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AN OVERVIEW OF ^{14}C ANALYSIS IN THE STUDY OF GROUNDWATER

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ABSTRACT. This paper provides a summary overview of the current state-of-art in the radiocarbon dating of groundwater. While the use of natural ^{14}C measurements in applied hydrogeology still presents a difficult challenge, meaningful dates can be achieved if they are determined and interpreted in conjunction with the analyses of other isotopic species that occur in the natural environment. Although ^{14}C dating of groundwater can be, and often is, carried out as a matter of routine, any specific case study requires its own scientific design and effort. As is widely recognized, and discussed in considerable detail throughout the scientific literature, there are many hydrogeochemical reactions and/or physical processes that can alter the natural ^{14}C enrichment measured in environmental materials. Fortunately, for fresh groundwater resources such effects are in general well defined and therefore of limited significance. The primary challenge in applied groundwater dating is with the development of the appropriate theoretical background against which ^{14}C dates can be used to calibrate numerical analogues of the groundwater system. The hydraulic properties of each of the widely used finite-element models can be well estimated from numerous piezometric data and extrapolations. In contrast, only a few groundwater ages can be provided for the calibration of those models that are complex functions of aging mixture and sometimes also hydrochemical reactions.

INTRODUCTION

The application of conventional radiocarbon dating using the inorganic carbon contained in speleothems was first proposed by Franke (1951). Soon afterwards Deevey et al. (1954) reported a significant reduction in the ^{14}C specific activity of the dissolved inorganic carbon (DIC) compounds in lake water due to the participation of geologically old carbonate where this occurs within the catchment—the so-called "hard water effect" or "reservoir effect" as was later coined by Olsson (1980). The direct dating of groundwater based on the measured ^{14}C activity was introduced by Muennich (1957, 1968). However, it soon became evident that the initial ^{14}C activity (N_o) imparted during groundwater recharge is determined in large part by the ongoing hydrogeochemical mass balance reactions towards establishment of the carbonate/CO_2 equilibrium state. In general, therefore, the appropriate N_o value used to determine a ^{14}C age for the DIC tends to be set at less than 100% modern carbon (pMC) i.e., the theoretical equivalent to time zero on the conventional ^{14}C time scale.

By international convention the ^{14}C age (t) in years BP (before AD 1950) of groundwater DIC is calculated from its measured ^{14}C activity (N) and according to the relationship

$$t = \tau/\ln 2 \ \ln(N_o/N) , \qquad (1)$$

where τ is set at either the Libby half-life of ^{14}C (5570 yr) or the physical half-life of 5730 yr.

In addition to any initial uncertainty over the actual ^{14}C activity (N_o) set at recharge, the apparent decrease in ^{14}C activity due to radioactive decay during subsequent storage in the aquifer can also be distorted by the superimposed influence of hydrochemical reactions, physical processes, and geohydraulic mixing. Consequently, the great challenge in applied groundwater dating is to resolve and quantify the true age controlled effect of radioactive decay from other possible influences on the measured ^{14}C activity.

HYDROCHEMICAL REACTIONS

Objective ^{14}C dating of groundwater requires recognition and quantification of those hydrochemical reactions that will have altered the ^{14}C activity of the DIC in addition to the immutable rate of radioactive decay. Quantification of the isotopic composition from such processes is essential since ultimately their collective influence will determine the ^{14}C activity of the DIC sample and hence the most appropriate method for its numerical conversion to a meaningful age for the water. There are two stages in the aquifer recharge and storage processes that have to be accounted.

1. First are those reactions that occur during groundwater recharge. These take place in the unsaturated zone that represents an open system for isotopic exchange via the soil zone and the free atmosphere. The general trend is towards a lowering of the ^{14}C activity imparted to the DIC. The extent to which this initial dilution occurs is in turn dependent on the geochemical and petrological characteristics of the catchment.
2. Once transferred to the saturated zone of the aquifer, the groundwater can be subject to secondary hydrochemical reactions. Any resultant isotopic alterations that take place during this period of groundwater storage and aging do so within the constraints of a closed geochemical system.

The Initial ^{14}C Activity of DIC

When rainwater enters the topsoil, it encounters an atmosphere that contains very high concentrations of CO_2 generated by the biological decomposition of dead organic matter and/or root respiration. Dissolution of this CO_2 produces hydrocarbonic acid which will in turn react with any soil carbonate present until either calcite saturation or $CaCO_3/CO_2$ equilibrium is reached.

$$CO_2 + H_2O + CaCO_3 \leftrightarrow 2HCO_3^- + Ca^{2++} \tag{2}$$

In the pH range 6–8, which is common for fresh groundwater, the DIC consists of HCO_3^- and CO_2. The relative concentration of these components is determined and controlled by the partial pressure of CO_2 in the topsoil and the ambient temperature.

It is necessary to distinguish between open and closed system conditions (Wigley 1977). In open systems, calcite saturation is reached by utilization of the essentially unlimited reservoir of carbon contained as soil CO_2 within the unsaturated zone. On entering the closed geochemical system, represented by the saturated zone, the groundwater is separated from this open CO_2 reservoir and calcite saturation is approached when reactable dissolved CO_2 is in equilibrium with the carbonate ions. Under most natural conditions these hydrochemical reactions actually occur in geochemical states that are transitional between open and closed systems.

