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Infiltration of river water to a shallow aquifer investigated with ^{3}H/^{3}He, noble gases and CFCs

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Abstract

Noble gas isotopes (^{3}He, ^{4}He, Ne, Ar, Kr, Xe), tritium (^{3}H), chlorofluorocarbons (CFCs) and dissolved oxygen (O_2) were seasonally measured in a small groundwater system recharged by infiltration of river water at Linsental, northeastern Switzerland. All Groundwater samples contained an excess of atmospheric noble gases (‘excess air’) usually with an elemental composition equal to air. The concentrations of atmospheric noble gases in the groundwater were used to calculate the excess air component and the water temperature at recharge. The noble gas temperatures (NGTs) in the boreholes close to the river vary seasonally, however, the average NGT of all samples lies close to the mean annual temperature of the river water. Groundwater ages were calculated using the tritium/helium-3 (^{3}H/^{3}He) dating method. The water ages of the samples obtained near the river depend on the amount of recently infiltrated river water and are young during times of active river discharge. In contrast, the mean water age of about 3 years of the deep aquifer remained nearly constant over the sampling period. The observed CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) concentrations are significantly higher than the atmospheric equilibrium concentrations and therefore CFCs do not provide any direct information on the residence time of the groundwater. Nevertheless, the CFC excess in the groundwater shows a linear increase with the ^{3}H/^{3}He age. Additionally, both accumulation of radiogenic He ($^4He_{rad}$) and O_2 consumption are strongly correlated with residence time. All these correlations can be interpreted either in terms of mixing of recently infiltrated river water with older groundwater or in terms of accumulation/consumption rates. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: River infiltration; Noble gases; Tritium–helium-3 dating; Chlorofluorocarbon; Recharge temperature; Oxygen

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1. Introduction

Young groundwater is commonly used for drinking water, e.g. over 80% of Switzerland’s potable water resources come from groundwater (Hartmann and Michel, 1992). In alpine and prealpine countries a significant amount of this young groundwater is recharged by infiltration of river water. However, the knowledge about the time scale on which a particular groundwater is renewed is often poor. This situation may lead to mis-management and encourages the over-utilization of the groundwater as fresh water resource. Furthermore, if residence times are unknown, it is difficult to evaluate the potential effects of contamination and to develop strategies to protect the quality of the groundwater.

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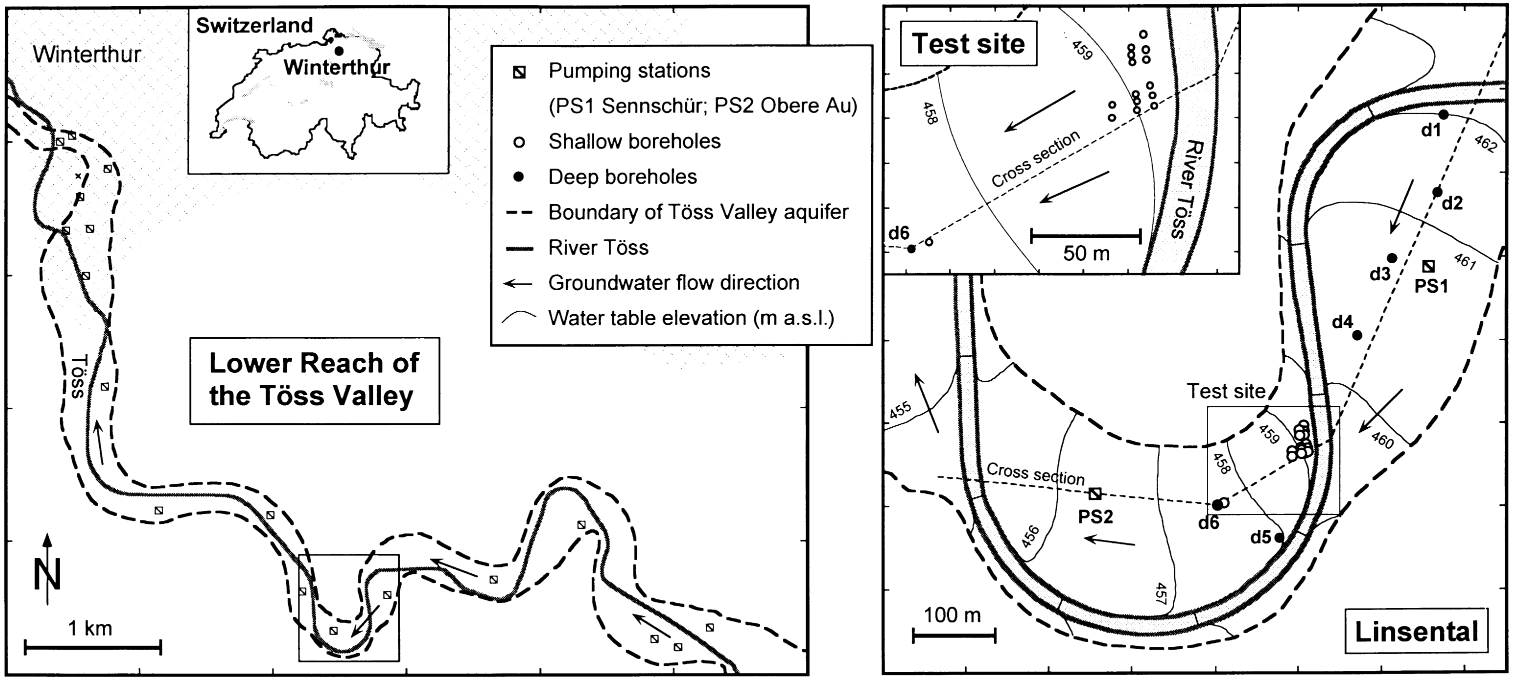

Fig. 1. Schematic map of the Linsental, a part of the Töss Valley, Switzerland, close to the city of Winterthur. The thin dashed line indicates the position of the vertical cross section shown in Fig. 2.

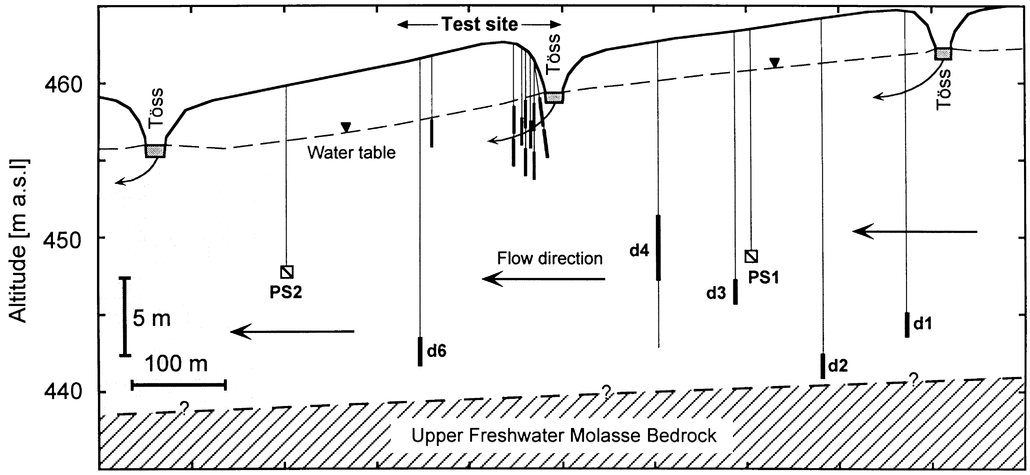

Fig. 2. Vertical section through the Linsental aquifer. Well screens (in bold) are at the bottom of each borehole. Sample of borehole d4, which is filtered along the whole length, was taken at 11 m below the water table.

