Residence time of Chalk groundwaters in the Paris Basin and the North German Basin: a geochemical approach

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Abstract—The comparative geochemical and isotopic study of confined and unconfined Chalk groundwaters of the Paris Basin and the N German Basin proves a significant chemical evolution during groundwater flow from the recharge zones to the deep confined aquifer. Different time dependent geochemical parameters have been tested as dating tools: Cation ratios (Sr^{2+}/Ca^{2+}, Mg^{2+}/Ca^{2+}), N–NO_3^-, noble gas contents as paleotemperature indicators (Ne, Ar, Kr, Xe), radiogenic He, ^{13}C, ^{14}C, ^{18}O, ^2H, ^3H. Cation ratios and ^{13}C show the importance of incongruent dissolution processes in the Chalk aquifer. Water–rock interactions were taken into account in a multi-step dissolution model to determine radiocarbon groundwater ages. The oldest waters in the confined part of the Paris basin Chalk with maximum ^{14}C ages of 14,000 a B.P. contain pleistocene recharge components as can be shown by a stable isotope depletion and noble gas temperatures significantly lower than in recent groundwaters. Chalk waters at the Lägerdorf site in Northern Germany show a distinct stratification with respect to residence times and hydrochemistry. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The Chalk is an aquifer of major economic importance in NW Europe, in particular in Great Britain and in France. The geochemistry of groundwaters in relation to their residence time in the Chalk has been studied in detail for the confined parts of the London Basin (Smith *et al.*, 1975, 1976; Downing *et al.*, 1979; Edmunds *et al.*, 1987; Elliot, 1990) and N Norfolk (Hiscock *et al.*, 1996). Hydrochemical and isotopic research on the Chalk of the Paris Basin has up to now focused on the unsaturated zone (Dever *et al.*, 1982; Vachier *et al.*, 1987; Moulin, 1990) and on the unconfined parts of the aquifer (e.g. Kloppmann *et al.*, 1994). A detailed review of previous work is given by Edmunds *et al.* (1993). Some aspects of the hydrochemistry of two of the rare local Chalk-outcrops in the N-German Basin have been studied by Löhnert (1977) and Schönfeld and Grube (1990). An intimate knowledge of hydrochemical baseline conditions and of groundwater age in the Paris basin Chalk is needed in order to estimate vulnerability of the confined part of this aquifer to pollution during expected future exploitation. The present study attempts to establish residence times of Chalk groundwater in France and Germany on the background of the general chemical evolution from recharge to discharge areas. Various quantitative and qualitative geochemical age-indicators were used which allows a critical comparison of dating methods. Several models for radiocarbon dating were tested and an adapted model accounting for the specific conditions in the Chalk aquifer was established. Tritium and NO_3 concentrations are used as semi-quantitative indicators of mixing processes with recent groundwaters; stable isotopes and noble gas concentrations deliver the first paleoclimatic evidence from Chalk groundwater in France and Germany.

HYDROGEOLOGICAL SETTING AND SAMPLING SITES

In the Paris Basin the Chalk outcrops over about 75,000 km^2, in the central part of the basin, about 25,000 km^2 of the aquifer are covered by Tertiary strata (Fig. 1). At outcrop, the Chalk is extensively exploited for drinking water and irrigation but up to now abstraction from the confined parts of the

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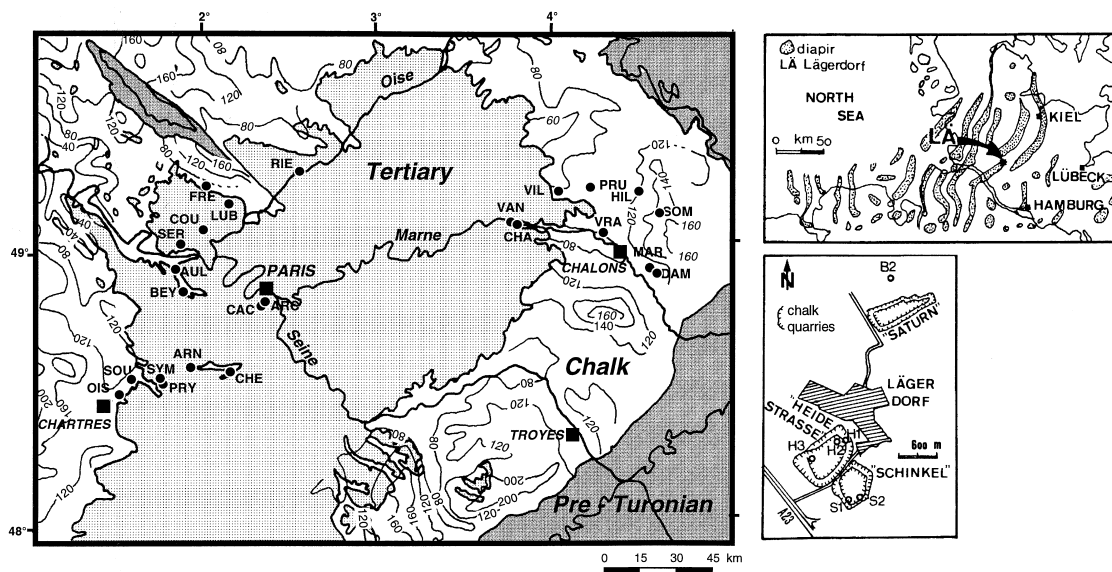†Corresponding author.

Fig. 1. (a) Sampling sites in the Paris Basin (Ch = Chalk, S = Senonian, T = Turonian, conf. = confined, unc. unconfined or semi-confined). Groundwater levels after Crampon *et al.* 1993. *Champagne*: MAR (Marson, Ch(S), unc.); DAM (Dampierre, Ch(T), unc.); HIL (St. Hilaire, Ch(S), unc.); SOM (Somme Suippe, Ch(S), unc.); VRA (Vraux, Ch(S), unc.); PRU (Prunay, Ch(S), unc.); VIL (Villers-aux-Noeds, Ch(S), unc.); VAN (Vandières) and CHA (Chatillon sur Marne): Ch(S), unc. during pumping. *Hurepoix and Paris region*: OIS (Oisème, Ch(S), unc.); SOU (Soulaires, Ch(S), unc.?); SYM (St. Symphorien, Ch(S), conf.); PRY (Prunay en Yvelines, Ch(S), conf.); ARN (St. Arnoult, Ch(S), conf.); CHE (St. Chéron, Ch(S), conf.); CAC (Cachan, Ch(S), conf.); ARC (Arcueil, Ch(S), conf.). *Oise region*: BEY (Beynes, Ch(S), unc.); AUL (Aulnay, Ch(S), unc.); SER (Seraincourt, Ch(s), unc.); COU (Courcelles, Ch(S), conf.); LUB (St. Lubin, Ch(S), conf.); FRE (Fresnes Léguillon, Ch(S), unc.); RIE (Rieux, Ch(S) + Thanetien, conf.) (b) Sampling sites in the Lägerdorf Chalk (North German Basin, Campanian-Maastrichtian): H1, H2, H3 (Chalk, quarry "Heidestraße"), S1, S2 (Chalk, quarry "Schinkel"), B2 (Quaternary, quarry "Saturn").

aquifer has been limited to a few zones in the central Paris region, especially to the river valleys, where permeabilities are relatively high.

