A CONTRIBUTION TO THE INTERPRETATION OF ^{14}C GROUNDWATER AGES CONSIDERING THE EXAMPLE OF A PARTIALLY CONFINED SANDSTONE AQUIFER

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ABSTRACT. Previously described models and a new model were compared to determine the initial ^{14}C content of groundwater in a partially-confined and unconfined sandstone aquifer (Fränkisches Albvorland, Germany). Isotope and chemical data were derived from samples of water, soil-CO_2, and solid carbonates. The various ^{14}C models lead to important differences in resulting groundwater ages.
From the relationship between ^{14}C and ^{2}H or ^{18}O concentrations of groundwater, it must be assumed that chemical and/or physical carbon isotope exchange between the DIC and the solid carbonate has occurred provided the groundwater with lower ^{18}O and ^{2}H concentrations was generated during the Pleistocene. Groundwater ages deduced from ^{14}C and ^{39}Ar concentrations showed discrepancies which can be explained if carbon isotope exchange between DIC and solid carbonate as well as mixing of recent and fossil waters is considered.

TEST SITE

The area under study lies south of Nuremberg, southern Germany. The unconfined area is in the northwest (Fränkisches Albvorland) where sandstone layers of Keuperage crop out, partially interrupted by discontinuous clay lenses "Zwischenletten". Nearly all surface waters receive discharging Keuper groundwater (Andres and Geyh, 1970; Rietzler, ms). The confined area is in the Frankenalb and its foreland where the sandstones are entirely covered by thick clay layers of the upper "Mittlere Keuper" (Feuerletten), Lias and Dogger. The Danube and Altmühl rivers receive the discharge from this area.

MODEL CONSIDERATIONS FOR DETERMINING INITIAL ^{14}C CONCENTRATION

In humid climates ^{14}C produced and oxidized in the atmosphere is introduced via soil-CO_2 into groundwater which dissolves ^{14}C free carbonate (Münnich, 1957). This concept led to the chemical mixing model (equation 1) and the isotope mixing model for calculating the initial ^{14}C concentration, A_o (Ingerson and Pearson, 1964):

$$A_{o,1} = (N_{CO_2} + 0.5\ N_{HCO_3})\ A_g *)\qquad(1)$$

$$A_{o,2} = \frac{\delta^{13}C_{DIC} - \delta^{13}C_s}{\delta^{13}C_g - \delta^{13}C_s}\ A_g \qquad(2)$$

A_o can be subsequently increased if the soil carbonates contain ^{14}C or if carbon isotope exchange takes place between DIC and soil-CO_2 in the unsaturated zone of the groundwater recharge area. Vogel (1970) deduced empirically an initial ^{14}C concentration of $A_o = (85+5)\%$modern. The simple models described by equation 1 and 2 were further developed by considering additional carbon isotope exchange

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	Symbols:
A_o:	initial ^{14}C concentration
$A_{o,1}, A_{o,2}$:	initial ^{14}C concentration calculated by the chemical mixing model respectively isotope mixing model
A_g:	^{14}C concentration of soil-CO_2
B:	calculated carbon exchange factor
$\delta^{13}C_g$, $\delta^{13}C_s$:	$\delta^{13}C$ value of soil-CO_2 and solid carbonate
$\delta^{13}C_{DIC}$, $\delta^{13}C_{b\ ex}$, $\delta^{13}C_{s\ eq}$:	measured $\delta^{13}C$ value of DIC, calculated $\delta^{13}C$ values of DIC before carbon exchange takes place, and $\delta^{13}C$ of DIC in equilibrium with the solid carbonate
$\varepsilon_{g/aq}, \varepsilon_{g/s}, \varepsilon_{s/HCO_3^-}$:	carbon isotope fractionation between gaseous CO_2 - dissolved CO_2, gaseous CO_2 - solid carbonate, and solid carbonate - bicarbonate
N_{CO_2}, $N_{HCO_3^-}$:	mol-fraction of aqueous CO_2 and HCO_3^-
DIC:	Dissolved Inorganic Carbon

