

HYDROGEOLOGIC INTERPRETATION OF THE  $^{14}\text{C}$  CONTENT OF GROUNDWATER

- A STATUS REPORT -

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1) Introduction

When routine  $^{14}\text{C}$  analyses of groundwater were started in the sixties the physicists knew that the conventional  $^{14}\text{C}$  ages would have to be corrected for dilution of the  $^{14}\text{C}$  content with fossil carbon from soil lime, and it was believed that the determination of groundwater velocities would be of hydrogeologic interest. Surprisingly, the first groundwater ages that were determined seldom fitted the classic hydrogeologic conceptions (GEYH & GRO-SCHOPF 1978) and in some cases were even in disagreement with the geologic expectations (KLITZSCH et al. 1976). Since then, new conceptions for the interpretation of the  $^{14}\text{C}$  content in groundwater have been developed which may be divided in two groups :

- those which make corrections for reactions in the water and between it and its environment, considering the various sources of carbon isotopes in the groundwater (hydrochemical models),
- and those which consider primarily the hydrodynamics (hydrodynamical models).

2) Hydrochemical models

Hydrochemical models deal with the transformation of conventional  $^{14}\text{C}$  ages of groundwater into actual ages. Groundwater and aquifer are considered as closed boxes; groundwater motion, convection and dispersion are not considered (piston-flow model). The following effects have been discussed so far :

- soil carbonate dissolution (initial  $^{14}\text{C}$  content),
- hydrochemical secondary reactions,
- stable isotope corrections ( $\delta^{13}\text{C}$  correction),
- isotope exchange, and
- radiocarbon diffusion.

### 2.1. Soil carbonate dissolution (initial $^{14}\text{C}$ content)

The conception of groundwater dating by radiocarbon (MÜNNICH 1957, 1968) is based on the dissolution of fossil soil carbonate by contemporary biogenic carbon dioxide during the process of groundwater regeneration. The  $^{14}\text{C}$  content of the finally dissolved carbonic acid in the groundwater (initial  $^{14}\text{C}$  content) is theoretically lower by 35-45 % than that of contemporaneous wood or atmospheric carbon dioxide. This is confirmed for samples from karst springs. Because carbonates containing radiocarbon accumulate in sediments during the summer (GEYH 1970), the initial  $^{14}\text{C}$  content of the majority of groundwater samples is greater than this theoretical range. The highest  $^{14}\text{C}$  content is found for groundwater recharged in crystalline areas since the carbonates available there are formed contemporaneously with the groundwater regeneration. The deviation of the initial  $^{14}\text{C}$  content of groundwater from that of contemporaneous wood accounts for the exaggerated conventional  $^{14}\text{C}$  ages of groundwater samples.

Table 1 : Initial  $^{14}\text{C}$  content [%modern] of groundwater from catchment areas of different geology, and differences  $\Delta$  between conventional  $^{14}\text{C}$  ages and actual water ages [a](GEYH 1972).

Recharge area	[%modern]	- $\Delta$ [a]
Karst regions, deep Pleistocene sand dunes and sandstone	55-80	4800-1800
Regions with sediment cover (e.g. loess)	80-90	1800- 850
Crystalline areas	90-100	850- 0

## 2.2. Hydrochemical secondary reactions

Hydrochemical interactions between groundwater and rock in the aquifer may change the  $^{14}\text{C}$  content (WIGLEY 1977, WIGLEY et al. 1978), for instance if continuous dissolution and precipitation of carbonates occur. Computer programmes (e.g. WATEQF ISOTOP) have been developed (REARDON & FRITZ 1978) to calculate the corresponding effects on the  $^{14}\text{C}$  age of groundwater on the basis of hydrochemical data. Unproved suppositions are that

- all hydrochemical reactions approached equilibrium,
- the  $^{14}\text{C}$  content in the groundwater is definitively determined by the initial and end conditions of the chemical reactions and is independent the reaction paths, and
- the  $^{14}\text{C}$  content of soil lime is zero.

In the case of fresh water (low mineralization), the calculated age corrections do not differ from those derived from the initial  $^{14}\text{C}$  content. An example is the results from a Triassic sandstone aquifer in England (Table 2; BATH et al. 1978).

Table 2 : Mean of the differences between the conventional and hydrochemically corrected  $^{14}\text{C}$  ages, recalculated initial  $^{14}\text{C}$  contents and average of the  $\delta^{13}\text{C}$  values for water samples from a Triassic sandstone aquifer in England.

Number of wells	initial $^{14}\text{C}$ content	difference in ages [yr]	$\delta^{13}\text{C}$ [‰]
31	$63 \pm 4$ %modern	$-3700 \pm 490$	$-11.9 \pm 1.0$
7	$50 \pm 2$ %modern	$-5600 \pm 350$	$-9.1 \pm 0.5$

Two kinds of groundwater are found in the aquifer indicated by different initial  $^{14}\text{C}$  contents and  $\delta^{13}\text{C}$  values. However, the differences between the hydrochemically corrected data and those derived from a constant initial  $^{14}\text{C}$  content (Table 1) have a range of only  $\pm 500$  years. This range may be indeed smaller since in the field the required accuracy of the hydrochemi-

cal data and especially that of  $\pm 0.01$  for the determination of the pH values can seldom be realized (PEARSON et al. 1978).

