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ENVIRONMENTAL ISOTOPE STUDY (^{14}C,^{13}C,^{18}O,D,NOBLE GASES) ON DEEP GROUNDWATER CIRCULATION SYSTEMS IN HUNGARY WITH REFERENCE TO PALEOCLIMATE

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ABSTRACT. We have studied environmental isotopes and noble gases in groundwater samples from various locations in the Great Hungarian Plain along two selected hydrogeological cross-sections of ca 100km. The ^{14}C groundwater ages were corrected hydrochemically and compared with age information derived from excess helium due to ^4He from α-decay of U and Th and their daughter nuclides within the aquifer and to He accumulation from the crustal (and mantle) He flux. In correcting the ^{14}C groundwater ages, we considered carbonate dissolution under open and closed system conditions in the infiltration areas. Non-radioactive reduction of the $^{14}C/^{12}C$ isotope ratio also plays an important role due to the addition of "dead" carbon species to groundwater along its subsurface pathway. High (corrected) ^{14}C ages, which fall into the last global cold period, are supported by significantly lower heavy stable isotope values as well as lower temperatures derived from the noble gases Ne, Ar, Kr and Xe.

INTRODUCTION

Experience in isotope dating of fresh groundwater pumped from deep, (semi-) confined, porous aquifer systems in various sediment basins of the globe has shown that the age of deep groundwaters from ca 100–1000m depth often ranges from a few thousand to several tens of thousands BP. Ages of this order are to be expected if the groundwater flow velocity is considered, relating the time scale to the length scale of groundwater circulation. The hydraulic conductivity of sediments pumped by deep wells ranges from $K_f = 10^{-6}$m/s (poor aquifer) to 10^{-4}m/s (good aquifer). Using 10^{-3} as typical for the hydraulic gradient Darcy velocities $v_f = 10^{-9}$ to 10^{-7}m/s equivalent to $v_f = 3*10^{-2}$ to 3m/y are to be expected. With $n = 0.1$ for the porosity these filter velocities correspond to distance velocities of $v = 0.3$ to 30m/y. Basin-wide groundwater flow over a length scale of some 10–>100km then gives a groundwater flow time (age) in the order of thousands of years.

Deep groundwater ages fall into the time span of ^{14}C dating, which still plays an important role in deep groundwater research. However, problems in obtaining reliable ages from ^{14}C activities of groundwater derive from the fact that the $^{14}C/^{12}C$ isotope ratio of the dissolved inorganic carbon (DIC = $H_2CO_3 + HCO_3^- + CO_3^{2-}$), expressed in percent modern carbon (pMC), is not affected only by ^{14}C decay as is assumed when simply relating the measured $^{14}C/^{12}C$ ratio of the sample (^{14}C content) to modern carbon by the law of radioactive decay.

$^{14}C/^{12}C$ in groundwater is (strongly) affected by various hydrochemical processes that go along with the chemical evolution of the carbonate system of groundwater. These chemical effects usually act in the same direction as does radioactive decay. Thus, uncorrected ^{14}C groundwater ages often appear too high. Isotope-geochemical models simulate the hydrochemical evolution of the ^{14}C/^{12}C isotope ratio of groundwater DIC along the subsurface pathway, in order to correct the measured ^{14}C groundwater data for non-radioactive effects and derive reasonable ^{14}C groundwater ages (for review, see Fritz & Fontes, 1980).

Groundwater ^{14}C is due to soil CO_2 in the infiltration area. If in the unsaturated soil zone solid carbonate is available for solution the maximum possible bicarbonate concentration is reached. Although reaction with the solid consumes CO_2 the partial pressure (pCO_2) controlling the solution process does not drop ("open" system). ^{14}C being restored in the gas phase by soil respiration reaches 100 pMC in the liquid. If, on the other hand, no solid carbonate is available in the unsaturated zone, the water can carry along only the CO_2 allowed by straightforward gas solution. Only this amount of dissolved CO_2 can then be used later to dissolve solid carbonate in the saturated zone. During the reaction the system is "closed," only some bicarbonate ($\approx$DIC) is formed, and the ^{14}C remains between 50 and 70 pMC.

DIC, δ^{13}C and pH of groundwater can be used to distinguish between carbonate dissolution under open and closed system conditions, respectively (Deines, Langmuir & Harmon, 1974). On this basis better information on the initial ^{14}C content is obtained, and more reliable ^{14}C ages can be calculated.

The ^{14}C/^{12}C ratio of the groundwater carbonate system may have been changed further by later carbonate dissolution under the influence of "dead" volcanic CO_2 and CO_2 from microbial oxidation of fossil organic carbon (Dörr, Sonntag & Regenberg, 1987) along the groundwater path. Where this reduction of the ^{14}C/^{12}C ratio is accompanied by an equivalent increase of DIC, *ie,* the absolute ^{14}C content = ^{14}C atoms/L water has remained constant, this isotope dilution effect can easily be corrected by the change of DIC. If, however, carbonate precipitation comes into play, complex hydrochemical correction models are needed.

The problems of ^{14}C groundwater dating make it necessary to search for independent checks of the ^{14}C ages evaluated. Fortunately, we can use the strong climatic change from the late Pleistocene cold period, with maximum glaciation at ca 18,000 BP, over the Holocene warm period to the present climatic conditions. The higher temperature contrast between the subtropical ocean and the mid-latitude continental areas in the Pleistocene cold period in comparison to the present is reflected by a steeper decrease of the stable isotopes δD and δ^{18}O in precipitation in the direction of atmospheric moisture flow. For this reason, deep groundwater of late Pleistocene age is isotopically depleted by ca -12‰ in δD and by -1.5‰ in δ^{18}O, in comparison to the isotopic composition of Holocene and modern groundwater at the same locality. Moreover, paleotemperature data can be obtained from atmospheric noble gases, Ne, Ar, Kr and Xe, dissolved in groundwater due to the temperature dependence of their physical solubility in water (Mazor, 1972).

