



^{36}Cl in modern groundwater dated by a multi-tracer approach ($^3\text{H}/^3\text{He}$, SF_6 , CFC-12 and ^{85}Kr): a case study in quaternary sand aquifers in the Odense Pilot River Basin, Denmark

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Abstract

^{36}Cl produced by thermonuclear bomb testing has been proposed as an additional tool to date or at least to identify recent groundwater components. In order to investigate the behaviour of ^{36}Cl in shallow groundwater a multi-tracer approach ($^3\text{H}/^3\text{He}$, SF_6 , CFC-12 and ^{85}Kr) was used to characterise and date the groundwater of a quaternary sands aquifer which is located on the Island of Funen near the city of Odense, Denmark. Recharge to the semi-confined shallow aquifer occurs through permeable sand windows and fractured tills at the surface. Locally, however, mixing with older pre-bomb water from the underlying limestone aquifer may occur. The integrated analyses of the available tracer data allowed a well constrained age structure determination of the investigated water system.

The $^{36}\text{Cl}/\text{Cl}$ ratios measured in groundwater were used to reconstruct the fallout rates for radioactive ^{36}Cl at Odense. The calculated fallout values exceeded the fallout estimated based on data from the Dye-3 ice core in Greenland. Recycling of the bomb peak fallout seems to be the most probable reason of the high values measured. The local extent of this process is difficult to quantify, which impedes the use of ^{36}Cl for dating.

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1. Introduction and aquifer characterization

The investigated area is located on the Island of Funen around the city of Odense, Denmark. Geologically, the site is situated in a complex setting of quaternary glaciofluvial sand aquifers with confining sandy and clayey tills (Fig. 1). The semi-confined glaciofluvial sands which

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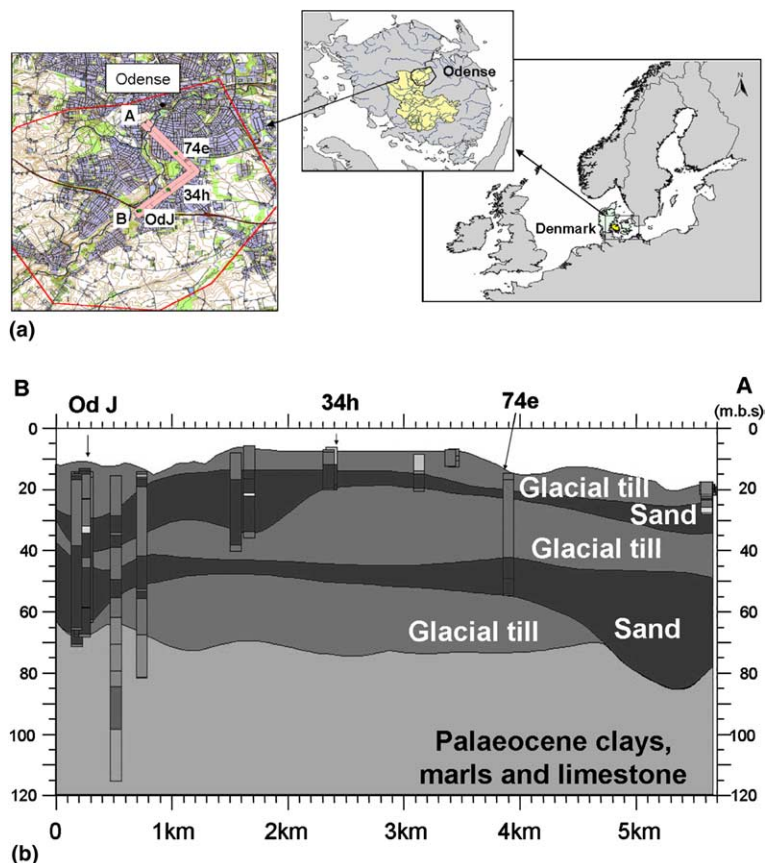


Fig. 1. (a) Location of the investigated area. The area includes the southern part of the city of Odense. (b) Geological cross-section with well locations (Geological Survey of Denmark and Greenland).

constitute the main aquifer on the island overlies a sequence of mainly Palaeocene marls and clays of varying thickness (typically 10–20 m) which form the lower boundary of the quaternary aquifer system. Recharge occurs through sand windows and lenses and through fractures and root holes in the tills. The potentiometric head is at depths between 4 and 10 m.b.s. Screened intervals (5–14 m) within the sands are at depths ranging from 18 to 56 m.b.s. A Palaeocene limestone aquifer is underlying the Odense shallow aquifer and the Palaeocene marls and clays (see the aquifer cross-section in Fig. 1) and in some areas deep wells may extract water from this aquifer or create hydraulic contact to the sand aquifers above.

