

1 **Application of ^{36}Cl as a dating tool for modern groundwater**

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29

1 **Abstract**

2 The $^{36}\text{Cl}/\text{Cl}$ ratios of groundwater samples were measured by AMS in order to investigate
3 the potential use of ^{36}Cl as a dating tool for modern groundwater. Groundwater samples were
4 obtained from several piezometers in the Oderbruch in northeastern Germany. The shallow
5 confined aquifer of the area is mainly recharged by the infiltration from the River Oder. From
6 the results of measurements, the pre-bomb and the recent background $^{36}\text{Cl}/\text{Cl}$ ratios in the basin
7 of the Oder were estimated to be $7\text{--}9 \times 10^{-14}$. The ^{36}Cl fallout values estimated from the $^{36}\text{Cl}/\text{Cl}$
8 ratios of the Oderbruch samples, which were dated by the $^3\text{H}/^3\text{He}$ method, show good agreement
9 with Dye-3 ice core data. These results suggest that the distribution of ^{36}Cl in groundwaters
10 reflects the influence of the ^{36}Cl bomb pulse. This, in turn, suggests that the distribution of
11 $^{36}\text{Cl}/\text{Cl}$ in modern groundwaters could reveal groundwater ages and flow systems in a region.

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15 Residence time; Groundwater dating; Environmental tracer

16

17 **1. Introduction**

18 Tritium (^3H) has been one of the most useful environmental tracers for dating of modern
19 groundwater (age ~50 years) [1,2]. Since large quantities of ^3H were produced during
20 atmospheric thermonuclear testing, ^3H concentrations in precipitation reached a peak around
21 1963, resulting in a “bomb pulse” in the hydrological cycle. However, due to the short half-life
22 of ^3H (12.33 years [3]), the ^3H bomb pulse has been attenuated significantly through radioactive
23 decay. This leads to a need for another tracer or dating method applicable in modern
24 groundwater studies. Recently, several tracers have been successfully utilized; e.g., tritiogenic
25 ^3He (^3He produced by ^3H decay; $^3\text{H}/^3\text{He}$ method) [4], CFCs (Chlorofluorocarbons) [5], SF_6 [6]
26 and ^{85}Kr [7]. Tritiogenic ^3He and CFCs, especially, are extensively used in groundwater studies.
27 It is of note that when applied in the field, these tracers require complete isolation of the
28 samples from the atmosphere because they are gas tracers.

1 As an alternative, the application of bomb-produced chlorine-36 (^{36}Cl) was proposed by
2 Bentley et al. [8]. ^{36}Cl is a long-lived radioisotope of chlorine with a half-life of 3.01×10^5 years
3 [3]. Natural ^{36}Cl is mainly produced in the following three ways: (1) cosmic-ray spallation of
4 ^{40}Ar in the atmosphere; (2) cosmic-ray spallation of K and Ca, and neutron activation of ^{35}Cl
5 near the surface rocks and (3) neutron activation of ^{35}Cl in the deep subsurface [9]. Amongst
6 these three sources, (1) cosmic-ray spallation in the atmosphere is the main natural source of
7 ^{36}Cl in groundwater. The ^{36}Cl produced in the atmosphere is mixed with marine-derived stable
8 chlorine (from seaspray) and falls onto the earth's surface, with the greatest fallout occurring at
9 mid-latitudes [9].

10 In addition, significant amounts of ^{36}Cl were produced by neutron activation of ^{35}Cl in
11 seawater during thermonuclear testing on small islands or on barges (primarily between 1954
12 and 1958), and this bomb- ^{36}Cl was injected into the atmosphere [10]. Fallout of this bomb- ^{36}Cl
13 has been preserved in ice cores, e.g., the Dye-3 cores from Greenland [11,12], show a ^{36}Cl peak
14 in the late 1950s (several years prior to the ^3H peak). The bomb-pulse ^{36}Cl is thought to have a
15 latitudinal distribution with greatest deposition at mid-latitudes [10].

16 Chlorine is geochemically conservative in hydrological cycle because it has a high electron
17 affinity and it exists primarily as Cl^- in the environment, except under low pH condition [9].
18 This makes chlorine an ideal tracer in hydrology and also makes sampling for ^{36}Cl very
19 straightforward. With these advantages, and its long half-life, ^{36}Cl has been applied to the dating
20 of very old groundwater in such regions as the Great Artesian Basin of Australia [13] and the
21 Milk River Aquifer of Canada [14].