The He content of deep groundwater frequently exceeds the expected level in equilibrium with atmospheric helium by orders of magnitude. This excess helium originates from the α-decay of U and Th and of their daughter nuclides in the aquifer material as well as from the He release of deeper rock layers of the earth's crust, which causes a diffusional flux of this crustal helium penetrating the various groundwater bodies before eventually entering the atmosphere. Thus, the amount of excess helium accumulated in groundwater bears information on the groundwater mean residence time and can be compared with corrected ^{14}C ages.

SAMPLE COLLECTION AND MEASUREMENT

For carbon isotope analysis the DIC in large groundwater samples of 50L each was converted into $BaCO_3$ with the conventional field chemical treatment. In the laboratory, the carbonate samples were transferred into pure CO_2 for radiometric ^{14}C analysis in large low-level (CO_2) proportional counter systems and for mass spectrometric measurement of $\delta^{13}C$ with an accuracy of ±0.1‰. Water samples of 250ml each were used for mass spectrometric determination of δD and $\delta^{18}O$ (accuracy ±1‰ and ±0.1‰, respectively) and for tritium analysis by low-level gas counting after electrolysis enrichment by a factor of 5 to 7. The tritium data of the groundwater are below the detection limit, which is 0.5 TU (2σ).

For noble gas analysis, well water was passed under high pressure and gas bubble control through a commercial copper tube, 8mm inner diameter and 1m long, with pinch-off clamps at its ends. The copper tube allows gastight sampling of ca 40ml water. In the laboratory this sample container was attached to a vacuum line system, where the water sample was quantitatively degassed. A 2% fraction of the extracted raw gas mixture was then passed through a hot titanium sponge (800°C) to get rid of all chemically active gas components. The remaining noble gases were then separated by adsorption on nitrogen-cooled activated charcoal followed by controlled heating and finally measured in a static mass spectrometer, 120mm radius and 60° deflection (type MM 1200, VG Instruments). The overall precision of the temperature data derived from Ar, Kr and Xe after air excess correction is ca ±0.5°C (1σ, Rudolph, Rath & Sonntag, 1984).

AREA OF INVESTIGATION

The sedimentary basin of the Great Hungarian Plain (GHP) in the eastern part of Hungary (Fig 1) is up to several thousand meters deep. Its sediments were formed in the late Tertiary and Quaternary. Two large groundwater flow systems can be distinguished: an intermediate flow system through Quaternary (Q) layers and a regional system through underlying Pliocene (P_2) layers with semi-permeable Pliocene sediments (P_3) as confining beds in between. The geology and hydrogeology are described by Erdélyi (1976). Figure 1 shows groundwater sampling sites along two hydrogeological cross-sections presented in Figures 2 and 3. Groundsurface topography and hydraulic head contour lines of cross-section C-A-B indicate large-scale groundwater flow from the recharge area marked by A to the discharge areas B and C (Fig 2). Cross-section DC illustrates the conditions of the regional deep groundwater flow through the permeable Pliocene sediments P_2 from the infiltration area at D to C, where discharge occurs by deep groundwater ascent through the confining layers P_3 and by mixing with the groundwater in the Quaternary sediments above.

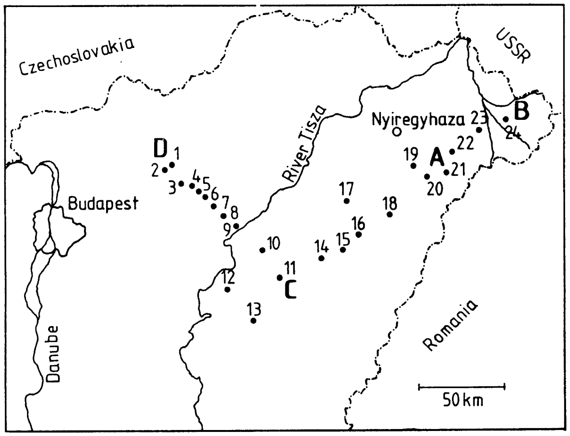

Fig 1. Deep groundwater sampling sites along two cross-sections in the Great Hungarian Plain

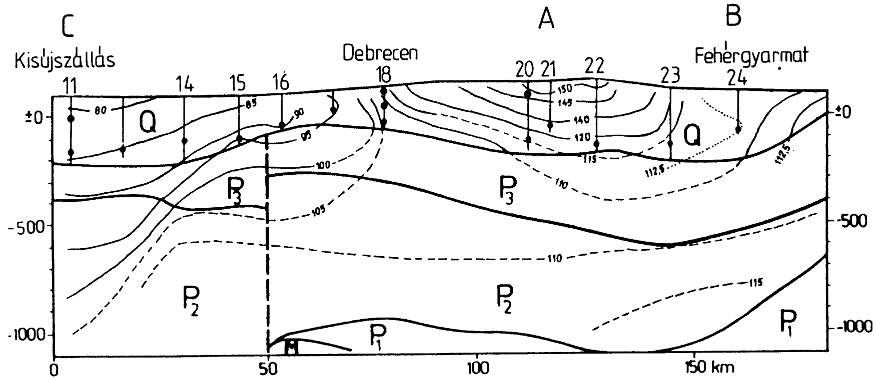

Fig 2. Hydrogeologic cross-section CAB with hydraulic head contour lines (in meters asl) and well positions in the Quaternary groundwater flow system (Q). P_2 = Middle Pliocene flow system, P_3 = confining beds (Upper Pliocene), P_1 = Lower Pliocene, M = Miocene