Denmark and the island of Funen (55° N) are located in a humid temperate zone with an estimated average annual precipitation of about 780 mm. The estimated net recharge of the shallow semiconfined aquifer is 240 mm/a (Hinsby et al., 2003).

A set of modern residence time isotopic indicators ($^3\text{H}/^3\text{He}$, ^{85}Kr , SF_6 and CFC-12) was used to resolve the age structure of the shallow groundwater. In the

past, several studies have demonstrated the applicability of each of the adopted tracer methods (Schlosser, 1989; Busenberg and Plummer, 1992; Plummer et al., 1993; Cook and Solomon, 1997; Beyerle et al., 1999; Plummer and Busenberg, 1999; Bauer et al., 2001). The benefit of the simultaneous application of several methods lies in the possible identification of processes that could erroneously affect the interpretation of data of a single method (for example CFC degradation, Plummer and Busenberg, 1999).

In this paper, the $^{36}\text{Cl}/\text{Cl}$ ratio and the Cl concentration in groundwater were analysed to reconstruct a budget of ^{36}Cl that was produced by testing thermonuclear weapons during 1952–1958. The main objective of this part is to investigate the use of the ^{36}Cl fallout for tracing and dating groundwater. High levels of ^{36}Cl in groundwater indicate, similarly to ^3H , that recharge has occurred since the bomb peak tests. Records of the ^{36}Cl fallout were reconstructed by Bentley et al. (1986) and Synal et al. (1990) from the Dye-3 ice core, Greenland (see Fig. 2). The ^{36}Cl isotope has a half-life of 301 Ka; therefore, radioactive decay can be neglected

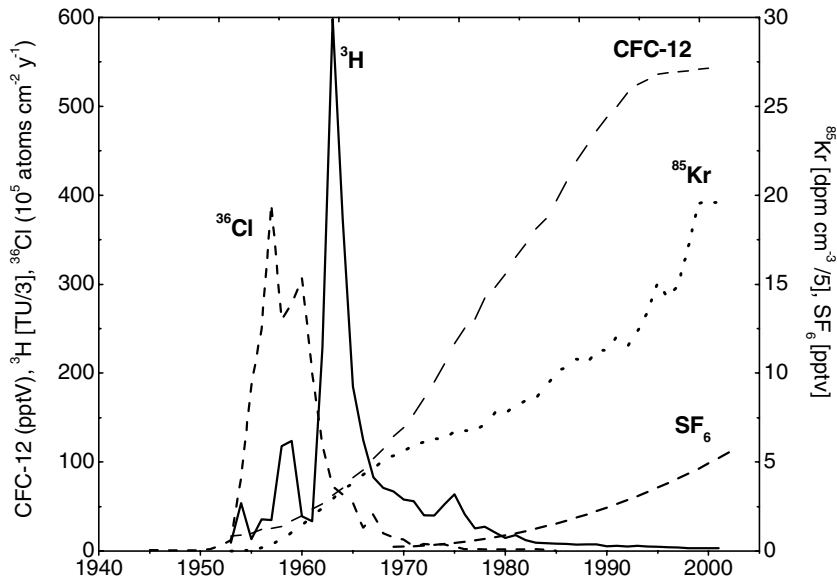


Fig. 2. ^3H concentration in precipitation at Odense (IAEA/GNIP database, 2001), ^{36}Cl fallout predicted at Dye-3 ice core, Greenland, by Synal et al. (1990) and atmospheric concentrations of ^{85}Kr (IAR Freiburg), CFC-12 (Walker et al., 2000) and SF_6 (Maiss and Brenninkmeijer, 1998) used as input functions in the area of Odense.

for the time scale involved in this study. According to the reconstructed fallout at Dye-3, ^{36}Cl has been washed out from the atmosphere since the bomb tests and the actual fallout rates almost reach natural levels. However, according to recent studies (which included direct measurement of ^{36}Cl fallout at different sites, and the ^{36}Cl concentration in different environmental components such as plants, soil, surface waters, groundwaters, etc.), storage and recycling of Cl in the biosphere seems to maintain a background ^{36}Cl activity chronically elevated above natural levels (Milton et al., 1994, 1997; Cornett et al., 1997; Scheffel et al., 1999; Blinov et al., 2000; and Milton et al., 2003). The present study contributes new data to a better understanding of the behaviour of this isotope in nature.

2. Methods

Three wells (34h, 74e and Od J) were sampled in the first half of 2001 for the analysis of $^3\text{H}/^3\text{He}$, ^{85}Kr , SF_6 , CFC-12 and the $^{36}\text{Cl}/\text{Cl}$ ratio (Fig. 1). Two depths were sampled from Od J, one mixed sample from the complete screened section, and one sample from the bottom of the screen. Field measurements of dissolved O_2 concentration, water temperature, pH and E_h were also performed.