Geochemical Modeling

The initial reactants in the CO_2 /carbonate exchange have different origins and consequently quite distinct carbon isotope signatures i.e., specific ^{14}C activity and the stable-isotope composition ($\delta^{13}C$). The biogenic derived CO_2 has a ^{14}C activity close to 100 pMC (percent modern carbon) and a $\delta^{13}C_{PDB}$ value of about –23‰. ^{13}C is enriched (less negative $\delta^{13}C$) compared to common terrestrial organic matter since atmospheric CO_2 with a $\delta^{13}C_{PDB}$ value of –8 to –7‰ diffuses into the topsoil. Soil lime is considered to be of marine origin with a $\delta^{13}C_{PDB}$ value close to 0‰ and is so old as to be essentially free from ^{14}C i.e., an activity of 0 pMC.

Therefore, it is the relative contribution from dissolved bicarbonate and carbon dioxide that determines the carbon isotope composition that characterizes the DIC in freshly recharged groundwater. The initial ^{14}C activity ranges from 80 to 100 pMC, and from 54 to 84 pMC for open and closed conditions, respectively. The corresponding ranges of stable isotope composition ($\delta^{13}C_{PDB}$) are –17 to –16‰ and –13 to –12‰ (Clark and Fritz 1997).

Various theoretical models have evolved to estimate appropriate values of N_o based on hydrochemical evolution processes in conjunction with the stable carbon isotope composition of DIC (Mook 1976; Clark and Fritz 1997). The approach was pioneered by Ingerson and Pearson (1964) who proposed the quantification of N_o as a function of the $\delta^{13}C_{PDB}$ values of the DIC, soil CO_2 and soil lime. This basic model assumed closed system conditions (100 pMC for soil CO_2 and ^{14}C free carbonate, and perfect stoichiometry for carbon exchange).

Gonfiantini (1972) replaced the relationship and introduced the isotope fractionation (ε) between dissolved bicarbonate and CO_2. The appropriate value of ε depends upon the temperature and pH; it ranges from +7 to +10‰. In this instance:

$$N_o = N_{(bio)}\,(\delta^{13}C_{DIC} - \delta^{13}C_{carb})/(\delta^{13}C_{bio} + \varepsilon - \delta^{13}C_{carb}) \tag{3}$$

Where N_{bio} is assumed to be 100 pMC and the indices "bio" and "carb" refer to the soil CO_2 and soil carbonate, respectively.

Geyh and Wendt (1965) introduced the concept of chemical balance for the numerical estimation of N_o. The method is dependent on knowing the concentrations of CO_2 and HCO_3^- in the groundwater, though in practice it is difficult to determine that of CO_2 precisely. Tamers et al. (1967) improved this approach by replacing the CO_2 concentration term by the difference between total dissolved inorganic carbon (TDIC) and the HCO_3^- concentration. Both models assume closed system conditions.

More complicated process-oriented models that recognize both the hydrochemical balance and the isotope fractionation have been developed subsequently (Mook 1976; Reardon and Fritz 1978). Fontes and Garnier (1979) even included mixing–matrix exchange, i.e. rock/water interactions.

A computer program (NETPATH) has been developed (Plummer et al. 1994) to simulate the progressive changes in carbon isotope geochemistry along the groundwater flow path based on the prevailing hydrochemical conditions.

Limitations of the Theoretical Models

Processes and Model Conditions. It must be recognized that in practice the objective application of any theoretical model is constrained. A first consideration is the fact that most natural groundwater systems tend to exhibit the complex interaction of several hydro-geochemical and/or physical mixing processes. Moreover, calcite saturation and isotopic equilibrium, although often assumed in theory, are not always achieved in nature. Consequently, although the overall effect of multiple processes in determining the initial ^{14}C activity of DIC can be quantified as the product of the individual dilution factors (Clark and Fritz 1997), it is important to recognize that the preferred isotopic and hydrochemical initial field parameters employed in the calculation are seldom known precisely.

Objective application of the NETPATH program (Plummer et al. 1994) is for example limited by the prerequisite that the pattern of samples intended for ^{14}C measurement must reflect a hydrologic flow path which in itself cannot be located precisely.

Isotopic Field Parameters. It is presumed in all models that the initial ^{14}C activity of the participating soil carbonate is zero. However, Geyh (1972) showed that the ^{14}C enrichment of soil lime from immediately below the decalcified zone can exhibit values as high as 75 pMC and a mean of 15 pMC obtains in humid regions. During the warm season the evaporation of recently recharged groundwater tends to result in a precipitation of calcite crystals and an accumulation of excess ^{14}C in the unsaturated zone. Freezing in the unsaturated zone can have a similar effect.

In coastal areas the predominant contributor to the carbonate reservoir contained in the topsoil is young mollusc shells which are relatively rich in natural ^{14}C. Similarly, in karst areas, Holocene aged tufa may be exposed and/or present as carbonate filling in geological fractures. Likewise, it is possible that weathering of Felspar by the action of biogenic CO_2 will add small amounts of bicarbonate with a ^{14}C activity of 100 pMC to the DIC. However, as was highlighted by Ehhalt and Vogel (1963), this is a very slow, and therefore relatively insignificant process. In such instances the reservoir-effect corrected ^{14}C ages of groundwater will be apparently too small.

Tamers et al. (1975) have contended that the realistic precision that can be achieved in groundwater dating is constrained to a considerable degree by any thorough error analyses that recognizes the ranges of ^{14}C activity and ^{13}C enrichment that can obtain for the various carbonaceous parameters involved. This opinion is well exemplified via the frequently used "Gonfiantini model" (Equation 2). If we adopt an uncertainty range of ±2‰ for the $\delta^{13}C$ values that are assumed for both the biogenic CO_2 and the soil carbonate and ±1‰ for DIC, then the modeled dating precision for Holocene groundwater will be ±2700 yr. This in stark contrast to the ±1000 yr (1 σ) error associated with and arising from the conventional ^{14}C age measurement. In practice, however, the results of many case studies show that the scatter of ^{14}C groundwater dates is far less—generally within a ±500-yr envelope (Geyh 1992), the reason being that although the scatter of the initial $\delta^{13}C$ values encountered in restricted recharge areas is not accurately known, this is nevertheless of significantly less magnitude than the global ranges.

