Application of $^{14}$C-groundwater dating to non-steady systems

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Abstract Most case studies on $^{14}$C groundwater dating deal with steady-state systems in which recharge and discharge of groundwater is balanced, as is usual in humid regions. Under such circumstances groundwater flow velocities, flow directions, and regional values of the porosity and hydraulic conductivity can be determined and boundary conditions useful for numerical modelling can be obtained. In arid and semiarid regions, non steady state conditions dominate the groundwater systems. Groundwater discharge exceeds recharge and a large proportion of such resources may be considered as fossil. The question arises what hydrogeologically relevant information can be obtained from such systems and with which isotope hydrological methods. This paper explains the potential and the drawbacks of isotope hydrological methods in semiarid and arid regions using the aquifer systems of the Ad-Dawwa Basin in Syria as an example.

INTRODUCTION

Mazor & Nativ (1992; 1994) distinguished between two aquifer systems: passive and active ones. Passive aquifer systems are, for instance, found in very old basins filled with connate water. It is assumed that there is no horizontal pressure gradient and groundwater does not flow. In contrast, groundwater recharge and discharge is balanced in active aquifer systems, resulting in steady state flow conditions. In such cases the gradients of the piezometric surface allow the calculation of the Darcy velocity, $v_D = K\Delta$ with $K$ as the hydraulic conductivity and $\Delta$ as the gradient of the water table. The (tracer) velocity $v_T$, determined for instance by the $^{14}$C method, is related to $v_D$ by $v_T = v_D/n$, where $n$ is the total regional porosity of the area of study which can be calculated if both velocities are determined (Geyh et al., 1984). The often cited problem of
the uncertainty in the calibration of the $^{14}$C time scale for groundwater is of minor importance in the case of fresh water resources as the correction is usually constant (Geyh, 1992).

In arid and semiarid regions, active aquifer systems must be further subdivided into non-steady and steady-state aquifer systems. In non-steady state systems groundwater recharge has been frequently interrupted as a result of a changing paleohydrology (Fig. 1). Comprehensive studies have been carried out on the last 30,000 years in the Eastern Mediterranean (Geyh, 1994). After each cessation of groundwater recharge the water head started to decline (Burdon, 1977). The groundwater was flowing with decreasing velocity as a result of the decreasing groundwater gradient. Consequently, the discharge rate also diminished.

The groundwater ages determined e.g. by the $^{14}$C method do still reflect the steady state conditions of the former pluvial when the groundwater was recharged. However, the piezometric surface of such systems does not. Hence, the $^{14}$C age differences no longer allow an estimation of the present tracer velocity and direction. Instead, periods of groundwater recharge can be accurately evaluated, which is indispensable for numerical modelling of such aquifer systems (Fig. 2) and paleohydrological studies (Geyh & Plöethner, 1995). If steady-state conditions are assumed and the limited periods of groundwater recharge are not taken into account when modelling, the actual groundwater recharge is greatly overestimated (Verhagen et al., 1991; Geyh et al., 1995). The relative areal age distribution gradient will not change though the absolute ages will increase. Even more complicated is the situation where the gradient of the water resource is a superposition of a relict water body and of some contemporary groundwater recharge (Geyh et al., 1995). Under such conditions mass transport modelling depends on isotope hydrological dates.

![Fig. 1 Paleohydrological situation in the eastern Mediterranean, based on distribution of $^{14}$C dates from groundwater and stalagmite data (Geyh, 1994).](image)
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Fig. 2 Distinct ancient groundwater bodies stored in an aquifer reflect periods of intensive groundwater recharge. The tracer velocity is overestimated if the gap between two pluvial periods, which is frequently not known, is not considered.

AREA OF STUDY

The area of study stretches from the 2000 m high Anti Lebanon Mountains in the west to the Ad-Dawwa Basin with the Sabkha Al-Mouh in the east (Fig. 3). The east flank of the Anti Lebanon Mountains form the Al-Qalamoun Basin with precipitation of 150-300 mm year$^{-1}$. In the western area near Palmyra and the Sabkha Al-Mouh it amounts to a maximum of 100 mm year$^{-1}$. The Turon/Cenoman/Coniac aquifer in the Ad-Dawwa Basin is confined. Catchment areas are the Anti Lebanon Mountains as well as the Northern and Southern Palmyrides. The latter form a water divide along a fault stretching from southwest to northeast. Due to the increase in agricultural and mining activities in this area, hydrogeological and geohydraulic modelling has been undertaken with cooperation between the Arab Center for Studies in Arid Zones and Dry Lands (ACSAD) and the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR). An environmental isotope study was included in order to asses the potential of this technique.