The Cretaceous Chalk is a very pure and fine grained limestone with microporosities varying between 20 and 40% (Megnien, 1978). Fissure porosity (1%) can be regarded as hydraulically inactive in the unsaturated zone (Vachier *et al.*, 1987) but controls groundwater flow: fissures are well developed beneath valleys where hydraulic conductivity can attain 1×10^{-3} to 4×10^{-3} m·s^{-1} (Megnien, 1978) and decreases considerably under Tertiary cover. The maximum thickness of the Chalk is about 700 m in the basin centre. It is underlain by the Gault clays and the marls of Briennes and overlain in the central part of the basin by up to 50 m of clays and sandy clays of the lower Eocene (Sparnacian). The limestones and marls of the Tertiary cover include two gypsum horizons (Lutetian and Ludian), mainly in the centre of the basin. In order to compare confined and unconfined conditions we selected 3 sectors (Fig. 1) in the central Paris Basin: the Champagne, the Hurepoix and the Oise regions. The samples were taken from abstraction boreholes and wells in the Senonian and Turonian Chalk exploited for common, private and industrial use.

The geology of the N German Basin is complicated by a strong diapirism of Permian and Rhetian salt. The upper Cretaceous and Danian Chalk is generally buried under more than 1000 m of continental Tertiary and Quaternary sediments and outcrops very locally on the top of salt domes. The Lägerdorf Chalk outcrop (Campanian-Maastrichtian, Koestler and Ehrmann, 1986) is exploited up to a depth of −90 m. Artificial lowering of the groundwater level provokes local groundwater outflow on the walls and at the bottom of the Chalk quarries which allows sampling at different depths.

ANALYTICAL METHODS

Samples were filtered in the field through 0.45 μm filters. Samples for ^{14}C analysis were taken by precipitating BaCO$_3$ by addition of excess BaCl$_2$ to 60 l of water previously brought to pH 12 by addition of NaOH. Temperature ($\pm 0.1^\circ$C), pH (± 0.1), Eh (± 10 mV), conductivity (± 100 μS·cm^{-1}) and alkalinity (± 0.2 meq·l^{-1}) were measured in the field. Major anion determinations were performed by ion chromatography, major cation and trace element analysis by ICPMS and ICPOES at the British

Geological Survey (Wallingford, U.K.). δ^2H was determined by mass spectrometry on H_2 gas reduced over Zn at 450°C (Coleman et al., 1982), $\delta^{18}O$ was determined on CO_2 equilibrated with 3 ml of degassed sample at 25°C (Epstein and Mayeda, 1953 in: Gonfiantini, 1981). Carbon dioxide samples for $\delta^{13}C$ were prepared for mass spectrometry by acidifying 100 ml water samples using orthophosphoric acid. ^{14}C activity was determined by liquid scintillation counting on benzene synthesised from CO_2 (Fontes, 1971). Samples for noble gas analysis were taken under pressure in sealed Cu tubes (Andrews et al., 1989) and analysed by quadrupole mass spectrometry in the noble gas laboratory of Reading (U.K.) University.

HYDROCHEMICAL BACKGROUND

In many respects, downgradient hydrochemical evolution in the Paris Basin Chalk is similar to that in the London Basin. Water–carbonate rock interactions and redox processes are the main controls for both major and minor elements. Anthropogenic and atmospheric inputs play an important role whereas cation exchange and mixing with interstitial "connate" Chalk waters seem to be of minor importance compared to the London Basin, at least in the rather superficial zone of the aquifer treated in our study.

The presence of Permian salt domes in the underground of the N German Basin has a strong impact on the geochemistry of its deep groundwaters (Löhnert, 1966; Bauhus, 1988; Löhnert et al., 1992). Mixing processes with saline solutions, cation exchange and water–Chalk interactions determine the chemical composition of waters from the Lägerdorf Chalk.

Paris basin. The dominant components of shallow Chalk-groundwaters are Ca^{2+} and HCO_3^- with rather constant concentrations around 5 meq·l^{-1}. Unconfined waters are saturated with respect to calcite and show bivalent cation ratios (Mg/Ca, Sr/Ca) equal or slightly superior to those of the Chalk matrix. Na^+, Cl^-, SO_4^{2-} concentrations can be attributed to atmospheric inputs (Kloppmann et al., 1994). Drainage from Tertiary strata may constitute a supplementary source for SO_4. All unconfined groundwaters are oxidising and contain dissolved O_2 and NO_3, the latter up to the limit of potability. $N–NO_3^-$ and K^+ may be of anthropogenic origin although they are not correlated.

The deep, confined groundwaters are of Ca–Mg–HCO$_3$ or Ca–Mg–SO$_4$–HCO$_3$ type. High Ca concentrations are related to the occurrence of gypsum in the tertiary cover and may attain 20 meq·l^{-1} in the Paris region. In other parts of the confined Chalk Ca^{2+} contents are lower thanthe mean concentrations in the unconfined part due to a partial replacement by Mg^{2+}. No significant rise in SO_4 can be observed on the Vexin profile but in the Paris region concentrations may attain 38 meq·l^{-1} and Chalk groundwaters reach saturation with respect to gypsum and celestite. We observe a slight increase in Na^+ in the confined zone possibly due to some cation exchange whereas Cl^- is nearly constant: The influence of interstitial saline waters seems to be less important than in the London Basin Chalk. In the confined area desorption of K^+ from clay minerals may lead to concentrations up to 20 mg·l^{-1} and to an decrease of the Na/K ratio. Redox conditions both in the unconfined and the confined Chalk in France and Germany were analysed elsewhere in detail (Kloppmann et al., 1996). Deep groundwaters are anaerobic with measured redox potentials negative. A zonation of redox conditions in the direction of groundwater flow has been demonstrated. $N–NO_3^-$ disappears at the same time as dissolved O_2 does, Fe, Mn and H_2S become detectable further downgradient.

The most striking feature of the *Lägerdorf Chalk* groundwater is its high salinity and the rise of temperature and mineralisation with depth. We observe an excellent correlation between temperature, Cl^- and most major cations and trace elements: mixing seems to occur between shallow groundwaters of Ca–Na–HCO$_3$–Cl type and deep groundwaters in which Na and Cl dominate. Na^+/Cl^- ratios <1 indicate the importance of cation exchange at depth (Na leaves solution for Ca). All groundwaters are reducing with low NO_3 concentrations and enriched in Fe and Mn.

QUANTITATIVE AND QUALITATIVE INDICATORS OF GROUNDWATER RESIDENCE TIME

Carbon isotopes

The crucial point in the use of C isotopes for the estimation of groundwater "age" are the various sources and sinks for dissolved inorganic C (TDIC). Dating requires the distinction of the effect of radioactive decay of ^{14}C from other mechanisms of ^{14}C input, output or dilution. All dating models yield an initial ^{14}C activity A_0 which is considered as starting point of radioactive decay after all other effects have been taken into account. Chalk presents particular chemical and physical properties which must be taken into consideration to produce realistic corrected ages. A short outline of chemical and isotopic evolution during infiltration and groundwater flow will provide the criteria an adapted model has to fulfil as well as a range of values for input parameters. In a schematic summary we may distinguish 4 phases in the Chalk groundwater evolution:

(1) Infiltrating water will equilibrate with the gaseous phase in the Chalk soil according to Henry's law. TDIC will be slightly depleted in ^{13}C with respect to the gaseous phase ($H_2CO_3^*$ is the predominant species at this stage and $e(CO_{2(g)}-H_2CO_3^*)$ is negative). The $A^{14}C$ of TDIC $A^{14}C_l$ is similar to $A^{14}C_g$ of the soil gas (100 pmc).

