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APPLICATION OF NATURAL ISOTOPES IN GROUND WATER HYDROLOGY

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ABSTRACT

^{18}O, deuterium and tritium may serve as tracers and be used to determine the origin of groundwater. The radioactive isotopes ^{14}C and T can be used to date water. Deuterium and ^{13}C may give information about evaporation and processes in the unsaturated zone.

INTRODUCTION

The naturally abundant isotopes of carbon, oxygen and hydrogen all have their specific contribution to ground water research. The first significance is to serve as ideal tracers, especially ^{18}O, deuterium and tritium, being materials of the water molecule itself. They are largely used to determine the origin of the ground water. The radio-active isotopes, ^{14}C and T, have a special feature, that of dating water. By comparing the ages of samples within a water body, a flow direction and velocity may be deduced. Finally, deuterium and ^{13}C can reveal more specific information, viz. the degree of evaporation before or during infiltration and the occurrence of hydrologic and chemical processes in the unsaturated zone.

The isotopes will be discussed in the logic and practical order of the analyses, of which the radioactivity measurements are the most time and costs consuming.

DEFINITIONS

The stable isotopic compositions are given relative to the internationally adopted standards (Craig, 1957, 1961a);

for deuterium (^{2}H)

$$\delta^2 = (^2\mathrm{H}/^1\mathrm{H})_{\mathrm{sample}} / (^2\mathrm{H}/^1\mathrm{H})_{\mathrm{SMOW}} - 1;$$

for carbon-13 (^{13}C):

$$\delta^{13} = (^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sample}} / (^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{PDB}} - 1;$$

for oxygen-18 (^{18}O):

$$\delta^{18} = (^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{sample}} / (^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{SMOW}} - 1;$$

the δ-values are, as usual, given in per mil (‰). Tritium (^{3}H) activities are stated in Tritium Units (T.U.), defined as the specific activity of water in which the concentration ratio

$$^3\mathrm{H}/^1\mathrm{H} = 10^{-18}$$

Radiocarbon activities are referred (in %) to the international standard activity, which is 0.95 times the specific activity of the NBS oxalic acid standard sample, and corresponds by definition to organic material grown in A.D. 1950.

OXYGEN-18

Although the ^{18}O/^{16}O ration in *precipitation* is not quantitatively understood, the general phenomena have been explained. According to the Epstein model (Epstein, 1956), tropospheric water

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vapour, originating from the regions around the thermal equator (about 5°N.Lat.) and moving towards the poles, condensates little by little. This process of slowly proceeding removal of vapour leads to progressive depletion in ^{18}O of the precipitation with progressive distance from the equator. Dansgaard, (1964) found this phenomenon to obey a linear relation between δ^{18} of the total yearly precipitation and the average yearly surface air temperature (in degrees Celsius):

$$\delta^{18} = 0.7\,t - 13.6 \qquad (6)$$

A similar mechanism that explains this so-called latitudinal effect also gives rise to an increasing depletion in ^{18}O with increasing altitude in mountain ranges – altitudinal effect – and with progressive distance from the continental coast-continental effect. Re-evaporation of rain on the continent causes the atmospheric vapour to become additionally depleted in ^{18}O. Consequently, the continental precipitation contains less ^{18}O than is indicated by temperature for oceanic rain.

Concluding we can say that δ^{18} of precipitation is more or less specific for a special area. Due to the extensive network of stations co-operating with the IAEA in Vienna (IAEA, 1969) in collecting water samples for isotope analyses, rather good estimates can be given for the δ^{18} of annual precipitation in certain areas, especially if the climate is moderate.

The ^{18}O content of the *ground water* should reflect that of the precipitation in the catchment area (Mook, 1970), or rather equals the δ^{18} value of the rain during the periods of maximum infiltration and so of maximum precipitation. Thus, it will not be far off δ^{18} of annual rainfall. In moderate climates this is especially true since the rain in the wet autumn has an ^{18}O content about half way between the summer maximum and winter minimum.