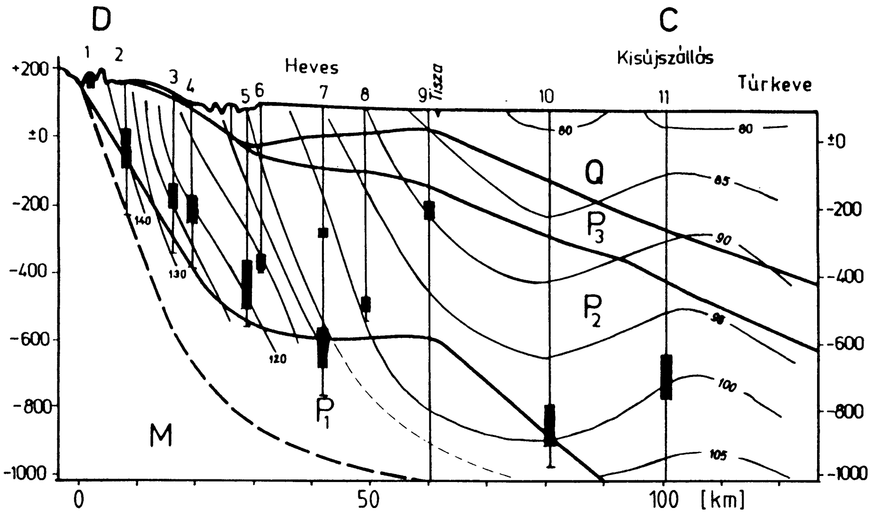

Fig 3. Hydrogeologic cross-section DC with hydraulic head contour lines and well positions in the Pliocene flow system (symbols same as Fig 2)

RESULTS AND DISCUSSION

Quaternary Flow System (CAB)

The isotope, noble gas and relevant hydrochemical data of the groundwaters sampled along cross-section CAB are listed in Table 1. Starting with recharge area A, $\delta^{13}C$ and DIC can be interpreted as resulting from carbonate dissolution under open as well as closed-system conditions. Assuming $\delta^{13}C_c = 0$ to $+2‰$ for the soil carbonate present, these groundwater data can be matched with $\delta^{13}C_g = -23$ to $-25‰$ for the gaseous CO_2 of ca 7–9% partial pressure in the soil air as far as closed-system conditions are concerned (Deines, Langmuir & Harmon, 1974; Garrels & Christ, 1965). For open-system dissolution, $\delta^{13}C_g = -22‰$ and 2–3% CO_2 partial pressure are assumed. As mentioned above, an initial ^{14}C content of $A_o = 100$ pMC is to be expected for open systems, whereas values ranging from 54–62 pMC were calculated by means of Pearson's (1965) $\delta^{13}C$ correction model for the closed system approach.

^{14}C groundwater ages obtained by deriving the measured ^{14}C contents even from these lower initial values seem to be too high, compared with age data obtained from excess helium in groundwater. This follows from Figure 4, which shows the He_{ex} data *vs* ^{14}C ages calculated for open- and closed-system conditions. The straight lines marked by 1 to 3 represent He_{ex} exclusively due to U and Th decay in the aquifer accumulated over time (age). The equivalent He accumulation rates A, noted in the figure caption, were derived from U = 1.3 ± 0.4ppm and Th = 12 ± 3ppm as average values for the U and Th content of 39 sediment samples (Deák *et al*, 1987) and from 0.2 (line 1) and 0.3 (line 2) as estimates for total porosity. Line 3 is based on the lowest