(2 and 3) Water containing $H_2CO_3^*$ ($f(CO_2)$) will be able to dissolve the carbonate matrix. Wigley (1975) showed the distinction of dissolution in a system closed to soil CO_2 from dissolution in an open system to be crucial for radiocarbon dating. In the unsaturated zone of the Chalk in the Champagne region (Moulin, 1990) the system becomes closed several meters below the surface. We should therefore consider two successive dissolution phases, the first one in an open, the second in a closed system.

(4) Once saturation with respect to the least soluble magnesian calcite phase is reached, isotopic and chemical evolution can continue by incongruent dissolution (concurrent dissolution and precipitation of carbonate phases) in particular in the fine-grained porous carbonate milieu of Chalk. Waters seem to undergo isotopic "exchange" but Pearson (1991) shows that the observed isotopic evolution can be modelled with incongruent dissolution techniques (Wigley *et al.*, 1978). During this step cation ratios in the liquid phase will differ from those in the solid solution of the Chalk matrix: trace elements like Sr and Mg will be preferentially released into the liquid phase, the reprecipitated carbonates will be purer calcites than the original matrix (Moulin *et al.*, 1989) The final point of isotopic evolution depends on ε_{ml}, the isotopic fractionation factor between TDIC (subscript l) and mineral phase (subscript m) and Γ, the ratio of dissolution and precipitation rate. Wigley (1976), using ε values from Deines *et al.* (1974) to reinterpret data of Smith *et al.* (1976), shows an important reduction of model ages of Chalk groundwater if considering an incongruent dissolution phase. Mook's new set of fractionation factors (Mook, 1979, adopted by Pearson, 1991) leads to smaller ε_{ml} values and to a correspondingly small correction of ages. We have to consider (after Wigley *et al.*, 1978)

$$\varepsilon_{ml} = 1000 \cdot \left(\frac{\alpha_{mg}}{\sum_j x_j \alpha_{jg}} - 1 \right)$$

where

$\varepsilon_{ml} =$ additive fractation factor between TDIC and the mineral phase

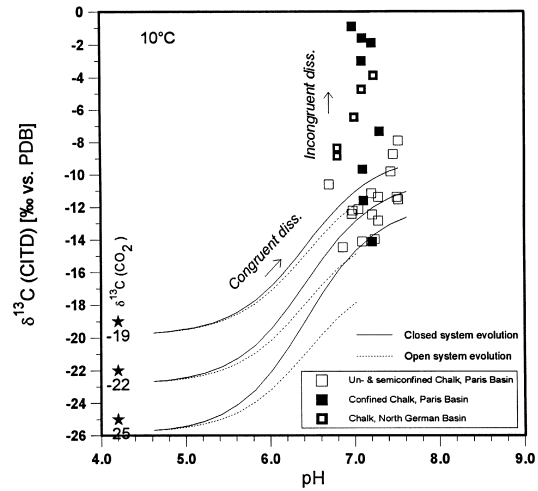$\alpha_{mg} =$ fractionation factor between gaseous phase and mineral phase

Fig. 2. $\delta^{13}C$ of TDIC of Chalk groundwaters from the Paris and N German Basin plotted against pH. The isotopic evolution by congruent dissolution of calcite in an open or closed system is modelled for T = 10°C, $PCO_2 = 10^{-1.5}$ atm and $\delta^{13}C$ values of the gaseous phase varying between −25‰ and −19‰ *vs.* PDB.

$\alpha_{jg} =$ fractionation factor between gaseous phase and carbonate species j

$x_j =$ molar fraction of the carbonate species j

ε_{ml} depends on temperature and pH and would be around 2.5‰ at a pH of 7 and a temperature of 10°C.

Characteristics of gaseous and mineral phase

Gaseous phase. The observed alkalinity/pH range of Chalk groundwaters can be modelled either by carbonate dissolution in an open system with a $logPCO_2$ (atm) between −1.3 and −2.4 or in a closed system with $logPCO_2$ (atm) between −1.0 and −1.5. Observed $logPCO_2$ (atm) values in the unsaturated zone of English and French Chalk range from −3.0 to −2.0 (Pitman, 1978; Dever *et al.*, 1982; Moulin, 1990), those for Chalk groundwaters in England may attain −1.4 (Pitman, 1978; Heathcote, 1985). The most probable model seems to be an evolution in a hybrid system (Wigley, 1975) with $logPCO_2$ (atm) values below −1.3 atm. Most of the directly measured $\delta^{13}C_g$ values of the gaseous phase in the unsaturated French and English Chalk vary between −25 and −20‰ *vs.* PDB (Dever *et al.*, 1982), a mean value of −22‰ seems justified for model calculations.

Mineral phase. The $\delta^{13}C_m$ depends on the stratigraphic position of the solid phase sample (Pomerol, 1984) and the degree of alteration. It may be influenced by dissolution–precipitation processes, especially in the unsaturated zone. Nevertheless the isotopic composition of Chalk in NW
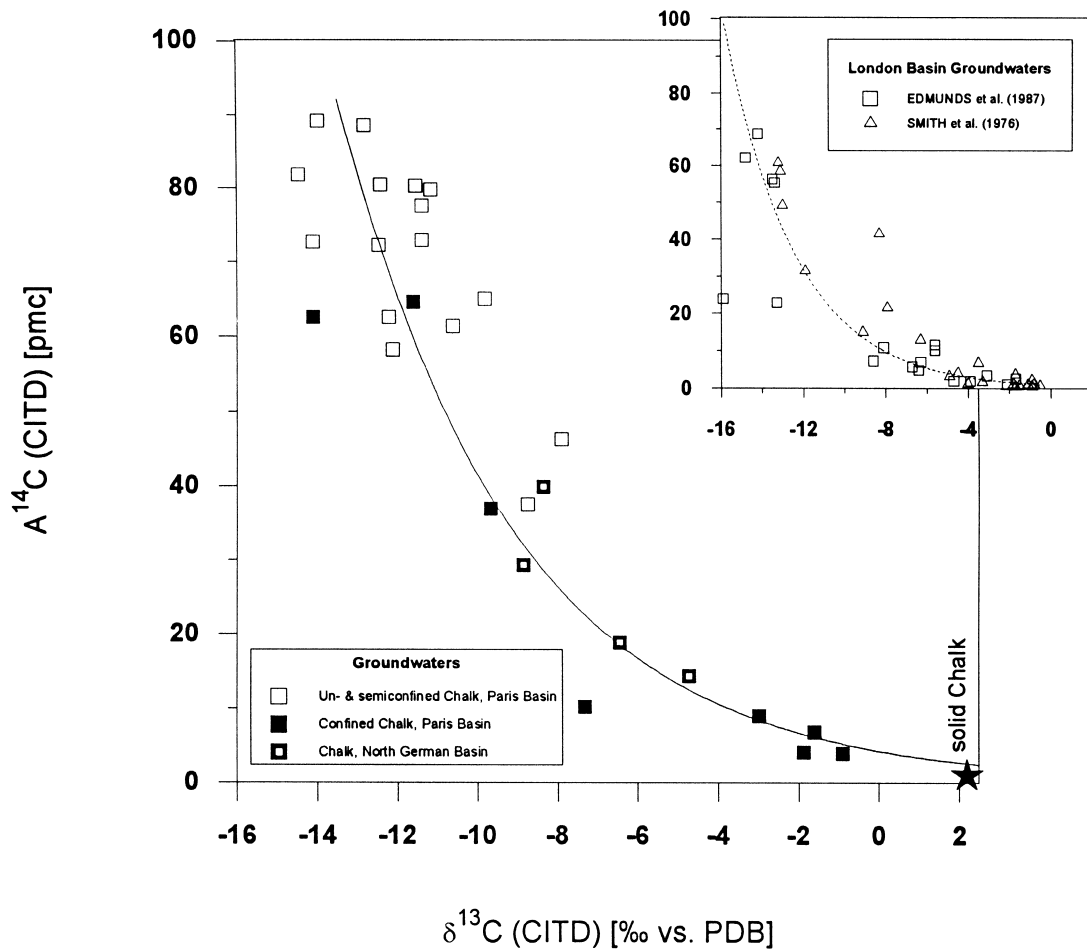
Fig. 3. Radiocarbon activities of Chalk groundwaters of the Paris Basin, the N German Basin and the London Basin (Smith *et al.*, 1976; Edmunds *et al.*, 1987) plotted against $\delta^{13}C$ of TDIC. The distribution of points is fitted by an exponential function.