While the basic models tend to assume that soil CO_2 is entirely of biogenic origin and hence characterized with a $\delta^{13}C$ value of –25‰ there the is an almost inevitable ongoing exchange with atmospheric CO_2 which requires a more realistic value of –22‰. Furthermore, in arid and semi-arid regions, C_4 type vegetation (sugar cane, corn, sorghum, grasses in the savanna) is liable to dominate the soil CO_2 and imprint much heavier ^{13}C enrichment (typically $\delta^{13}C_{PDB}$– = –13‰). Usually the vegetation consists of an unknown assemblage of both types of plants and with relative variations in previous years.

Where bacterially mediated reactions occur, these are invariably accompanied by large shifts in isotopic fractionation. The prime example here is methanogenesis (Clark and Fritz 1997). Since the extent of the induced isotopic fractionation is generally site specific and unknown in most instances it is not possible to adjust the measured radiometric (^{14}C) enrichment of the DIC to achieve a realistic ^{14}C date.

Empirical Approaches

Many empirical approaches have been applied to estimate N_o and hence determine directly the calibration factor used to define the assumed age of DIC in groundwaters. Frequently this is simply use of the fixed correction value of 85 pMC as proposed by Vogel and Ehhalt (1963).

As an alternative, Geyh (1972) calculated a range of N_o values that would be more applicable to describe the initial ^{14}C activity of DIC in spring water from specific geological settings. These estimates (Table 1) are often found to compare well with the more stringently determined N_o values modeled independently and in relation to other isotopic parameters.

Another relatively simple approach to determining the appropriate "reservoir correction" value was proposed by Vogel (1970). The procedure involves measurement of the conventional ^{14}C age of

DIC sampled at recorded intervals along the groundwater flow path in confined aquifers and the subsequent linear extrapolation of these data back towards the catchment region where the actual water age can be assumed at close to zero. The method is exemplified in Figure 1.

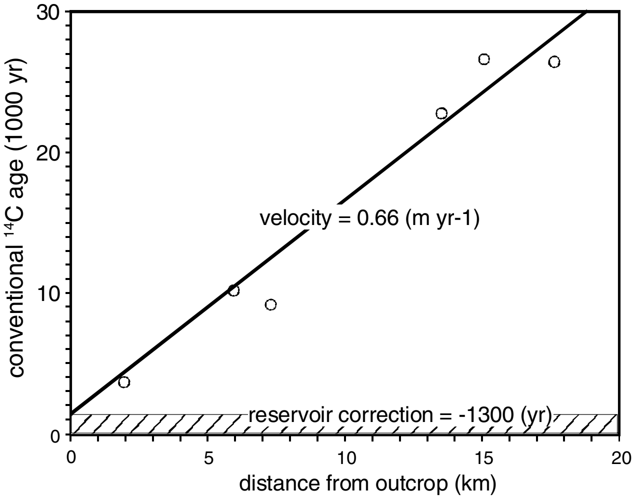

Figure 1 Increase in ^{14}C ages of DIC in groundwater as a function of distance from the catchment area (after Vogel 1970) as used to estimate the initial ^{14}C activity

Table 1 Initial ^{14}C activity values and corresponding reservoir (age) corrections for different geological settings (Geyh 1972)

Catchment geology	Initial ^{14}C activity (pMC)	Reservoir age correction (yr BP)
Crystalline	90–100	−1000 to zero
Loess covered	85	−1300
Uncovered karst, dunes	55–65	−5000 to −3500

Another very successful approach, developed by Verhagen et al. (1991), is summarized in Figure 2. It is applicable in systems where the groundwater may have incorporated post-nuclear CO_2 i.e., as evidenced by the occurrence of measured ^{14}C activities greater than 100 pMC, and involves the construction of a “^{3}H/^{14}C” or alternatively a “^{85}Kr/^{14}C” diagram. The appropriate initial ^{14}C activity is then assumed to occur where the curve intersects the tritium detection limit. The basic reasoning here is that a groundwater sample that does not contain “bomb” tritium will also be free of anthropogenic ^{14}C.

In fractured aquifer systems (open system) the mean residence time (MRT) rather than the water age of groundwater may be estimated by applying the exponential model to the specific activity of tritium and ^{14}C. In the case of ^{14}C there are two unknown parameters, viz., the initial ^{14}C activity and MRT. Since any spring or well-water sample has its specific MRT, by applying this method to the measured ^{3}H and ^{14}C activities of several samples from the same catchment, the initial ^{14}C activity is obtained in addition to the MRT (Geyh 1972).