22 In the case of the ^{36}Cl bomb pulse, the long half-life makes decay attenuation negligible on
23 the time scale of several decades to centuries (in contrast to ^3H). Thus, the ^{36}Cl bomb pulse
24 provides a potential dating tool covering the last ~50 years. Although it has been applied to
25 studies of the unsaturated zone (soil waters) to estimate recharge rates [15,16], there are few
26 studies applying the ^{36}Cl bomb pulse to groundwaters [17]. Therefore, in this study we attempt
27 to relate ^{36}Cl content variations to groundwater residence times and investigate the potential use
28 of the ^{36}Cl bomb pulse as a dating tool for modern groundwater.

1

2 **2. Materials and methods**

3 *2.1. Study sites and groundwater sampling*

4 The Oderbruch is a large polder (reclaimed land) area which is located in northeastern part
5 of Germany (Fig. 1). At the east side of the area, the Oder flows northward on the border
6 between Germany and Poland into the Baltic Sea. The Oder begins in the Oder Mountains of the
7 Czech Sudeten in the eastern part of Czech Republic. Hydrogeology and groundwater chemistry
8 of the Oderbruch have been intensely investigated [18–21]. Surface elevation of the investigated
9 area is 2–3 m above sea level. The area lies mainly below the river water level, and the river
10 base is highly permeable because it consists of coarse sand and gravel. Consequently, river
11 water is permanently infiltrating into the shallow aquifer as shown in Fig. 2. The aquifer
12 consists of fine to medium sized sands and the thickness is about 20–30 m on the average. It is
13 underlain by a glacial till (thickness ~120 m) and overlain by an alluvial loam (thickness
14 0.4–4.0 m). Along the river banks of the area, the aquifer is confined up to about 3 km inland
15 (Figs. 1 and 2) and recharged by river water infiltration only.

16 Six groundwater samples of 100 ml were obtained from confined area in September 2003.
17 Sampling points are located along the major groundwater flow direction (Fig. 1). At each point,
18 groundwater samples were obtained from piezometers at two depths (5–7 m and 19–21 m below
19 ground surface). These depths correspond to upper and lower parts of the aquifer. Since the
20 groundwater ages of the same sampling depths had been estimated by the $^3\text{H}/^3\text{He}$ method in
21 2001 [18,21], this area was well suited for this study.

22

23 *2.2. Sample preparation and measurements*

24 Groundwater samples were analyzed for Cl^- and ^{36}Cl . All samples were filtered through 0.20
25 μm membrane filter (DISMIC-25cs, Advantec, Tokyo, Japan). The Cl^- concentrations of
26 aliquots were determined by ion chromatography (Dionex DX-500).

27 For ^{36}Cl AMS analysis, groundwater samples were prepared as AgCl . Excluding samples
28 with high Cl^- concentrations (generally more than 50 mg/l), each groundwater sample

1 containing more than 1 mg of Cl was heated on a hot plate to concentrate it to 10–20 ml.
2 Figure 3 shows the sample preparation scheme employed in this study. For the purpose of
3 eliminating the isobaric interference from ^{36}S in the ^{36}Cl AMS measurement, a sulfur reduction
4 process was included in the sample preparation scheme. The procedure was performed in an
5 air-conditioned room to prevent the addition of sulfur contamination and also under dark
6 conditions to avoid decomposition of the AgCl.

7 At first, each sample was acidified with 13 M HNO_3 , and then 0.3 M AgNO_3 solution was
8 added to precipitate AgCl. The AgCl precipitate was separated by centrifugation and dissolved
9 in 3 M NH_4OH . In order to precipitate sulfur (in the form of SO_4^{2-}) as BaSO_4 , saturated
10 $\text{Ba}(\text{NO}_3)_2$ solution was added. The BaSO_4 precipitate was removed by filtration and the filtrate
11 was acidified by the addition of 13 M HNO_3 to precipitate AgCl again. This sulfur reduction
12 process was repeated. After these steps, the AgCl precipitate was re-dissolved and
13 re-precipitated in order to further exclude remaining impurities. Finally, the AgCl precipitate
14 was washed three times with 0.01 M HNO_3 and twice with 99.5% $\text{C}_2\text{H}_5\text{OH}$, and then dried in
15 the oven at 130°C for 3 hours. The overall chemical yield of chlorine was, on the average, about
16 80%. For subsequent AMS measurements, a benzene solution saturated with fullerene (C_{60}) was
17 added to each sample ($\sim 10\ \mu\text{l}$ per 1 mg of AgCl) and the sample was re-dried just before the
18 target pressing.