Europe is quite constant (mean values: 2.5‰ for the Paris Basin (Dever, 1985), 2.35‰ for the London Basin (Edmunds *et al.*, 1993), 2.7‰ for Lägerdorf (Schönfeld *et al.*, 1991).

Isotopic evolution of groundwater

The possible isotopic evolution paths during congruent dissolution for different $\delta^{13}C_g$ values are shown in Fig. 2. Even if we take into account a rather highly enriched gas phase and a closed system the congruent dissolution model fails to explain isotopic compositions of most of the confined groundwater samples. It is likely that it is incongruent dissolution which leads to those high $\delta^{13}C_l$ values approaching 0‰ (−0.5‰ seems to be an equilibrium value both in the Paris and the London Basin). The theoretical equilibrium $\delta^{13}C_l$ (Wigley *et al.*, 1978) for $\delta^{13}C_m = 2.2$‰, pH = 7, $\Gamma = 1$ (ratio of dissolution to precipitation rate) and T = 10°C would be of the order of −0.3‰.

We observe an exponential correlation of ^{14}C and ^{13}C values of TDIC (Fig. 3). The scatter of points representing unconfined groundwaters reflects possibly a large variation of hybrid system conditions during infiltration. Variability decreases as the waters approach pure closed system conditions. The exponential correlation may be due to the superposition of two processes:

1. incongruent dissolution (isotopic "mixing" between a pole reflecting open system conditions and a pole near the isotopic composition of the solid phase) would lead to a linear correlation between $A^{14}C$ and $\delta^{13}C$.

2. radioactive decay which is exponential in time and affects only ^{14}C.

A large variety of chemical and isotopic models has been developed in order to calculate the initial ^{14}C activity A_0. We have tested the behaviour of some selected models in the context of chalk groundwaters:

Table 1. Values and statistical distribution of model parameters for radiometric age calculation

Parameter	Distribution	Constant value	Min/Max	Mean	Standard dev.
$\delta^{13}C_g$	normal			-22‰PDB	1.3‰
$\delta^{13}C_{min}$	normal			2.2‰PDB	0.3‰
$\log PCO_2$ (atm)	normal			-2	0.3
Γ	rectangular		0.9/1.1		
pH_{lim}	rectangular		6.5/8.0		
$A^{14}C_g$	const.	100 pmc			
$A^{14}C_{min}$	const.	0 pmc			

The Ingerson and Pearson (1964) model is based on the assumption of isotopic mixing by congruent dissolution in a closed system. If part of the isotopic evolution of groundwater takes place under open system conditions there would be a tendency to over-correct ages of less evolved groundwaters (low $\delta^{13}C_l$ values). On the contrary, ages of groundwaters near isotopic equilibrium with the matrix are under-corrected (too high) as isotope fractionation is not taken into account.

The Fontes and Garnier model (Fontes and Garnier, 1979; Fontes, 1992) is a combined chemical/isotopic model based on the "Tamers" model (Ingerson and Pearson, 1964) with correction for "exchange" by an additional factor. This factor becomes very high for evolved groundwaters ($\delta^{13}C_l \geq -5$‰) resulting in negative A_0 values in which case ages are not defined.

The IAEA model (Salem et al., 1980) assumes initial isotopic equilibrium of liquid and gaseous phase analogous to open system conditions. For higher $\delta^{13}C_l$ values behaviour is similar to the Ingerson and Pearson model. It avoids over-corrections for less evolved groundwaters but does not take into account fractionation between liquid and solid phase. The concept of Salem et al. (1980) seems nevertheless to approach rather closely the conditions observed in the Chalk aquifer.

We adopted a combined model using the approaches of Deines et al. (1974) and Wigley (1975) to model groundwater evolution by congruent dissolution in a hybrid system. It is possible to allow conditions to vary between a nearly closed and a pure open system. pH has been chosen as a master variable for this purpose. Isotopic evolution beyond calcite saturation is supposed to proceed by incongruent dissolution in a closed system. This part of the evolution is based on the concept developed by Wigley et al. (1978) and Pearson (1991). Input parameters for the model are soil pCO2, $\delta^{13}C_g$, $\delta^{13}C_{min}$, $A^{14}C_g$, $A^{14}C_{min}$, Γ and the pH at which the system closes (tab. 1). A Monte Carlo sampling procedure (as proposed by Pearson, 1991, 1994) has been used to allow systematic variations of the input values with a given statistical distribution (gaussian or homogeneous) in order to quantify errors in the corrected ages. Details are given by Kloppmann (1995). The high absolute errors for several old groundwaters reflect their proximity to isotopic equilibrium with matrix carbonates (especially for Courcelles). Most unconfined groundwaters of the Paris Basin have recent radiocarbon "ages". On both sides of the confined boundary local mixing of older and younger components may lead to intermediate ages of several thousand years (example: $4 \times 10_3$ a for Beynes with unconfined Chalk under the alluvium of the Meauldre valley). Some groundwaters in the deep confined chalk attain ages close to 10^4 a and more and might contain a Pleistocene component (Arcueil and Cachan in the Paris region, Courcelles, St. Lubin and Rieux in the Oise region).

Gonfiantini (1988) has proposed a method to interpret exponential $^{14}C/^{13}C$ correlations in terms of "exchange" kinetics. It makes use of the slope of the fit line in a log–log diagram assuming that "exchange" (or incongruent dissolution) is a first order reaction. Resulting reaction half-lives for incongruent chalk dissolution in the London and the Paris Basin range between $3–5 \times 10^3$ a, much higher than values obtained in laboratory (Mozeto et al., 1984) but lower than the 11×10^3 a obtained for a karstic limestone aquifer in Libya (Gonfiantini, 1988).