Consequently, knowledge of the mean residence time and recharge dynamics of an aquifer is central for the protection and sustainability of groundwater resources.

The present study is part of a larger interdisciplinary research program which evaluates the possible impacts of a planned natural renaturalization of the Swiss prealpine river Töss (Fig. 1). Along its flow, the river Töss infiltrates through the riverbed and feeds the groundwater into the adjacent alluvial aquifer which provides drinking water for about 100 000 people. During the last century, the river Töss was canalized, but in recent years the effects of this canalization and of a potential renaturalization of the river Töss have been discussed in detail. In case of renaturalization, the river bed could potentially move closer to the pumping stations leading to lower groundwater residence times which may have a negative effect on the drinking water quality. To develop objective criteria to decide on the planned renaturalization, a series of hydrogeologic, flow-modeling, biological and isotopic studies have been initiated in a part of the Töss Valley called Linsental.

The main focus of this contribution is to determine the spatial and temporal variability of the mean groundwater residence times and to differentiate between recently infiltrated river water and older groundwater. To reach these objectives, the following tracers were used: (1) tritium (^3H) in combination with its decay product tritiogenic ^3He ($^3He_{tri}$); (2) dissolved chlorofluorocarbons (CFC-11, CFC-12); (3) dissolved oxygen (O_2); (4) radiogenic ^4He ($^4He_{rad}$); and (5) dissolved atmospheric noble gases.

The $^3H/^3He$ dating method offers a direct measure for the time since groundwater had its last gas exchange with the atmosphere (Tolstikhin and Kamenskiy, 1969; Schlosser et al., 1988) and provides quantitative groundwater residence times. Furthermore, excess in CFCs, deficits in O_2 and accumulation of $^4He_{rad}$ were established as qualitative indicators for older groundwater in the Linsental aquifer. All these indicators and the tritiogenic ^3He are based either on an excess or a lack of dissolved gases compared to the initial concentration in groundwater. This initial concentration can be derived from the concentrations of the atmospheric noble gases Ne, Ar, Kr, and Xe dissolved in groundwater.

2. Study area

The Töss valley is located 20 km north-east of Zürich, Switzerland. Its formation has been attributed to the fluvial erosion of the former glacial deposits through lateral migration of the river to the Upper Fresh Water Molasse bedrock. Subsequently, the bedrock was overlain with reconstituted Quaternary gravels from fluvial deposition forming the Töss

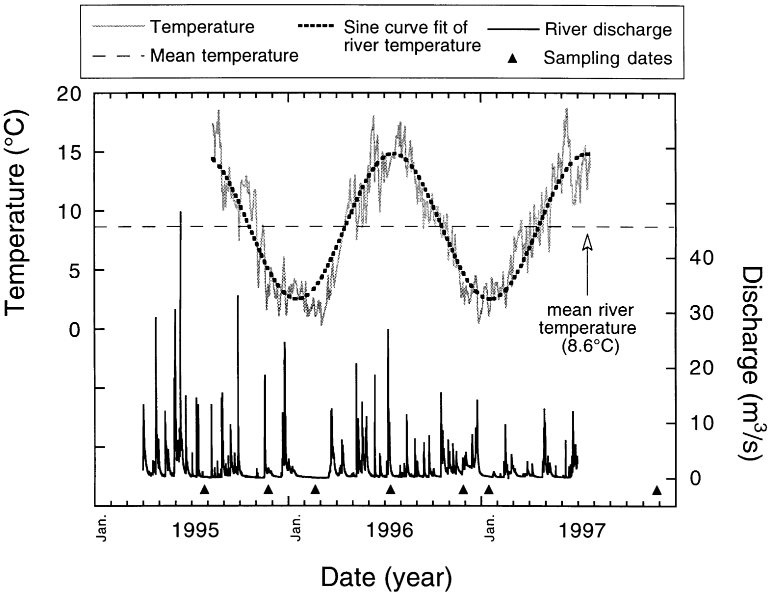

Fig. 3. Daily discharge of the river Töss compared with the daily mean temperature of the river for the time period between 1995 and 1997.

Valley aquifer (Kempf et al., 1986). The Töss Valley aquifer is more than 40 km long with its lower boundary being the low permeable molasse bedrock.

The Linsental aquifer is in the lower reach of the Töss Valley and has a maximum thickness of 25 m and an average width of 200 m (Figs. 1 and 2). Spatially the aquifer is highly heterogeneous with a range of hydraulic conductivities of 10^{-2} m s^{-1} in gravels to 10^{-5} m s^{-1} in clay lenses. Generally, the mean vertical hydraulic conductivity (K_V) in an alluvial aquifer is an order of magnitude smaller than the horizontal hydraulic conductivity (K_H) (Bouwer, 1978). This anisotropy can be attributed to the fluvial depositional history of the river. From field observations and pumping tests, the K_H of the gravels was found to fall in the range of 10^{-2}–10^{-3} m s^{-1} (Kempf et al., 1986). Assuming a porosity between 0.2 and 0.3, which is typical for fluvial deposits, and a mean hydraulic gradient of the Linsental aquifer of about 10 m km^{-1} (Fig. 1), the horizontal groundwater velocity can be estimated to be of the order of 10–100 m d^{-1}.

Hydraulically, the Linsental aquifer is predominantly influenced by withdrawal of groundwater as a potable water resource from the pumping stations Sennschür (PS1) and Obere Au (PS2) (Fig. 1) and by infiltration from the river Töss. The latter is controlled by the river discharge, the respective aquifer and river water levels, and the hydraulic conductivity of the river bed. During recent years, several boreholes were installed in the Linsental from which sampling is possible between 3 and 25 m below surface. Closely spaced boreholes were drilled in the vicinity of the river to observe the local river infiltration ('test site' in Figs. 1 and 2).

Local precipitation controls the runoff dynamics of the river Töss. During floods, the discharge is two orders of magnitude higher than in dry periods (Fig. 3). River temperatures vary between 18°C in summer and 0°C in winter. The mean annual temperature of the riverine water is 8.6°C (Fig. 3) and is slightly lower than the mean annual air temperature of 9.2°C at the altitude of the Linsental (460 m a.s.l.) (Schüepp, 1981).

3. Methods

3.1. Sampling and analysis

More than 60 samples of groundwater and river water from the Linsental were collected between

1995 and 1997. Groundwater samples were taken from 18 boreholes and two pumping stations by submersible pumps. The water for the noble gas, ^{3}H and CFC analysis was immediately transferred to 45 ml copper tubes and sealed with pinch-off clamps (Kipfer, 1991). The O_2 concentration was directly measured by Winkler titration.

Usually all noble gases (^{3}He, ^{4}He, Ne, Ar, Kr, Xe) were measured, with the exception of samples taken in July 1995 and January 1997 when only the ^{3}He, ^{4}He and Ne concentrations were analyzed. The ^{3}H concentration was measured in about every third sample, as variations in ^{3}H concentrations were expected to be small assuming residence times of a few months only. The CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) concentrations were measured for most of the samples except for those taken in November 1996/97.