### 2.3. $\delta^{13}\text{C}$ corrections

$\delta^{13}\text{C}$  values for dissolved carbonic acid in groundwater are sometimes considered to be a function of the initial  $^{14}\text{C}$  content since the  $\delta^{13}\text{C}$  values of biogenic carbon dioxide ( $\approx -25\%$ ) and soil carbonate ( $\approx 0\%$ ) are different. In the most simple case the stoichiometric ratios of both components are used ; MOOK (1972) also included isotope fractionation. However, lack of accurate initial  $\delta^{13}\text{C}$  values for both components and of the initial  $^{14}\text{C}$  content of soil lime makes any  $\delta^{13}\text{C}$  correction questionable (TAMERS 1975). The  $\delta^{13}\text{C}$  values and the  $^{14}\text{C}$  content for soil carbonates have a broad scatter (GEYH 1970, SALOMONS & MOOK 1976) and those for soil carbon dioxide vary with the season (RIGTHMIRE 1979) and therefore with the climate.

### 2.4. Isotope exchange

Isotope exchange between dissolved carbonic acid and carbonate in the aquifer would decrease the  $^{14}\text{C}$  content in the groundwater, however, it will not change the  $\delta^{13}\text{C}$  values (MÜNNICH 1968). If this process is restricted to a monomolecular layer -- which can be assumed -- and the aquifer is considered to consist of carbonate balls ( $\emptyset = 0.1-2.0$  mm) the increase in the  $^{14}\text{C}$  ages of groundwater would be maximum 25-35 % (Fig. 1) for usable aquifers ( $k_f \geq 10^{-5}$  m/s). This increase is smaller if only part of the rock in the aquifer is carbonate. However, the effect has never been large enough to interfere with the hydrogeologic interpretation of the  $^{14}\text{C}$  data (PEARSON & HANSHAW 1970).

### 2.5. Radiocarbon diffusion

The diffusion model by SONNTAG (KLITZSCH et al. 1977) deals with  $^{14}\text{C}$  transport between adjacent stories containing groundwater of different ages. In

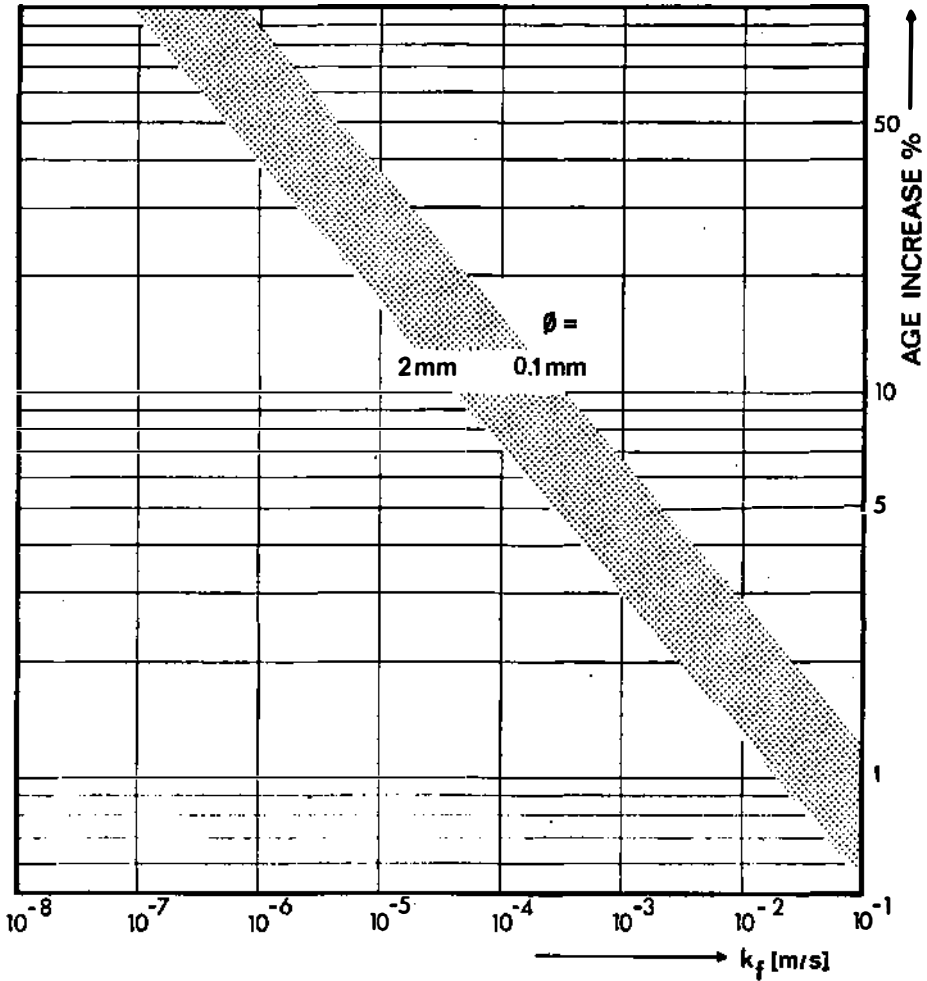


Fig. 1 Increase of the conventional  $^{14}\text{C}$  ages due to isotope exchange between the dissolved carbonic acid of the groundwater and the carbonate in the aquifer as a function of the hydraulic conductivity  $k_f$  and the grain size of the disintegrated rock particles in the aquifer. It is assumed that isotope exchange is restricted to a monomolecular layer (MUNNICH 1968).

the long term, the  $^{14}\text{C}$  concentration of interstage groundwater may become increased on the order of 10 %modern. However, in nature the effect of radiocarbon diffusion on groundwater ages is usually masked by the effect of vertical groundwater convection (see section 3.3).