Groundwater "ages" in the Lägerdorf chalk have a tendency to increase with depth and to be correlated with salinity. Close to the bottom of the chalk quarries mean ages of $> \times 10^3$ a have been calculated. Results are shown in Table 2.

Cation ratios

It was shown for the London Basin Chalk (Edmunds et al., 1987) that the bivalent cation ratios Mg/Ca and Sr/Ca are directly related to groundwater residence time and may be used as a qualitative age indicator. The rise of the Sr concentration from a mean value around 0.2 mg/l in the unconfined Chalk to maximum values of 13 mg/l in the confined area is less important than the downgradient Mg enrichment in solution. Concentrations in the deep groundwater of the Lägerdorf quarries are similar to those in the deep confined Paris Basin Chalk. Molar Sr/Ca rations show a very significant rise from 0.09% which corresponds to the mean ratio in the Chalk matrix (Moulin, 1990) to 7.9% and 5.0% in the deep confined groundwater in

Table 2. Indicators for residence time, modelled radiocarbon ages for French and German Chalk groundwaters

Location	TDIC mmol/l	N-NO$_3$ mmol/l	Mg/Ca	Sr/Ca ‰	A^{14}C pmc	δ^{13}C ‰ PDB	Modelled "age" mean ± 1 (years)	δ^{18}O ‰ SMOW	δ^{2}H ‰ SMOW	^{3}H TU	mean noble gas temp. °C	Ne-index	He content cm^3 gas (STP)/cm^3 H$_2$O *E^{-8}
MAR	3.1	0.33	0.03	0.90	65.0	–9.8	800 ± 860	–7.96	–51.6				
DAM	4.3	0.31	0.05	0.85	72.9	–11.4	950 ± 860	–7.76	–51.1				
SOM	4.0	0.54	0.02	0.17	80.3	–11.5	230 ± 840	–7.69	–51.2				
HIL	3.95	0.32	0.01	0.66	77.6	–11.4	430 ± 860	7.40	–53.3				
VRA	4.1	0.61	0.03	0.45	79.8	–11.2	30 ± 850	–7.38	–51.4				
PRU	3.87	0.57	0.02	2.72	46.3	–7.9	1980 ± 870	–7.45	–48.4				
VIL	5.95	0.55	0.1	9.51	72.2	–12.5	1630 ± 800	–7.54	–51.0				
CHA	6.85	0.36	0.23	6.96	89.2	–14.0	560 ± 600	–7.85	–51.2				
VAN	6.5	0.91	0.2	6.59	88.6	–12.8	180 ± 780	–7.01	–47.4				
OIS	6.1	0.45	0.09	0.72	81.8	–14.5	1390 ± 520	–7.20	–41.7				
SOU	4.65	0.32	0.14	0.92	58.3	–12.1	3120 ± 800	–7.42	–46.0				
SYM	5.3	0.54	0.11	0.80	72.7	–14.1	2260 ± 590	–6.99	–45.7				
PRY	4.3	0.16	0.13	0.96	62.6	–14.1	3480 ± 590	–6.65	–45.2	<2	10.9	1.22	4.3
ARN	5.15	0.23	0.14	1.80	64.6	–11.6	1950 ± 810	–7.19	–48.4	35	12.1	1.18	8.1
CHE	5.2	0.12	0.23	3.14	36.9	–9.7	5200 ± 830	–7.29	–49.8	15	11.6	1.09	5.5
CAC	4.5	0.00	0.88	17.92	9.0	–3.0	8640 ± 1380	–8.27	–58.1	<2	3.1	1.50	29.1
ARC	4.3	0.00	0.83	14.30	6.8	–1.6	6980 ± 2490	–8.14	–56.0	<2	5.3	1.44	44.3
BEY	5.8	0.26	0.90	7.56	37.5	–8.7	4170 ± 800	–6.86	–46.2				
AUL	5.9	0.64	0.40	2.90	61.4	–10.6	1630 ± 820	–6.81	–46.0				
SER	6.0	0.34	0.29	3.24	80.5	–12.4	700 ± 800	–7.19	–47.7				
COU	5.8	0.00	0.90	78.57	3.9	–0.9	8790 ± 3100	–8.12	–54.8	<2	8.2	1.35	80.6
LUB	6.2	0.00	1.57	53.23	4.1	–1.9	12250 ± 2100	–8.20	–59.4	<2	2.5	1.29	37.2
FRE	5.7	0.62	0.11	0.95	62.6	–12.2	2580 ± 800	–7.07	–48.9				
RIE	5.45	0.00	0.72	35.84	10.2	–7.3	13780 ± 850	–7.86	–57.1	<2	8.3	1.38	19.7
H1	6.35	0.00	0.66	49.82		–3.9	-	–7.65	–52.5	7			
H2	6.05	0.02	0.47	33.23	14.3	–4.7	7900 ± 1000	–7.14	–50.0	4			
H3	5.45	0.02	0.23	8.12	39.9	–8.4	3580 ± 850	–7.31	–50.7	13			
S1	5.45	0.06	0.42	28.88	29.3	–8.9	6520 ± 830	–7.94	–51.8				
S2	5.8	0.08	0.59	39.61	18.9	–6.5	7760 ± 890	–7.92	–54.5	<2			

Paris Basin and Lägerdorf Chalk, respectively. Mg/Ca ratios approach the value of 1 which has been interpreted as an equilibrium value for the London Basin. Several confined groundwaters are saturated in dolomite. Strontium concentrations may be partly controlled by saturation with respect to celestite in the high SO_4 groundwaters of the Paris region (Table 2).

The concomitant change of Sr/Ca and $\delta^{13}C_l$ in the unconfined Chalk of the Champagne region (Kloppmann et al., 1994) suggests that both parameters are controlled by the same process. It can be demonstrated that incongruent dissolution of Sr or Mg substituted calcite would enrich those trace elements in the liquid phase (Edmunds, 1980; Stumm and Morgan, 1981; Denis and Michard, 1983) while precipitated carbonates are "purer" than the original matrix. The same mechanism would lead to an enrichment of ^{13}C in the TDIC. A diagram Mg/Ca versus $\delta^{13}C_l$ shows a rather good linear correlation (r = 0.8) of both parameters (Fig. 4). The groundwater evolution in fact parallels the diagenetic transformation of the marine Chalk sediment in a freshwater environment (Edmunds et al., 1987). A quantitative interpretation of the observed trace element behaviour in terms of residence time is difficult because of potential sources and sinks other than incongruent dissolution. Apart from the influence of "connate" interstitial water in the chalk which seems to be less important in the Paris Basin than in the London Basin, mixing with Sr and Mg rich Tertiary groundwaters may play a role for some sites in the Paris region. The good correlation of Sr and Mg with Cl in the Lägerdorf Chalk indicates mixing with brines in the deeper part of the aquifer.
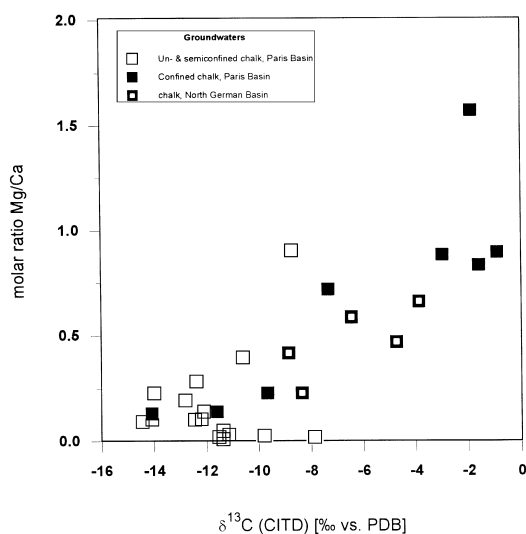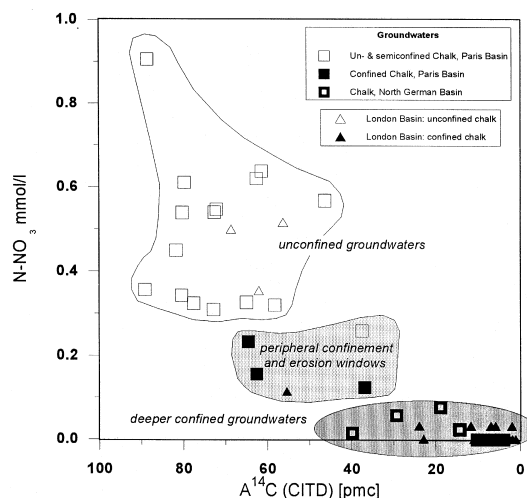

