Distribution of ^{36}Cl/Cl in a river-recharged aquifer: Implications for the fallout rate of bomb-produced ^{36}Cl

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ABSTRACT

Distribution of ^{36}Cl/Cl ratios in a river-recharged aquifer was investigated in the Oderbruch area, northeastern Germany. The aquifer is confined up to 3.5–4 km inland, where it changes to an unconfined condition. The ^{36}Cl/Cl ratios in the confined area were in the range between 4.6×10^{-14} and 23.1×10^{-14}, showing a peak at 2–3 km away from the river. A plot of ^{36}Cl/Cl vs. reciprocal Cl$^-$ concentrations indicated possible effect of the Cl$^-$ concentration variation on the observed ^{36}Cl/Cl ratios. After accounting for this effect, the estimated ^{36}Cl fallout rates for the last 30 yrs show reasonable agreement with the Dye-3 data and the mid-latitude background value. The results suggest that a local ^{36}Cl fallout curve can be constructed from groundwater when dispersive mixing is of minor importance.

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1. Introduction

Bomb-produced ^{36}Cl can offer a potential dating method for young groundwaters (residence time <60 yrs) [1]. Its advantages as a hydrological tracer stem from the geochemically conservative behavior of chlorine, and the long half-life of ^{36}Cl, which makes decay attenuation negligible on the time scale of several decades to centuries [2,3]. As tritium (^{3}H) has become less effective recently, the ^{36}Cl bomb pulse can be an alternative, as well as other environmental tracers (e.g. CFCs, SF$_6$ and ^{85}Kr).

Dating of young groundwaters relies upon the historical tracer concentrations in the atmosphere, except for the ^{3}H/^{3}He method. Likewise, the knowledge of the ^{36}Cl fallout history for the past ~60 yrs is the basis for the application of bomb-produced ^{36}Cl. Accordingly, the most straightforward approach for investigating the potential use of the ^{36}Cl bomb pulse is to reconstruct ^{36}Cl fallout rates from ^{36}Cl/Cl ratios in groundwater, and then compare them with historical fallout records [4,5].

Fallout rates of ^{36}Cl in Denmark reconstructed by Corcho Alvarado et al. [4] exceeded latitude-corrected estimates based on the Dye-3 ice core data [6]. They attributed it to storage and recycling of chlorine (including bomb-produced ^{36}Cl) in the biosphere [7,8].

In our previous study [5], estimated ^{36}Cl fallout rates in Germany showed a consistent pattern with the Dye-3 fallout data, while the influence of the observed Cl$^-$ concentration variation in the aquifer was not clear.

Extending the previous work, here we present new ^{36}Cl fallout estimates from groundwater data for further investigating the utilization of bomb-produced ^{36}Cl as an age-dating tracer. An updated observation well network enabled us to obtain a more detailed distribution of ^{36}Cl/Cl ratios in a river-recharged aquifer in the Oderbruch, Germany. Results provided insights into the Cl$^-$ variation in groundwater and local ^{36}Cl fallout rates.

2. Study area and sampling

The Oderbruch area is located in the northeastern part of Germany along the border to Poland (see Refs. [5,9,10] for detailed site descriptions). It is a large polder area covering more than 800 km^2, which has been artificially drained during the past 250 yrs. The climate is characterized by a mean annual precipitation of 489 mm (1961–1990) and a high evapotranspiration rate (greater than precipitation) [9].

The field site is situated in the vicinity of the Oder River, where the surface elevation is about 2–3 m above sea level. The area lies mainly below the river water level, and the river base is highly permeable because it consists of coarse sand and gravel [10].