For the noble gas mass spectrometric analysis, the samples were quantitatively degassed on a vacuum line by water vapor transport through a capillary on liquid nitrogen cooled cold traps. The light noble gases He and Ne were analyzed according to the procedures described by Kipfer et al. (1994). After He and Ne analysis, the extracted water vapor (about 0.5 g) and all other condensable gases were released from the cold traps by heating to 180°C. After passing through a molecular sieve (3 Å pore diameter) to remove the water vapor, the gas was expanded to a 2 l reservoir. A split of 0.7 cm^3 was taken, passed through a series of getters to remove the reactive gases, and then admitted to the mass spectrometer for simultaneous analysis of Ar, Kr, and Xe. To improve the precision of the Xe measurement, in a larger gas split only the Xe concentration was measured. This time the Xe was separated from the other heavy noble gases by freezing on a cold trap at $-$ 100°C and later releasing it by heating to 180°C. The degassed water was transferred into the original copper tube and after several months the sample was reanalyzed for ^{3}He produced by the decay of ^{3}H.

For information on experimental details on noble gas, ^{3}H and CFC measurements refer to Beyerle et al. (1999), Kipfer et al. (1994) and Hofer and Imboden (1998), respectively.

The gas amounts of the samples are regularly calibrated against an air standard. Aliquots of an internal freshwater standard are routinely analyzed for the purpose of quality control. The typical precision of the ^{3}He/^{4}He ratios and the He, Ne, Ar, Kr concentrations for water samples, expressed as the reproducibility of the noble gas concentration of the water standard, are typically better than ± 1% (1σ error). The typical precision of ^{3}H measurements is better than ± 1 TU, whereas the analytical error of the CFC measurement is less than ± 5%. Since the water samples were measured within 4 months after sampling, anoxic degradation of CFC-11 during storage is not significant compared to the error of the CFC-11 measurement (Hofer and Imboden, 1998).

3.2. Evaluation of noble gas temperature and excess air

The equilibrium concentration of dissolved atmospheric gases in groundwater (e.g. noble gases, CFCs and O_2) is determined by the individual partial pressure in the atmosphere, the water temperature at the groundwater table and the solubility of the gas, i.e. its Henry coefficient. In contrast to surface waters, at recharge groundwater commonly dissolves an excess of atmospheric gases in addition to the expected equilibrium concentration (‘excess air’) (Heaton and Vogel, 1981). The formation of excess air is poorly understood. Nevertheless, it has to be taken into account to calculate the initial concentration of dissolved gases in groundwater at recharge.

The amount of excess air and the recharge temperature both can be determined by measuring the concentration of Ne, Ar, Kr, Xe in groundwater, because the physical processes responsible for dissolution of atmospheric noble gases can be adequately modeled (see Aeschbach-Hertig et al., 1999). It is usually assumed that the elemental composition of the excess air component corresponds to unfractionated atmospheric air, i.e. air bubbles trapped during recharge and later dissolved completely (Andrews, 1992). Therefore it is possible to calculate the two unknown variables, i.e. noble gas temperature (NGT) and excess air component from the known noble gas concentrations. Usually He can neither be used to derive the NGT nor the amount of excess air, because radiogenic He and tritiogenic ^{3}He often accounts for most of the observed ^{3}He and ^{4}He excess. In some aquifer systems, the composition of the excess air appears to deviate from that of atmospheric air. Partial loss of the excess air due to diffusive gas exchange at

Table 1
Noble gas temperature (NGT), tritium concentration (^3H) and $^3H/^3He$ ages of river Töss, the shallow boreholes from the test site (depth: 3–8 m) and the deep borehole d6 (depth: 19 m)

Date	NGT (°C)			^3H (TU)			$^3H/^3He$ age (days)	
	River[a]	Shallow[b]	Deep (d6)[a]	River[c]	Shallow[b]	Deep (d6)[c]	Shallow[b]	Deep (d6)[c]
26 July 1995	–	–	–	28.2 ± 0.9	27.2 ± 0.4	24.4 ± 1.2	20 ± 30	640 ± 130
24 November 1995	5.7 ± 0.1	9.3 ± 0.2	8.4 ± 0.2	30.1 ± 0.7	25.8 ± 1.0	26.8 ± 1.3	450 ± 70	620 ± 110
21 February 1996	4.7 ± 0.2	7.2 ± 0.3	8.3 ± 0.2	26.2 ± 0.6	25.2 ± 0.6	24.1 ± 0.6	400 ± 130	660 ± 100
12 July 1996	13.9 ± 0.1	10.2 ± 0.8[d]	8.1 ± 0.2	31.8 ± 0.8	26.8 ± 0.7	26.0 ± 0.7	40 ± 60	450 ± 70
27 November 1996	–	8.8 ± 0.2	8.9 ± 0.2	–	29.1 ± 0.7[c]	26.8 ± 0.7	70 ± 30[c]	550 ± 100
14 January 1997	–	–	–	34.9 ± 0.8	29.5 ± 1.3	27.3 ± 0.6	140 ± 30	450 ± 100
26 November 1997	–	–	9.1 ± 0.2	–	–	26.9 ± 0.7	–	560 ± 100
Average[e]	8.1 ± 5.1	8.9 ± 1.3	8.6 ± 0.4	30.2 ± 3.3	27.3 ± 1.7	26.0 ± 1.3	190 ± 190	560 ± 90

[a] NGT and its error derived from Ne, Ar, Kr, and Xe concentrations by fitting temperature and excess air to minimize the sum of the weighted squared differences between measured and predicted concentrations (Aeschbach-Hertig et al., 1999).

[b] Error is equal to the standard deviation between the values for each shallow borehole.

[c] Error is equal to the analytical error of the measured value (1σ error).

[d] Satisfactory fit only if an additional parameter for partial re-equilibrium after formation of excess air (degassing) is assumed.

[e] Error is equal to the standard deviation between the values for each sampling date.

the water table has been proposed as a conceptual model to interpret the measured noble gas abundance pattern in such situations (Stute et al., 1995b). Thus, one additional parameter, the degree of re-equilibration may be needed to describe noble gas concentrations in groundwater. To calculate NGT we used the fitting procedure established by Aeschbach-Hertig et al. (1999). Solubility data of noble gases in water are taken from the following references: Weiss (1971) for He and Ne; Weiss (1970) for Ar; Weiss and Kyser (1978) for Kr and Clever (1979) for Xe, respectively.

The NGT measures the soil temperature at recharge and corresponds typically to the annual mean air temperature (Stute et al., 1995a). Differences between annual mean air temperature and NGT may occur in cases where infiltration rates are very high, the water table is very close or far from the surface, or where water predominately infiltrates during warmer/colder periods (Stute and Schlosser, 1993). However, no data about NGT are available for river bank infiltrated groundwater.