Water samples for noble gases, ^3H and CFC analysis were immediately transferred to 45 ml Cu tubes and sealed with pinch-off clamps. Water for SF_6 analysis was sampled in 500 ml gas sampling cylinders. The analyses were performed at the EAWAG and ETH laborato-

ries (Switzerland) following the procedures described by Hofer and Imboden (1998), Beyerle et al. (2000) and Hofer et al. (2002).

For ^{85}Kr analysis several hundred litres of water were degassed in the field and the extracted gas was compressed into evacuated cylinders. Krypton was separated by gas chromatography and the ^{85}Kr activities were measured by low level gas proportional counting at the Physics Institute, University of Bern, Switzerland (Loo-sli et al., 1986, 1999).

The analyses of $^{36}\text{Cl}/\text{Cl}$ ratios were performed at ETH Zurich according to the method described by Ssynal et al. (1990). Chloride analyses in rain water were performed by the Geological Survey of Denmark and Greenland on samples collected by the Odense Water Company (1963–1995). Precipitation rate at Odense was taken from the IAEA/WMO (2001, Global Network of isotopes in precipitation, accessible at www.iaea.org/).

3. Results and discussion

3.1. Measurements

Groundwater temperatures range between 9 and 10.3 °C, and pH between 6.8 and 7.2. The excess air, expressed as the Ne excess, ranges between 17% and 25%. This parameter was used to correct the SF_6 , CFC-12 and ^3He concentrations for concentrations above gas solubility limits. The aquifer has generally

anoxic conditions (Table 1), (O_2 : < 0.1 mg/l; E_h : < -33 mV). Nitrate concentrations vary, but are generally low or very low (<1 mg/l) indicating on-going or recent NO_3 reduction. Sulphate reduction is generally not observed (Hinsby et al., 2003).

^{85}Kr , 3H and CFC-12 above the detection limit (DL) were observed in all the samples, in accordance with the geological situation which points to modern recharge (Table 2). A CFC-12 concentration in excess of air equilibrated water was observed in one sample and attributed to contamination (c). The concentration of SF_6 in one sample was below DL.

The $^{36}Cl/Cl$ ratios and the Cl concentrations in groundwater were measured at all of the wells and the results are presented in Table 2. The lowest Cl concentrations were observed in the deepest well, Od J.

3.2. Tracer dating

Measured concentrations were converted into corresponding atmospheric input concentrations based on the in situ water temperature, elevation of the recharge area and the excess air content (Schlosser, 1989; Busenberg and Plummer, 1992, 2000; Plummer et al., 1993, 1999; Holocher et al., 2002). No corrections are necessary for ^{85}Kr , if no significant isotopic fractionation occurs during gas/water partitioning in the quasi-saturated zone of the aquifer. Noble gas data support this assumption as the measured $^{22}Ne/^{20}Ne$ and $^{40}Ar/^{36}Ar$ ratios agree with the atmospheric ratios and hence, exclude any significant isotope fractionation. As a first approximation, the tracer data were interpreted assuming piston flow (PF) and neglecting hydrodynamic dispersion and mixing of different water components. Using the local

input functions (Fig. 2) residence times between 14 and 48 a were calculated (Fig. 3) (Corcho Alvarado et al., 2002). Low SF_6 concentrations close to the DL allowed only the estimation of a minimum age of about 30 a for wells 74e and Od J. The comparisons of tracer ages depict two obvious discrepancies: CFC-12 ages are generally older compared to the other tracers and $^3H/^3He$ ages for well Od J are younger. These considerable discrepancies between the apparent tracer ages indicate that additional processes have to be taken into account which are not included in the simple piston-flow model. The most probable ones are presented in Fig. 3 and include mixing, dispersion and tracer degradation.

CFC-12 is expected to behave non-conservative under reducing conditions. It is known from similar studies that CFCs can be degraded in such conditions (Busenberg and Plummer, 1992; Plummer and Busenberg, 1999), and degradation has been found in other reducing sand aquifers in Denmark (Hinsby et al., 1997, 2004). As sorption is estimated to be insignificant for the investigated type of aquifer sediments (Engesgaard et al., 2004; Hinsby et al., 2004), degradation stays the most probable explanation for the CFC deviations. Because of the increasing input function, this results in an over-estimation of residence times.

$^3H/^3He$ ages correspond to the residence time of the original 3H -bearing water component while the other tracers indicate a mean age which is the combined result of the age of the young water component and dilution with an older tracer-free water component. Mixing of different water components, either by dispersion or by different origins, is therefore potentially the reason for the deviation of the $^3H/^3He$ ages at well Od J (Kipfer et al., 2002).