Within a groundwater stratum large variations in δ^{18} cannot be expected. This is obvious if one considers the restricted extent of the infiltration area and the very slow infiltration and movement of the water underground in the order of meters per year.

The special importance of measuring $^{18}O/^{16}O$ in ground water samples is (i) to establish whether all samples collected belong to the same origin so that the later comparison of groundwater ages is allowed; this condition requires δ^{18} to be equal within a few tenths of a per mil; (ii) to determine the origin of the groundwater; on a flat continent or along the coastline a few hundred kilometers can amount to one per mil difference in ^{18}O content; in the mountains differences are considerably larger.

In a regional aquifer local deviations of δ^{18} values from that expected for average precipitation can be caused in several ways.

(i) Depending on the levels of the piezometric surface, river or lake water can infiltrate into the ground through the river bed or the bottom of the lake. This water, if originating from afar, can have a much different ^{18}O content.

(ii) Infiltration of sea water is often easily recognizable. If the ground water sample collected is merely a mixture of the fresh ground water and the sea water the δ^{18} must be simply linearly related to the chlorinity Cl by:

$$\delta^{18} = \delta^{18}_{\mathrm{fresh}}\,(1 - Cl/Cl_{\mathrm{mar}}) + \delta^{18}_{\mathrm{mar}}\,(Cl/Cl_{\mathrm{mar}}), \quad (1)$$

where $\delta^{18}_{\mathrm{mar}}$ ($\approx 0‰$) and Cl_{mar} ($\approx 20‰$) refer to the sea water and $\delta^{18}_{\mathrm{fresh}}$ to the fresh groundwater component, while the chlorinity of the fresh water is taken as zero. The other possibility is that the original fresh ground water has dissolved salt from deep layers; by this, δ^{18} of the water is not affected.

Deuterium

(iii) Another occurrence of deviations in ^{18}O from average precipitation is found if the water has been subjected to a fairly large degree of evaporation before infiltration, for instance in shallow pools or lakes. As a consequence of the evaporation process the linear relation between the *deuterium* and the ^{18}O content of the water, which holds for meteoric waters (Craig, 1961b; Dansgaard, 1964):

$$\delta^{2} = 8\delta^{18} + 10‰, \qquad (8)$$

is not obeyed. Instead, a relation is found having a smaller slope:

$$\delta^{2} = 4(\text{or } 5)\,\delta^{18} + \ldots ‰ \qquad (9)$$

Assuming a slope of 4 to 5 for the ^{18}O-^{2}H diagram, the measured δ^{18} and δ^{2} can be extrapolated back to the intersection with the "meteoric line" resulting in the original δ^{18} of the precipitation. This reasoning is not valid for the evapotranspiration process (Gat and Tzur, 1967). The isotope effect involved in this process, though not specifically known, is probably small, since the uptake of water by the roots requires no significant fractionation and the net transport through the plant is almost unidirectional.

In case a preliminary ^{18}O survey of the water samples collected from the aquifer under investigation points to a good homogeneity of the water body – a conclusion which often cannot be drawn from the chemical composition of the samples – it is worthwhile to carry out further and more laborious analyses.

TRITIUM

Principally the radioactive hydrogen isotope, having a half-life of 12.3 year, would be applicable to determine the age of relatively young underground water masses. Since the natural (pre-bomb) tritium level in atmospheric vapour and precipitation is about 5 T.U. (Roether, 1967) and the detection limit approaches 0.1 T.U., ages – i.e. periods of time between infiltration and sampling- of less than 65 years would have been measurable, if it were not that the tritium abundance has completely been disturbed by the nuclear weapon tests which enormously increased the amount of tritium present in especially the stratosphere. Periodically, largely during the spring, tritium in injected back into the troposphere. As a consequence, the tritium content in precipitation on the northern continent reached a peak early 1963 of up to 10,000 T.U. The level on which the (damped) seasonal oscillation is superimposed has meanwhile (1971) come down to values between 30 and 150 T.U., with lower figures for the northern continent.