3.3. $^3H/^3He$ dating of groundwater

Tritium (^3H), the radioactive isotope of hydrogen with a half-life of 12.38 years (Oliver et al., 1987), has been extensively used to study hydrologic systems such as oceans, lakes and groundwater. Most studies used the ^3H release from nuclear bomb tests in the atmosphere as a time marker. In addition, ^3H has been combined with its decay product $^3He_{tri}$ (tritiogenic ^3He) to determine the so called $^3H/^3He$ water age (Schlosser et al., 1988; Solomon et al., 1992; Aeschbach-Hertig et al., 1998). Since residence times in the Linsental aquifer are expected to be on the order of months, ^3H alone cannot be used. The $^3He/^3H$ ratio provides information on the groundwater age. The concentration of dissolved ^3He increases as soon as the groundwater is isolated from the atmosphere, because ^3He produced by ^3H decay can no longer escape. Therefore the $^3He_{tri}/^3H$ ratio is a measure for the time elapsed since a water parcel was last in contact with the atmosphere. The $^3H/^3He$ age τ is defined as (Tolstikhin and Kamenskiy, 1969):

$$\tau = \frac{1}{\lambda} \ln \left(1 + \frac{[^3He_{tri}]}{[^3H]} \right) \tag{1}$$

where $\lambda = 0.0556\ yr^{-1}$ is the decay constant of ^3H and $[^3H]$ the measured ^3H concentration. It is usually expressed in tritium units (TU). 1 TU corresponds to a $^3H/^1H$ ratio of 10^{-18} and decays to $2.488 \times 10^{-15}\ cm^3STP(^3He)\ g(H_2O)^{-1}$. $[^3He_{tri}]$ is defined as the fraction of the total ^3He produced by ^3H decay, i.e. the difference between the measured concentration

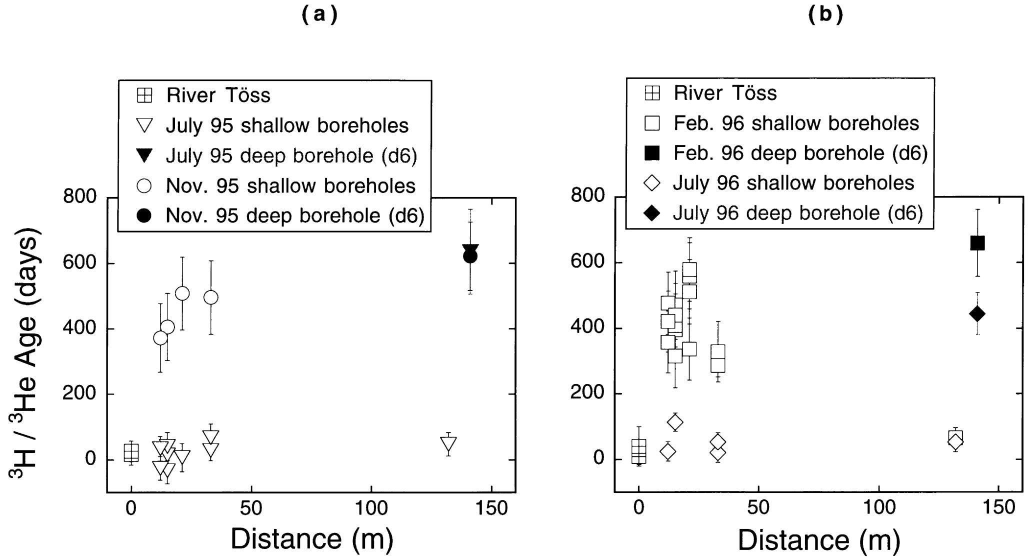

Fig. 4. ^{3}H/^{3}He groundwater ages of samples taken at the test site versus distance from the river Töss (cf. Figs. 1 and 2).

[$^3He_{meas}$] and the concentrations of all other ^{3}He components ([$^3He_{eq}$]: equilibrium, [$^3He_{air}$]: excess air, [$^3He_{ter}$]: terrigenic):

$$[^3He_{tri}] = [^3He_{meas}] - [^3He_{eq}] - [^3He_{air}] - [^3He_{ter}] \tag{2}$$

The equilibrium concentration in water [$^3He_{eq}$] is determined by the water temperature and the ambient pressure during recharge. Solubility data for He and Ne isotopes are taken from Weiss (1970) and from Benson and Krause (1980). The atmospheric excess [$^3He_{air}$] can be calculated from the Ne or also from the ^{4}He excess, provided the latter is exclusively of atmospheric origin. Isotopic and elemental compositions of the atmosphere are taken from Ozima and Podosek (1983). The [$^3He_{ter}$] can be derived from the terrigenic ^{4}He, if the ^{3}He/^{4}He ratio of the injected He is reasonably well known. In this study the [$^3He_{ter}$] was calculated using the average ^{3}He/^{4}He production ratio in crustal rocks of 2×10^{-8} (Mamyrin and Tolstikhin, 1984). However, since the radiogenic ^{4}He component in the groundwater of the Linsental is in the range of a few percent, the [$^3He_{ter}$] is almost negligible. As an example, the 1.2 year old groundwater sample taken from the pumping station PS1 has the following relative ^{3}He fractions: 80% [$^3He_{eq}$], 14% [$^3He_{air}$], 6% [$^3He_{tri}$], and 0.04% [$^3He_{ter}$] assuming a radiogenic ^{3}He/^{4}He ratio of 2×10^{-8}.

4. Results and discussion

4.1. ^{3}H/^{3}He groundwater ages

Between 1995 and 1997 ^{3}H concentrations hardly varied in the Linsental aquifer (Table 1), but were significantly larger than the average ^{3}H content in precipitation of northern Switzerland (17.7 ± 1.8 TU in 1993, Aeschbach-Hertig, 1994). Local tritium enrichments are reported from other highly industrialized parts of Switzerland (Völkle et al., 1996). Whereas ^{3}H variations in the groundwater are small (deep: 26.0 ± 1.3 TU, shallow: 27.3 ± 1.7 TU), ^{3}H fluctuates considerably in the river water (30.2 ± 3.3 TU). Assuming the mean ^{3}H of the river to be constant over time, the differences in ^{3}H concentrations between the river and the groundwater can be roughly interpreted in terms of a residence time that is in the order of 2 to 3 years.

More precise estimates of groundwater residence times can be gained if ^{3}H and $^3He_{tri}$ are combined to calculate ^{3}H/^{3}He ages according to Eqs. (1) and (2). For water samples in which ^{3}H was not measured, ^{3}H

Table 2
^{3}H/^{3}He groundwater ages of the samples from the deep boreholes (d1–d6) and the pumping stations Sennschür (PS1) and Obere Au (PS2) from different sampling dates

^{3}H/^{3}He age (days)							
d1	d2	d3	d4	d5	d6	PS1	PS2
960 ± 100[a]	750 ± 100[b] 800 ± 100[e] 910 ± 90[a]	190 ± 40[b] 320 ± 40[e]	550 ± 70[b]	290 ± 90[a]	560 ± 90[c]	480 ± 90[d]	290 ± 90[d]

[a] 26 November 1997.
[b] 12 July 1996.
[c] Average, cf. Table 1.
[d] 27 November 1996.
[e] 14 January 1997.

concentrations were assumed to be equal to the average ^{3}H concentration of the Linsental aquifer (Table 1). The tritiogenic ^{3}He was calculated using the following assumptions: (1) during recharge the water temperature is either equal to the calculated NGT or the measured groundwater temperature, (2) the pressure at the water table corresponds to a mean atmospheric pressure at the altitude of the Linsental (960 mbar at 460 m a.s.l.) and (3) the observed non-tritiogenic ^{3}He excess originates from the complete dissolution of air, and in case of a radiogenic ^{4}He component, from terrigenic He injection with a ^{3}He/^{4}He ratio of 2×10^{-8}.