in an open or closed system, and dissolution precipitation reactions (Mook, 1976; Fontes and Garnier, 1979; Reardon and Fritz, 1978; Wigley, Plummer, and Pearson, 1978; Mozeto, 1981). The temporal alteration of $A_{o,1}$, if recognizable by changes of the ^{13}C concentrations, can be expressed approximately by a factor B in equation 1 (Eichinger, ms):

$$A_o = B \cdot A_{o,1} \tag{3}$$

In B, the measured $\delta^{13}C$ value is related to calculated $\delta^{13}C$ values obtained without isotope exchange and with isotope exchange under the condition of isotope equilibrium between DIC and solid carbonates:

$$B = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{s\ eq}}{\delta^{13}C_{b\ ex} - \delta^{13}C_{s\ eq}} \tag{4}$$

$\delta^{13}C$ can be derived from the stoichiometric formation of DIC, considering isotopic fractionation during CO_2 dissolution in water (for fractionation factors, see Mook, 1980):

$$\delta^{13}C_{b\ ex} = N_{CO_2}(\delta^{13}C_g - \varepsilon_{g/aq}) + 0.5\ N_{HCO_3^-}(\delta^{13}C_g - \varepsilon_{g/aq} + \delta^{13}C_s) \tag{5}$$

If a carbon isotope equilibrium is established between DIC and solid carbonate, then $\delta^{13}C_{DIC} = \delta^{13}C_{s\ eq}$ and

$$\delta^{13}C_{s\ eq} = N_{CO_2}(\delta^{13}C_g - \varepsilon_{g/s}) + N_{HCO_3^-}(\varepsilon_{s/HCO_3^-}) + \delta^{13}C_s \tag{6}$$

ISOTOPE HYDROLOGY AND HYDROCHEMISTRY

A_o can be obtained from equation 3 if the originally existing initial ^{14}C concentration $A_{o,1}$ was changed through carbonate reactions, ion exchange, carbon isotope exchange between DIC and solid carbonates, and/or outgassing of CO_2 accompanied by carbonate precipitation. The conditions for the use of equation 3 (as well as for all the other models) are:
$\delta^{13}C$ values of soil-CO_2 and reacting solid carbonates

must be known; the groundwater under investigation does not
originate from surface water recharge, i e, surface water
that underwent carbon isotope exchange with atmospheric
CO_2; outgassing of CO_2 did not take place without
accompanying carbonate precipitation; no admixture of CO_2
of magmatic or fossil organic origin occurred.

^{13}C IN SOIL-CO_2. Most published $\delta^{13}C$ values of soil-
CO_2 from humid climates lie between -28 and -19‰. For the
area here under study, a $\delta^{13}C$ value of ca (-23 ± 1)‰ can be
deduced for modern soil-CO_2. Taking into account the
influence of fossil fuel combustion since the beginning of
industrialization, a $\delta^{13}C$ value of ca (-21 ± 1)‰ is assumed
for old groundwater and the pertinent soil-CO_2.

^{13}C IN SOLID CARBONATE. ^{13}C concentrations were measured
on 62 samples of rock from 6 deep cores and 9 samples from
surface outcrops. The samples from the "Mittleren Keuper"
and "Oberen Keuper" gave $\delta^{13}C$ values between -14 and -3‰
with a mean value of -7.9‰; those from Jurassic formations
range from 0 to +2‰ with a mean of +1‰, which means that
an uniform $\delta^{13}C$ value for the solid carbonate cannot be
assumed.