19 The $^{36}\text{Cl}/\text{Cl}$ ratios of the samples were measured by AMS at the Tandem Accelerator
20 Complex, University of Tsukuba [22]. At the Tsukuba AMS system, which was developed on
21 the 12UD Pelletron tandem accelerator, the tri-carbon molecular ion ($^{12}\text{C}_3^-$) is used as a pilot
22 beam to stabilize the terminal voltage of the tandem accelerator (9 MV for ^{36}Cl -AMS). Due to
23 the addition of the saturated fullerene solution to each sample as mentioned above, $^{12}\text{C}_3^-$ ions
24 are produced in the ion source concurrently with Cl^- ions. Stable $^{35}\text{Cl}^-$ ions are measured as a
25 current using a Faraday cup just after a 120° magnet just downstream of the ion source, while
26 the $^{36}\text{Cl}^-$ ions of interest are injected into the accelerator with $^{12}\text{C}_3^-$ and accelerated. Through
27 two steps of charge changing, $^{36}\text{Cl}^{13+}$ ions are transported to a ΔE - E detector, distinguished from
28 $^{36}\text{S}^{13+}$ background and counted.

1 After ^{36}S background correction using a blank sample prepared from a NaCl reagent, the
2 $^{36}\text{Cl}/^{35}\text{Cl}^-$ (counts/ μC) ratio derived from such measurements of a sample is normalized to the
3 counts/ μC ratio obtained for a standard sample yielding the $^{36}\text{Cl}/\text{Cl}$ ratio of the sample. The
4 standard samples are prepared by dilution of the NIST ^{36}Cl standard (SRM 4943) with NaCl
5 reagent [23]. The calculated $^{36}\text{Cl}/\text{Cl}$ ratio of the standard sample is 4.47×10^{-11} . At the Tsukuba
6 AMS system, the background level of $^{36}\text{Cl}/\text{Cl}$ measurement is 2×10^{-14} [22]. Details of the
7 $^{36}\text{Cl}/\text{Cl}$ calculations and measurement errors have been described previously [23].

8 In this study, the ^{36}Cl data are used in the form of $^{36}\text{Cl}/\text{Cl}$ ratios; these ratios are used in
9 further discussions rather than ^{36}Cl concentrations in order to minimize the possible influences
10 of dilution and/or evaporation processes on the interpretation of the results.

11 **3. Results and discussion**

12 Table 1 lists Cl^- concentrations, ^{36}Cl data and $^3\text{H}/^3\text{He}$ data [18,21] for the samples. The Cl^-
13 concentrations decrease from ~ 100 mg/l to ~ 24 mg/l with distance from the Oder.

14 One possible cause of the decrease is mixing between the groundwater and infiltrating water
15 from the surface. Although the aquifer is essentially confined up to 2144 F & T, the groundwater
16 is recharged to some extent by infiltration through the unsaturated zone (50–70 mm/year [18]).
17 The Cl^- concentration in the infiltrating water would be 2.1–9.5 mg/l. These values were
18 calculated from 434 mm of mean annual precipitation (1951–1980) [18] with 0.34–1.1 mg/l of
19 Cl^- concentration (south Germany [24]), and 50–70 mm of mean annual recharge rate [18]. The
20 mixing rate of the infiltrating water would be 78–84%, when the infiltration is responsible for
21 all of the reduction in Cl^- concentrations.

22 However, the mean annual recharge rate (50–70 mm) is very small compared to the
23 thickness of the aquifer (~ 20 m; Fig. 2). Accordingly, the mixing of 78–84% of the infiltrating
24 water should not have occurred. Other phenomena such as change in evaporation rate may have
25 caused the variation in Cl^- concentration of the Oder. This kind of variation has no effect on
26 $^{36}\text{Cl}/\text{Cl}$ ratio.

27 The possible mixing rate of the infiltrating water would be $\sim 18\%$ as calculated from 70

1 mm/year of recharge rate for 50 years (as discussed later) and 20 m of the thickness of the
2 aquifer. In this case, Cl^- derived from the infiltrating water is only 0.5–2% of total Cl^- in the
3 groundwater. This contribution would not cause serious effect to the original $^{36}\text{Cl}/\text{Cl}$ ratio.
4 Therefore, any influence of the Cl^- concentration variations on the $^{36}\text{Cl}/\text{Cl}$ ratios of groundwater
5 samples does not appear to be a significant driver of the observed variations of the $^{36}\text{Cl}/\text{Cl}$ ratios
6 of the six samples.