Note that in case of low water ages ($<$ 3 years) and approximately constant ^{3}H concentrations as in the Linsental aquifer, the ^{3}He$_{tri}$ concentration is almost linearly related to the calculated ^{3}H/^{3}He age and the age error induced by the measured ^{3}H value is negligible. The error in the calculated age is mainly caused by errors of the ^{3}He/^{4}He ratio and the concentrations of He and Ne. If no radiogenic He component is present in a given sample, ^{4}He is used instead of Ne for excess air correction. This excess air correction leads to smaller errors in age because the ^{3}He/^{4}He ratio is measured with a better precision than the ^{3}He/Ne ratio (about ± 40 days instead of ± 100 days).

The ^{3}H/^{3}He ages in the Linsental aquifer show a distinct variation over time. The samples from the deep part of the aquifer have an almost constant water age, whereas water ages of the shallow aquifer depend on the time of sampling (Table 1). Occasionally the mean age of the shallow part is similar to the age of the deep groundwater, at other times most ages from the shallow boreholes do not differ significantly from zero. This variation of the water ages is shown in Fig. 4 in which ^{3}H/^{3}He ages are plotted against the horizontal distances from the river. Samples with younger water ages can be interpreted as a binary mixture between locally infiltrated river water in different proportions and older groundwater. As the local infiltration is reduced or even cut off, only older groundwater remains and therefore the ^{3}H/^{3}He age of the groundwater close to the river is comparable to the age of the deep aquifer.

To illustrate this, in February 1996 the mean water age of the shallow aquifer was 400 days with a standard deviation of ± 130 days. This mean residence time of the shallow part of the aquifer is comparable to the groundwater age of the deep aquifer of 660 ± 100 days leading to the conclusion that local river infiltration was small. In contrast, the mean water age of the shallow groundwater in July 1996 had decreased to 40 ± 60 days (Table 1, Fig. 4(b)) which indicates that locally infiltrated river water dominates. Indeed, in winter there was no major flood recorded in the Töss valley for almost 30 days prior to the February sampling, whereas in July 1996 heavy rain and flooding events were common (see Fig. 3).

In Table 2 the ^{3}H/^{3}He water ages of the deep boreholes reaching the molasse bedrock are compared to the water ages found in the pumping stations (PS1, PS2) which extract groundwater a few meters above the molasse bedrock. The pumping stations operate at about 100 l min^{-1} for 5–6 h in the evenings. Samples

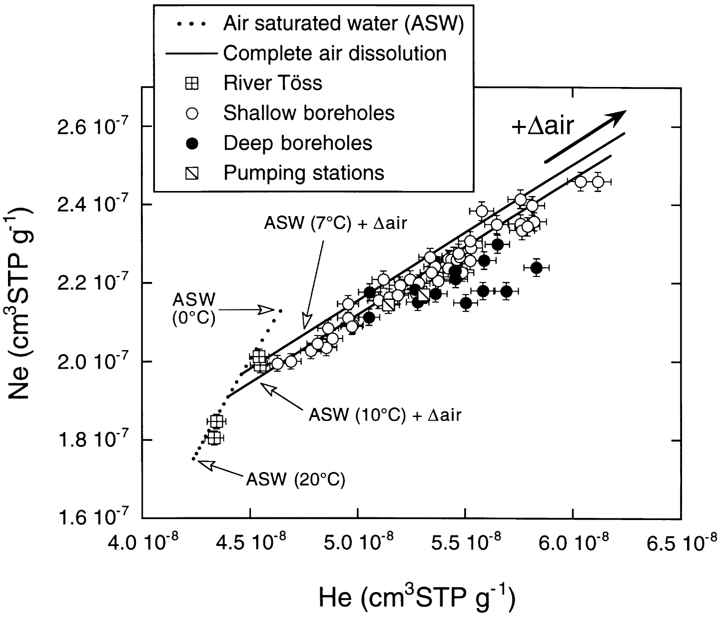

Fig. 5. He versus Ne concentrations from the Linsental aquifer and the river Töss. Error bars correspond to the analytical error (1σ).

were taken in the morning subsequent to pumping during 30 min. The water ages in the pumping stations were found to be about 1 year. The mean age is much higher than the communal water supply authorities previously expected and is far larger than the threshold of 10 days quoted in the groundwater regulations (Pedroli, 1982). Model calculations using current average pumping rates as boundary conditions indicate that the youngest components of water attracted by the pumping stations have residence times from infiltration to the well along a single flow track of more than 10 days (Mattle, 1999). Assuming that the pumped water in PS1 is a binary mixture of recently infiltrated river water (age $\approx$ 0 days) and older groundwater that is similar to the one at the nearby borehole, d1 (960 ± 100 days), the older component accounts for roughly 50%. A similar mixing ratio for PS2 can be estimated, assuming that the older component is equal to the one at the nearby borehole, d6 (560 ± 90 days).

4.2. Noble gas data from the Linsental aquifer

Groundwater is commonly supersaturated with atmospheric air (excess air). Since the light noble gases are far less soluble in water than the heavier noble gases, He and Ne react more sensitively to excess air than Ar, Kr and Xe. Indeed, measured He and Ne concentrations confirm that the supersaturation of noble gases is essentially controlled by the complete dissolution of air, as usually the elemental ratio of the light noble gas excess is in agreement with the atmospheric value ($[\mathrm{Ne}_{\mathrm{ex}}]/[\mathrm{He}_{\mathrm{ex}}] = [\mathrm{Ne}_{\mathrm{air}}]/[\mathrm{He}_{\mathrm{air}}] = 3.47$; Fig. 5). But in some samples, He tends to be enriched relative to Ne which is indicative of a small non-atmospheric He component, most probably of radiogenic origin. This interpretation is in accordance with the observation that the largest ^{4}He excesses are found in the oldest groundwater samples (see Section 4.5).

The noble gas temperature (NGT) and the amount of excess air of the samples were determined by using the optimization algorithm of Aeschbach-Hertig et al. (1999). In fact, although the river water is close to equilibrium, all groundwater samples contain appreciable amounts of excess air, even those from wells within meters of the river bank and with near zero ^{3}H/^{3}He ages. The amount of excess air in the groundwater varies between 5×10^{-4} and 3×10^{-3} cm^{3}STP g^{-1} (5–30 % ΔNe). Except for four of the 47 samples, it is not necessary to assume a fractionation of the excess air in order to achieve a good