The consequence of this serious disturbance is that tritium cannot be used for simply dating ground water, because a small local infiltration of recent water with a high tritium content will completely upset age measurements within a water body.

Nevertheless, tritium analyses are indispensable in isotope hydrology. The applications are threefold. The occurrence of a measurable quantity of tritium in a ground water sample which is, according to ^{14}C, of considerable age (more than some hundred years), indicates that recently infiltrated water has been admixed into the aquifer or that the sample is contaminated during the sampling procedure. It seems to be very difficult to make a realistic estimate of the contribution of recent water and thus of the correction to be applied to the ^{14}C result, since the tritium activity in the rain water concerned is unknown to even the order of magnitude. The only thing one can do is philosophize about minimal or maximal amounts of contamination. On the other hand, an admixture in some way of young water does not necessarily mean that the ^{14}C content has been influenced. The fact is that if the young water does not contain an appreciable – compared to the old water – concentration of inorganic carbon, the ^{14}C age cannot have been changed by the addition at all. Anyhow, the ^{14}C age of the water, to be discussed later, must be considered as a minimum age as far as this problem is concerned.

A second, more independent use of tritium research is to be found in the movement of shallow ground water, or, so to speak, the fast component of the ground water movement, in which case tritium can be used as a tracer. Since 1962 the tritium concentration in precipitation is characterized by a very irregular pattern superposed on the seasonal variation mentioned above. To study the fast ground water movement one could try to trace tritium spikes, detected in the precipitation, in the ground. The author does not know of any serious and successful attempt in this respect so far. Based on measurements or estimates of the average tritium level in rainfall during the last decade, a few examples of dating shallow ground water have been presented (Münnich et al., 1967).

Another possibility would be to determine the water balance of a hydrologically restricted area by comparing the input and output of tritium in the area. Part of the precipitation will be drained off quickly, another part will infiltrate and remain in the area for a longer period of time. Thus, the regional small rivers or canals partly contain precipitation fallen in the preceding period, partly older groundwater, which was drained into the small streams due to the increase of groundwater levels.

The most favourable time for this field of research, the years shortly after the nuclear weapon tests, has passed by. On the other hand, the recent, less irregular tritium activities show the advantage that a tritium input can be determined more reliably and with less sampling.

CARBON-13

The application of the stable carbon isotopes is probably the most disputed subject in isotope hydrology nowadays. The major problem in dating ground water with ^{14}C is the uncertainty of the original (i.e. during infiltration) ^{14}C content of the water or rather of its inorganic carbon content. Anyhow , ^{14}C must be correlated with the stable carbon isotopic composition, both being determined by processes in the soil.

As Vogel and Ehhalt (1963) pointed out originally, a δ^{13} value of dissolved bicarbonate of −12‰ is to be considered normal. A value of −11.5 ± 0.5‰ follows from the formation of the bicarbonate ions out of one molecule of soil CO_2 (δ^{13} = −24.5 ± 0.5‰ and one molecule of soil (marine) limestone ($\delta^{13} = 1.5 \pm 0.5$‰) by the reaction $H_2O + CO_2 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$. The same process causes the carbon-14 content in the groundwater bicarbonate to be 0.5 (100 + 0)% = 50%.

It must be emphasized that the value of −11.5‰ refers to dissolved bicarbonate instead of total dissolved carbon. Unfortunately, many radiocarbon laboratories give δ^{13} values of the total carbon content and fail to give the proper results of the chemical analyses of the water, by which one would be able to calculate δ^{13} of dissolved bicarbonate. The fact is that the latter gives the relevant information as will be pointed out.