## 2.6. Conclusion

Hydrochemical corrections seem to change the conventional  $^{14}\text{C}$  ages of fresh groundwater by rather constant values which is why they are seldom necessary in practical hydrogeologic interpretations. The study of this subject, however, may improve our understanding of the complex process by which the carbonate system approaches hydrochemical and isotopic equilibrium and may help derive absolute groundwater ages for paleohydrogeological studies.

## 3. Hydrodynamic models

Hydrodynamic models are used to interpret the isotopic content of groundwater as hydrologic parameters rather than ages. Hydrodynamic models are based on the hydrodynamic situation of the aquifers being investigated.

Groundwater as a fluid medium is always in motion. And convection, dispersion and other processes result in mixing of groundwater of different ages. The effect of natural processes under undisturbed conditions over millennia on the  $^{14}\text{C}$  content of groundwater is often similar to that of extensive groundwater exploitation over a few decades. However, the change in the  $^{14}\text{C}$  ages resulting from either of these processes is in general considerably greater than that estimated by the hydrochemical corrections.

### 3.1. Exponential model

An exponential model is used to interpret the  $^{14}\text{C}$  and  $^3\text{H}$  contents of water samples taken from springs and wells in hard rock areas, especially in karst regions. It is assumed that well water and long-term spring water (base flow) consist of different old components whose proportions decrease exponentially

with increasing age. As the  $^{14}\text{C}$  and  $^3\text{H}$  contents of atmospheric  $\text{CO}_2$ , e.g. rain, have varied during the last few decades due to the atom bomb tests, it is possible to determine mean residence times (MRT) up to 100-150 years of water from wells and of base flow spring water and their initial  $^{14}\text{C}$  contents (TAMERS 1975, GEYH & GROSCHOPF 1978). There is a frequently confirmed relationship between the annual base flow discharge of the spring, the porosity and the thickness of the corresponding aquifer, the size of its catchment area and the radiometric MRT.

**Table 3 :** Sizes [ $\text{km}^2$ ] of the catchment areas of karst springs in SW Germany determined radiometrically and geologically.

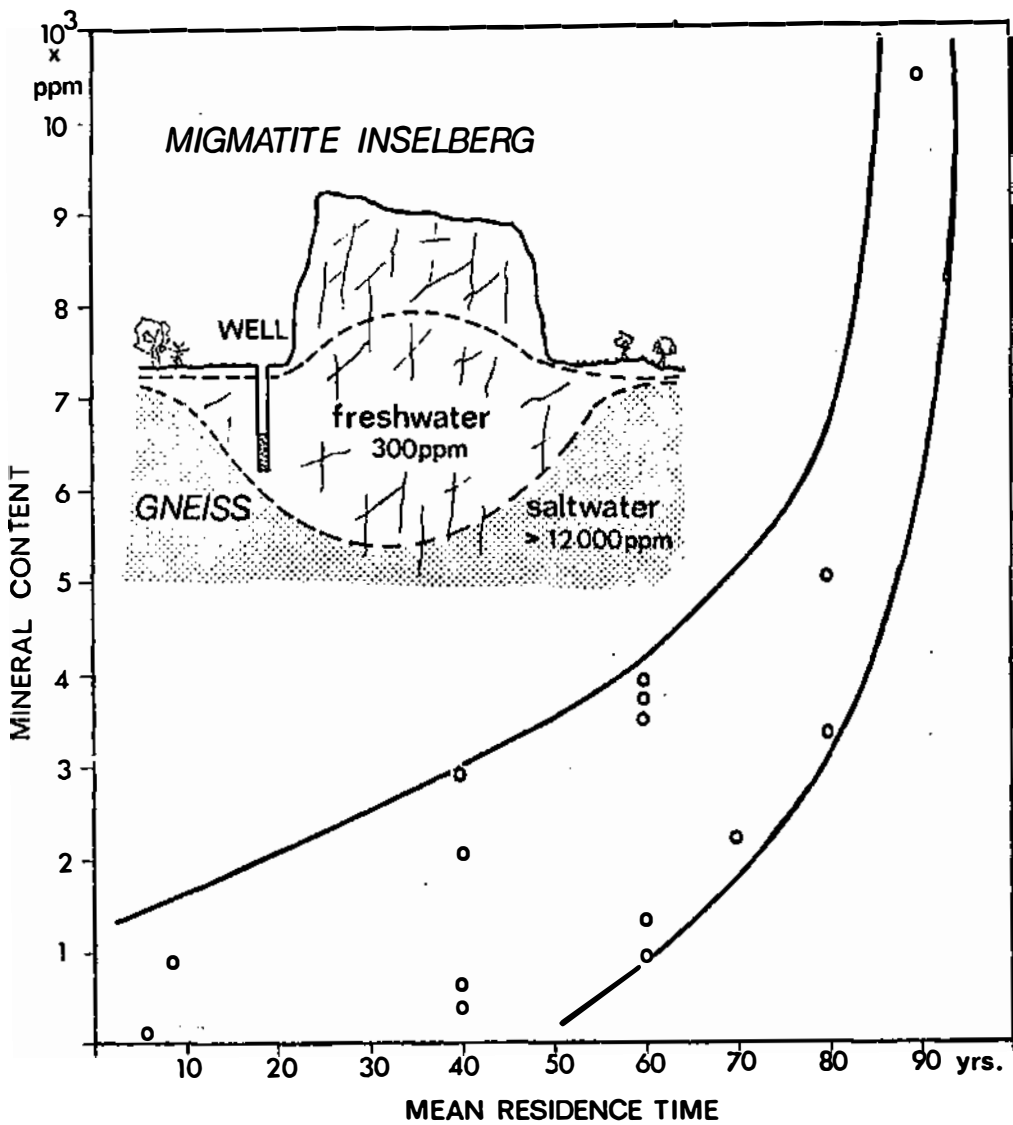
spring	rad.	geol.	spring	rad.	geol.
Rohrach	55	50-61	Gallengehren	80-90	110
Lone	30-40	30	Pfeffer	66-76	70
Blautopf	149	150-175	Kocher, schwarz	28-35	40

The validity of the radiometrically determined MRT is reflected for example by their relationship to the mineral content of groundwater samples taken in the crystalline peneplain of NE Brazil (Fig. 2). On the basis of these and other results the previous conception for selecting drilling sites of wells was changed. The yield of the new wells was statistically greater by a factor of 2 and the mineral content was less than previous wells, which had a mean of 3600 ppm, by a factor of 7 (GEYH 1979).