RESULTS AND INTERPRETATION OF THE ISOOTPE ANALYSES

Groundwater recharge

A hydrochemical survey of the groundwater within the Ad-Dawwa Basin showed that the central part contains predominantly fresh water while highly saline groundwater is
found along the foothills of the Northern and Southern Palmyrides. In contrast to the dip of the geological layers to the west it was assumed that the recharge of fresh water in the Anti Lebanon Mountains (with more than 1000 mm year\(^{-1}\) annual rainfall) displaced the saline water in the basin to the east. Surprisingly, the \(^{14}\)C dates of groundwater show that very recent groundwater containing tritium is highly mineralized while the huge fresh water resources in the centre of the basin have \(^{14}\)C water ages exceeding 20 000 years BP. Obviously, in the present, groundwater recharge is so limited that it can only dissolve salt formed by weathering of the rock during the year and transport it into the aquifer. As a result, Holocene groundwater can only be expected to be within the aquifer below the Palmyrides to a maximum of 10% of the total resources of the area in the study.

In order to estimate groundwater recharge rates \(^{14}\)C depth profiling is recommended. In unconfined aquifers \(^{14}\)C water ages increase with depth. The gradient allows an estimate of the groundwater recharge rates for former pluvial periods (Vogel, 1970; Geyh \textit{et al}., 1992; Geyh & Plöethner, 1995). The presupposition is that the costly layered sampling during the drilling of an exploratory well can be carried out. Another technique uses the \(^{3}\)H value of samples from freshly pumped dug wells. For this, the \(^{3}\)H input function of the study area must be reconstructed for previous decades using e.g. the tritium values for the rainfall in any neighbouring area (IAEA, 1969-1990). If the \(^{3}\)H
level is lower than the detection limit an estimate of the maximum recharge rate in the order of mm year$^{-1}$ can be made (Geyh & Plöethner, 1995).

Localization of the catchment area

One of the most controversially discussed hydrological question is whether or not groundwater recharge occurs in the Al-Qalamoun Mountains and discharge happens via the Nabek Basin into the Damascus Basin. The centre of the Al-Qalamoun Basin is assumed to act as a natural water divide.

Stable isotope analyses of $^2$H and $^{18}$O has given an answer to this problem (Fig. 4). All delta values of the contemporary fresh water from the Anti Lebanon Mountains as well as of the precipitation of the Al-Qualamoun Mountains fit the Mediterranean Meteoric Water Line with the following relation (MMWL; Gat & Carmi, 1970):

$$\delta^2H = 8 \delta^{18}O + 22$$

All groundwater samples fall in a band between the MMWL and the MWL:

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

The data for groundwater from the Al-Qualamoun Basin and that for the area south of

![Fig. 4 $\delta^{18}$O/$\delta^2$H plot with the data from the Anti Lebanon on the Mediterranean Meteoric Water Line. All the data from the fossil groundwater of the study area form a band which may be interpreted as a mixture of Mediterranean and continental precipitation. The data from the Al-Qualamoun basin as well as the data from the groundwater south of the Southern Palmyrides form an unique cluster while those from the northern Ad-Dawwa Basin are isotopically lighter and might have been recharged in the Palmyrides at lower altitude. It is improbable that this aquifer was recharged from the Al-Qalamoun Basin.](image)
the Southern Palmyrides form one cluster (mean = \(-8.47 \pm 0.34\%\)). This indicates that they may both have the same catchment area and water age. In contrast, the old groundwater from the northern Ad-Dawwa Basin is isotopically heavier (mean = \(7.62\% \pm 0.30\%\)) and can only have been recharged at a lower altitude (Fig. 5). As the Anti Lebanon Mountains are too high, the Southern and Northern Palmyrides are considered as catchment areas rather than the Al-Qalamoun Mountains.

As in this region the so-called "Chamsien" depression in late spring supplies precipitation of continental origin (MWL; Geyh & Wagner, 1982; Geyh et al., 1982) the groundwater might be a mixture of both continental and Mediterranean sources. In former pluvial periods the continental rainfall seems to have contributed more to the groundwater recharge than today.

Groundwater age determination

The \(^{14}\)C age determination of groundwater is based on the estimation of the initial \(^{14}\)C value. The first result gave a \(^{14}\)C value for the young karst water from Ras El-Maara (71 pMC; 12 TU) from which a reservoir correction between 3000 and 3500 years is derived. Gonfiantini’s model (1972) yields 3600 years assuming that \(C_3\) vegetation

**Fig. 5 Spatial distribution of the \(\delta^{18}\)O values showing that the groundwater of the Ad-Dawwa Basin north of the Southern Palmyrides is isotopically heavier than that south of this mountain chain.**
dominated during the groundwater recharge (Geyh et al., 1992). For the sediment covered catchment of the Palmyrides a reservoir correction of only −1300 years was found (Geyh et al., 1992).