TABLE 1

Q – flow system

Sample no.	Location	Filter depth (m)	δD (‰)	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)	^{14}C (pMC)	A_o closed (pMC)	^{14}C age system (yr)	He age (yr)	Dilution factor	^{14}C age (yr BP)	HCO_3^- (mg/l)	CO_2 (mg/l)	Cl^- (mg/l)	Ca+Mg (meq/l)	Na+Ka (meq/l)	DIC (mmol/l)
11.1	Kisújszállás	93–106	−79.3	−10.6	−19.4	1.1±0.2	61			0.34	24,300	780	58.0	37.0	2.6	11.2	14.1
11.2	Kisújszállás	239–257	−78.5	−10.5	−29.0	2.1±0.3	61			0.28	17,300	976	56.1	43.3	2.1	15.1	17.3
12.1	Törökszentmiklós	239–281	−88.5	−12.1	−19.3	<0.5	61			0.26	>28,600	1024	65.8	15.0	3.1	14.1	18.3
12.2	Törökszentmiklós	390–405	−83.7	−11.6	−25.4	0.5±0.2	61			0.24	27,900	1195	37.0	30.2	2.6	17.8	20.4
13.1	Mezötúr	161–170	−87.1	−12.0	−23.4	<0.4	61			0.28	>31,000	1040					17.1
13.2	Mezötúr	492–500	−83.2	−11.6	−23.6	<0.8	61			0.26	>24,700	1134		42.3	1.2	18.6	18.6
14	Püspökladány	192–215	−83.3	−10.8	−8.7	1.5±0.5	61			0.55	25,700	510	20.0	24.0	1.3	7.7	8.8
15	Kaba	182–209	−82.0	−10.5	−10.3	5.0±0.7	61			0.56	15,900	512	4.1	37.6	1.5	8.0	8.5
16	Hajdúszobozló	120–129	−83.2	−11.0	−5.7	4.3±0.3	61			0.49	16,000	549	31.4	43.9	2.2	8.0	9.7
17	Balmazújváros	85–98	−79.6	−11.2	−15.7	1.0±0.3	61			0.62	30,000	447	21.3	7.9	3.8	3.8	7.8
18.1	Debrecen	25–49	−66.1	−9.1	−10.0	42.5±0.3	61	2930	<940	0.64	0	414	44.4	7.7	5.5	1.5	7.8
18.2	Debrecen	70–92	−72.4	−10.0	−15.2	20.0±0.3	60.8	9200	<6880	0.64	5500	366	36.2	17.0	4.4	2.1	6.8
18.3	Debrecen	138–181	−69.2	−9.8	−15.1	19.0±0.3	60.4	9570	<52200	0.64	5880	390	30.6	7.5	5.7	0.9	7.1
19	Geszteréd		−66.7	−9.8	−15.6	36.2±0.5	62.4	4500	<1250	0.64	810	408	43.6	12.6	6.0	1.1	7.7
20.1	Nyiradony	244–254	−69.6	−9.9	−15.3	23.6±0.3	61.2	7880	<625	0.64	4190	338	36.0	4.3	5.9	0	6.4
20.2	Nyiradony	55–61	−67.8	−9.6	−12.8	24.6±0.2	59.2	7260	<1880	0.64	3570	451	43.0	35.0			8.4
21	Nyirlugos	110–175	−68.0	−9.7	−14.5	44.0±0.4	62.0	2840	<940	0.64	0	457	22.6	14.7	7.3	0.6	8.0
22	Nyirbátor	297–313	−69.1	−9.9	−12.5	21.1±0.8	54.0	7770	<20900	1	7770	155	6.0	10.0	0.8	2.0	2.7
23	Máészalka	226–251	−73.9	−10.2	−12.8	17.1±0.9	51.2	9070	<14400	1	9070						
24	Fehérgyarmat	165–189	−89.4	−11.7	−15.5	8.1±0.2	62.0	16800	<64100	0.64	13,140	396	32.3	11.2	3.5	3.3	7.2

TABLE 1 (cont'd)

Sample no.	Noble gas conc (cm^3 STP/g) He · 10^8	Ne · 10^7	Ar · 10^4	Kr · 10^8	Xe · 10^9	He excess [cm^3 STP/g] · 10^8	Air excess [cm^3 STP/g] · 10^3	Noble gas temperature (°C) Ne	Ar	Kr	Xe
11.1	905	2.05	3.49	8.5	12.7	900	0.6	12.3	14.5	12.2	10.3
11.2	1280	2.70	4.10	9.5	13.7	1270	3.9	9.7	10.7	9.6	8.7
12.1	214	2.60	4.50	10.6	15.1	208	2.9	5.6	5.6	5.5	5.9
12.2	958	2.43	4.29	10.2	14.2	952	2.1	6.9	6.8	6.6	7.4
13.1	377	2.60	4.59	10.5	15.1	371	2.9	5.7	4.7	6.1	6.3
13.2	819	2.63	4.54	10.5	15.1	813	3.1	5.6	5.3	5.7	5.9
14	1050	2.19	4.34	10.6	15.4	1040	0.6	4.8	5.0	4.6	4.9
15	1030	2.53	4.69	11.2	16.4	1030	2.2	3.4	3.2	3.3	3.7
16	1390	2.26	4.29	10.1	14.6	1390	1.1	6.3	5.9	6.5	6.5
17	289	2.62	4.31	10.0	14.0	282	3.3	7.8	7.7	7.4	8.1
18.1	5.3	2.14	3.87	9.0	13.4	0.3	0.9	9.7	10.0	10.4	8.8
18.2	7.7	2.31	3.98	9.1	12.8	2.2	1.9	10.2	9.8	10.4	10.4
18.3	23.4	2.72	4.31	9.3	12.6	16.7	4.1	10.1	8.5	10.5	11.3
19	7.6	2.90	4.31	9.6	12.8	0.4	5.0	10.1	9.5	9.9	11.1
20.1	4.9	2.12	3.79	8.8	12.4	<0.2	0.9	11.1	11.0	11.2	11.1
20.2	7.5	2.80	4.21	9.4	13.3	0.6	4.5	10.1	10.1	10.3	9.8
21	7.8	2.99	4.15	9.3	12.7	0.3	5.7	11.6	12.1	11.4	11.4
22	13.2	2.63	4.12	9.3	12.7	6.7	3.6	10.4	10.1	10.2	10.9
23	10.6	2.47	4.07	9.3	13.0	4.6	2.7	9.9	9.7	10.0	10.1
24	27.7	2.64	4.63	10.8	15.7	20.5	3.0	4.7	4.4	4.9	4.9
	±3.4%	±2.1%	±1.7%	±1.6%	±1.4%	±(0.05+3.4%)	±0.3		±0.5		

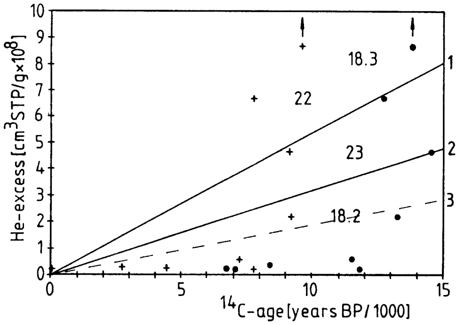

Fig 4. Excess helium in groundwater from the Quaternary flow system *vs* uncorrected ^{14}C ages based on initial ^{14}C content as expected for carbonate dissolution under open (+) and closed (•) system conditions. Lines 1 to 3 represent accumulated He_{ex} due to *in-situ* He production. The *in-situ* He accumulation rate $A_1 = 5.4*10^{-12}$ cc He STP/(g H_2O yr) (1) was obtained from [U] = 1.3ppm and [Th] = 12ppm for average values of the U and Th content of 39 sediment samples and n = 0.2, porosity. The accumulation rate $A_2 = 3.2*10^{-12}$ cc STP/(g*yr) (2) is based on the same numbers for U and Th, but on porosity n = 0.3. $A_3 = 1.9*10^{-12}$ results from the lowest U and Th content found and n = 0.3.