Fig. 5. Nitrate concentrations plotted against radiocarbon activities of Chalk groundwaters of the Paris Basin, the N German Basin and the London Basin (Edmunds et al., 1987).

Tritium

The lack of an appropriate ^3H input function for the Paris basin, the inherent restrictions of the method and a possible role of mixture makes limits interpretation of ^3H data to a semi-quantitative approach.

Most analysed samples from the confined Paris basin chalk have ^3H concentrations below detection limit (2 TU) with exception of St. Arnoult (35 TU) and St Cheron (15 TU). Low ^{14}C activities indicate nevertheless long residence times for those two groundwaters. Samples with similar characteristics have been observed in the London basin (Downing et al., 1979). We can state a common hydrogeological situation: the samples derive from the proximity of erosion windows in the Tertiary cover which favours mixing between recently recharged and deep groundwaters from the confined zone. ^{14}C ages are in this case minimum ages for the old component and overall reflect of a mixing.

Lägerdorf samples from different depths contain between <2 and 13 TU. There is a tendency for a decrease in ^3H concentrations with sampling depth. At the base of the quarries (<−80 m below sea level) we reach a zone of slow circulation without significant influence of recent recharge.

Nitrates

In general high ^3H values coincide with high NO_3 concentrations which may be used as a qualitative indicator of a young groundwater component. In a diagram $N–NO_3$ vs. $A^{14}C$ (Fig. 5) the different groups of groundwater are clearly separated. Unconfined groundwaters form a group with mean

Fig. 4. Molar Mg/Ca ratios versus $\delta^{13}C$ of TDIC for Chalk groundwaters of the Paris Basin and the N German Basin.

NO_3 concentrations of 0.5 mmol/l and mean activities of 70 pmc. These are modern groundwaters with NO_3 input due to agricultural activity. Nitrate concentrations in deeper confined groundwaters with ^{14}C activities ranging from 3.9 to 40 pmc are near or below the detection limit. An intermediate group of groundwaters (Beynes, Prunay, St. Arnoult, St. Cheron) comes from zones near the border of confinement which would allow some mixing between recent groundwaters which have not undergone significant denitrification and older NO_3-free groundwaters.

Stable isotopes of water

First attempts to interpret stable isotope ratios of chalk groundwaters in terms of paleotemperature were undertaken by Smith *et al.* (1976) based on the "classical" equations of the study of Dansgaard (1964). Since then, new global and regional temperature dependence equations have been published with further studies on the Chalk (Edmunds *et al.*, 1987; Elliot, 1990).

Stable isotope ratios ($^{18}O/^{16}O$ and $^2H/^1H$) may reveal information about the climatic history of groundwater. Temperature effects may be masked by other isotope effects (Rozanski, 1985) and $\delta^{18}O$/ temperature relationships seem to be highly dependent on local conditions of condensation, vapour origin and mixing processes (Andrews, 1994). Estimations of recharge temperatures have therefore

to take into account regional climatic input functions.

For the Paris Basin Chalk we observe a fairly well defined $\delta^{18}O/\delta^2H$ relationship:

$$(\delta^2H = 9.12(\pm 0.91) \bullet \delta^{18}O + 17.58(\pm 6.74)$$

which is in reasonable agreement with world precipitation (Yurtsever and Gat, 1981) and regional precipitation (Dever *et al.*, 1990) which excludes significant ***evaporation*** of infiltrating waters. Compared with London Basin chalk groundwaters (Smith *et al.*, 1976; Edmunds *et al.*, 1987) the Paris Basin values are better correlated and show larger variations for $\delta^{18}O$ and δ^2H. Lägerdorf chalk samples lie on a poorly defined regression line with a lower slope and an evaporation effect on stable isotopes cannot be ruled out.

The large W–E extension of the study area in the Paris Basin (200 km) allows an estimation of the influence of the ***continental effect*** (Sonntag *et al.*, 1978) on the stable istotope composition of Chalk groundwaters. The observed W–E depletion (Fig. 6) of unconfined and peripherally confined groundwaters is $0.46 \pm 0.07‰/100$ km for $\delta^{18}O$ and $3.5 \pm 0.5‰/100$ km for δ^2H (r = 0.81, n = 20). This gradient is similar to the one observed for winter rainfalls at 10 European IAEA stations (Rozanski *et al.*, 1982) and higher than the gradient for summer rains. This observation is compatible with predominant groundwater recharge in winter (Vachier *et al.*, 1987). The continental effect is higher than the mean gradient defined for "recent"
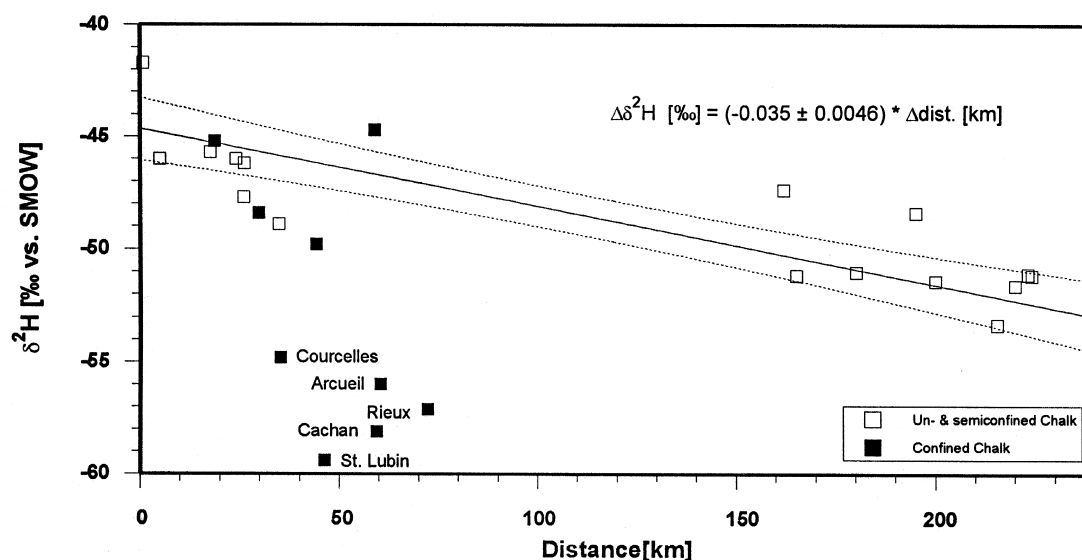

Fig. 6. Projection of δ^2H values of Paris Basin Chalk groundwaters on a W–E profile. The best fit (full line) and the error at 95% confidence level (dotted lines) have been calculated for all values with the exception of the isotopically depleted group of deep confined groundwaters in the western part of the basin. E–W depletion reflects a continentality effect, depletion of confined groundwaters a temperature effect.