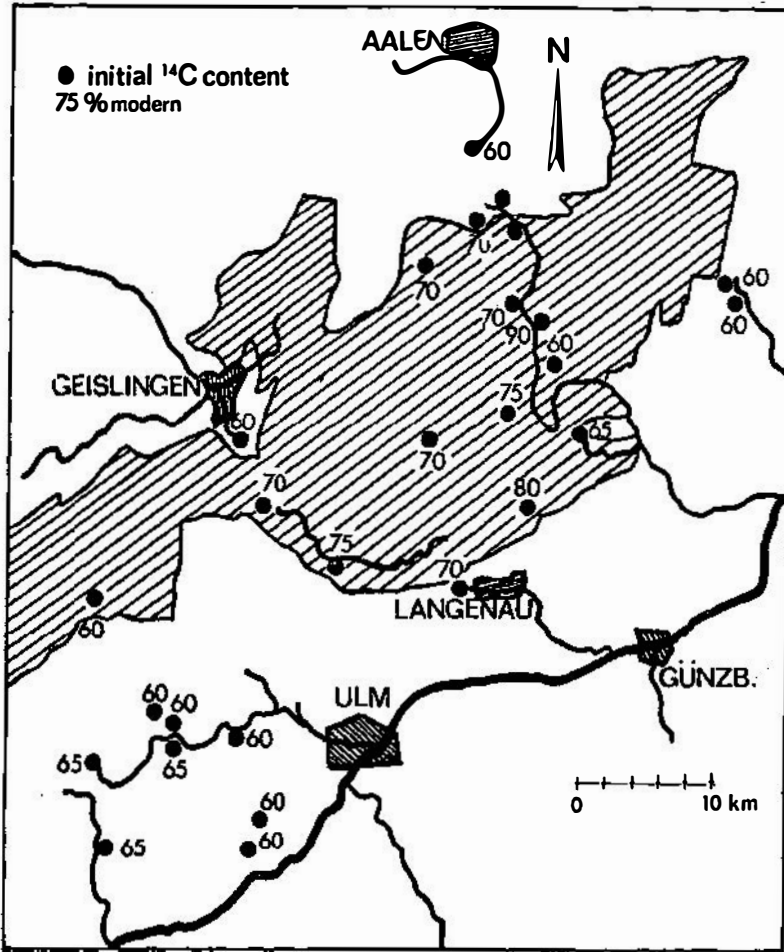
Another application of the exponential model is the determination of the initial  $^{14}\text{C}$  content (GEYH & GROSCHOPF 1978) which shows a sensitive relation to the kind of soil cover of the catchment area (Fig. 3). Especially in hydrogeologically untouched regions the technique has been very helpful.

### 3.2. Base flow model

In heavily karstified limestone regions, e.g. in the Frankian Alb, there are joint karst water bodies with a great storage volume and continuous recharge. Mean residence times determined by tritium are much greater than



**Fig. 2** Interrelation between the radiometrically determined mean residence times of joint groundwater samples from the hard rock pen-  
 eplain in NE Brazil and their mineral contents (GEYH and KREYSING  
 1973).