measured U and Th contents and the higher porosity values. The "*in-situ*" He groundwater ages $T_{He} = He_{ex}/A$ in Table 1 were calculated with the He_{ex} accumulation rate A_2 of line 2, which is considered the most probable. These He ages are upper limits for real groundwater ages, because the experimental He_{ex} may have a considerable crustal flux component. Crustal He seems to be present in groundwaters No. 18.3, 22 and 23 as shown by the data points above line 2 (Fig 4). These water samples were pumped from layers close to the base of the Quaternary aquifer system, where the diffusional flux of crustal helium is highest. The data points of samples No. 18.1, 18.2, 19, 20.1, 20.2 and 21 are located below line 2, which suggests that the ^{14}C ages based on the above-mentioned initial values for open- and closed-system conditions are obviously too high. This age discrepancy can be solved by proper correction factors, which account for non-radioactive decrease of the $^{14}C/^{12}C$ in groundwater due to additional carbonate dissolution in the aquifer by dead CO_2. In this case, these are derived from microbial oxidation of fossil organic carbon in the sediments as suggested by the low ^{13}C content of the groundwater, which cannot be separated by $\delta^{13}C$ from the carbonate dissolution due to CO_2 of atmospheric origin. This age comparison suggests "isotope dilution factors" of 0.64 and 0.39 as the average values for preceding carbonate hardness contribution under closed- and open-system conditions, respectively. The addition of dead carbon to the carbonate system of the groundwater is also indicated by the DIC data, which seem to be too high to be entirely related to carbonate dissolution by carbonic acid from modern soil CO_2. This because the CO_2 content of soil air needed to explain these data are by about half an order of magnitude higher than experimental soil CO_2 data from various soil sites (Dörr & Münnich, 1987).

The corrected ^{14}C groundwater ages in Table 1 are based on initial ^{14}C values A_o derived from the $\delta^{13}C$ data for closed-system conditions. For samples 18.1–21 from infiltration area A, and 22–24 from flow section AB, correction for isotope dilution was made using the above average 0.64 correction factor. Although crustal helium in the He_{ex} of samples 18.3, 22–23 (Fig 4) would yield apparent *in-situ* He ages considerably higher than the uncorrected ^{14}C ages with no need for any dilution correction, the same correction factor was applied because of the uniform DIC values (except sample 22!).

The He_{ex} in samples 11.1–17 from flow section AC is so high that it must be entirely due to He from the crustal flux. Thus, we corrected the ^{14}C groundwater ages by means of the DIC increase along this flow section. The isotope dilution factors in Table 1 are composed of 0.64 as mean dilution factor for groundwater from the infiltration area and an additional one, which is simply the quotient of DIC = 7.5 mmoles/l as the mean value for the infiltration area and DIC of the individual groundwater sample. The average initial content in the infiltration area, $A_o = 61$ pMC is used as initial content of samples 11.1–17. The very low $\delta^{13}C$-values in C (11.1–13.2, down to –29‰) point to the influence of C due to CH_4 oxidation. The corresponding increase of hardness is included in our simple chemical correction.

Pliocene Flow System (DC Section)

The hydraulic head contour lines in cross-section DC (Fig 3) indicate deep groundwater flow through permeable Pliocene sediments (P_2) from the recharge area D at the foot of the northern mountains to the lowest part of the Great Hungarian Plain (GHP), where discharge occurs by groundwater ascent through the semi-permeable (leaky) confining beds (P_3) and mixing with the groundwater of the Quaternary flow system above.

The hydrochemical data of the deep groundwater sampled along DC show a continuous increase of $Na^+ + K^+$, HCO_3^- and thus of DIC in flow direction, whereas $Ca^{2+} + Mg^{2+}$ (Table 2) are decreasing. This signals cation exchange, Ca(Mg) *vs* Na(K), along the groundwater pathway (Deák *et al*, 1987), which may go along with carbonate dissolution within the aquifer (Pearson & Swarzenki, 1974) and thus with dilution of the $^{14}C/^{12}C$ isotope ratio in the DIC due to addition of dead carbon of $\delta^{13}C = 2.4$‰ (see previous section). The linear correlation between $\delta^{13}C$ and 1/DIC (Fig 5) indicates that the carbonate dissolution along the subsurface pathway is influenced by isotopically heavy carbon due to the cation-exchange effect; also eventually due to CO_2 of volcanic origin or hydrothermal destruction of solid carbonates (Miocene volcanism in Hungary), in contrast with light CO_2 from fossil organic matter of the Quaternary flow system. This correlation suggests DIC = 4.8mmoles/l for sample 1 at the beginning of the deep groundwater flow (Fig 5, by extrapolation, there are no chemical data available for sample 1). The comparatively high ^{14}C content and the low $\delta^{13}C$ there makes us think that ^{14}C has entered the groundwater predominantly by carbonate dissolution under open-system conditions, where a CO_2 partial pressure of 0.6% ($\delta^{13}C_g = -24$‰) were needed to form the DIC value of 4.8mmoles/l (Garrels & Christ, 1965). Apart from samples 1, 2.1 and 2.2, the excess He in all other Pliocene groundwater is too high for *in-situ* origin and thus has to be interpreted as He accumulated from the crustal flux (for model, see below). Correction of the ^{14}C groundwater ages for the isotope dilution effect, therefore,