Table 1
Field measurements and noble gas data

Well	Screen depth (m.b.s.)	Temperature (°CC)	E_h (mV)	O_2 (mg/l)	pH	4He (10^{-8})	$^3He/^4He$ (10^{-6})	Ne (10^{-7})	Ne excess (%)
34h	18–23	9.0	-33	<0.1	6.8	6.44 ± 0.08	2.24 ± 0.02	2.53 ± 0.04	25
74e	26–39	10.3	-78	<0.1	7.0	8.42 ± 0.10	2.13 ± 0.02	2.45 ± 0.04	22
Od J	46–56	9.2	-56	<0.1	7.2	6.54 ± 0.08	2.03 ± 0.02	2.51 ± 0.04	24
Od J deep	46–56	9.2	-78	<0.2	7.1	6.44 ± 0.08	2.02 ± 0.02	2.37 ± 0.04	17

Noble gas concentrations expressed in cm^3 STP per g of water.

Table 2
Tracer concentrations in groundwater samples

Well	^{85}Kr (dpm/cm ³ Kr)	3H (TU)	$^3He_{Tritogenic}$ (TU)	SF_6 (pptV)	CFC-12 (pptV)	Cl (mg/l)	$^{36}Cl/Cl$ (10^{-12})	^{36}Cl (10^7 atoms/l)
34h	18.5 ± 5.8	10.8 ± 0.2	24.4 ± 1.1	1.36	791 (c)	66.7	0.09	10.3 ± 0.6
74e	5.9 ± 1.1	11.0 ± 0.3	39.4 ± 1.2	<DL	98	54.4	0.15	13.5 ± 0.8
Od J	4.5 ± 0.7	10.2 ± 0.2	20.1 ± 1.0	0.25	80	27.4	0.17	8.0 ± 0.3
Od J deep	4.8 ± 1.3	10.2 ± 0.3	21.4 ± 1.0	0.10	13	27.3	0.18	8.3 ± 0.9

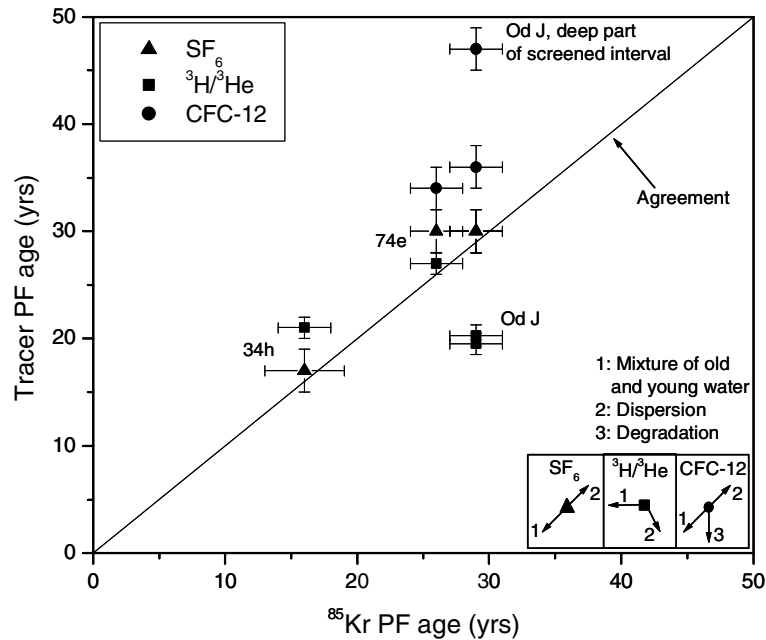


Fig. 3. SF₆, CFC-12 and ³H/³He PF ages vs. ⁸⁵Kr PF age at 3 wells of the Odense sands aquifer (2 screen intervals at Od J). Arrows indicate direction of age correction if the simple piston flow model is complemented with additional processes. Deviations from the 1:1 correlation can mainly originate from degradation for CFC12, dispersion and admixture of an old water component for ³H/³He.

In the following exercise, the data were interpreted with a simplified model that analytically accounts for dispersion (described by the parameter *Pe*, which defines the relative importance of advective and dispersive flow), the ratio of mixed older (tracer free) water component (*m*) and the mean residence time (τ) of the young component (Zuber and Maloszewski, 2001). The three model parameters p_i (τ , *Pe* and *m*) are determined by inverse modelling (Purtschert et al., 1999), minimizing the sum of weighted squared deviations,

$$\chi^2 = \sum_i^n \frac{(C_{out}^i(p_i) - C_{meas}^i)^2}{\sigma_i^2}, \quad (1)$$

where *C* is the tracer concentration (meas the measured, out the modelled), *i* the ⁸⁵Kr, ³H, ³He or SF₆, σ_i the experimental 1 σ -errors.

The weights σ_i^2 give preference to the most precise data. CFC-12 was excluded from the fitting procedure considering that an additional process (degradation) is modifying the concentration in groundwater which is not included in the dispersion model. In all cases, the very low values of χ^2 (see Table 3) indicate a good fitting.