The mass spectrometric measurement of δ^{13} actually is performed of the total amount of CO_2 gas (ΣC) evolved by acidifying the water sample. To know δ^{13} (HCO_3^-) a correction must be applied for the other inorganic carbon compounds, viz. dissolved carbon dioxide and carbonate (Mook and Koene, 1972; Mook, 1970):

$$\delta^{13}(HCO_3^-) = \delta^{13}(\Sigma C) - \frac{C_{CO_2}}{\Sigma C} \cdot \epsilon^{13}_{HCO_3}(CO_2\,aq) - \frac{C_{CO_3}}{\Sigma C} \cdot \epsilon^{13}_{HCO_3}(CO_3^=)$$

where C_{CO_2} and C_{CO_3} are the concentrations, $\epsilon^{13}_{HCO_3}$ (CO_2aq) and ϵ_{HCO_3} ($CO_3^=$) the temperature dependent isotope fractionations, with respect to dissolved bicarbonate, of dissolved carbon dioxide and carbonate ions respectively. To calculate this correction it is sufficient to have the temperature and pH of the water sample and eventually the chlorinity.

One can think of several reasons why the actual δ^{13} (HCO_3^-) figures differ from the expected "normal" −11.5 ± 0.5‰ and consequently the ^{14}C content of recent groundwater from 50%. First, the δ^{13} values of the soil CO_2 as well as of the soil limestone may be different from those given. Observations have shown that the carbon isotopic composition of the humus carbon dioxide is more or less specific for the kind of vegetation. With the exception of desert plants which can have δ^{13} values of around −10‰, the variations do not seem to be more than 1 or 2‰, so that −24.5 ± 0.5‰ generally is a reliable average for a relatively extended infiltration area. We have some evidence that a larger uncertainty could be due to variations in δ^{13} of the soil limestone. The isotopic composition of soil limestone has not been investigated thoroughly as yet, but some preliminary results in certain areas showed δ^{13} values as low as −3 to −4‰.

The process of isotope exchange which could be responsible for the decrease in ^{13}C content of the limestone might also alter δ^{13} and consequently the ^{14}C content of the bicarbonate in the early or even a later stage of the groundwater movement. This would come to a decrease in ^{14}C and thus larger ages would result. Although there is no definite evidence, some authors assume that the influence of exchange in this respect is negligible (Thilo and Münnich, 1970).

The source of inorganic carbon in the groundwater may be different. The dissolution of limestone could be brought about by other compounds than the soil CO_2, for instance by hydrogen ions or by wheathering rocks. Here no addition of ^{14}C to the groundwater is involved so that if part of the formation of bicarbonate is due to these processes the ^{14}C age of the water is too large. The occurrence of this complication however is easily recognized by δ^{13} which should be closer to that of the limestone (+ 1.5‰).

Another reason for increased δ^{13} values (> −10‰) could be the isotopic exchange with atmospheric CO_2 at the surface, which process can occur before infiltration or before sampling, for instance from an open well. By this, the ^{13}C content – and the ^{14}C content attendant upon it – will increase in the direction of an equilibrium situation where $\delta^{13} \approx +1$‰ and $^{14}C \approx 100\%$. In a moderate climate this effect is not likely to be observed, as opposed to tropical areas, where it often agrees with an increase in ^{18}O and D content by evaporation.

The infiltration of sea or lake water also affects the ^{13}C content of the ground water. The δ^{13} of ocean bicarbonate is about +2‰ while that in a lake can have any value between −12‰ and +2‰ depending on the residence time of the water. Again, as is observed with ^{18}O, there is a linear relation between δ^{13} (ΣC) and the degree of contamination. x, as, for sea water, is indicated by the chlorinity where the δ^{13} values refer to the total carbon content in this case, and the subscripts to the uncontaminated water and contaminant, respectively.

$$\delta^{13} = \delta^{13}_{\text{fresh}} \; (1 - x) \frac{\Sigma C_{\text{fresh}}}{\Sigma C} + \delta^{13}_{\text{cont}} \; x \, \frac{\Sigma C_{\text{cont}}}{\Sigma C},$$