European groundwaters of 1.7‰/100 km for δ^2H (Rozanski, 1985).

The significant isotopic depletion of some deeper confined Chalk groundwaters in the western part of the Paris Basin may be due to a lower *recharge temperature* at the time of infiltration. Compared with groundwaters from the recharge zone, this group is depleted by 10.5‰ with respect to ^{2}H and by 1.1‰ with respect to ^{18}O. Several studies of "paleowaters" in deep confined European aquifers (summarised by Rozanski, 1985) reveal a similar shift with a mean amplitude of 12.2‰ for ^{2}H and attribute it to a Pleistocene component in the deep groundwaters. The group of depleted groundwaters in the Paris Basin has ^{14}C activities < 10 pmc and ^{3}H concentrations < 2 TU with mean ^{14}C ages ranging from $7–13 \times 10^3$ a (Fig. 9). In attempting to relate the isotope shift to a change of surface air temperature we have to consider several independent isotope effects. Most of them (isotopic enrichment of the ocean surface as a source of water vapour, diffusion within the aquifer, Davidson and Airey, 1982, mixing with a modern fraction) would lead to an underestimation of the temperature shift whereas an increase of evaporation would have the opposite effect (Craig and Ingraham, 1994). It seems to be oversimplified to take into account global temperature relationships because of the high geographic variability of these equations (Andrews, 1994). We may consider as representative for the central Paris Basin the following relationship derived for 10 day means of rainfall events (1982–1985) in the Champagne region (Vachier *et al.*, 1987):

$$\delta^{18}O = 0.26\ T\ (°C) - 9.5‰$$

The temperature shift between recent and old groundwaters in the western Paris Basin would be at least 4.4°C. Taking into account an ocean surface isotopically enriched by 1.3‰ (^{18}O) (Duplessy *et al.*, 1980) would lead to values as high as 10°C which is compatible with the temperature shift at the Pleistocene–Holocene boundary (see discussion below). In the Lägerdorf quarries stable isotope ratios are closely related to salinity, depth of sampling and groundwater temperature. Deep groundwaters seem to be depleted in heavy isotopes which may indicate a temperature effect. Similar conclusions have been drawn for deep Tertiary aquifers in the North German Basin (Bauhus, 1988).

Noble gases

Several studies of deep confined European groundwaters have used the temperature dependence of inert gas solubilities to model paleo-recharge temperatures (Andrews and Lee, 1979;

Bath *et al.*, 1979; Rudolph *et al.*, 1984; Andrews *et al.*, 1985, 1987; Deak *et al.*, 1987; Edmunds *et al.*, 1987; Stute and Deak, 1989; Elliot, 1990; Rauber *et al.*, 1991; Stute *et al.*, 1992). Eighteen samples from 8 sites in the western part of the central Paris Basin have been analysed for their noble gas contents. Recharge temperatures have been calculated after correction for altitude and excess air (correction procedure in Elliot, 1990). Two samples, Arcueil(1) and St. Lubin(1), show signs of degassing and were not considered in the interpretation. The mean noble gas temperatures for the 3 sites adjacent to the recharge area (Prunay, St. Arnoult, Cheron) are close to the interannual mean of air temperature in the Paris region (11.4°C at Paris/Montsouris, 1900–1981). Recharge temperatures for deep confined groundwaters (Paris region, Vexin, Oise valley) are significantly lower by 3 to 9°C. Using ^{14}C ages as a first approximation of residence times it is possible to locate this shift between $8 \times 10^3–10^4$ a (Fig. 9). These data are compatible with various paleoclimatic studies of continental sediments in western Europe (Atkinson *et al.*, 1987; Guiot, 1987, 1990; Ponel and Coope, 1990; Rind *et al.*, 1986) which fix the last major temperature increase at the end of the Younger Dryas at 10^4 a BP. A predominant component in the deep confined Chalk groundwaters seems to have been recharged under periglacial conditions.

With noble gas concentrations and stable isotope ratios we dispose of two independent "thermometers": both parameters are in fact well correlated (Fig. 7). Their relationship can be described by the following linear equation:
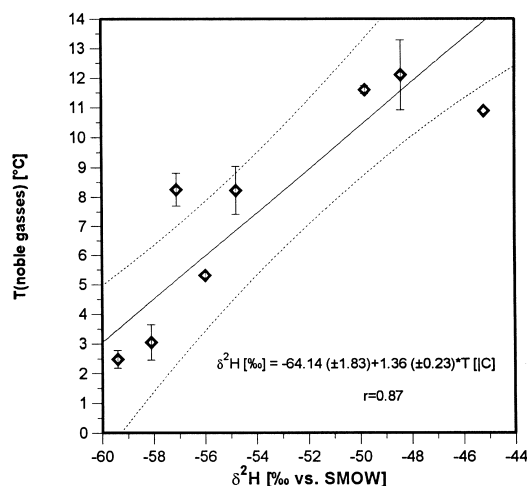

Fig. 7. Mean recharge temperatures calculated on the basis of noble gas concentrations of Chalk groundwaters in the western part of the Paris Basin plotted against δ^2H values. The best fit (full line) is represented together with the error at 95% confidence level (dotted lines).
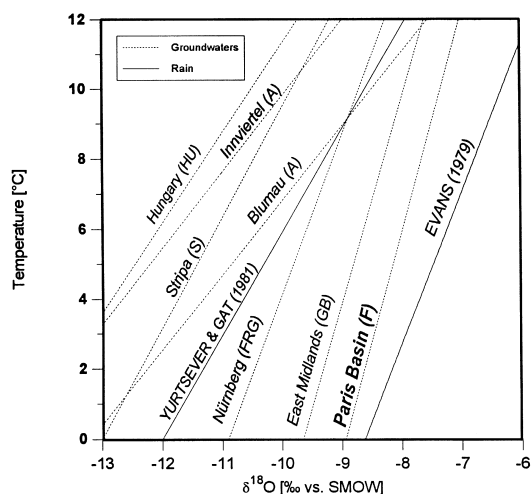
Fig. 8. Correlations between temperature (noble gas temperatures for groundwaters, atmospheric temperatures for rainfall) and $\delta^{18}O$ values for different sites in Europe: East Midlands (Triassic sandstones) after Andrews et al. (1985), Paris Basin Chalk (this study), Nürnberg, Germany (Keuper sandstones) after Rudolph et al. (1984), Blumau, Austria (clastic tertiary sediments) after Andrews et al. (1984), Innviertel, Austria (molasse) after Andrews et al. (1985), Stripa, Sweden (granites) after Andrews et al. (1987), Hungary after Deak et al. (1987). The precipitation lines have been fitted to data from IAEA stations in western Europe under oceanic influence (Groningen, Isfjord Radio, Lista, Reykjavik, Valentia after Evans et al., 1979) and from 91 IAEA stations (Yurtsever and Gat, 1981).