The resulting mean residence times of the young component (τ) range from 17 to 27 a. In the deepest well Od J, an admixture of between 30 and 40% of old water was concluded. This is in perfect agreement with the fact that the screen of well Od J is located in

Table 3

Parameters that best fit the dispersion model to the measurements

Well	Dispersion model			
	τ	<i>m</i>	<i>Pe</i>	χ^2
34h	17	100	23	0.4
74e	27	100	5500	0.0
Od J	23	66	9562	2.7
Od J deep	22	70	6431	1.4

τ , mean residence time of the young component [a]; *m*, mixing ratio of the young component (%) and *Pe*, Peclet number ($v\alpha/D$). The dimensionless χ^2 -value indicates the goodness of the fit as the weighted sum of deviations between measured and modelled concentrations (see Eq. (1)).

the deepest part of the aquifer (Table 1, Fig. 1) where a hydraulic contact with the underlying limestone aquifer can be expected.

Dispersion seems to be of minor importance for the analytical solution (Table 3). The values of the *Pe* number indicate that advection transport predominates over dispersion. In the shallower part of the aquifer (34h) dispersion is more pronounced, than in the deeper part (74e).

Assuming that degradation is the only process affecting the CFC-12 concentration the degradation rate of CFC-12 at the Odense site can be estimated to be in

the range of $0.8\text{--}3.6 \times 10^{-4} \text{ day}^{-1}$. This is agreement with the CFC-12 degradation rate of $0\text{--}6 \times 10^{-4} \text{ day}^{-1}$ (best fit $3 \times 10^{-4} \text{ day}^{-1}$), corresponding to a half life of about 6 a, which was found in a similar Danish aquifer (Hinsby et al., 2004).

In the above described multi-tracer analysis, the aquifer is treated as a steady state system. The resulting age structure is representative for the most recent, spatially averaged groundwater residence time. A several years record of ^3H in precipitation and in two wells (34h and 74e) offers a possibility of reconstructing residence times in the past (Fig. 4). The time lag between the bomb peak in precipitation and in groundwater indicates residence times of approximately 10 and 20–25 a at the wells 34h and 74e, respectively. Within the uncertainties, these results indicate faster travel times to the wells (about 2–7 a) than those obtained from the other isotopic tracer dating, but are still in relative good agreement. For well 34h, where the highest disagreement was obtained, groundwater dating was performed more than 10 a after the well was shut down and this may be part of the explanation as the fraction of young groundwater may change during pumping. The relative high dispersion impact estimated by the model might be explained by the non-stationarity not included in the analytical expression. The screen of this well is positioned in the upper shallow part of the aquifer system, where seasonal variation in recharge is influencing the flow system and consequently may affect the groundwater age distribution.

3.3. Origin of ^{36}Cl in young groundwaters

^{36}Cl has different origins in the environment (Fig. 5). In groundwater two sources can be distinguished: (i) ^{36}Cl in precipitation and (ii) ^{36}Cl added in the subsurface.

- (i) ^{36}Cl concentrations in recharge can be calculated from the fallout rate F_{Cl} (atoms/ $\text{m}^2 \text{ s}$), the annual precipitation P (mm) and the evapotranspiration E (%) according to (Bentley et al., 1986):

$$[^{36}\text{Cl}]_{\text{Nat}} = \frac{F_{\text{Cl}} \cdot 31\,536\,000}{P} \cdot \left(\frac{100}{100 - E} \right). \quad (2)$$

The fallout rate is the sum of a natural fallout (F_{nat}), due to interaction of cosmic rays with ^{40}Ar , ^{36}Ar and ^{35}Cl in the atmosphere, and ^{36}Cl that was produced by atmospheric nuclear weapon testing (F_{bomb}) in the years 1952–1958 (Bentley et al., 1986). A globally averaged F_{nat} of $48 \text{ atoms m}^{-2} \text{ s}^{-1}$ was calculated by Phillips (1999), a value that is up to 4 times higher than other estimates (Lal and Peters, 1967; Bentley et al., 1986; Masarik and Beer, 1999). The F_{bomb} was reconstructed from ice core analyses (Fig. 2) and reached values up to $10^4 \text{ atoms m}^{-2} \text{ s}^{-1}$ (Bentley et al., 1986; Synal et al., 1990). Hence, in young groundwater bomb ^{36}Cl completely overwhelms the natural fallout by several orders of magnitude.