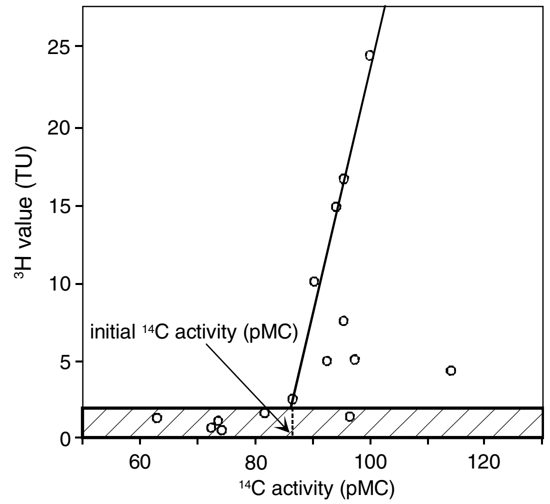

Figure 2 ^{3}H/^{14}C diagram as used to estimate the initial ^{14}C activity in DIC of groundwater from the northern Kalahari (Verhagen et al. 1974)

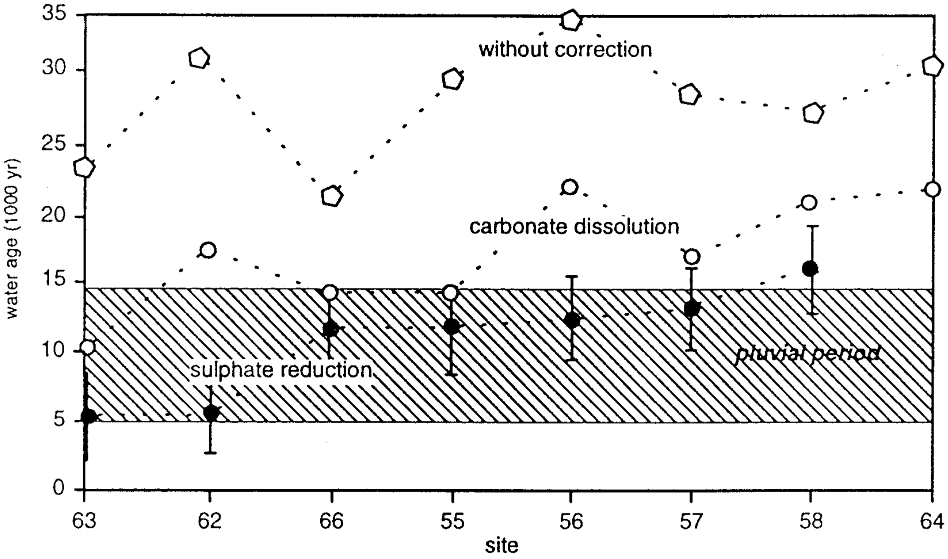

Figure 3 Application of different hydrochemical models to estimate the initial ^{14}C activity of DIC in groundwater from the Ad Rhuma aquifer in Oman based on palaeohydrological information (after Clarke et al. 1996)

In favorable circumstances, paleohydrological, paleoclimatological, and prehistoric information can also be usefully employed in estimating the initial ^{14}C activity or to check its accuracy (Geyh 1992; Clark et al. 1996). An example that incorporates this approach as described by Clark et al. (1996) is summarized in Figure 3 above. In this instance, supplementary correction models were applied to account for the influence of both carbonate dissolution and sulphate reduction (Clarke and Fritz 1997) and to ensure that the ^{14}C ages of the DIC corresponded with the paleohydrological situation.

Rogojin et al. (1998) used the measured ^{234}U excess to calibrate the ^{14}C timescale of groundwater. A good correlation was established between the uranium isotope ratios and ^{14}C ages of DIC in groundwaters sampled from the oxygenated parts of a limestone and a sandstone aquifer in Israel.

Natural ^{14}C Activity in DOC

Dissolved organic carbon (DOC) in groundwater consists of organic liquids, hydrocarbons, methane, and humic components. It is produced in soils and peat layers by microbacterial degradation of organic detritus and via the oxidation of lignite or kerogen. The youngest recognized constituent of groundwater DOC is the group of organic compounds classed as fulvic acids (FA). These are the most promising molecules for dating groundwater DOC (Geyer et al. 1993; Aravena et al. 1993). The more abundant humic acids (HA) are less suitable.

In general, the concentration of fulvic acids in groundwater is low, often providing as little as 1 mg C/liter. Since the component carbon of fulvic acids can derive from a variety of pedogenic and/or geogenic sources all of which are of potentially variable age, the composite natural ^{14}C activity (N) can be expected to be significantly lower than 100 pMC. Geyer et al. (1993) reported values from 34 to 100 pMC but noted the greatest frequency of results occurred within the range 75–100 pMC. Given this situation, any quantification of an appropriate N_o value (see Empirical Approaches, above) must be recognized as an empirical estimate. Therefore, the initial expectation that conventional ^{14}C dating of DOC could overcome the hydrogeochemical problems inherent in dating DIC has not been fulfilled. Nevertheless, comparative dating of DOC is often a useful supplement to parallel dating of the component DIC in selected groundwaters.

Secondary Reactions

While hydrochemical reactions in the saturated zone can reduce the residual ^{14}C activity of DIC independent of, and in addition to, the ongoing radioactive decay process, DOC is not susceptible to such reactions. However, it must also be recognized that the possible admixture into the bulk DOC of fossil derived fulvic acid will signal erroneously old ^{14}C ages (Geyh 1991).

Oxidation of Organic Matter and Subsequent Carbonate Dissolution

The most serious and frequently observed hydrochemical reaction that can disturb the ^{14}C activity of DIC is the formation within the saturated zone of CO_2 from fossil organic matter contained in the aquifer system. This reaction is facilitated by the consumption of dissolved oxygen (up to 6 mg/liter) or the reduction of any sulphate and/or nitrate present. Once formed, the CO_2 is likely to enable the dissolution of additional fossil carbonate. Many aquifers contain fossil organic material and many groundwaters exhibit high concentrations of sulphate. Where such conditions prevail, the measured stable isotope enrichments (δ^{13}C values) are no longer applicable for either estimating the initial ^{14}C activity (Figure 4) or to correct for secondary non-decay changes to the ^{14}C activity of the DIC. The impediment here stems from the fact that there are two independent sources of carbon with divergent δ^{13}C and ^{14}C activity values viz., fossil organic matter with respectively –25‰ and 0 pMC, and soil carbonate with respective isotope signatures of 0‰ and 0 pMC. As is shown in Figure 4, both the apparent age and concentration of DIC increases due to the input of fossil derived CO_2 while the coincident δ^{13}C values change in an irregular pattern (Geyh and Kantor 1998).