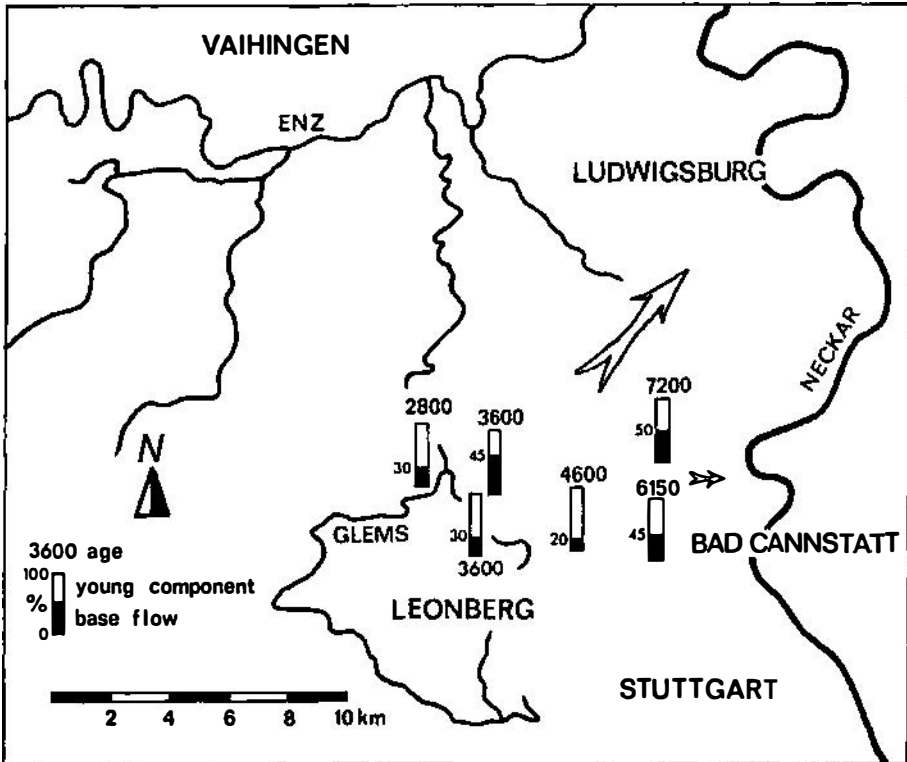


**Fig.3** Differing initial  $^{14}\text{C}$  contents of samples from karst springs in the Swabian Alb in relation to the kind of soil cover of the catchment areas. Regions with thick sediment cover are shadowed (GEYH GROSCHOPF 1978).

those based on the radiocarbon content. This can be explained by a mixing of an old tritium-free water (base flow) with a young component whose isotope content is described by the exponential model. It has been applied for example to water samples taken from wells situated in the assumed catchment area of the mineral springs at Bad Canstatt (Fig. 4). The base flow ages proved that the springs at Bad Canstatt are recharged in their neighborhood and not far away in the Black Forest. The MRT of the young component does not exceed 30 years and the ages of the base flow range from 3000 to 9000 years. The deduced direction of the base flow is in agreement with the isometric lines. However, the base flow velocity of 1-3 m/a contradicts that derived from the water budget and the radiometric MRT ( $v \approx 200$  m/a). Thus, more than 99 % of the discharge of the springs should consist of the young component while the well water samples contained only 50-70 %. The discrepancy is the result of pumping (Fig. 5). In a karst water body the young component flows with a comparably high velocity above a slowly moving base flow. The pump in the well accelerates both components to the same velocity which is why the base flow is overrepresented in well water samples with respect to the spring water. This example makes obvious once more that the natural and the artificial hydrodynamic situation has to be studied before it can be known whether the isotope content must be interpreted as an age or as a hydrogeological parameter. In the given example, the base flow ages reflect the natural groundwater budget while the base flow proportion of the samples is a quantitative indication of the mining of this old groundwater body.

### 3.3. Convection model (hydraulic model)

A convection model has been developed (GEYH & BACKHAUS 1978) for confined aquifers which are separated by a rather impermeable layer (aquitarde) from an unconfined aquifer containing young water (Fig. 6). If a hydrostatic pressure difference exists between the two, a vertical groundwater flow results. In the case of flow upwards, a few decimeter water column are already sufficient to cancel the effect from  $^{14}\text{C}$  downwards movement by diffusion (see section 2.5). Then, the conventional  $^{14}\text{C}$  ages of the groundwater samples corrected hydrochemically (see section 2) reflect the paleohydrogeologic situation.



**Fig. 4** Content and age of the base flow calculated from the  $^{14}\text{C}$  concentration of pumped water samples taken from wells in the recharge area of the mineral springs at Bad Cannstatt (GEYH 1969).

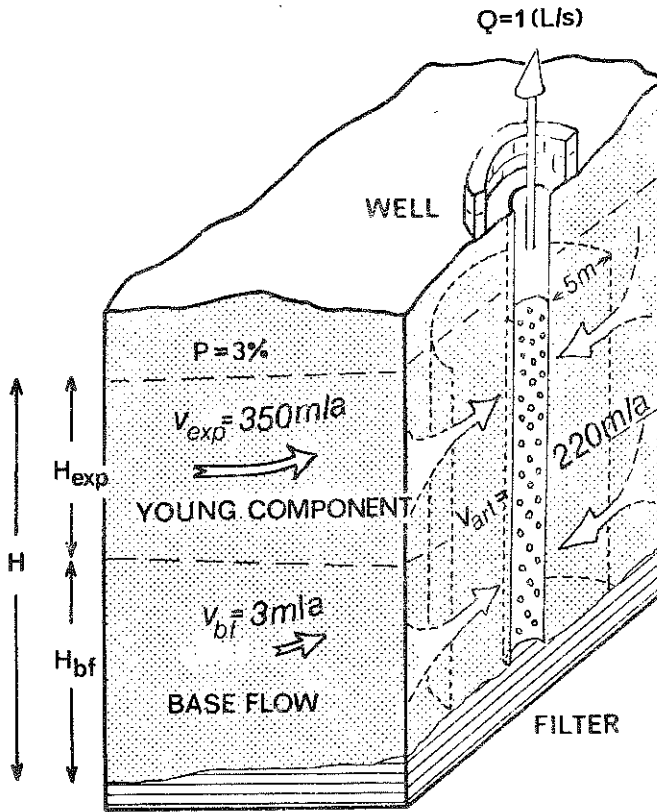


Fig. 5 Schematic presentation of the effect of pumping to the flow velocities of both the young component and the base flow (GEYH 1979).