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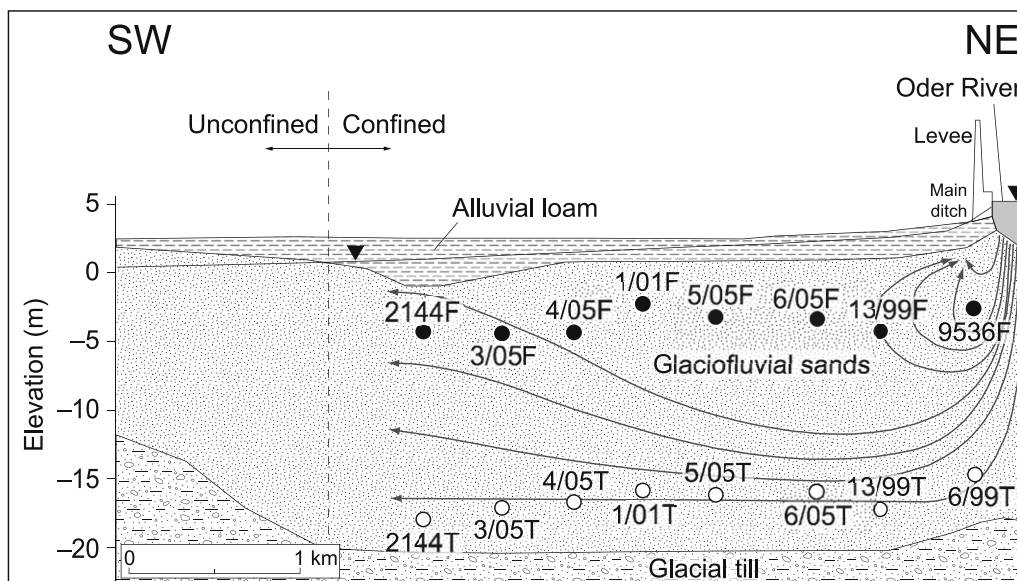 E-mail address: tosaki@tac.tsukuba.ac.jp (Y. Tosaki).

Fig. 1. Cross-sectional illustration of the aquifer along the main groundwater flow direction (modified from Sültenfuß and Massmann [11]). The arrows in the aquifer show groundwater flow paths based on the ^{3}H/^{3}He ages and a three-dimensional flow model [9,12]. Closed and open circles indicate the depths of filter screens of shallow and deep piezometers, respectively. The figure has been vertically exaggerated for clarity.

Consequently, the river water is perennially infiltrating laterally into the shallow aquifer as shown in Fig. 1.

The aquifer consists of fine to medium-sized sands and the thickness is about 20–30 m on the average. It is underlain by a glacial till layer (thickness ~120 m) and overlain by an alluvial loam layer (thickness 0.4–4.0 m) with a low hydraulic conductivity [10]. Along the river banks, the aquifer is confined up to about 3.5–4 km inland (Fig. 1) and recharged by river water infiltration only.

A sample from the Oder River and 16 groundwater samples were collected in March 2006. The sampling points are located along the major groundwater flow direction in the confined area (Fig. 1). Groundwater was sampled at two depths at each point, which correspond to upper and lower parts of the aquifer. According to ^{3}H/^{3}He dating studies [9,11,12], the range of time scale investigated was from a few yrs to over 50 yrs ago.

3. Analyses

Prior to analyses, all samples were filtered with a 0.20 μm membrane. Chloride (Cl$^-$) concentrations were measured by an ion chromatography (Ion Analyzer IA-100, Dkk-Toa). Dissolved silica (SiO$_2$) concentrations were determined with an ICP-AES system (ICAP-757, Nippon Jarrell-Ash) at the Chemical Analysis Division, Research Facility Center for Science and Technology, University of Tsukuba.

The ^{36}Cl/Cl ratios were measured by accelerator mass spectrometry (AMS) at the Tandem Accelerator Complex, University of Tsukuba [13], with the diluted NIST ^{36}Cl standard (^{36}Cl/Cl = 1.000×10^{-11} [14]). For ^{36}Cl-AMS, AgCl was precipitated from the samples according to the standard procedure (see Ref. [5] for details). Depending upon the Cl$^-$ concentration, the sample volume for ^{36}Cl-AMS varied between 5 and 40 mL (typically corresponding to ~1 mg of Cl). Process blanks prepared from NaCl reagent gave ^{36}Cl/Cl ratios on the order of 10^{-15}.

4. Results and discussion

Fig. 2 shows ^{36}Cl/Cl ratios, Cl$^-$ and SiO$_2$ concentrations along the distance from the Oder River. In accordance with our previous