Chloride concentrations in rainwater in the area range between 1 and 73 mg/l with a mean of 15 mg/l. An evaporation rate of 70% will increase the mean input

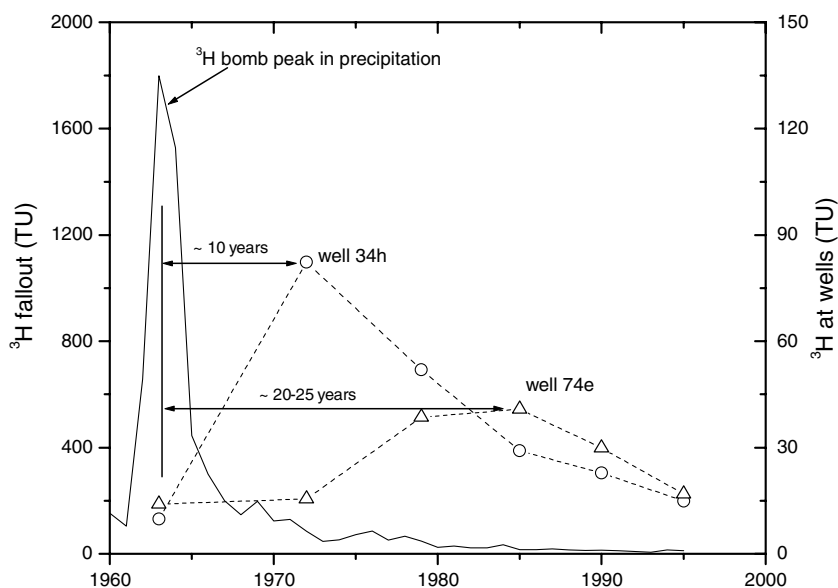


Fig. 4. ^3H time series for Odense precipitation and for wells 34h (○) and 74e (△).

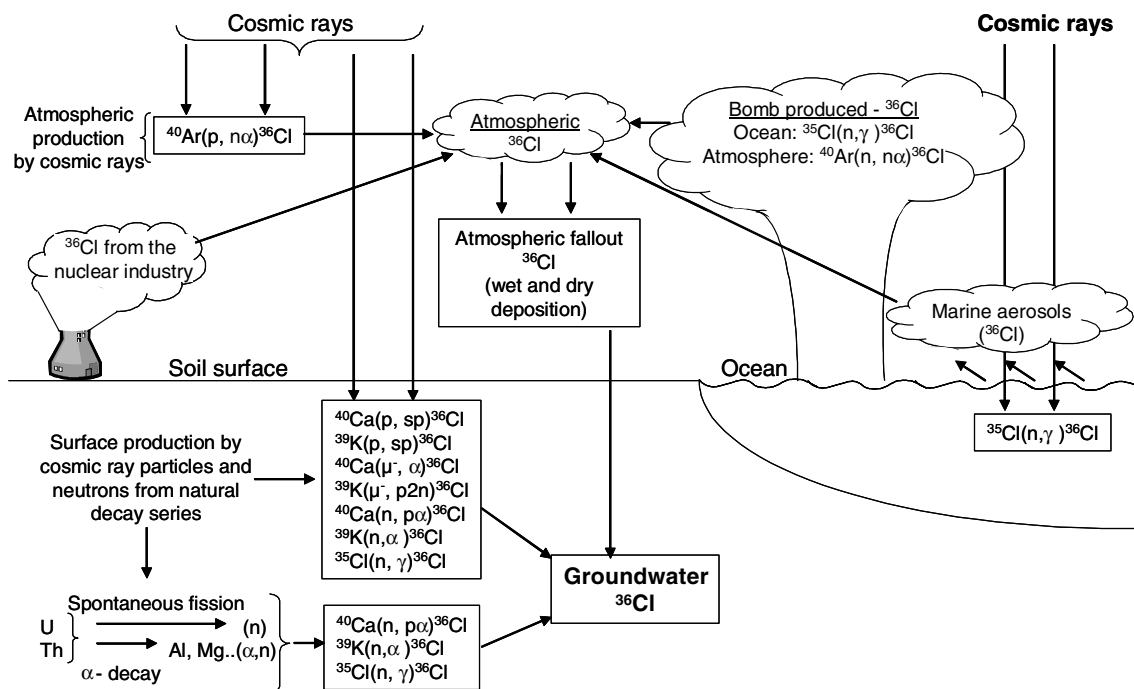


Fig. 5. A schematic representation of the main sources of ^{36}Cl in the environment and the input to groundwater.

concentration to about 50 mg/l, which is comparable to the measured concentrations found in the investigated groundwater (Table 2). However, subsurface Cl sources with high $^{36}\text{Cl}/\text{Cl}$ ratios may significantly contribute to the total ^{36}Cl , even if only a small amount of Cl is added to the water.

