2).

Como se puede ver en la figura, esta ecuación se ajusta bastante bien a las curvas experimentales al mismo tiempo que sigue su evolución temporal.

CONCLUSIONES

En general se obtuvieron dos ecuaciones: La primera que relaciona al coeficiente de dispersión con el caudal y la velocidad del flujo del río y que
solo es válido para la zona alta del río Bogotá y bajo las condiciones hidráulicas existentes en el momento de las medidas; la ecuación resultante es: 
\[ D = 8,093 (Qv)^{0.371} \]. La segunda ecuación, descrita anteriormente, relaciona las curvas de paso del trazador en función de varios parámetros.

Para la zona baja del río Bogotá no se sacó ninguna conclusión en ese momento.
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