study [5], the ^{36}Cl/Cl ratios showed a bomb-derived peak at 2–3 km away from the river followed by rather low/pre-bomb ratios encountered at ~3.5 km river distance (see Ref. [9] for ^{3}H/^{3}He
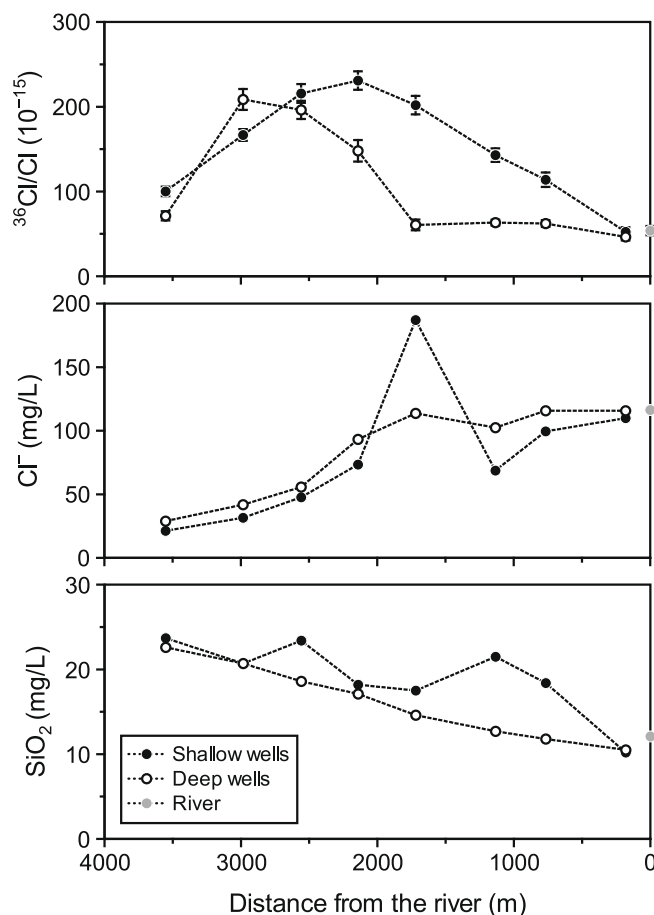

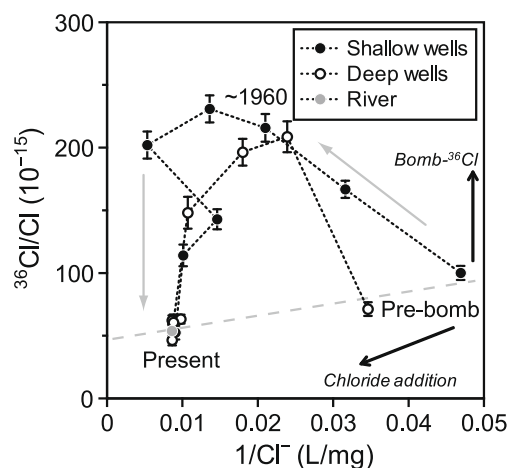**Fig. 2.** Distributions of ^{36}Cl/Cl ratio, Cl$^-$ and SiO$_2$ concentrations along the distance from the Oder River.

Fig. 3. ^{36}Cl/Cl ratios plotted against reciprocal Cl$^-$ concentrations. Trends of stable chloride addition and bomb-produced ^{36}Cl addition are shown by the black arrows. The dashed line indicates the two-component mixing trend between pre-bomb water and a Cl$^-$ source to yield the present river water value.
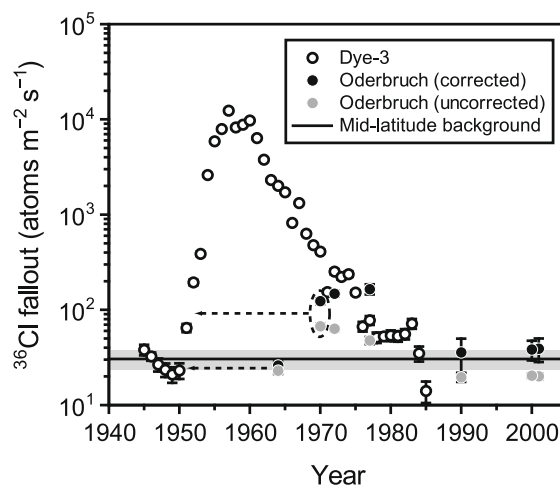

Fig. 4. Comparison of the estimated fallout values from the Oderbruch groundwaters and the Dye-3 fallout data. Infiltration year of each sample is based on ^{3}H/^{3}He data [9]. Also shown is the recent background flux estimated for mid-latitude [19].

Table 1
^{36}Cl/Cl ratios and Cl$^-$ concentrations for the river water and the deep groundwaters.