TABLE 2

P_2 flow system

Sample no.	Location	Filter depth (m)	Depth of basal P_2 (m)	Distance from recharge area (m)	δD (‰)	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)	^{14}C (pMC)	Dilution factor	^{14}C age (yr BP)	HCO_3^- (mg/l)	CO_2 (mg/l)	Cl^- (mg/l)	Ca+Mg (meq/l)	Na+Ka (meq/l)	DIC (mmol/l)
1	Abasár (D)	11–19	102	1600	–67.3	–9.58	–16.2	77.0±0.7	1	2160						
2.1	Gyöngyös	140–194	245	7900	–64.4	–9.42	–15.3	49.7±0.9	.94	5280	244	49.3	9.5	4.2	0.1	5.1
2.2	Gyöngyös	191–239	245	7900	–62.1	–9.46	–13.8	37.7±0.5	.91	7250	280	29.4	8.1	3.8	1.0	5.3
3	Karácsond	274–330	408	17400	–81.9	–11.45	–13.7	5.7±0.7	.91	22900	220		69	3.0	2.6	>3.6
4	Nagyfüged	282–332	490	25200	–88.2	–12.04	–11.3	8.8±0.7	.77	18000						(6.2)
5	Tarnaméra	435–594	633	30000	–81.7	–11.42	–9.9	3.0±0.6	.68	25800	403	22.6	6.4	1.8	5.0	7.1
6	Boconád	446–467	653	33100	–82.9	–11.24	–10.7	1.9±0.3	.59	28500	414	56.8	10.5	2.3	4.8	8.1
7.1	Heves	360–387	673	42000	–93.1	–12.36										
7.2	Heves	674–772	673	42000	–80.1	–11.21	–5.2	1.2±0.5	.48	30600	573	20.7	10.0	1.1	8.5	9.9
8	Hevesvezekény	541–568	673	48900	–90.9	–12.05										
9	Kisköre	291–299	673	60400	–88.3	–11.95										
10	Kunhegyes	886–991			–84.7	–11.09										
11	Kisúszállás (C)	720–850			–75.6	–8.00										

TABLE 2 (cont'd)

Sample no.	Noble gas conc (cm^3 STP/g)					He excess [cm^3 STP/g] $\cdot 10^8$	Air excess [cm^3 STP/g] $\cdot 10^3$	Noble gas temperature (°C)			
	He $\cdot 10^8$	Ne $\cdot 10^7$	Ar $\cdot 10^4$	Kr $\cdot 10^8$	Xe $\cdot 10^9$			Ne	Ar	Kr	Xe
1	6.0	2.22	3.64	8.4	11.6	0.7	1.7	13.4	13.7	13.2	13.4
2.1	8.7	2.53	4.08	9.3	13.5	2.6	3.0	9.6	9.9	9.9	9.1
2.2	6.7	2.25	4.12	9.9	14.6	1.4	1.2	7.2	7.8	7.2	6.6
3	194	2.48	4.37	10.4	14.9	190	2.3	6.2	6.2	6.0	6.2
4	22.4	3.33	5.28	12.0	16.8	14.0	6.5	2.6	1.7	2.6	3.5
5	100	2.61	4.56	10.3	14.6	94	3.0	5.7	5.0	5.5	6.5
6	50.1	2.62		10.7	14.6	44	3.1	6.0		5.1	6.8
7.1	28.6	2.58	4.75	10.8	15.6	22.5	2.6	4.3	3.1	4.8	5.0
7.2	170	2.51	4.56	10.7	15.0	164	2.4	5.1	4.5	4.8	6.0
8	41.6	2.49	4.66	10.9	15.5	36	2.1	4.3	3.4	4.3	5.1
9	75.3	2.47	4.21	9.9	14.2	69	2.4	7.6	7.9	7.5	7.5
	±3.4%	±2.1%	±1.7%	±1.6%	±1.4%	±(0.05+3.4%)	±0.3	±0.5			

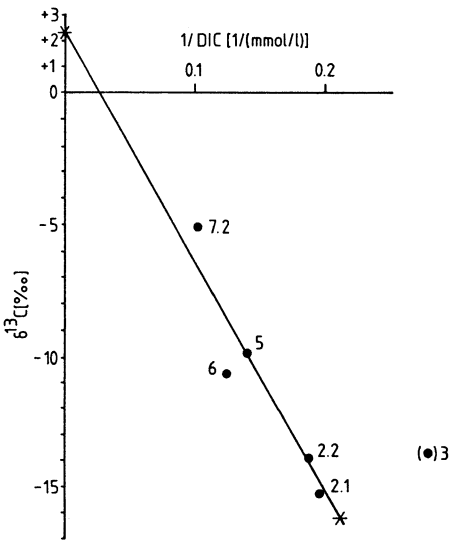

Fig 5. $\delta^{13}C$ – 1/DIC relationship for groundwater from the Pliocene flow system.
mixing line; numbers identify the groundwater samples
* = endmembers of the

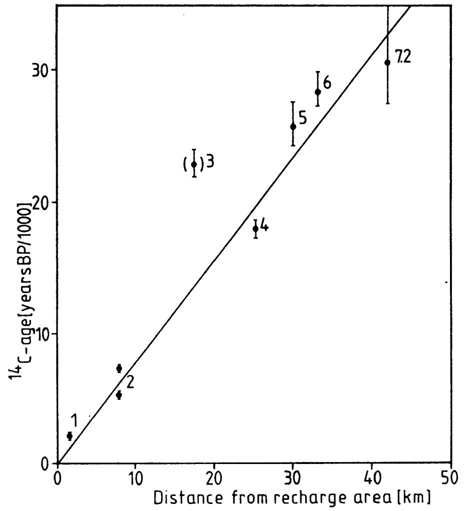

Fig 6. Corrected ^{14}C ages of groundwater from the Pliocene flow system *vs* distance from the recharge area. The slope of the linear regression line gives 1.3m/yr for the mean groundwater flow velocity across the entire flow system.

was made with 4.8/DIC as the correction factor, where 4.8mmoles/l is taken to be representative for DIC of groundwater in the infiltration area.