There is no areal trend to the $^{14}$C groundwater ages within the Ad-Qalamoun Basin (Fig. 6). This is not surprising in a fractured hard rock aquifer. In contrast, there is a trend of increasing $^{14}$C groundwater ages south of the Southern Palmyrides from 15 000 to 35 000 years BP corresponding to a former maximum tracer velocity of 6 m year$^{-1}$. The $^{14}$C groundwater ages from the Ad-Dawwa Basin range from 20 000 to 30 000 years, but do not show any pronounced trend. The hydrochemical composition of the groundwater might not have changed the $^{14}$C values as seen by many fresh and mineralized water samples with the same $^{14}$C age collected from neighbouring wells within the Palmyra region.

The stable carbon isotope analyses yield a further indication that groundwater from the Al-Qualamoun does not flow toward the Ad-Dawwa Basin. The $\delta^{13}$C values in the Ad-Dawwa Basin range from $-9.1$ to $-12.0\%_o$, typical of the C$_4$-assimilating plants in the catchment area, while those from Al-Qualamoun have the range $-6.2$ to $-9.4\%_o$ of a mixed C$_4$ and C$_3$ vegetation.

Based on the $^{14}$C ages of groundwater and the corresponding $\delta^{13}$C values, the groundwater resources of the Ad-Dawwa Basin are believed to have been formed during former pluvial periods (Geyh & Wagner, 1982; Geyh et al., 1982). The slight increase of the $^{14}$C ages towards Palmyra is interpreted as decreasing admixture of Holocene groundwater towards the east rather than reflecting groundwater flow. From this follows the question how an aquifer can be filled within such a short time, as an age gradient cannot be seen. There is only one possibility: that the aquifer was empty. This apparently absurd idea is validated if we consider that the Pleistocene Mediterranean sea level was more than 100 m deeper than that during the Holocene. Consequently, the hydrostatic pressure of the deep aquifers was also lower than today. We will assume that the water head of the Cenoman/Turon/Coniac aquifer was 10 m above that of the underlying Jurassic aquifer during this time. Then, the intermediate aquitard of 200 m thickness and a $K$ value of $10^{-9}$ m s$^{-1}$ still allows a 2 mm year$^{-1}$ seepage of groundwater as occurs today in the Nubian aquifer in North Africa (Verhagen et al., 1991). Supposing a porosity maximum of 10%, the aquifer will be emptied at the latest 10 000 years after a hyperarid period. Such long lasting periods are not uncommon in the Mediterranean and might have occurred between 40 000 and 20 000 years BP when the aquifer became refilled within a very short time. The humid belt needs only to have shifted by several 100 km towards the north.

At the beginning of the early Holocene the aquifer was mostly filled with groundwater, and only in the east near the catchment area was there some space for freshly recharged groundwater (Geyh & Wagner, 1982; Geyh et al., 1982). The border of its occurrence in the central Ad-Dawwa Basin is west of Al Sira (no. 37) at the exposure of the T2 aquifer. Holocene groundwater is otherwise only found along the Palmyrides. Hence, it is confirmed that no more than 10% of the total groundwater resources are of Holocene origin.

The 10 000 year smaller groundwater ages along the Northern Palmyrides compared to those of the wells at Sabkhet al-Mouh in the south support the idea that both have different source regions. The very old groundwater of this Sabkha was recharged in the west along the Anti Lebanon Mountains. If groundwater was later locally recharged, it
has since been evaporated or discharged. Today, ascending groundwater is the major source of the groundwater resources in this area. The stable isotope balance excludes mixing of Pleistocene and Holocene groundwater along the Northern Palmyrides.

The reliability of the $^{14}$C ages of groundwater exceeding 20 000 years BP was checked several times. The water $^{14}$C ages from the 200 m deep well Al-Hafne 9 (no. 20/21) and the well SM 8 (no. 33/39) did not vary outside the confidence interval during 15 years of pumping. However, careless analytical work during sampling can easily result in contamination or an apparent decrease of the $^{14}$C age.