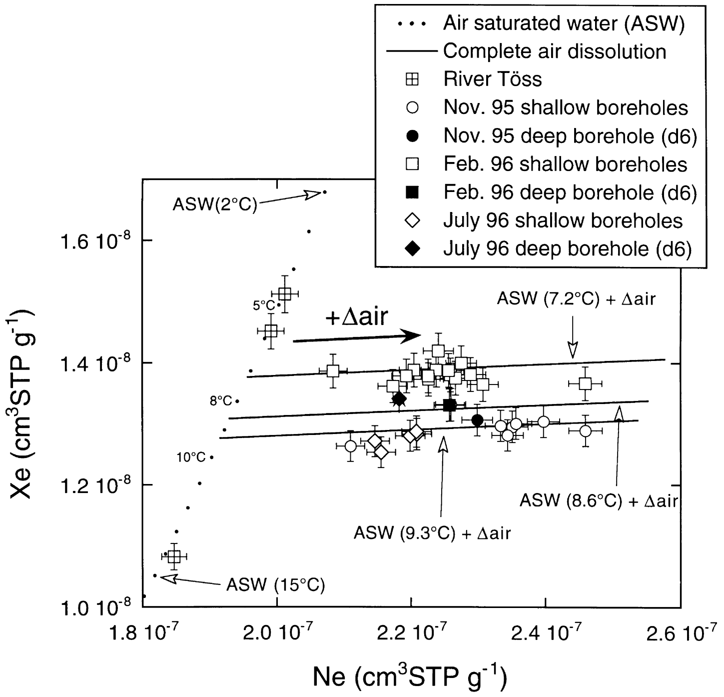

Fig. 6. Ne versus Xe concentrations from the Linsental aquifer and the river Töss.

fit. Since most of the samples have a, albeit small, radiogenic He component, the inclusion of He to fit NGT and excess air is usually not possible.

For the 42 samples with unfractionated excess air, temperature can be determined with a precision of ±0.2°C, ranging from 6.6 to 9.6°C. Thus, if we take the error estimate at face value, the scatter of the noble gas temperatures must indicate real temperature variations. The effects of temperature and excess air on noble gas concentrations can be visualized in a graph of Xe versus Ne concentrations (Fig. 6). Xe reacts most sensitively to temperature, whereas Ne reflects mainly the effects of excess air. The noble gas data form clusters which are separated from each other mainly by different Xe concentrations. These concentration clusters indicate different regimes of groundwater recharge at different temperatures and therefore samples from shallow depths tend to exhibit seasonal variations. The samples taken in February 1996 have the highest Xe concentrations, corresponding to the lowest temperatures, yielding a mean temperature of 7.2°C with a standard deviation of only ± 0.3°C. The relatively warm mean NGT of 9.3°C from November 1995 suggests that this groundwater was infiltrated not in late autumn but during summer (Table 1). The NGTs of the deep borehole (d6) are almost constant over time (mean 8.6°C) and correspond well to the mean annual temperature of the river Töss (8.6°C, Fig. 3). It appears that the mean NGT is closer to the mean river temperature than to the mean atmospheric temperature of 9.2°C. The variability of calculated NGTs is small compared to the fluctuation of the river temperature, as in general the amplitude of temperature oscillations exponentially decreases with depth in soils and groundwater (e.g., Stute and Schlosser, 1993; Matthess, 1982).

The four samples taken from the shallow part of the aquifer during July 1996 have similar Xe concentrations as the November samples (Fig. 6). However, the NGT cannot be satisfactorily fitted assuming that excess air corresponds to unfractionated air. Yet, a model with an additional parameter for partial re-equilibration after formation of the excess air yields reasonable fits (Stute et al., 1995b; Aeschbach-Hertig et al., 1999). With this model, the mean NGT of the samples from July 1996 is 10.2°C (Table 1).

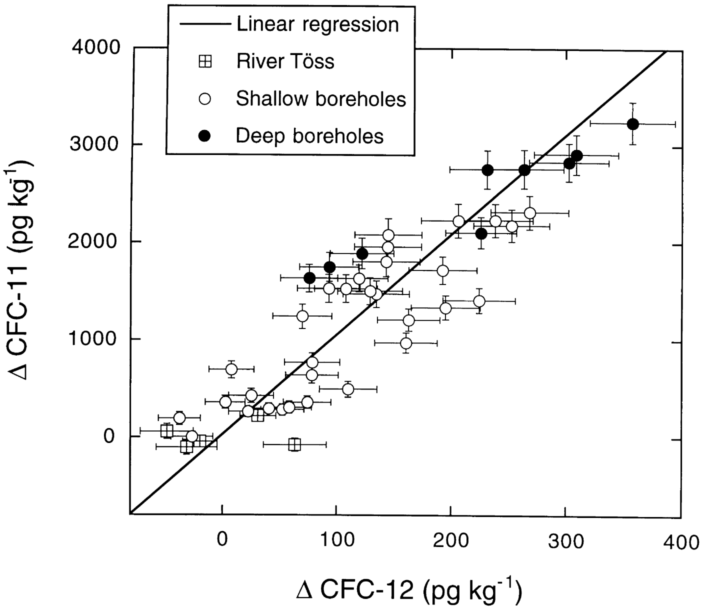

Fig. 7. CFC-12 excess (ΔCFC-12) plotted against CFC-11 excess (ΔCFC-11) in the Linsental aquifer yielding a ΔCFC-11/ΔCFC-12 ratio of 10 ± 1.

Unfortunately, the error of the calculated NGT is considerably higher than that derived with the simple excess air model. The mean temperature error for the five samples taken in July is ± 0.6°C, although noble gas concentrations were determined with a precision of ± 1%.

The major conclusions of this section are that excess air is formed within days after infiltration and within meters from the river, and that this excess air is mainly unfractionated. If this is the case, infiltration temperatures can be determined with high precision (± 0.2°C), allowing to easily detect seasonal variations of only about ± 1°C.

4.3. CFCs excess caused by contamination

Chlorofluorocarbons (CFCs) have been used in hydrology to date groundwaters (Thompson and Hayes, 1979; Busenberg and Plummer, 1992; Dunkle et al., 1993). In the Linsental aquifer, the following two reasons exclude the direct application of the CFC method to obtain information about the groundwater residence times: Atmospheric CFC concentrations did not increase significantly during the last few years (Elkins et al., 1993), and even more importantly, CFC concentrations in the Linsental aquifer are in excess compared to the expected initial concentration in groundwater.

As for all atmospheric gases, the initial concentration of CFCs in groundwater is determined by the atmospheric concentration, atmospheric pressure, solubility and the amount of excess air. The solubility is controlled by the recharge temperature of the groundwater, with CFC-11 being more soluble in water than CFC-12 (Warner and Weiss, 1985). The impact of excess air on CFC concentrations is very small, e.g. a typical supersaturation of 15% in Ne (dissolution of atmospheric air of 1.5×10^{-3} $cm^3STP\ g^{-1}$) corresponds to a CFC excess of only about 1%.

The CFC content of the atmosphere in the Linsental is deduced from the riverine CFC concentration, assuming that the river Töss is in atmospheric equilibrium as indicated by the noble gas concentrations (Figs. 5 and 6). The calculated atmospheric CFC abundances are almost constant over the entire observation period. The mean atmospheric CFC concentration is slightly higher than modern atmospheric values (Cook and Solomon, 1997), possibly caused by local industrial activity (400 vs. 300 pptv for CFC-11 and

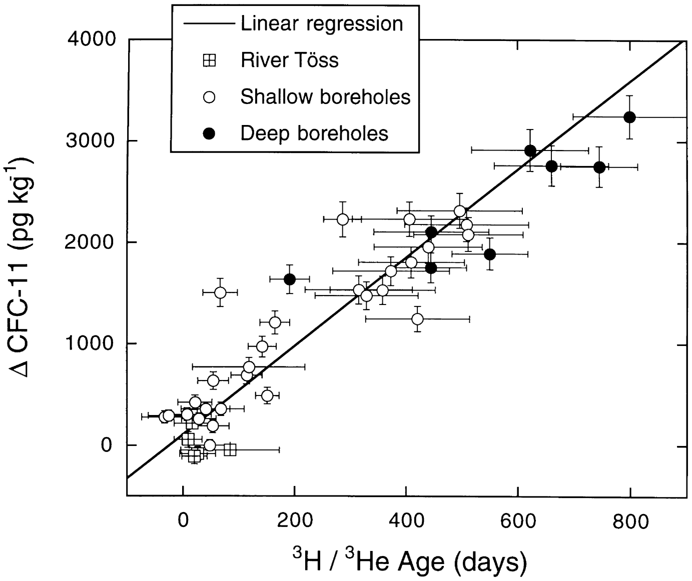

Fig. 8. CFC-11 excess (ΔCFC-11) plotted against calculated ^{3}H/^{3}He groundwater age in the Linsental aquifer.