(ii) After recharge, ^{36}Cl in groundwater may originate from the following sources

- ^{36}Cl produced cosmogenically in shallow depths through interaction of secondary particles of cosmic radiation in both the rock and the water phases. The most important reactions are spallation of K and Ca and neutron activation of ^{35}Cl . The in situ production in the water phase depends on the Cl content and the depth below surface. Resulting $^{36}\text{Cl}/\text{Cl}$ ratios are commonly negligible considering the small exposure times of the water in the environment (see Table 4). Additionally, ^{36}Cl released from rocks into the water due to weathering produces a ^{36}Cl flux which varies in different geological environments and for different altitudes a.s.l. (Phillips, 1999). Typical values at latitude 40°N are below $25 \text{ atoms m}^{-2} \text{ s}^{-1}$ and therefore comparable to the natural atmospheric deposition fluxes.
- At greater depths, ^{36}Cl is produced by neutron irradiation of ^{35}Cl either in the rock matrix or in the Cl dissolved in the groundwater. The subsurface n -flux is mainly controlled by the U and Th

concentrations in the rock. Calculated and measured equilibrium $^{36}\text{Cl}/\text{Cl}$ ratios commonly range from 5 to 30×10^{-15} in most rocks (Bentley et al., 1986) and below 1×10^{-15} in halites (Fabryka-Martin et al., 1987).

- Other possible ^{36}Cl sources could be the addition of chlorinated solvents such as TCE and BTEX, which were observed in some of the groundwater at Odense; and road salting, which can be significant locally because a large proportion of the catchment lies within the city limits. Most solvents are manufactured with Cl derived from brines which were made from evaporite deposits (sea water, halites). Equilibrium $^{36}\text{Cl}/\text{Cl}$ ratios for sea water are below 4×10^{-15} (Finkel et al., 1980) and for halite formations below 1×10^{-15} (Fabryka-Martin et al., 1987). Salts used for treating roads during winter time have the same origin from evaporite deposits; therefore similar $^{36}\text{Cl}/\text{Cl}$ ratios would be expected.

The contributions of the different ^{36}Cl sources are summarized in Table 4. Subsurface sources are relatively low compared to precipitation sources. ^{36}Cl fluxes (Eq. 4) and $^{36}\text{Cl}/\text{Cl}$ ratios were converted into ^{36}Cl concentrations in water using precipitation and evaporation rates and Cl concentrations, respectively, which are valid in the area of investigation. Bomb ^{36}Cl was estimated using the fallout rate depicted in Fig. 6 (Synal et al., 1990) and the corresponding residence times from the tracer data.

Table 4
Summary of sources of ^{36}Cl in groundwater at Odense and estimations of their magnitudes

	^{36}Cl flux (atoms/m ² /s)	$^{36}\text{Cl}/\text{Cl}$ ratio (10^{-15})	[Cl] (mg/l)	[^{36}Cl] (10^6 atoms/l)
Present in precipitation				
Natural atmosphere-produced fallout	48 ^a		15 ^b	< 7 ^c
Bomb produced fallout	22–428 ^d		15 ^b	3–58 ^c
Subsurface sources				
In situ produced in shallow groundwater		<1 ^c	27–67	<1
Weathering from shallow rocks	<25 ^a		<40 ^f	<3 ^g
Dissolution of Cl bearing minerals (e.g. halite)		5 ^h	<40 ^f	<4
Addition of chlorinated solvents		1–4 ^h	<40 ^f	<3
Road salting		1–4 ^h	<40 ^f	<3
Calculated input to groundwater (mean value) ⁱ				
Measured values (mean value) ^j		120	61	123
Input from other sources ^k				
				82

^a Phillips (1999).

^b Mean value of Cl^- concentration in precipitation. Data from the Geological Survey of Denmark and Greenland.

^c Calculated using Eq. (2) from Bentley et al. (1986). A precipitation rate of 780 mm and an evaporation of 70% were used (Hinsby et al., 2003).

^d Calculated from the Dye-3 ice core data, Greenland (Synal et al., 1990) considering a latitudinal correction factor of 2.5 (Bentley et al., 1986). The range originates from the different recharge years estimated with the box model approach (between 1974 and 1984).

^e Calculated using an averaged neutron flux at shallow depths (between soil surface and 20 m.b.s.) taken from Fabryka-Martin (1988).

^f Assuming an input of Cl^- to groundwater of 40 mg/l which is most probably an overestimation.

^g Calculated using a recharge rate of 280 mm/a (Hinsby et al., 2003).

^h Data from Bentley et al. (1986), Fabryka-Martin et al. (1987) and Finkel et al. (1980).

ⁱ Sum of the mean value of each subsurface and precipitation source.

^j Value corresponds to the mean of the youngest (34h) and the oldest (74e) groundwaters investigated at Odense.

^k Difference between “measured values” and “calculated input to groundwater”.