Clarke and Fritz (1997) proposed a correction scheme for this reaction based on the measured H_2S concentration, but the precise determination of this parameter is difficult in groundwater samples. A correction scheme proposed in 1972 by Hans Oeschger of Berne offers a more suitable solution to this program. On the presupposition that the organic carbon was entirely fossil derived and that the

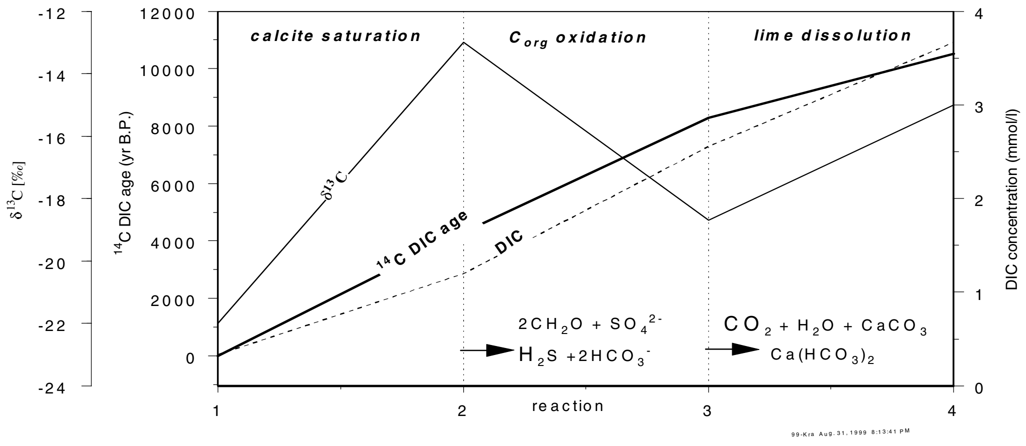

Figure 4 Schematic diagram of the changes in ^{14}C age, DIC concentration and $\delta^{13}C$ values of DIC of groundwater due to oxidation of fossil organic matter and the subsequent dissolution of fossil carbonate (Geyh and Kantor 1998)

DIC concentration was determined precisely, then the age of the DIC could be determined from the product of the measured ^{14}C activity and the DIC concentration viz.,

$$t\ (\text{yr BP}) = 5730/\ln 2 \times \ln\ (DIC_o \times N_o)/(DIC \times N)\ . \tag{4}$$

Most recently, Harrington and Herczeg (1999) suggested using the $^{87}Sr/^{86}Sr$ isotope ratio as the basis for application of a suitable correction to the ^{14}C activity of DIC which had been influenced by input to the groundwater of CO_2 formed by the oxidation of fossil organic matter. This involves the application of a two-component mixing model in which the end-members are distinguished by their respective $^{87}Sr/^{86}Sr$ isotope ratios.

Dissolution of Dolomite

Although the dissolution of magnesium subsequent to the calcite saturation is a slow process, it is common under closed conditions in the aquifer. Two carbonate molecules are released into a solution for each Mg^{2+} ion and consequently result in an increase in DIC concentration. Even in instances where this reaction is buffered by calcite precipitation, the “Oeschger correction” (Equation 4) can be used, whereas the alternative “Gonfiantini correction” may not be applicable (Clark and Fritz 1997).

Admixture of Fossil Carbon Dioxide

The admixture of geogenic or magmatic CO_2 (from deep crustal or mantle sources) is often associated with thermal metaphormism and usually accompanied by an increase of the mineralization of the groundwater. Complex hydrochemical reactions may occur. This situation is generally indicated by the occurrence of heavier $\delta^{13}C$ values i.e., more positive than approximately –9‰ and DIC concentrations that exceed approximately 8 mMol carbon/liter. The NETPATH program (Plummer et al. 1994) can be used to model the corresponding evolution of the ^{14}C activity and the hydrochemical composition. However, this approach requires that hydrochemical equilibrium has been established, that the possibility of outgassing of CO_2 can be excluded (which is seldom the case in practice), and that the flow path of the analyzed groundwater is entirely localized.

Methanogenesis and/or the Admixture of Fossil Methane

The process of methanogenesis, which involves the microbacterial degradation of detrital organic matter, in accordance with Equation 5, can occur in both the unsaturated and the saturated zones of aquifer systems.

$$2CH_2O \rightarrow CO_2 + CH_4 \tag{5}$$

The biochemical pathway is invariably marked by a significant fractionation of the carbon isotopes. Attempts to quantify an appropriate correction for the ^{14}C activity of the DIC are usually unsuccessful since the source organic matter is likely to have finite but unknown ^{14}C activity, and some CO_2 is liable to have outgassed from the groundwater prior to carbonate dissolution. The "Oeschger correction" (Equation 4) can be applied, but as discussed previously, only if it may be assumed that the source organic matter is fossil (essentially ^{14}C free) and that no loss of CO_2 gas has occurred.

The incorporation of thermocatalytic, abiogenic, or mantle fossil methane is often associated with the admixture of fossil CO_2 into the groundwater. Gas will expel after exchange with the dissolved CO_2 resulting in an uncontrolled loss of ^{14}C. In any case, methane is seldom found in resources of fresh groundwater (Geyh and Kuenzl 1981).