SPRINGS AND WELLS.The investigation, made between May 1979
and September 1980, included many spring and well waters.
From the unconfined towards the confined area, the water in
deep wells shows increasing concentrations of Ca^{2+}, Mg^{2+},
HCO_3^-, Na^+, K^+, as well as increasing pH-values, and
saturation indices for calcite, dolomite, and gypsum.
        The following relationships between isotope concentra-
tions and hydrochemical parameters are evident:
1) $\delta^{18}O$ and δ^2H values show a clear tendency towards
lower values for those groundwaters with ^{14}C
concentrations below 10% modern. If we assume that these
waters infiltrated ca 10 000 to 13 000 years ago at the end
of the last glacier time (Rudloff, 1980), the measured ^{14}C
concentrations of 10% modern would indicate that initial
^{14}C concentrations were in the range of 33 to 48% modern,
considering only decay. In contrast, the chemical mixing
model yields an $A_{o,1}$ value of < 50% modern. These
differing initial concentrations lead to the assumption,
that carbon isotope exchange may have affected ^{14}C
concentrations.
2)The change from alkaline earth to alkali bicarbonate
groundwaters is caused by cation exchange whereby a decrease
in alkaline earth ions parallels a decrease of ^{14}C

concentration in the confined aquifer.

A clear relationship also exists between ^{14}C and ^{13}C concentrations of the DIC, or bicarbonate whereby the $\delta^{13}C$ values become more positive with decreasing ^{14}C concentrations. This change cannot be explained by increasing calcite dissolution alone. Therefore carbon isotope exchange between DIC and solid carbonate was also taken into account.

CALCULATION OF THE INITIAL ^{14}C CONCENTRATIONS

YOUNG GROUNDWATER (WITH ^{3}H, $>$ 10 TU). The only possibility for determining initial ^{14}C concentration independent of chemical or biologic reactions, is to measure ^{3}H (Geyh, 1972) or ^{85}Kr concentrations (Salvamoser, ms). In this case, applicability of the hydrologic exponential model is assumed and permits the determination of A_O and mean residence time of groundwater (Eichinger, ms). Figure 1 compares initial ^{14}C concentrations for young spring and well waters obtained from the hydrologic exponential model (EM) and the chemical mixing model (CMM). Compared to the hydrologic exponential model, the CMM shows, on the average, a 5% modern higher initial ^{14}C concentration for 18 wells and 11 springs (table 1). However, this difference is not significant. Regarding well waters alone, the average difference is 3% modern, and, if spring waters are compared, the difference amounts to 6% modern (table 1). A difference of at most 20% modern is observed among well waters (see fig 1, sample 6.64).This great variation of A_O is possibly related to infiltration of surface waters which had undergone carbon exchange with the atmosphere. For spring waters, only samples from aquifers with an estimated $\delta^{13}C_S$ value of ca 1‰ (Malm) were used and differences of at most 14% modern were observed.

Almost equal A_O values are found for the model described in equation 3 and for the isotope mixing model; for the Fontes-Garnier model, A_O is determined to be ca 5% modern higher, for the Mook model, ca 17% modern higher, and for the Reardon-Fritz model, ca 18% modern higher. The A_O values calculated with the Reardon-Fritz model assumed a carbonate controlled pH range of 6.3 to 7.0 and PCO_2 range of $10^{-1.7}$ to $10^{-1.5}$ atm for the recharge area (table 1).

Those models in which the carbon isotope of the DIC is assumed to be in equilibrium with the soil-CO_2 in the unsaturated zone of the recharge area, show considerably higher A_O values compared with the hydrologic exponential and other models.
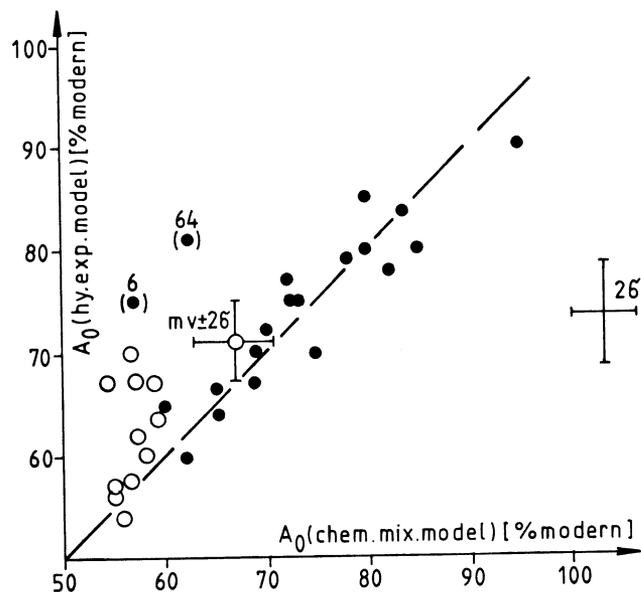
Fig 1. Initial ^{14}C concentration calculated by the hydro-
logic exponential model (Salvamoser, ms) and the chemical
mixing model. Samples are from wells($\bullet$) and springs (o).
Numbers 6 and 64 have not been considered. mv=mean value of
the mean with 95% confidence level.