Sample	Distance (m)	Cl$^-$ (mg/L)	^{36}Cl/Cl (10^{-15})
Oder	0	116.4	54 ± 5
6/99T	181	115.8	46 ± 4
13/99T	766	115.8	62 ± 4
6/05T	1134	102.4	63 ± 4
5/05T	1719	113.7	61 ± 6
1/01T	2142	93.3	148 ± 13
4/05T	2558	55.7	196 ± 11
3/05T	2984	41.8	209 ± 12
2144T	3551	28.9	71 ± 5

ages). The Cl$^-$ concentrations showed a decreasing trend with the distance, from ~120 to ~20 mg/L within the confined area.

Since possible recharge from the surface cannot account for this trend [5], it would be related to the past Cl$^-$ variation in the river water. An increasing trend in Cl$^-$ concentration with time has actually been observed in the upper Oder River, which was possibly caused by the inflow of saline waters from coal mine drainage [15]. Increased Cl loading from agricultural activities can also have affected the Cl$^-$ concentration in the river. A plot of ^{36}Cl/Cl vs. reciprocal Cl$^-$ concentrations (Fig. 3) confirms these effects, as shown by a mixing line through pre-bomb and present/recent waters.

A hydraulic model by Massmann [12] showed that only the deep wells are actually located along a groundwater flow path (see Fig. 1). This is supported by the distribution of SiO$_2$ concentrations along the distance (Fig. 2). Hence, further analysis and discussion focus on the deep confined groundwaters. Table 1 lists the ^{36}Cl and Cl$^-$ data for the river and the deep groundwaters.

In order to account for the effect of the Cl$^-$ variation, we considered a two-component mixing process. Extension of the mixing line in Fig. 3 provides a Cl$^-$ source end-member having a ^{36}Cl/Cl ratio of about $(5.0 ± 0.5) × 10^{-14}$ and an assumed Cl$^-$ concentration of 10,000 mg/L. Assuming the Cl$^-$ concentrations of the initial waters (i.e. before mixing) to be 20 mg/L (cf. lowest Cl$^-$ in Fig. 2), we calculated the initial ^{36}Cl/Cl ratio for each sample. Since 13/99T has a lower ^{36}Cl/Cl ratio than the ratio used for the end-member (Table 1), it was excluded from the calculation.

After accounting for the effect of chloride concentration variation, the ^{36}Cl/Cl ratios were converted into ^{36}Cl fallout rates by using the following mass balance equation [16]:

$$R = \frac{F \times 3.156 \times 10^7}{P \times 10^{-3} \times C_p \times 6.022 \times 10^{23}/35.45} \tag{1}$$

where R is the ^{36}Cl/Cl ratio, F is the ^{36}Cl fallout (atoms m^{-2} s^{-1}), P is the mean annual precipitation (mm), and C_p is the Cl$^-$ concentration in the precipitation (mg/L). It would be reasonable to assume C_p = 1 mg/L and P = 600 mm, according to a C_p distribution map [17] and a P distribution map [18].

In Fig. 4, the estimated ^{36}Cl fallout rates are compared with the Dye-3 data and mid-latitude background data [19]. According to Massmann et al. [9], the older two samples (3/05T and 2144T) showed much greater hydraulic ages (~70 and ~120 yrs, respectively) than ^{3}H/^{3}He ages, suggesting greater effects of dispersive mixing. With this consideration, the estimated ^{36}Cl fallout rates are in better agreement with the Dye-3 fallout data and the natural background ^{36}Cl flux than those from the uncorrected values. This result supports the assumed Cl$^-$ mixing process and its effect on the observed ^{36}Cl/Cl ratios. The agreement with the Dye-3 data for the last 30 yrs suggests that one can construct a local ^{36}Cl fallout curve from groundwater in case the dispersive mixing is of minor importance.

5. Conclusions

In this study, ^{36}Cl/Cl distribution was investigated in a river-recharged aquifer in the Oderbruch, northeastern Germany. Possible effect of variable Cl$^-$ concentrations was accounted for by using a two-component mixing model. With this correction, the estimated ^{36}Cl fallout rates were consistent with the Dye-3 ice core data. This supports the chloride mixing process assumed in this study.

The results imply that the ^{36}Cl fallout record can be estimated by measuring ^{36}Cl in systematically-sampled groundwaters. Modeling of ^{36}Cl/Cl distribution in a simple groundwater system can lead to an estimation of local bomb-produced ^{36}Cl fallout. Such information on the input of bomb-produced ^{36}Cl will increase the utility of bomb-produced ^{36}Cl as an age-dating tracer.

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