7 In this study, ages derived in a previous study using the $^3\text{H}/^3\text{He}$ method have been assigned
8 to the groundwater samples [18,21]. The $^3\text{H}/^3\text{He}$ method has been applied effectively in many
9 groundwater studies to date modern groundwater [4,25–27]. The $^3\text{H}/^3\text{He}$ ages were calculated as
10 follows [28]:

$$11 \quad t = \frac{T_{1/2}}{\ln 2} \ln \left(1 + \frac{[^3\text{He}_{\text{trit}}]}{[^3\text{H}]} \right) \quad (1)$$

12 where t is the $^3\text{H}/^3\text{He}$ age (years), $T_{1/2}$ is the half-life of ^3H (12.33 years), $[^3\text{H}]$ is the ^3H
13 concentration (TU; 1 TU means one ^3H atom in 10^{18} ^1H atoms), and $[^3\text{He}_{\text{trit}}]$ is the tritogenic
14 ^3He concentration (TU).

15 From the results of the $^3\text{H}/^3\text{He}$ dating [18,21], the residence times of these groundwater
16 samples range from a few years to ~50 years. In the $^3\text{H}/^3\text{He}$ dating study [18,21], dispersion and
17 diffusion of ^3He were not considered; accordingly, these factors were also not considered and
18 assumed to be unimportant for ^{36}Cl in this study. Figure 4 shows the $^{36}\text{Cl}/\text{Cl}$ ratios and initial
19 tritium concentrations (sum of ^3H and tritogenic ^3He) plotted against the distance from the Oder.
20 The $^{36}\text{Cl}/\text{Cl}$ ratios and the initial tritium concentrations showed similar variations with distance
21 from the Oder (i.e., along the major groundwater flow direction). High values derived from the
22 ^{36}Cl and ^3H bomb pulses were observed in two samples (1/01 F and 1/01 T; 2139 m away from
23 the river). It should be noted that sample 9561 F was somewhat enhanced only in initial tritium
24 concentration. This may be due to the timing difference between the ^{36}Cl and ^3H fallout pulses,
25 with the ^{36}Cl peak appearing significantly earlier than that of ^3H . Although the limited number
26 of data points does not allow definitive conclusions, this result suggests that ^{36}Cl was
27 transported with groundwater flow in almost the same way as ^3H .

1 To allow comparison of these data to the fallout history of bomb-produced ^{36}Cl , the $^{36}\text{Cl}/\text{Cl}$
2 ratios of the Oderbruch samples were converted into fallout values using the following equation
3 [29]:

$$4 \quad R = \frac{F \times 3.15 \times 10^7}{P \times 10^{-3} \times [\text{Cl}]_p \times 6.022 \times 10^{23} / 35.45} \quad (2)$$

5 where R is the measured $^{36}\text{Cl}/\text{Cl}$ ratio (in unit of 10^{-15}), F is the ^{36}Cl fallout (atoms $\text{m}^{-2} \text{s}^{-1}$), P is
6 the mean annual precipitation (mm), and $[\text{Cl}]_p$ is the Cl^- concentration in the precipitation (mg/l).
7 The mean annual precipitation (P) used was 434 mm [18], and $[\text{Cl}]_p$ was assumed to be 1 mg/l
8 (cf. 0.34–1.1 mg/l; south Germany [24]). The estimated fallout values from the Oderbruch
9 samples and measured fallout values at Dye-3 [12] are plotted together in Fig. 5. The ages
10 assigned to the Oderbruch groundwater samples are from the $^3\text{H}/^3\text{He}$ ages (Table 1) using 2003
11 as year zero.

12 As Fig. 5 shows, the trends of the estimated fallout values and the Dye-3 values are in
13 reasonable agreement except for one sample (2144 T). Although the $^3\text{H}/^3\text{He}$ age of the 2144 T
14 sample was calculated to be 42 years, this sample's initial tritium concentration is very low (3.2
15 TU; Table 1). This indicates that the 2144 T sample does not contain bomb pulse ^3H , and hence,
16 was composed of pre-bomb waters with an age of >50 years. Therefore, as shown by the arrow
17 in Fig. 5, the 2144 T sample should actually be plotted at about the time of the 2144 F sample.
18 With this correction, the variations in the estimated fallout values are consistent with the trends
19 in the fallout at Dye-3.