The corrected ^{14}C ages (Table 2) show a linear increase with distance from recharge area D (Fig 6). The slope of this straight line gives a constant groundwater distance velocity of 1.3m/yr over the whole pathway. The fact that sample 3 does not fit the general data trend might either be due to a hydrogeologic problem, eg, hydrochemistry (high Cl^-), or to wrong information about the filter depth.

Figure 7 shows the He_{ex} data *vs* flow distance. The curves represent estimates of *in-situ*-produced He accumulated over the flow time, which is the distance divided by the velocity derived from ^{14}C data. These estimates are based on the same *in-situ* He production rate, but on different numbers for the porosity of the Pliocene sediments reported by Deák *et al* (1987). Data points above these lines are considered as an indication of additional He accumulated from the crustal flux. The fact that the He_{ex} data points of the groundwater close to the infiltration area (samples 1, 2.1, 2.2) fall on these lines or even below suggests that the crustal flux component is negligibly small here. This because the downward directed groundwater flow component supresses the upward directed diffusion flux of crustal He (diffusion counteradvection problem). Crustal He, however, is accumulated along this section of the flow path, where the deep groundwater flow is quasi-horizontal or even upwards directed (in the discharge area).

For the horizontal flow, the He_{ex} evolution along the flow path (time) was simulated with Torgersen's model (Torgersen & Ivey, 1985). This

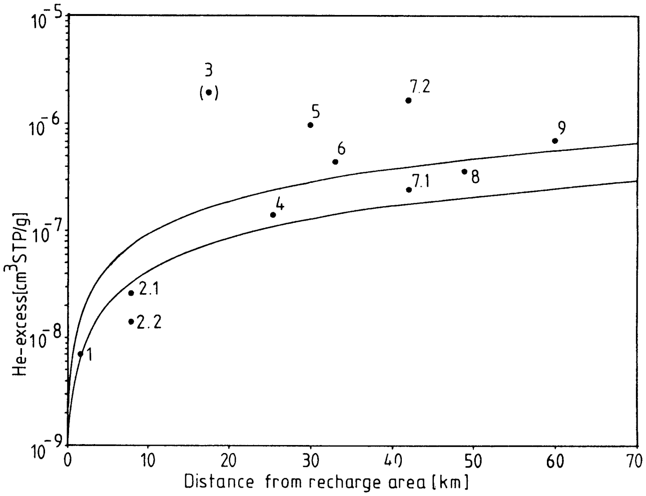

Fig 7. Excess He in groundwater from the Pliocene system *vs* distance from the recharge area. The curves represent estimates of the *in-situ*-produced He_{ex} component accumulated over the flow time (groundwater age), which is given by the distance divided by the mean flow velocity of 1.3m/yr. The *in-situ* accumulation rates $A = 5.4*10^{-12}$ cc STP/(g*yr) of the lower curve and $1.2*10^{-11}$ cc STP/(g*yr) for the upper are due to U = 1.3ppm and Th = 12ppm as mean values for the U and Th concentration in the sediments and to average porosities of n = 0.2 and 0.1.

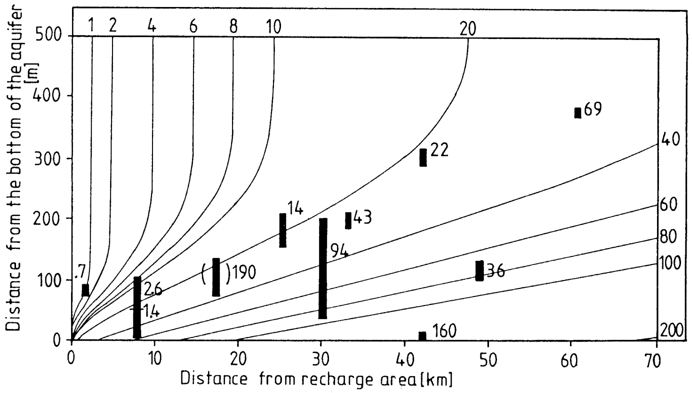

Fig 8. Isoline presentation of He_{ex} estimates for horizontal groundwater flow together with the He_{ex} data and positions of the well filters in the Pliocene flow system. All concentrations are given in terms of 10^{-8} cc He STP/g*H_2O. For the He_{ex} estimates, the following were used: *In-situ* accumulation rate $A = 5.4*10^{-12}$ cc STP/(g*yr), crustal He flux at the lower boundary $F = 8.4*10^{-4}$ cc STP/(m^2*yr) and an average groundwater flow velocity $v = 1.3$m/yr and a transverse dispersion coefficient $D = 0.4m^2/yr$.