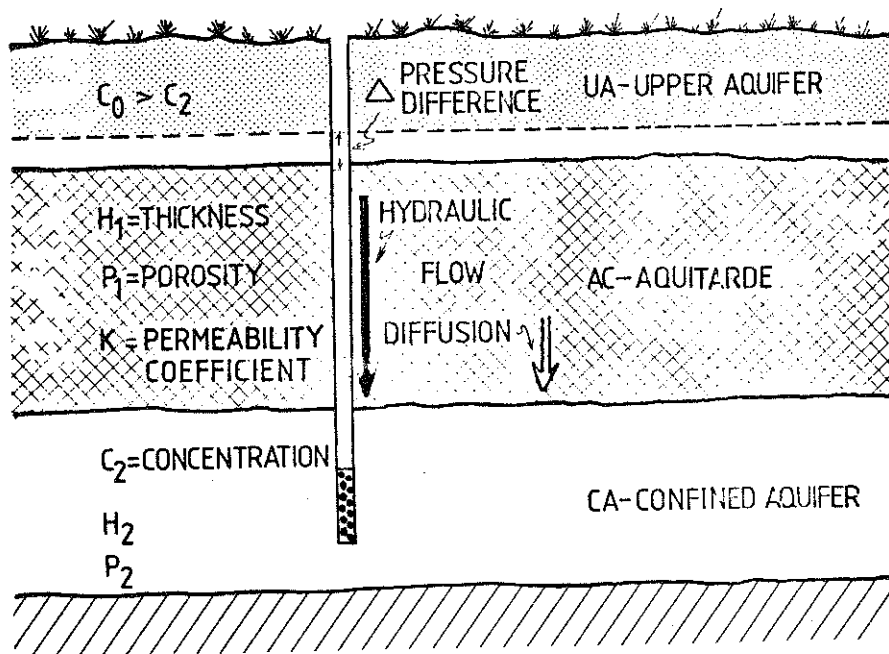


Fig. 6 Scheme of a confined aquifer separated from a shallow unconfined aquifer by an aquitard (GEYH BACKHAUS 1978).

If the young water from the unconfined aquifer penetrates the aquitarde, the  $^{14}\text{C}$  ages of the groundwater in the confined aquifer are diminished.  $^{14}\text{C}$  transport by diffusion can be neglected with respect to that by convection. A steady input of young groundwater yields a constant steady-state age (Fig. 7) in the final stage, such as can be found in large basins, e.g. in NW Germany. A few decimeters of hydrostatic pressure difference are sufficient to decrease infinite ages to a few millennia. In a sandstone aquifer north of Nurnberg we measured an unsystematic distribution of  $^{14}\text{C}$  ages in the direction of groundwater flow (Fig. 8). Applying the convection model, a hydraulic conductivity  $k_f = 3-4 \cdot 10^{-10}$  m/s and a flow velocity of 1 m/a were calculated from the  $^{14}\text{C}$  content. Pumping tests yield a  $k_f < 10^{-9}$  m/s. It is seen that in confined aquifers with an input of young groundwater, the  $^{14}\text{C}$  content is mainly a function of the hydraulic conductivity coefficient of the aquitarde rather than of the actual water ages.

The convection model is of course also valid for stable isotope, hydrochemical, or hydrothermal data. A steady admixture of water from an adjacent story changes the chemical content of the confined water. However, ion exchange processes in the aquitarde have to be taken into consideration as this may change the properties of the admixed water considerably.

### 3.4. Mining model

The mining model is derived from the convection model. Groundwater withdrawal from confined aquifers reduces the hydrostatic pressure and accelerates the admixture of young groundwater. As a consequence the  $^{14}\text{C}$  ages decrease (Fig. 9). The rate depends upon the aquifer geometry, the depletion rate, and the  $k_f$  value of the aquitarde.

The mining model has been applied to a confined aquifer in the Rhein/Neckar region (ARMBRUSTER et al. 1977) which has been in use for 20 years. The level of the pumping cone decreases by 0.2 m/a and should have theoretically lowered the initial groundwater ages to approx. 5800 years (GEYH & BACKHAUS 1978). The  $^{14}\text{C}$  ages of the groundwater scatter closely around 5000 BP. The tritium found in the samples of the confined aquifer need not be due to windows in the aquitarde but can be the result of seepage through it.