20 Although the Oderbruch samples do not capture the most diagnostic portion of the ^{36}Cl
21 fallout pulse, the results clearly suggest that the distribution of ^{36}Cl in the Oderbruch
22 groundwaters corresponds to the bomb pulse. Consequently, the Oberbruch results obtained here
23 support the contention that the ^{36}Cl bomb pulse can be used as an effective environmental tracer
24 in groundwater studies.

25 From the results obtained for the four pre- and post-bomb pulse samples, the pre-bomb
26 background $^{36}\text{Cl}/\text{Cl}$ ratio in the Oder basin, which extends from about 49°N to 53°N (including
27 areas upstream of the Oderbruch), is estimated to be $7\text{--}9 \times 10^{-14}$. These four results also suggest

1 that the $^{36}\text{Cl}/\text{Cl}$ ratio returned to pre-bomb levels by ~1980 (about 20 years ago), which is
2 consistent with the trends in the Dye-3 ice core data [12]. It is worth noting that the two samples
3 with somewhat higher $^{36}\text{Cl}/\text{Cl}$ ratios in Fig. 5 (1/01 F and 1/01 T) correspond to the tail part of
4 the bomb pulse.

5 Priller et al. [30] measured the $^{36}\text{Cl}/\text{Cl}$ ratios of wine samples spanning 1930–1980 from the
6 Rheingau region in western Germany (about 50° N). Their results have been interpreted as
7 reflecting the $^{36}\text{Cl}/\text{Cl}$ ratios of soil waters in each sampled year. The mean $^{36}\text{Cl}/\text{Cl}$ ratio they
8 obtained for the pre-bomb period was about $(5.1 \pm 2.2) \times 10^{-14}$ (which is slightly lower than the
9 result obtained in this study), while their peak value was $2\text{--}4 \times 10^{-12}$ for the years 1959–1961.
10 On the basis of Priller et al.'s results and the concordance between the Oberbruch and Dye-3
11 results (and if dispersion and mixing effects are negligible), the results obtained in this study
12 suggest that the groundwater ^{36}Cl bomb peak in the Oderbruch should reach a peak at a distance
13 of ~2.7 km from the Oder and the peak $^{36}\text{Cl}/\text{Cl}$ ratio value should be on the order of 10^{-12} .

15 **4. Conclusions and outlook**

16 $^{36}\text{Cl}/\text{Cl}$ ratios of groundwater samples were measured by AMS to evaluate the potential use
17 of ^{36}Cl as a dating tool for modern groundwaters. The ^{36}Cl fallout values estimated from the
18 $^{36}\text{Cl}/\text{Cl}$ ratios of $^3\text{H}/^3\text{He}$ dated Oderbruch samples show reasonable agreement with ^{36}Cl fallout
19 data from the Dye-3 ice core. This provides support for the contention that the variations of ^{36}Cl
20 in groundwaters reflect the input of bomb pulse ^{36}Cl , and hence, that the variations of $^{36}\text{Cl}/\text{Cl}$ in
21 modern groundwaters should reveal groundwater ages and flow systems in a region.

22 In contrast to the $^3\text{H}/^3\text{He}$ method, the utilization of ^{36}Cl in such studies requires spatially
23 extended sampling in order to map out the ^{36}Cl bomb pulse in the regional groundwaters.
24 However, because of its geochemical behavior, ^{36}Cl can be utilized in both the unsaturated zone
25 and the saturated zone. In the utilization of ^{36}Cl in groundwater dating studies, the possible
26 effects of dispersion on the ^{36}Cl concentrations and $^{36}\text{Cl}/\text{Cl}$ ratios in the groundwater should be
27 evaluated. In this regard, further investigations, involving denser sampling of the region, are
28 underway in the Oderbruch.