PHYSICAL PROCESSES

In addition to hydrochemical reactions and advective mixing it is necessary to recognize that other physical processes that can occur within the defined closed aquifer system have the potential to distort the relationship between recorded ^{14}C activity in DIC and straightforward radioactive decay.

Bicarbonate/Matrix Exchange

DIC in groundwater diffuses into the pores of the aquifer rock from where it loses ^{14}C by radioactive decay. Subsequent backwards diffusion the ^{14}C depleted DIC will lower the activity of the groundwater flowing through the wide fractures of the aquifer system. Maloszewski and Zuber (1984) showed that a simple relationship exists between the actual age of the water(t_{actual}) and the apparent DIC age (t_{app}) governed by the matrix porosity (n_{matrix}) and the fractural porosity (n_{frac}) of the aquifer rock viz.,

$$t_{actual} = t_{app} /(1 + n_{matrix} /n_{frac}) \ . \tag{6}$$

In carbonate aquifers, the term $(1 + n_{matrix} /n_{frac})$ may be approximated at 2 (Maloszewski and Zuber 1984).

Diffusion

Groening and Sonntag (1993) showed the hypothetical influence of a molecular-diffusive penetration of modern carbon into shallow phreatic aquifers obtained in field conditions. This effect resulted in an increase in the ^{14}C activity of DIC. The corresponding decrease, as reflected in the measured ^{14}C age of the DIC, was especially marked in the case of old ascending groundwater. Under such conditions a Pleistocene aged groundwater may signal an apparent Holocene recharge event. This process can be recognized by increased δ^{13}C values, since that of atmospheric CO_2 (–8‰) is heavier than that of DIC at approximately –12‰. Hence, the enrichment of the ^{14}C activity of DIC by the admixture of atmospheric CO_2 with its high ^{14}C activity can be estimated.

APPLIED HYDROGEOLOGY AND THE EFFECTS OF GEOHYDRAULICS

In applied hydrogeology the application of isotope hydrological methods is mostly in relation to the management of fresh groundwater resources that have to be exploited for drinking water supply. Therefore, there is usually a high concern over groundwater quality. Secondary hydrochemical reactions are restricted to one or two processes in freshwater systems only, and the induced changes in the isotopic composition can be accounted and corrected. Precise determination of the absolute age of the groundwater is seldom the main criterion. In most cases, it is sufficient to know whether or not the groundwater is being continuously recharged. If water balance modeling is required, then ^{14}C ages of the component DIC may be needed to allow calibration of the model or to improve the hydrogeological conception of the system in context of appropriate analyses.

Objections to applied groundwater dating are still voiced among hydrogeologists and isotope hydrologists. For the most part these criticisms tend to be based, quite unjustifiably, on a lack of experience and/or a misconception that the method is unreliable due to 1) the need for a critical evaluation of the initial ^{14}C activity, and 2) the effects of secondary isotopic changes induced via the subsequent hydrochemistry. Indeed, any tendency to apply the various isotopic and hydrochemical correction models to measured and interpret measured ^{14}C activities without a critical evaluation of the characteristic hydrogeochemical features of the natural aquifer system is likely to detract from the objective confidence that can be applied to the reliable ^{14}C dating of groundwater (Mook 1976; Clark and Fritz 1997). Without the necessary attention to selecting the most appropriate correction procedure, the resultant ages calculated for a specific sample of DIC can vary by up to 5000 years (Geyh 1992).

Experience gathered in numerous hydrological case studies of freshwater systems shows that secondary hydrochemical induced changes to the ^{14}C activity of DIC are the exception rather than the rule. Where they do occur, correction of the measured data is usually quite simple. The most common and more critical interference for objective dating are apparent shifts caused by the advective mixing of groundwaters of differing ages (e.g. Geyh and Backhaus 1979). However, the prime purpose of multi-environmental isotope analyses is often focused on conceptional modeling in order to yield qualitative or even quantitative hydrodynamic information rather than the determination of groundwater ages per se.

Natural System Conditions

Groundwater balance studies have to distinguish between stationary and non-stationary groundwater recharge. Neglecting this aspect in any groundwater budgeting exercise may result in a considerable overestimation of the sustainable resources (Verhagen et al. 1991).

Stationary Recharge Conditions

Groundwater flows from the recharge area to the discharge area, and during this passage the ^{14}C age of the component DIC increases. In active aquifer systems the rate of groundwater recharge is balanced by the discharge rate and a two-dimensional spatial of the ^{14}C ages of DIC reflects the actual groundwater flow direction and velocity. This information allows the basis for estimation of sustainable yield.

In the first instance, ^{14}C dates of DIC are usually interpreted under the assumption that the groundwater flow is analogous with *piston-flow* conditions and that any admixture within the groundwater mass can be discounted. This assumption may, however, only be valid in respect of confined aquifer systems. In phreatic aquifers, groundwater is recharged over the whole geographical extension resulting in a vertical component to the ^{14}C activity distribution and which is in turn a function of recharge rates (Vogel 1970).

If the aquifer has a constant thickness then there is no spatial distribution of the ^{14}C activity. This means that the ^{14}C age of DIC in groundwater from the same depth is constant from one location to another one. In practice, groundwater supplies from such aquifers are abstracted over a limited vertical range, which is determined by the filter length of the well. The resulting mixture of different aged waters can be described by the exponential model (Verhagen et al. 1991).

So-called "conceptional models" have been developed and applied to represent even very complex aquifer systems (e.g. Geyh and Backhaus 1979; Pearson et al. 1983; Wigely et al. 1984; Phillips et al 1989; Verhagen et al. 1991). The regionally valid hydraulic information derived via this approach is often superior to the local information obtained from pumping tests.