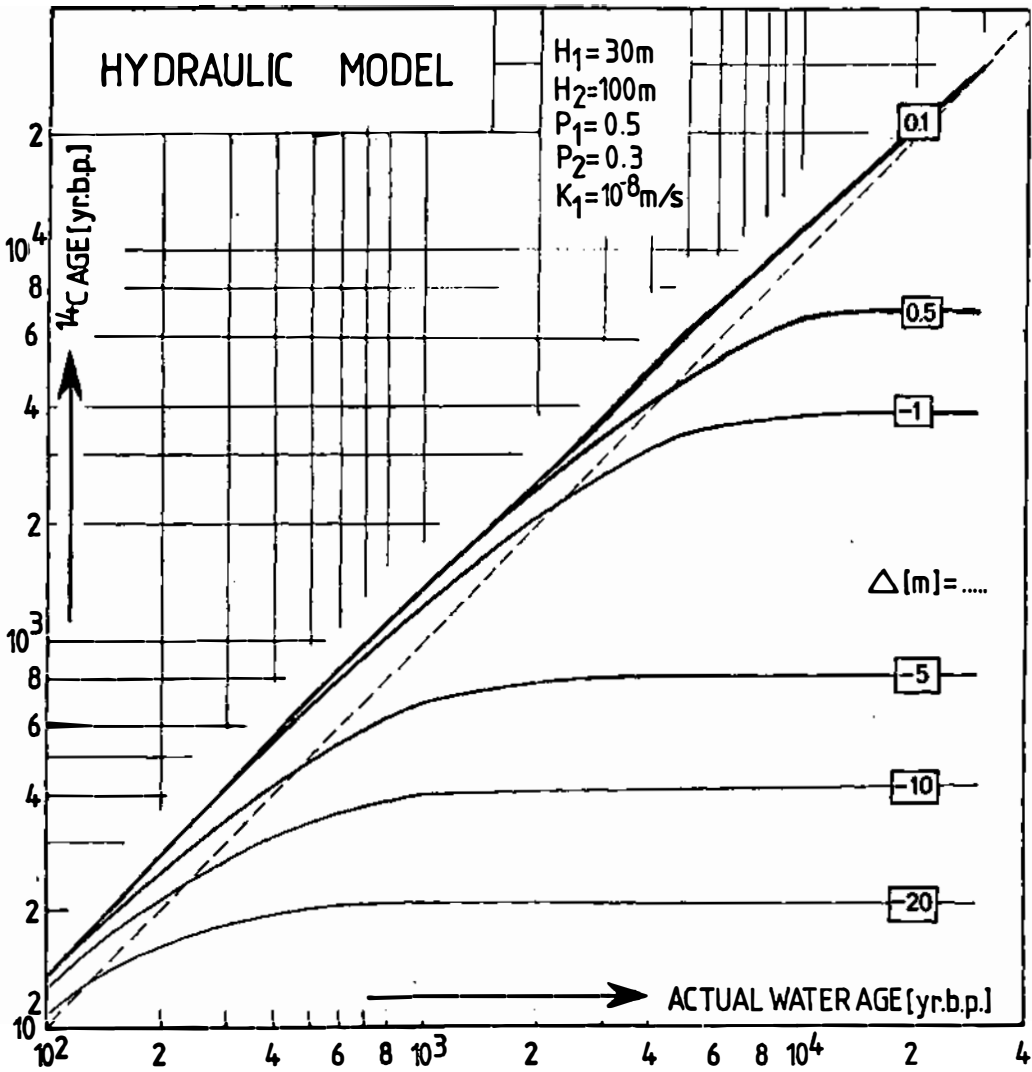
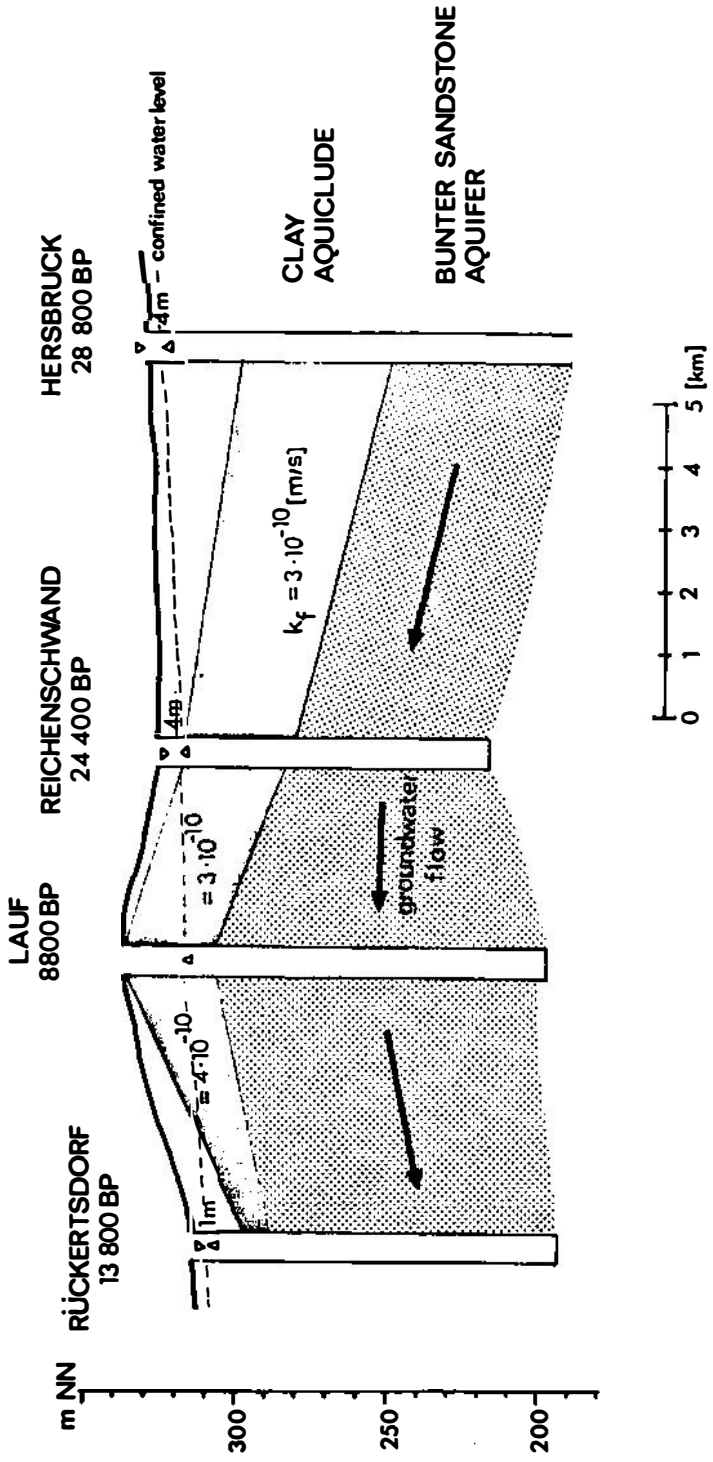


Fig. 7

Relationship between conventional  $^{14}\text{C}$  ages and actual ages of groundwater in case of vertical convection for a special case study (GEYH BACKHAUS 1978).



**Fig. 8** In flow direction scattering groundwater  $^{14}\text{C}$  ages for a sandstone aquifer  
 N from Nurnberg and  $k_f$  values of the aquitarde derived by the convection  
 model.