$$\delta^2H[\permil \ vs. \ SMOW] = -64.14(\pm 1.82)$$
$$+1.36(\pm 0.23) \cdot T[^\circ C](n = 8, \ r = 0.87)$$

The observed gradient $\Delta\delta^{18}O/\Delta T$ of 0.16 ($\pm$0.03) $\permil^\circ C^{-1}$ is quite close to the one measured for modern rainfall in the Champagne region (0.25 ($\pm$0.03) $\permil^\circ C^{-1}$, Dever et al., 1990). Temperature relationships of the same type have been obtained for rainfall and groundwater in western and central Europe (Fig. 8). There is a clear increase of $\Delta\delta^{18}O/\Delta T$ towards the interior of the continent. It can be noted that the value obtained for the Paris basin groundwater fits well in the general setting in Europe. It is similar to oceanic rainfall obtained for coastal stations by Evans et al. (1979) as well as that for groundwaters in the East Midlands of England (Andrews et al., 1985).

The Ne index indicating the amount of excess air (dissolved air bubbles from the unsaturated zone) reaches 1.5 for the old groundwaters compared with a value of 1.2 at the border of confinement. Wilson (1986) and Elliot (1990) observed a similar tendency in different British aquifer systems. This evolution (Fig. 9) may reflect a change of infiltration conditions due to a modification of the precipitation regime, of the physical structure of the unsaturated zone.

The α-decay of U an Th and their daughters in the solid phase is an important source of He in groundwater. The quantity of radiogenic He depends on the concentration of these radioelements in the rock matrix, on the porosity of the rock and on the residence time of groundwater in the aquifer. Radiogenic He production is predominant compared to atmospheric sources. For this reason, the He concentrations may not be used as a
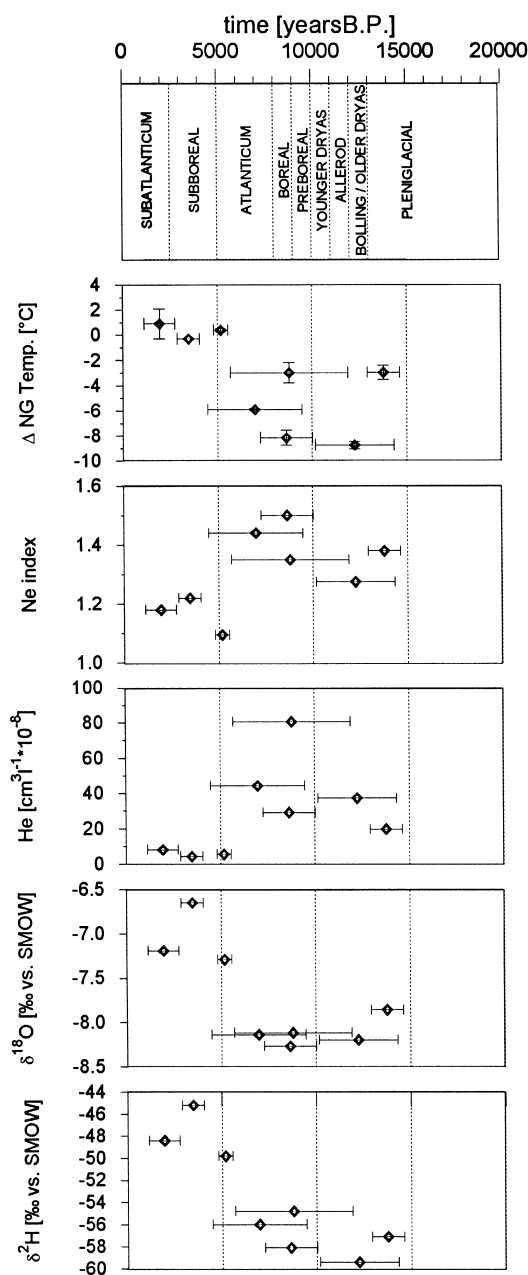

Fig. 9. Mean noble gas temperatures ($\pm 1\sigma$), Ne-index, He contents, $\delta^{18}O$ and δ^2H values of Western Paris Basin Chalk groundwaters plotted against radiocarbon "ages" ($\pm 1\sigma$).

paleoclimatic indicator. A quantitative estimation of groundwater residence time by means of He-contents would imply a distinction of *in situ* production in the aquifer and of He diffusion from deeper crustal or mantle sources based on He-isotope ratios. Only total He concentrations are disposable for the continental Chalk and they have to be interpreted in a qualitative way. Helium contents in the unconfined part of the aquifer are close to those expected for groundwaters in equilibrium with the atmosphere. The downgradient increase of He concentrations by a factor of 20 gives evidence of He diffusion or advection into the chalk groundwater, either from the chalk matrix itself or from the underlying formations. Recent investigations have proved the importance of He-flux in the deep aquifers of the Paris basin (e.g. Castro and Marty, 1994).

Helium concentrations in the chalk seem to be closely related to the residence time of groundwater estimated by radiocarbon dating (Fig. 9) and they allow the distinguishing of the two previously defined groups of groundwaters.

CONCLUSIONS

The geochemical character of Chalk groundwater in the Paris Basin and the N German Basin is closely related to residence time in the aquifer. Short term processes like ^{3}H decay and denitrification set time marks which allow recently recharged groundwater to be identified. Long term changes in the input function related to climatic evolution as well as low rate kinetics of water–rock interaction processes (incongruent dissolution) help to establish approximate residence times for old Chalk groundwaters. The combined use of different quantitative or semi-quantitative "dating tools" (cation ratios, δ^{13}C, radiocarbon activity; ^{3}H concentration, noble gas contents and stable isotope ratios) give a coherent image of the age structure within both investigated Chalk aquifers. Most groundwaters of the Paris Basin Chalk (at least the component available to pumping) have been recharged during the Holocene with an admixture of Pleistocene waters in the deep confined part of the aquifer. There is noble gas and stable isotope evidence for recharge during cooler periods since the last glacial maximum. In the Lägerdorf chalk a vertical stratification of the groundwater body in terms of age and chemical and isotopic characteristics can be seen. At depths of about 80 m we reach a zone of slow circulation and long term water–rock interaction with growing influence of brines derived from the underlying Permian salt.

Geochemical baseline conditions in the continental Chalk aquifer are very similar to those described for the London Basin which can be partly attributed to the geochemical and isotopic homogeneity of the European Chalk. Similar rock–water interaction mechanisms determine the concentrations of trace elements and the isotopic composition of dissolved inorganic C; the geochemical evolution tends to the same isotopic and chemical equilibrium values. Differences in the local and regional geological setting of the 3 sedimentary basins explain some particular hydrochemical features. The underlying Permian salt influences strongly the character of deep Chalk groundwaters in Northern Germany whereas in the Paris Basin salinity increase with depth is less important. Paleoclimatic evidence is clearer in the French Chalk than in the London Basin as both paleotemperature indicators, stable isotopes and noble gases give coherent results in the Paris Basin. In both cases "fossil" groundwaters have been encountered in the confined part of the Chalk aquifer, a result that must be taken into account for future exploitation of the groundwater resource.

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