Bomb derived ^{36}Cl is clearly the dominant ^{36}Cl source in the Odense groundwater. However, the observed ^{36}Cl concentration found in groundwater cannot be explained with the abovementioned sources alone. In Fig. 6, reconstructed ^{36}Cl fallout fluxes (through equation 2) at Odense are compared with fallout rates obtained from Dye-3 ice core (Greenland). Also shown are direct measurements of the ^{36}Cl fallout rates in annual atmospheric precipitation samples (wet and dry deposition) at different sites in Europe (Scheffel et al., 1999). There is a general disagreement between the ice core data and data from groundwater or from annual precipitation samples. On the other hand, calculated fluxes at Odense agree within the range of variation with direct measurements in Europe. The present measurements also reproduce the decrease of the fallout rate as a function of time but at a smaller rate than concluded from the Dye-3 ice core.

Recycling of the ^{36}Cl bomb peak fallout (Milton et al., 1994, 1997, 2003; Cornett et al., 1997; Scheffel et al., 1999; Blinov et al., 2000) might be the explanation for the extra ^{36}Cl measured in groundwater. Thereby, a part of the bomb ^{36}Cl is stored in the biosphere and reemitted into the troposphere in the form of CH_3Cl . This process might possibly reintroduce sufficient

amounts of ^{36}Cl into the atmosphere, and would be responsible for a large fraction of the present day atmospheric flux at Odense.

4. Conclusions

The combined application of a set of different residence time indicators for young groundwater allowed a consistent dating of four samples from three boreholes in the Odense aquifer. Considering the mixture of an older, tracer free, water component and dispersive mixing, it was possible to consistently interpret $^3\text{H}/^3\text{He}$, ^{85}Kr , and SF_6 concentrations in terms of groundwater residence time. Groundwater residence times inferred from analytical data are slightly younger than those implied by the delay in arrival of ^3H peaks for two wells. For CFC, neither mixing nor dispersion could provide a satisfactory explanation. Under reducing conditions, groundwater residence times obtained from CFC measurements tend to be too high due to degradation. Because it is difficult to quantify such a process, CFCs were excluded in the age estimations. Assuming degradation as the only responsible process for the discrepancy, a half life of be-

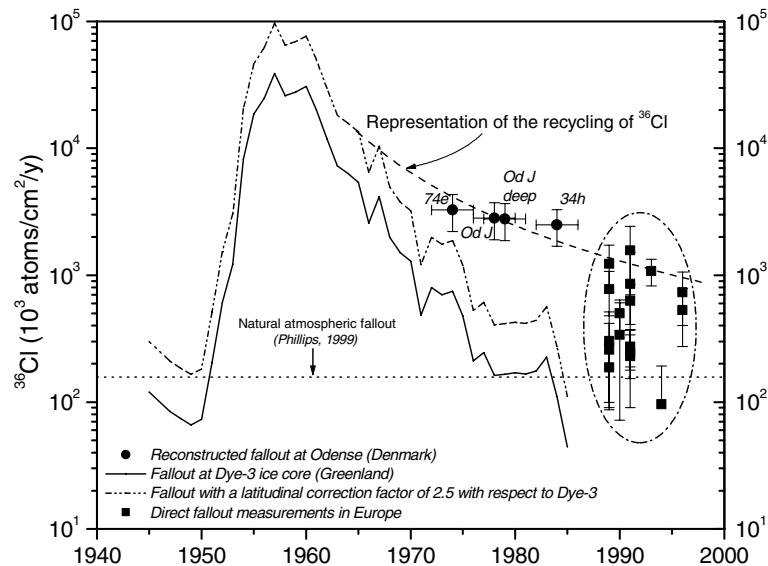


Fig. 6. ^{36}Cl fallout predicted at Dye-3 ice core (Synal et al., 1990) and fallout calculated after considering a latitudinal correction factor of 2.5. (●) fallout rates estimated at Odense from groundwater measurements (the error bars of the ^{36}Cl fallout based on evaporation rates from 60% to 80%) and (■) direct measurements of fallout rates at different sites in Europe (Scheffel et al., 1999). A schematic fallout rate considering recycling is shown by the dashed line. The dotted line represents the level of the natural atmospheric fallout (Phillips, 1999).

tween 5 and 24 a for CFC-12 is estimated under the prevailing conditions in the investigated area.

A ^{36}Cl budget of the tracer dated groundwater reveals some additional evidence that ^{36}Cl produced during atmospheric detonations of nuclear weapons is recycled in the environment. From groundwater samples, reconstructed ^{36}Cl fallout rates exceed estimations from ice core measurements by almost a factor of two. As a consequence, quantitative groundwater dating using thermonuclear ^{36}Cl is complicated lacking a well constrained local input function. However, because bomb ^{36}Cl exceeds natural background levels by several orders of magnitude it can be used, similar to ^3H in the last several decades, as an indicator for the presence of recent water components.

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