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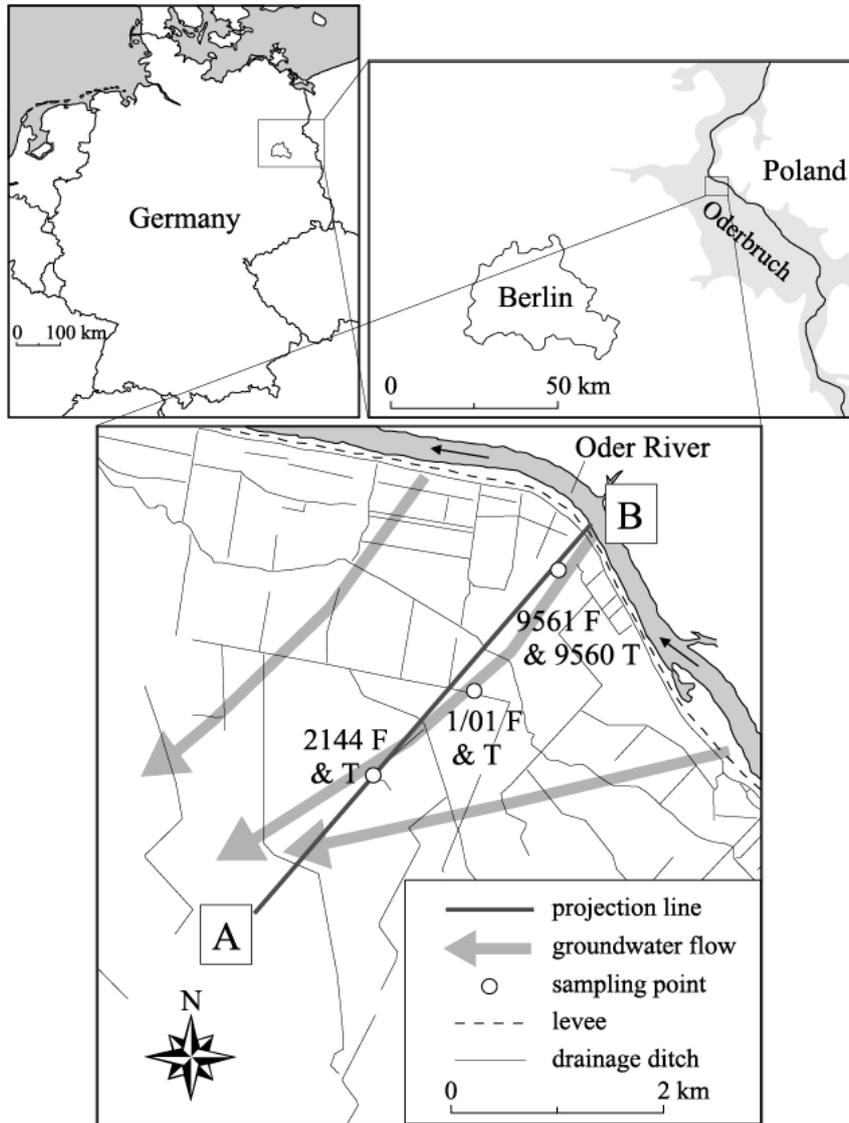
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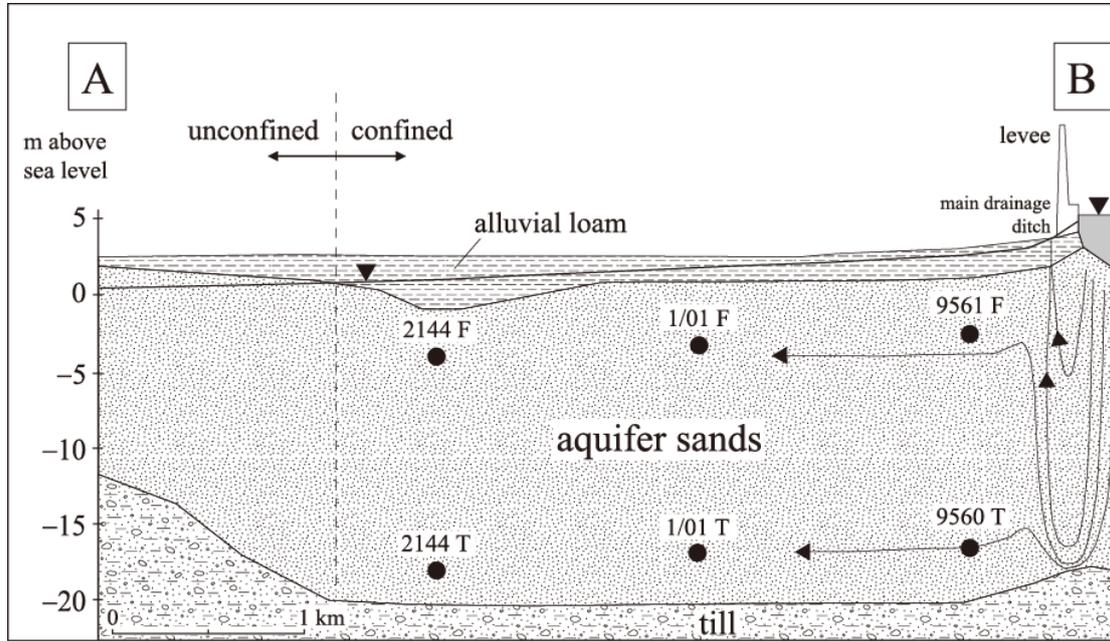
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5 Fig. 1. Location of the Oderbruch polder and groundwater sampling points along the projection
6 line (modified from Sültenfuß and Massmann [21]). Also indicated is groundwater flow
7 direction [18].