Tamers et al. (1975) carried out the first applied hydrological study on the exploitation of the deep groundwater of the Biscayne aquifer in southern Florida. The main objective was in support of a pollution prevention assessment. In another case study, Geyh et al. (1984) designed a conceptional model to determine regional hydraulic parameters of the aquitard in a leaky aquifer system north of Nuremberg, Germany, and to establish a water budget (Figure 5). This resulted in a revision of the original hydrogeological conception of the system. It was found that contrary to former ideas, 90% of the groundwater of the deep confined aquifer was in fact being recharged by seepage of shallow groundwater, and that the hydraulic conductivity of the aquitard was of the order of 10^{-10} m/sec.

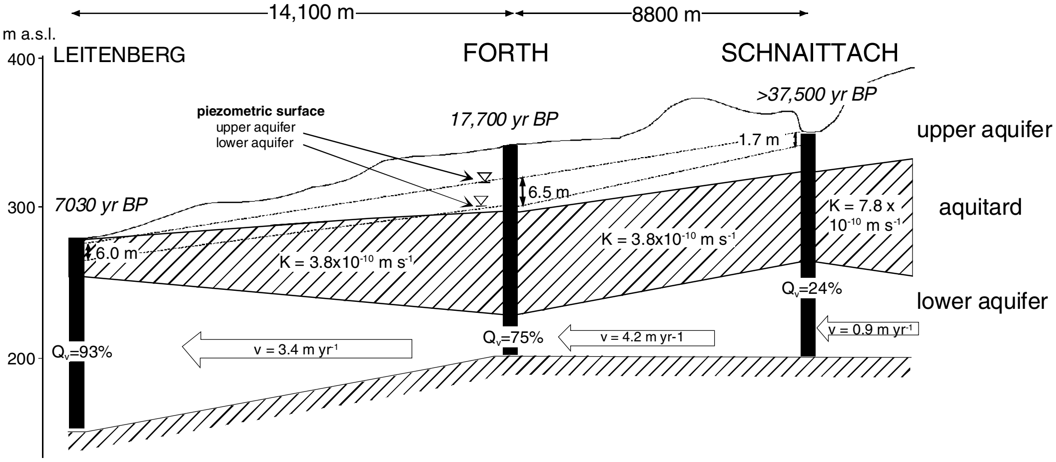

Figure 5 Hydrogeological section along the direction of groundwater flow in the study area, showing; the conventional ^{14}C ages of the deep groundwater, the regional hydraulic conductivity (m/s) of the aquitard, the percentage of vertical inflow of groundwater (Q_v) and the tracer velocity (Geyh et al. 1984)

The immediate challenge in the field of groundwater ^{14}C dating remains with the development of improved procedures that can enable ^{14}C dates measured for DIC to be applied more objectively in the calibration of finite-element numerical mass-transport models.

Non-Stationary Recharge Conditions

During the geological past, the hydrological conditions that prevail in modern arid and semi-arid regions oscillated between dry and pluvial periods (Geyh 1992). Furthermore, in present-day humid regions the paleo-hydrological conditions changed during the transition from glacial to interglacial periods and vice versa (Bath et al. 1979). Both scenarios exemplify the existence of non-steady-state recharge conditions during the past history of the particular aquifer system.

After any interruption of groundwater recharge the hydraulic gradient of the actual "decaying" fossil groundwater level reflects a superposition of the often negligible amount of recharged groundwater onto that of the fossil relict water body (Burden 1977). The two-dimensional spatial distribution of the ^{14}C dates of such fossil groundwater no longer represents the actual flow velocity (recharge rate) or the flow direction. The age pattern only records the flow conditions that prevailed during former pluvial periods (Figure 6). Consequently, groundwater recharge rates are overestimated if the paleo-hydrology of present arid and semi-arid regions is not taken into account in numerical flow modeling.

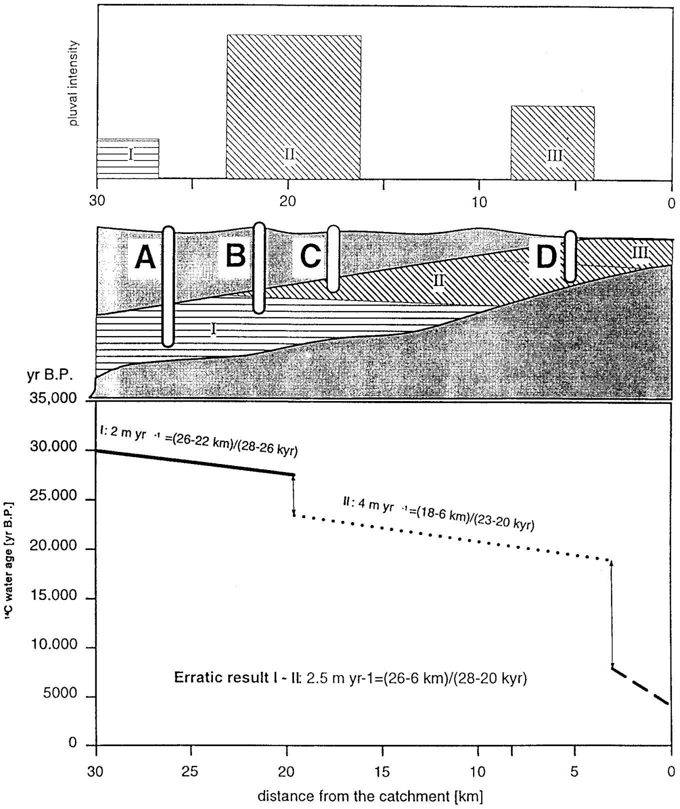

Figure 6 Scheme used to estimate the groundwater tracer velocity for the arid Near East in the past (Geyh 1994). Erratic results are obtained if a tracer velocity is calculated from ^{14}C dates of water recharged during different pluvial periods (e.g. from wells A and D).