620 vs. 550 pptv for CFC-12). For the given atmospheric CFC concentrations and the recharge temperatures, the expected CFC concentrations of the groundwater in the Linsental aquifer should be in the range of 800–1500 pg kg^{-1} for CFC-11 and of 300–500 pg kg^{-1} for CFC-12. However, the CFC concentrations in the Linsental aquifer vary from 1000 up to 4100 pg kg^{-1} for CFC-11 and from 320 up to 730 pg kg^{-1} for CFC-12. As a result it is concluded that the groundwater in the Linsental is influenced by non-directly atmospheric CFCs which limits the use of CFC for dating.

The CFC excess (ΔCFC) is derived by subtracting the calculated equilibrium concentration and the amount due to excess air from the measured CFC concentration:

$$[\Delta\mathrm{CFC}] = [\mathrm{CFC}_{\mathrm{meas}}] - [\mathrm{CFC}_{\mathrm{eq}}] - [\mathrm{CFC}_{\mathrm{air}}] \quad (3)$$

In the Linsental aquifer ΔCFC-11 increases linearly with ΔCFC-12 yielding a constant [ΔCFC-11]/[ΔCFC-12] ratio of 10 ± 1 (Fig. 7). Since this ratio is higher than the CFC-11/CFC-12 ratio both in air ($[\mathrm{CFC\text{-}11}_{\mathrm{air}}]/[\mathrm{CFC\text{-}12}_{\mathrm{air}}] \approx 0.6$) and in equilibrated water ($[\mathrm{CFC\text{-}11}_{\mathrm{eq}}]/[\mathrm{CFC\text{-}12}_{\mathrm{eq}}] \approx 3$, for 8–10°C), CFC-11 is enriched over CFC-12 in the CFC excess compared to atmosphere derived CFCs.

The comparison of ΔCFCs with groundwater age shows a linear increase as well (Fig. 8). Most probably, the observed CFC concentrations represent a mixture between locally infiltrated, uncontaminated river water and contaminated, older groundwater from the deep aquifer. Consequently, this older groundwater, which recharges and is contaminated at some distance, must have a constant CFC-11/CFC-12 ratio of around 10. About the source of the contamination we can only speculate. Either industrial pollution (Thompson and Hayes, 1979; Busenberg and Plummer, 1992) or sorption and desorption of the CFCs from soil surface are responsible for this CFC excess (Russell and Thompson, 1983). In Linsental, CFCs do not provide direct information on groundwater residence time, but they provide information on groundwater mixing and river bank controlled groundwater recharge.

4.4. Variation in the dissolved oxygen concentration

The concentration of dissolved oxygen generally decreases with residence time because of bacterial metabolic activity in the groundwater and can be used as an indicator of groundwater age. In alluvial aquifers oxygen consumption starts immediately after air-saturated river water infiltrates into the hyporheic zone which separates riverine water from

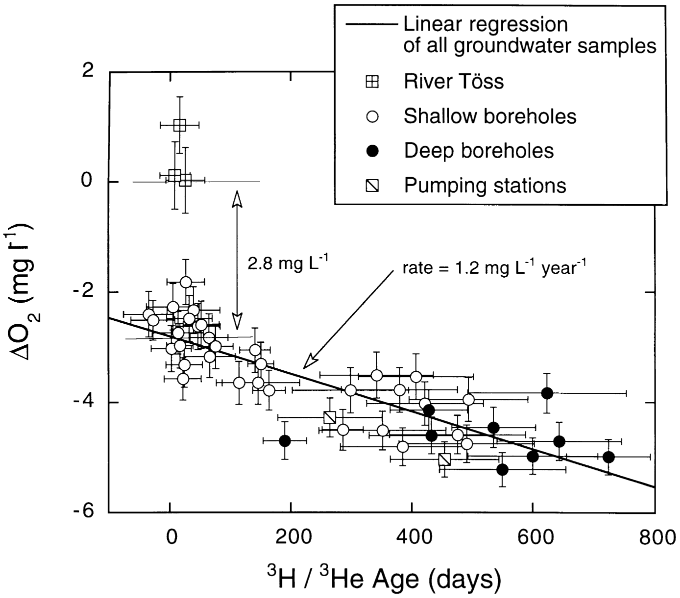

Fig. 9. Oxygen reduction (ΔO_2) plotted against calculated $^3H/^3He$ groundwater age.

groundwater (Triska et al., 1989). Due to high metabolic activity, the O_2 concentration sharply decreases during the passage of the water through the hyporheic zone. The hyporheic respiration rates of rivers are large (Malard and Hervant, 1999), e.g. about 4 mg $(O_2)\,l^{-1}\,h^{-1}$ for the Nekar river (Naegeli et al., 1995). After passing the hyporheic zone and reaching the 'real' groundwater flow, the O_2 degradation decreases by more than three orders of magnitude (Malard and Hervant, 1999). The strong variability of oxygen consumption in and below the hyporheic zone reflects mainly the availability of organic matter and bacterial activity.

In Fig. 9 the O_2 deficit in the Linsental aquifer is plotted against the calculated groundwater age. We define the reduction in O_2 as the difference between the measured O_2 concentration and the initial O_2 content at recharge which is given by the sum of the expected atmospheric equilibrium concentration and the excess air component:

$$[\Delta O_2] = [O_{2,\mathrm{meas}}] - [O_{2,\mathrm{eq}}] - [O_{2,\mathrm{air}}] \qquad (4)$$

Equilibrium and excess air O_2 can be derived from atmospheric noble gas concentrations. Note that in contrast to Eq. (4), O_2 consumption is commonly calculated relative to atmospheric equilibrium conditions although the existence of excess air is evident. In the Linsental aquifer samples with negligible $^3H/^3He$ age indeed do show a significant O_2 reduction of about 2.8 mg l^{-1} which can be easily explained by a fast O_2 consumption in the hyporheic zone within about an hour. However, the rate of change of dissolved O_2 in the groundwater, which has a measurable residence time, is only (1.2 ± 0.2) mg l^{-1} yr^{-1} (Fig. 9). As for the CFCs, the linear relation between ΔO_2 and $^3H/^3He$ age may also be interpreted in terms of mixing of riverine water after passing the hyporheic zone and older groundwater from the deeper aquifer.