The following process is considered to be of major importance since it must be held responsible for the fact that generally in young water ^{14}C values of up to 85% are found (Vogel, 1970), coupled with δ^{13} values below −11.5‰. In the unsaturated zone the dissolved bicarbonate can exchange carbon isotopes with an excess of carbon dioxide, if present. This exchange can proceed until an isotopic equilibrium is reached, where $^{14}C \approx 100\%$ and δ^{13} (HCO_3^-) is the fractionation apart from $\delta^{13}(CO_2)$, viz. ≈ −16‰. If we assume the ^{13}C and ^{14}C exchange to proceed proportionally to each other, the original ^{14}C content ($^{14}C_o$) can be calculated from:

$$\frac{\delta^{13} + 11.5}{-16 + 11.5} = \frac{^{14}C_o - 50}{100 - 50}\,, \tag{12}$$

where δ^{13} refers to the dissolved bicarbonate in the sample.

Some authors (Pearson, 1965; Tamers, 1967) prefer a different startingpoint for calculating the original ^{14}C content of ground water. Their treatment does not include the exchange process. Either based on the carbon isotopic or the chemical composition, $^{14}C_o$ is deduced by considering the total carbon content merely as a mixture of soil carbon dioxide and limestone.

CARBON-14

Once the original ^{14}C activity of the groundwater, that is during the infiltration, is known, the age of a water sample can be determined, on the premise that no further processes will change the ^{14}C content other than the radio-active decay. By age, in this respect, is meant the elapse of time between the moment of sampling and the moment of infiltration of the water into the ground. The conventional radiocarbon age is calculated from

$$t = -\frac{t_{\frac{1}{2}}}{\ln 2} \ln \frac{A_1}{A_o}$$

where A_1 and A_o refer to the measured and original specific activity, respectively, and $t_{\frac{1}{2}}$ to the half life. The "conventional radiocarbon age", t_{conv}, is revealed by applying $t½ = 5568$ year and A_o = NBS standard-activity, the more realistic "corrected age" by using $t½ = 5730$ year and $A_o = 85\%$ of the standard activity. The latter is taken as a reasonable approach to the original ^{14}C activity of "recent" groundwater as long as there is, in our opinion, no reliable way of determining this value from chemical data and from the stable carbon isotopic composition of the water.

It must be emphasized that a knowledge of this original ^{14}C content is often not relevant. The important application of carbon-14 in hydrology is found in the determination of the large-scale flow characteristics of a ground water body, viz. the direction and the velocity of the water movement. By analysing a series of samples from wells or borings, tapping from the same aquifer, isochrones can be established, i.e. geographical lines where the water is of the same age. According to Darcy's law, in aquifers with a homogeneous permeability these isochrones should coincide with the isohypses of groundwater, while, on the contrary, mutual deviations are due to inhomogeneities in permeability caused by, for instance, clay lenses or faults. Often it is required to know a value as good as possible of the overall permeability or rather of the velocity of the groundwater. From a geographical distribution of water samples the flow velocity between neighbouring wells or borings can be calculated from the age differences between the samples. From the equation

$$(t_2 - t_1)_{corr} = -8267 \ln \frac{A_2}{A_1}$$

it is seen that this age difference does not depend on the original ^{14}C content, A_o, which, therefore, is not relevant for calculating the flow velocities.

The investigation of ground water flow with radiocarbon is not limited to the horizontal component. The distribution of ^{14}C concentrations (or ages), to be expected in a vertical profile, has been calculated for specific cases (Vogel, 1967, 1970).

Carbon-14 can also be applied as a natural tracer like tritium. The possibilities to establish upwelling of ground water or infiltration of surface water into the ground are based on the differences between the ^{14}C activities observed. Also the possible leakage through soil layers of low permeability (clay) or along a bore-hole is an interesting application.

In tracer-studies the natural isotopes have great advantages over the use of artificial tracers in that they are completely harmless and the practical application hardly disturbs natural conditions, merely implying the collection of water samples in the field, while especially the hydrogen and oxygen isotopes act as ideal tracers, being an intrinsic part of the water molecule. Although the isotope studies are complex and timeconsuming, they offer a valuable tool that can supplement geohydrological and chemical methods in ground water research.

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