**Numerical ages and $^{14}$C ages**

Geohydraulic modelling has been undertaken to improve the groundwater budget for the Ad-Dawwa Basin. Its spatial extent is $160 \times 100$ km$^2$, the thickness of the aquifer is 250 m and the porosity is assumed to be 2.5% (10%). Adopting these values the total volume of the groundwater resource is $100 \times 10^9$ (400 $\times 10^9$) m$^3$. The values in brackets relate to the larger porosity and may be valid. New exploratory drillings for oil have shown that the aquifer is regionally heavily karstified.
Based on these estimates, a Russian consultant (Selkhozpromexport, 1987) postulated a groundwater recharge rate of 3% of the rainfall, corresponding to $58.2 \times 10^6$ m$^3$ year$^{-1}$. This should be balanced by the evaporation loss in the Sabkhet Al-Mouh, with an area of 230 km$^2$. If we adopt the hydraulic parameters of the German geohydraulic modelling, an extension of the aquifer by 200 (120) km, a maximum height $h_0$ of the groundwater level above the depression (Sabkhet Al-Mouh) of 400 (150) m and the $K$ value of $5 \times 10^{-5}$ m s$^{-1}$, the tracer velocity is 126 (79) m year$^{-1}$ for the porosity of 2.5% and 32 (20) m year$^{-1}$ for 10%. Adopting a north-south extension of the aquifer of 100 km, $78 \times 10^6$ ($49 \times 10^6$) m$^3$ year$^{-1}$ groundwater seems to be discharged, in agreement with the Russian estimate.

The Russian and German estimates of the evaporation loss of $58.2 \times 10^6$ m$^3$ year$^{-1}$ (we will use the published Russian value only) contradicts the hydrological situation. This value divided by 10% of the spatial extent of the aquifer ($16 \times 100 \times 10^6$ m$^2$), which is considered as the size of the catchment area of the Northern and Southern Palmyrides, yields a recharge rate of 36 mm year$^{-1}$ for the Cenoman/Turon aquifer though the annual precipitation is lower than 120 mm year$^{-1}$. The present-day climatic conditions in this region do not allow such high contemporary groundwater recharge.

The total groundwater volume divided by the mentioned recharge rate yields a head decay rate of 1720 (6870) years: both values conflict with the determined groundwater $^{14}$C age of more than 20 000 years. The water reservoir should show much smaller water ages and should already be considerably diminished having had no recharge in the last 4000 years BP.

We hoped for a better estimate of the mean residence time of the groundwater by using the theory of the outflow of an aquifer into a graben (Verhagen et al., 1991). We adopted a distance $r$ of 160 (120) km of our aquifer system, a maximum height $h_0$ of the groundwater level above the depression (Sabkhet Al-Mouh) of 400 (150) m, a $K$ value of $5 \times 10^{-5}$ m s$^{-1}$ and a porosity of 2.5%, and obtained a similar low head decay rate of 1290 (1940) years for $n = 10\%$ 5160 (7750) years. During the time $t$, the water head decreases by $1/e$. That means that the groundwater discharge has diminished during the last 20 000 years to about 5% of the Pleistocene value.

The next problem arises if we discuss the evaporation loss in the Sabkhet Al-Mouh over its extent of 230 km$^2$. The thickness of the aquitard is assumed to be 300 m and its $K$ value is assumed to be $10^{-9}$ m s$^{-1}$. For a difference between the water head of the confined and unconfined aquifers of 20 m, a maximum 0.48 x $10^6$ m$^3$ year$^{-1}$ can be lost, in contrast to the estimated ca. 50 x $10^6$ m$^3$ year$^{-1}$.

Our isotope hydrological results supplied conclusive arguments to solve the discrepancy between theoretical estimates and geohydraulic reality. According to them, ca. 90% of the groundwater resources in the Ad-Dawwa Basin have been discharged in the last 25 000 years, corresponding to $10 \times 10^9$ ($40 \times 10^9$) m$^3$, with an annual rate of $0.4 \times 10^6$ ($1.6 \times 10^6$) m$^3$ year$^{-1}$. This value agrees with the estimated evaporation loss in Sabkha Al-Mouh.

The groundwater $^{14}$C ages agree with the hydrological assessment only if the $K$ value of $5 \times 10^{-5}$ m s$^{-1}$ is reduced to $1 \times 10^{-5}$ m s$^{-1}$ or even less. Pumping tests in the centre of the Ad-Dawwa Basin (ACSAD, 1990) yielded transmissivities exceeding 1000 m$^2$ day$^{-1}$, but with a mean of 23 m$^2$ day$^{-1}$ = $1.1 \times 10^6$ m s$^{-1}$. Using 114 values, excluding those $>1500$ (4000) m$^2$ day$^{-1}$, the mean reduces to 230 (517) m$^2$ day$^{-1}$ = $11 \times 10^6$ ($24 \times 10^6$) m s$^{-1}$. The exclusion of the extreme values seems to be justified.
because wells drilled in fractured aquifers for groundwater exploitation represent optimum hydraulic conditions rather than the regional hydraulic situation. Based on this isotope hydrology based reflection Brunke (1994) adopted a hydraulic conductivity of $3.5 \times 10^{-6}$ m s$^{-1}$ for modelling.

**REFERENCES**