OLD GROUNDWATER (^3H CONTENT LOW OR UNDETECTABLE, < 1 TU).
The initial ^{14}C concentrations in relatively old ground-
waters with low or undetectable ^3H concentrations can only
be determined by hydrochemical models. The Fontes-Garnier
model and especially the Mook model show a very strong de-
pendence of A_0 of $\delta^{13}C$ values of soil-CO_2 and of solid
carbonate. Further, the Mook model shows, in some of the in-

TABLE 1. Initial ^{14}C concentration estimated from different models
for young groundwater samples (95% confidence level)

	No of samples	Hydrologic exponential model	Chemical mixing model	^{13}C isotope exchange model	Isotope mixing model	Fontes-Garnier model	Mook model	Reardon-Fritz model
				Initial ^{14}C concentration calculated from				
Springs	11	63 ± 3	57 ± 1	60 ± 2	62 ± 2	68 ± 4	80 ± 10	81 ± 1
Wells	18	77 ± 4	74 ± 2					
Both	29	72 ± 4	67 ± 4					

vestigated cases an unrealistic decrease of A_O with increasing δ^{13}C values of the solid carbonate and realistic δ^{13}C values of soil-CO_2. Both models result in incorrect values for A_O, if the $\delta^{13}C_g$ values approximate $(\varepsilon_{g/s} + \delta^{13}C_s)$ or $(\varepsilon_{g/HCO_3^-} + \delta^{13}C_s)$.

The described model (equation 3) mostly results in somewhat smaller A_O values than those from the isotope mixing model.

Because of the difficulties in the determination of the δ^{13}C values of groundwaters, soil-CO_2, and solid carbonate, the calculated ^{14}C concentrations often have such a wide range that the derivation of groundwater ages becomes meaningless.

PROFILE OF THE AREA

Initial ^{14}C concentrations calculated from different models were used to deduce flow velocities of the ground water, given in table 2. The first profile leads from the unconfined to the confined area, while the second profile only belongs to the deep wells in the unconfined area. Assuming that maximum isotope exchange ($\delta^{13}C_s = -8$‰) has occurred, calculated groundwater ages (equation 3) are lower than those obtained from the empirical model ($A_O = (85\pm10)$% modern) or the chemical mixing model. However, flow velocities (table 2) calculated from the differences in the groundwater ages prove to be independent from the type of model. They agree well with distance velocities calculated from hydraulic considerations in the first profile, while in contrast the distance velocities in the second profile show remarkably higher results.

TABLE 2. Groundwater flow velocities deduced from radiometric ages calculated with different ^{14}C models and from "Darcy's Law"

Groundwater flow [km]   Groundwater flow velocities [m/a]

Model		Measured ^{14}C values	Chemical mixing	Isotope mixing		^{13}C isotope exchange		"Darcy"
$\delta^{13}C_s$ [‰]				1	-8	1	-8	
confined	7	0.9 ± 0.1	1.1 ± 0.1	1.8	7	1.4 ± 0.3	-	1.4 ± 0.4
area	26	1.0 ± 0.1	1.1 ± 0.1	1.1	1.4	1.1 ± 0.1	1.6 ± 0.4	
unconfined	3.5	1.8 ± 0.5	1.6 ± 0.2	5.8	-	$5.8^{+13.1}_{-5.8}$	$1.8^{+2.0}_{-1.8}$	1.6 ± 4.0
area	13	0.9 ± 0.1	1.0 ± 0.1	1.1	1.9	1.0 ± 0.2	2.4 ± 1.0	