4.5. Radiogenic ^4He accumulation in the Linsental aquifer

Radiogenic ^4He ($^4He_{rad}$) has been widely used to estimate water residence times of up to 10^8 years in old groundwater systems (e.g., Andrews and Lee, 1979; Andrews et al., 1985; Torgersen and Clarke, 1985). Groundwater ^4He ages are based on the assumption that $^4He_{rad}$ is generated by the decay of U and Th in the aquifer matrix and accumulates continuously in the groundwater. However, the use of ^4He for calculating groundwater ages requires a detailed knowledge of the aquifer characteristics,

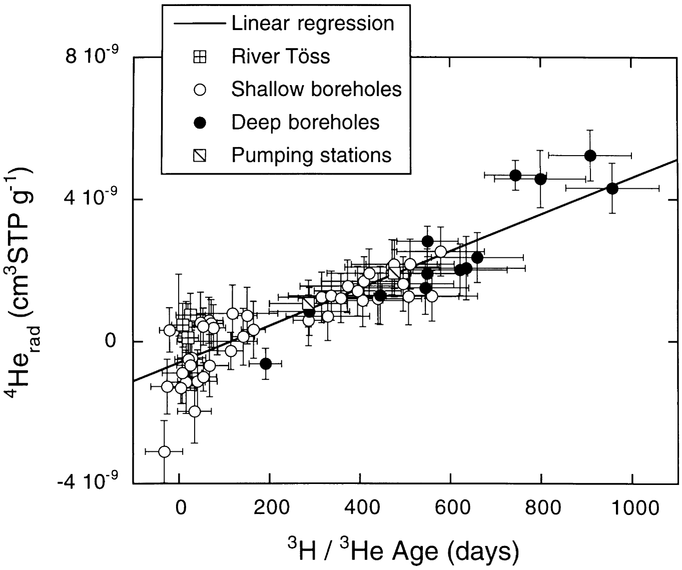

Fig. 10. Radiogenic ^4He ($^4He_{rad}$) plotted against calculated $^3H/^3He$ groundwater age yielding a ^4He accumulation rate of (1.9 ± 0.2) × 10^{-9} $cm^3STP\ g^{-1}\ yr^{-1}$.

such as porosity and the concentrations and spatial distributions of U and Th. Furthermore, the $^4He_{rad}$ accumulation rate is often much larger than the expected ^4He production due to U/Th decay in the aquifer matrix. Increased ^4He accumulation rates are explained either by (1) a ^4He-flux from the entire continental crust into the aquifer (Torgersen and Clarke, 1985), (2) ^4He transport from reservoirs in the upper most part of the continental crust (Lehmann and Loosli, 1991), or (3) by ^4He that accumulated over long time scales in the past in solid rock, which has relatively recently been eroded to form the aquifer matrix and now releases the stored ^4He by diffusion from the small grains (Solomon et al., 1996). Since the strength of an additional $^4He_{rad}$ source is highly uncertain, $^4He_{rad}$ accumulation rates can only be reasonable estimated if cross calibration with other dating methods is possible (e.g. $^3H/^3He$, CFC, ^{14}C, or hydrodynamic model ages).

The $^4He_{rad}$ in Fig. 10 is calculated as the difference between the measured ^4He ($^4He_{meas}$) and the atmospheric ^4He component given by the equilibrium concentration ($^4He_{eq}$) and the excess air component ($^4He_{air}$):

$$[^4He_{rad}] = [^4He_{meas}] - [^4He_{eq}] - [^4He_{air}] \qquad (5)$$

The in situ $^4He_{rad}$ production rate of gravel aquifers, as in the Linsental, is less than 10^{-11} cm^3 STP $g(H_2O)^{-1}\ yr^{-1}$ (Lehmann and Purtschert, 1997). However, the observed $^4He_{rad}$ increases with water age up to 5 × 10^{-9} $cm^3STP\ g(H_2O)^{-1}$ (Fig. 10). A linear fit through the data yields a ^4He accumulation rate of (1.9 ± 0.2) × 10^{-9} $cm^3STP\ g^{-1}\ yr^{-1}$. The observed $^4He_{rad}$ accumulation rate in the Linsental aquifer is at least two orders of magnitude larger than the expected in situ production rate. Furthermore, the estimated accumulation agrees within previous estimates of ^4He accumulation rates determined in different prealpine Swiss lakes (Aeschbach-Hertig, 1994). Although caution prevails in interpreting the available data on ^4He accumulation, the found constancy in the ^4He accumulation may indicate that the ^4He emanation seems to be constant within a factor of 5 in a region as large as Switzerland.

5. Summary and conclusions

This study demonstrates that the $^3H/^3He$ dating method provides valuable information on the recharge dynamics and residence time of a river bank infiltrated groundwater system. On the one hand deep groundwater in the Linsental is characterized by a relatively constant water age of about 2 years representing the mean residence time in the aquifer. On the other hand the measured $^3H/^3He$ ages of the shallow boreholes close to the river can be interpreted in terms of mixing of recently infiltrated river water with older groundwater. This idea is strongly supported by the fact that groundwater from the shallow boreholes have almost zero $^3H/^3He$ water ages subsequent to higher river discharge rates. The $^3H/^3He$ age data have important consequences for the water management in the Linsental. The water age at the pumping stations used for public water supply was found to be considerably higher than expected. The major conclusion from this result is that at least 50% of the pumped water originates from the deep aquifer.

Concerning the planned renaturalization of the Töss river at the test site, the two major results are: (1) Although the quantity of locally infiltrated river water depends on the discharge of the river Töss, the residence time of the deep groundwater is not affected by different infiltration regimes; (2) In contrast to the previous idea that the water of the pumping stations originates directly from the river Töss, at least half of the water comes from the deep aquifer which contains older groundwater. These results indicate that safety regulations for drinking water can be met even if the distance between the river and the pumping stations is reduced.

In the Linsental the non-tritiogenic ^3He component is mainly of atmospheric origin and can be deduced from the concentration of dissolved atmospheric noble gases. Additionally, knowing the noble gas recharge temperature and the amount of excess air, the initial concentration of any other dissolved atmospheric gas can be calculated. Consequently, any process that modifies this initial gas concentration during groundwater flow can be observed (e.g. accumulation, consumption and mixing).

CFCs cannot be used for dating purposes in the Linsental. Yet, the CFC excess increases linearly with $^3H/^3He$ age. This observation reinforces the conclusion that the shallow groundwater can be interpreted as a mixture between river water and deep groundwater, which has elevated concentrations of CFCs. Therefore CFCs are useful even though a non-atmospheric contribution is present. The knowledge of initial O_2 concentrations (equilibrium plus excess air component) and groundwater residence times, allows the rate of O_2 change to be quantified. In the Linsental the degradation of O_2 during groundwater flow was found to be much slower than the fast O_2 consumption in the hyporheic zone. Finally, the data from the Linsental aquifer allow us to calculate a ^4He accumulation rate of $(1.9 \pm 0.2) \times 10^{-9}$ cm^{3}STP g$(H_2O)^{-1}$ yr^{-1}, which is two orders of magnitude higher than the in situ production. This result shows that ^4He can be used as a dating tool also in young groundwaters provided that ^4He accumulation rates can be determined by calibration using, e.g. the $^3H/^3He$ dating method. However at present a generally accepted model for the accumulation of radiogenic ^4He in groundwater bodies is still missing.

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