This is well exemplified in the results of a comprehensive groundwater survey conducted in 1976 north of Khartoum, Sudan, and east of the Nile River (Verhagen et al. 1991). These data were in obvious conflict with those obtained by numerical geohydraulic modeling of the water budget. A rather simple one-dimensional mass transport model applied to the ^{14}C dates obtained from DIC indicated an actual infiltration rate of only 1.5 to 4.0 × 10^6 m^3/yr along the river bank as opposed to a value of

60 × 10^6 m^3/yr obtained by steady-state modeling—a situation where the actual groundwater availability is an order of magnitude smaller than that estimated erroneously via numerical modeling.

Anthropogenic Disturbance of Hydraulic Systems

During the last several decades, there has been a widespread disturbance of the natural balance between recharge and discharge of groundwater resources subject to human exploitation. This situation applies in both humid and arid regions of the world. The abstraction of groundwater has tended to lower the piezometric surface and increase the amount of percolation through aquitards that separate adjacent aquifers. As a result, the ^{14}C ages of DIC often changed without any hydrochemical indications. This apparent mobilization and mixing of groundwaters from different depths and/or between previously discrete aquifer systems provides clear evidence for over exploitation, and in extreme cases, "groundwater mining" (Figure 7; Geyh and Backhaus 1979).

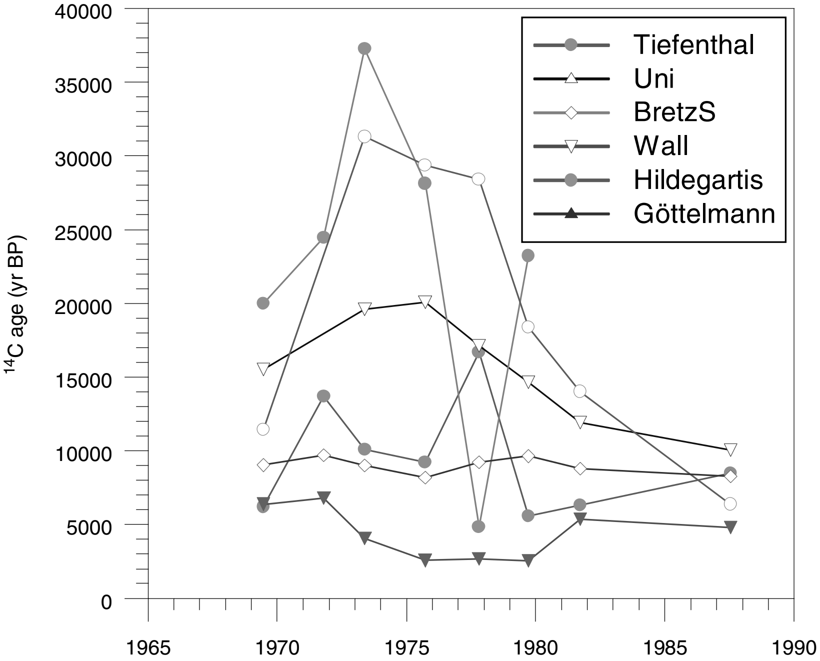

Figure 7 Temporal changes in the conventional ^{14}C ages determined for DIC from groundwater in the heavily exploited Mainz aquifer system

Monitoring of the temporal changes in ^{14}C activity of DIC in such aquifers has highlighted the considerable variation that can occur within a few years, and obviously raises doubts over the reliability of any ^{14}C ages so derived (Geyh 1986). For example, ^{14}C dates have been determined since 1968 from a 200-m-deep unconfined limestone aquifer in Mainz, Germany (Geyh and Sonne 1983). The measured ^{14}C activities show three deviating trends through time (Figure 7) that are significantly devoid of any local clustering. Analogous observations have been made in other unconfined and confined, fractured and sedimentary aquifers (Geyh and Soefner 1989; Verhagen et al. 1991). The only feasible explanation is that sometimes it is deep old groundwater that is mobilized and admixed, and at other times it is young shallow groundwater. A model that allows a quantitative explanation of these patterns has still to be developed.

Exploitation of temporal changes in the conventional ^{14}C dates measured for DIC to quantify the effects caused by groundwater abstraction can only apply where the aquifer system is characterized by simple hydraulic conditions. This was the case for the aquifer in the Azraq spring area described by Verhagen et al. (1991). Here, mixing of young groundwater from the basalt aquifer and old groundwater from the deep limestone aquifer is forced by anthropogenic depression of the water table.

CONCLUSION

^{14}C dating of the DIC in palaeowater is indispensable for paleohydrological and palaeoclimatological reconstructions and for applied hydrogeological studies. Numerical mass-transport modeling profits from the improvement of hydrogeological conceptions and the revision of boundary conditions. In the case of non-steady-state recharge conditions, maximum and minimum recharge rates in the past may be estimated from ^{14}C dates of DIC via numerical modeling.

^{14}C dates measured from DIC enable the determination of regional geohydraulic parameters and allow water balances to be checked. In most applications, complementary environmental isotope analyses of hydrogen and oxygen together with general hydrochemical measurements are recommended to facilitate a comprehensive and thorough interpretation of the ^{14}C dates (Cark and Fritz 1997).

A primary task towards a significant improvement in the applied ^{14}C dating of groundwater remains with the development of procedures that will enable ^{14}C activities measured from DIC to be confidently included in the calibration of finite-element and compartmental modeling exercises.

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