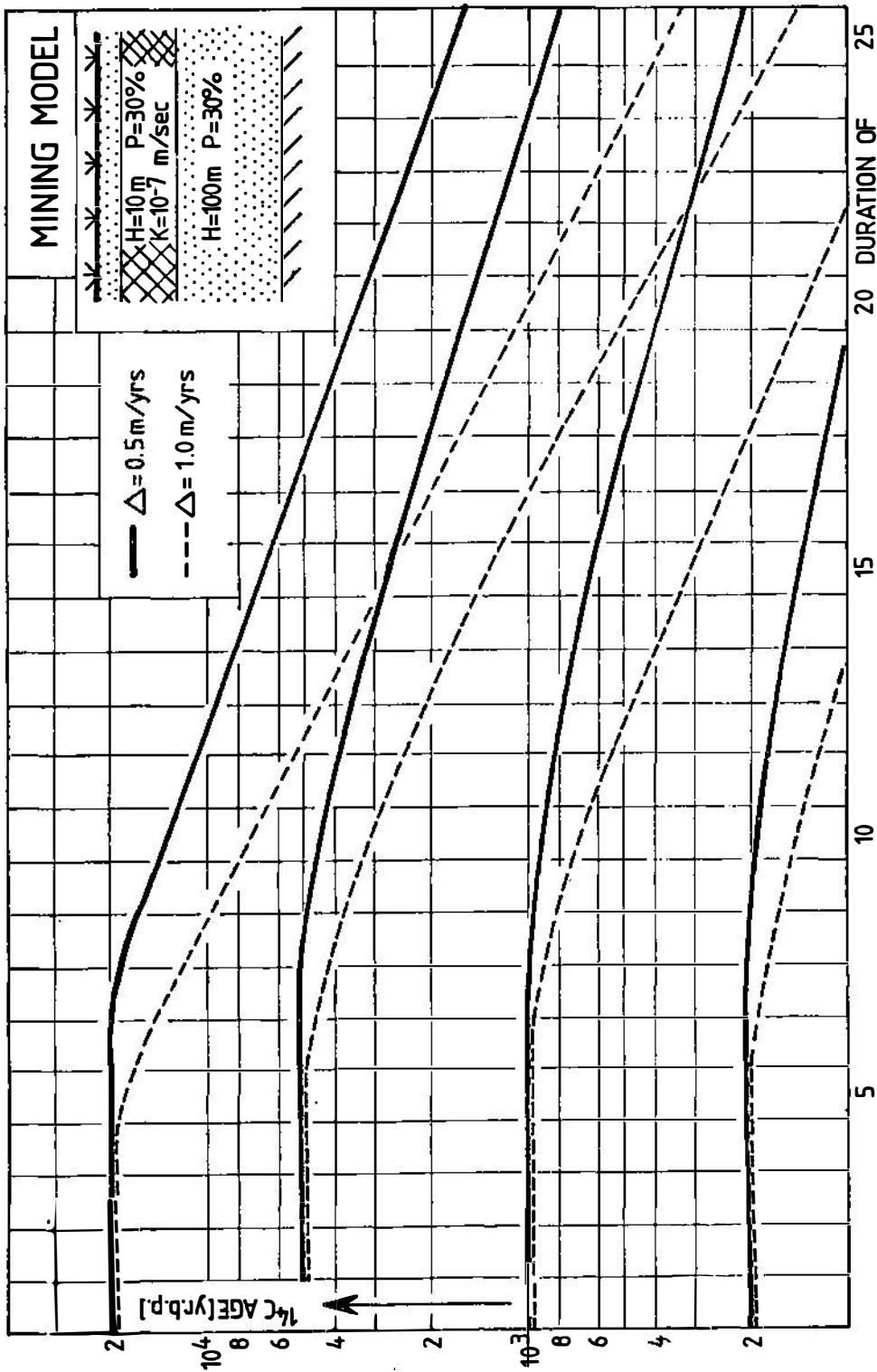


Fig. 9 Changes of the conventional <sup>14</sup>C ages of the groundwater in a confined aquifer at the Rhein/Neckar Region (ARMBRUSTER et al. =1977) due to groundwater mining as a function of its duration and the lowering rates of the water table (GEYH and BACKHAUS 1978).

In the last few years, the change of groundwater  $^{14}\text{C}$  ages as a result of groundwater mining has become the most extensive object of study for our laboratory. As seen in Fig. 9 an observation interval of two years is in general sufficient.

### 3.5. Mixing model

In hard rock regions sometimes fresh, brackish, and salty water occur side by side. Mixing lines are constructed from the hydrochemical or stable isotope data but the maximum salt content of the brine can only be obtained by plotting the  $^{14}\text{C}$  content versus salt content. The maximum salt content is at 0 ‰modern. In general the mixing occurs so fast that hydrochemical secondary reactions can be neglected (GEYH & MICHEL, in preparation).

### Summary

A comparison of the various interpretation models of the  $^{14}\text{C}$  content of groundwater shows that convection, dispersion and mixture seem to be more effective in changing the  $^{14}\text{C}$  content than any hydrochemical process. In many cases the  $^{14}\text{C}$  content reflects the hydrodynamic situation rather than the groundwater age. Hydrochemical corrections shift the conventional  $^{14}\text{C}$  ages of fresh groundwater by rather constant values which seldom affect the hydrogeologic interpretation. As several unmeasured parameters are assumed, most corrections of this kind are questionable. In hard rock areas, as well as in the case of groundwater mining, the mean residence times of the groundwater samples are too short for a change of the  $^{14}\text{C}$  contents due to hydrochemical secondary reactions.

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