COMPARISON OF THE GROUNDWATER AGES DERIVED FROM THE ^{14}C
AND ^{39}Ar CONCENTRATION

^{39}Ar measurements were made in some well waters in
this area for the comparison with ^{14}C groundwater ages
(Loosli and Oeschger, 1979). In most cases, the calculated
values of the groundwater ages were much smaller than the
^{14}C ages (fig 2 A). The reasons for these discrepancies
could be underground production of ^{39}Ar or gas exchange
with the atmosphere through the aquiclude (Loosli and
Oeschger, 1979). In addition, the ^{14}C concentration of the
DIC decreases through carbon isotope exchange with the solid
carbonate and the calculated groundwater ages with A_o =
85% modern are too high.
        In figure 2 A the calculated correlation between ^{14}C
and ^{39}Ar concentrations are plotted for three different
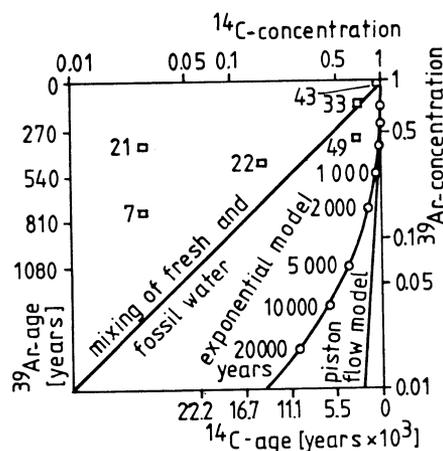mixing models. All measuring points should be on the right

Fig 2 A. Theoretical correla-
tion between ^{39}Ar and ^{14}C
concentration for three dif-
ferent mixing models. Data
(▫) are given for the test
side (Fränkisches Albvor-
land). The ^{14}C groundwater
ages are calculated with an
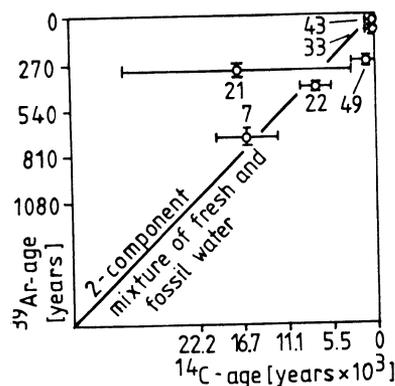initial ^{14}C concentration
of 85% modern (Loosli, 1980).

Fig 2B. ^{39}Ar and ^{14}C
groundwater ages. Initial
^{14}C concentration is
calculated from equation 3
with $\delta^{13}C_g$=-21%o and
$\delta^{13}C_s$=-8%o. ^{39}Ar
groundwater ages from
Loosli, (1980).

of the straight line for a mixing of recent and fossil wa-
ters. This is not the case, but when the ^{14}C groundwater
ages are calculated from equation 3, they then agree with
the ^{39}Ar groundwater ages (fig 2 B). With this
interpretation, the results of both dating methods could be
explained if mixing of water of different ages had occurred.
However, it would have to be assumed that substantial
amounts of groundwater leak through the nearly impermeable
layers of the Lias and that the ^{14}C concentrations of the
younger water decreased through geochemical processes.

CONCLUSIONS

The interpretation of isotope data from the unconfined
and confined aquifers in the project area clearly documents
the dependance of model calculations on the exact deter-
mination of input parameters. It is also possible that iso-
tope exchange between aqueous and solid carbonate modifies
the ^{14}C concentrations in these systems. However, com-
parison with ^{39}Ar data suggests that mixing of different
waters may occur even in the confined aquifer which would
invalidate the application of most model considerations on a
regional basis.

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