assumed constant thickness $H = 500$m and porosity $n = 0.2$ of the Pliocene aquifer and of constant flow velocity $v = 1.3$m/yr throughout the system and an *in-situ* accumulation rate $A = 5.4*10^{-12}$ cc He STP/(g H_2O yr). The best fit of the He_{ex} data presented in Figure 8 was obtained with the following: Diffusion flux of crustal He at the aquifer base $F = 8.4*10^{-4}$ cc He STP/m^2 yr and $D = 0.4m^2/yr$ for the coefficient of transverse dispersion, which is also taken as to be constant over the system. (Samples 2.1, 2.2 and 3 were omitted for this calculation.) Figure 8 shows the isoline presentation of the spatial variation of the calculated He_{ex} across the idealized rectangular cross-section together with the observed He_{ex} data and the position of the well filters. The number for the crustal He flux used is within the range of published data, $1.3*10^{-4}$ to $4.7*10^{-2}$ cc He STP/m^2 yr (Mamyrin & Tolstikhin, 1984). It is, however, considerably lower than that of $3.62*10^{-2}$ cc He STP/m^2 yr , which Torgersen & Ivey (1985) used for their model estimate of He_{ex} in the Jurassic aquifer system of the Great Artesian Basin in Australia. Our lower number might be due to the comparatively low geologic age (Tertiary) of the sediment of the Great Hungarian Basin, in which crustal He flow by molecular diffusion is still less developed as in the case of geologically older sediment basins. The number for the transverse dispersion coefficient is also small, since it exceeds the one expected for molecular diffusion by a factor of only 2.7 (coefficient of molecular diffusion in water (30°C): $D_{He} = 0.25m^2/a$ (Jähne, Heinz & Dietrich, 1987); the dispersion coefficient is referred to the water phase; the tortuosity has to be taken into account: $D_{He}^* = 0.25*0.6 = 0.15\ m^2/a$). This low transverse flow dispersion is presumably caused by a layered structure of the Pliocene aquifer in the form of an alternating sequence of permeable sand and poorly permeable clay layers some meters thick each, for which hydrogeologic evidence exists.

NOBLE GAS TEMPERATURES AND PALEOCLIMATE

Groundwater of late Pleistocene age appears as isotopically depleted in δD and $\delta^{18}O$ in comparison to local Holocene and modern groundwater. This depletion can be attributed to considerably lower temperatures prevailing in the last Ice Age. Reasonable paleotemperature data of an accuracy of ±0.5°C can be derived from the noble gases Ne, Ar, Kr and Xe dissolved in groundwater (Mazor, 1972) after proper correction for the noble-gas component of excess air (Heaton & Vogel, 1981) by means of Ne (Rudolph, Rath & Sonntag, 1984). These noble gas temperatures correspond to the annual mean soil temperature, which existed in the infiltration area close to the groundwater table when the investigated groundwater was formed.

The heavy stable isotope and noble gas temperature data in Tables 1 and 2 suggest that indeed δD and $\delta^{18}O$ and noble gas temperatures are linearly correlated (Deák *et al,* 1987). Figure 9 shows the noble gas temperatures *vs* the corrected ^{14}C groundwater ages. Data from location 11 are omitted here because it is in discharge area C where high mixing of groundwater components of different ages may occur. The variation of the mean annual temperature over the past 35,000 yr BP agrees surprisingly well with current paleoclimatic ideas.

This is particularly true for the temperature minimum at the time of maximum glaciation, for which Frenzel (1980) reported temperatures 5–13°C lower than at present. For the "Stillfried B" period (Fig 9) he expects 5°C lower temperatures for east Austria. δD and $\delta^{18}O$ show similar time variations, but with considerably higher scatter. Although, as shown here, deep groundwater bears valuable paleoclimatic information, problems do exist. Even when methodological problems of radioactive groundwater dating are solved, there are still problems of interpretation.

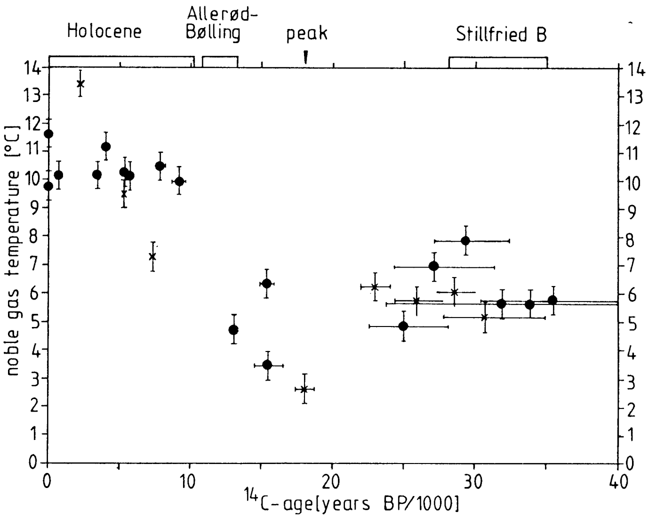

Fig 9. Noble gas temperatures *vs* corrected ^{14}C groundwater ages for the Quaternary flow system (•) and the Pliocene system (×).

If the groundwater samples are considered to have passed as a whole along a definite subsurface flow line ("piston flow"), the apparent age represents the transition time and thus the real groundwater age. If the groundwater samples consist of various components of widely different flow times due to strong flow dispersion, the apparent age has to be transformed into a reasonable number for the mean groundwater age by means of suitable tracer flow model. This is the reason why paleoclimatic data obtained from deep groundwater have a fairly limited time (age) resolution. That noble gas temperatures as well as stable isotopes δD and $\delta^{18}O$ *vs* the apparent ^{14}C groundwater ages (Fig 9) are reasonable indicators of paleoclimatic variation, suggests applying the piston flow model to the deep groundwater flow in the Great Hungarian Plain. This approach is supported by the fairly small number for the transverse dispersion coefficient, if we assume that the longitudinal coefficient does not exceed the hundred-fold of the transverse coefficient.

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