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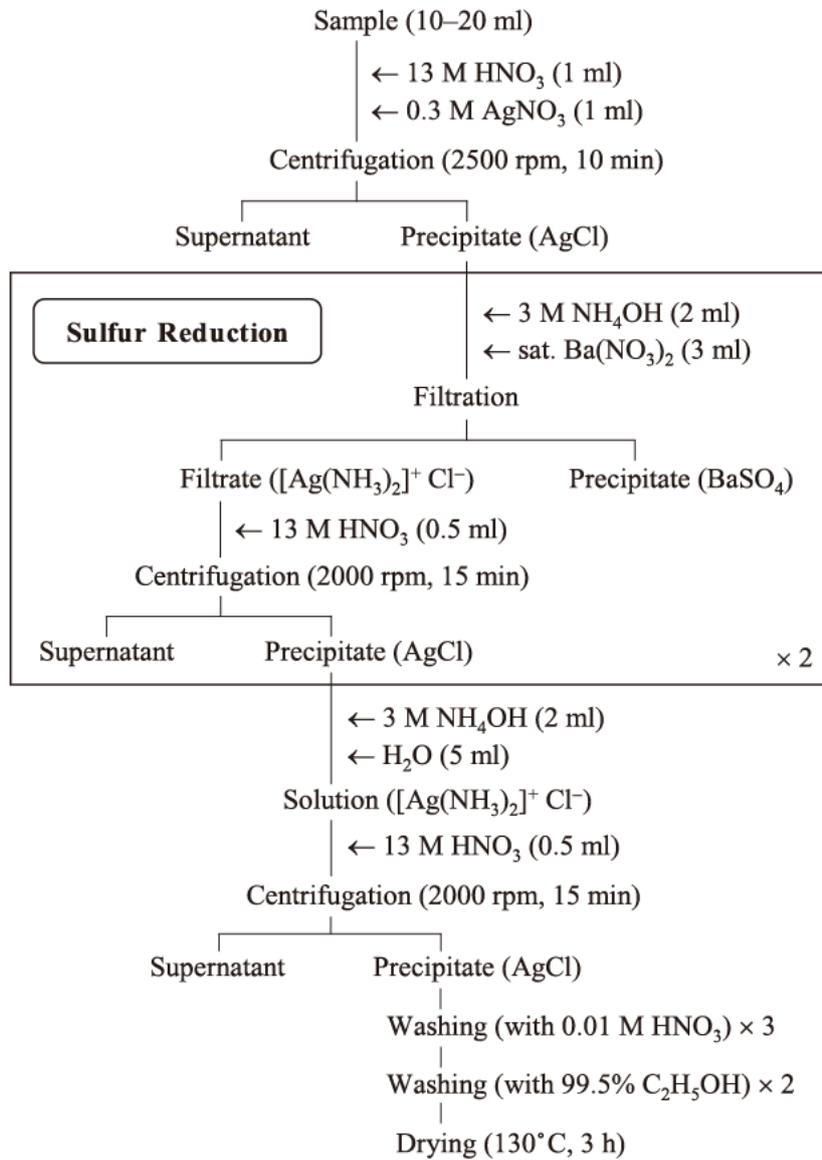
5 Fig. 2. Cross section along the projection line with major hydrological units (modified from

6 Sültenfuß and Massmann [21]). The projection line is shown in Fig. 1. The arrows in the aquifer

7 show groundwater flow paths. Black circles indicate the depths of filter screens of piezometers.

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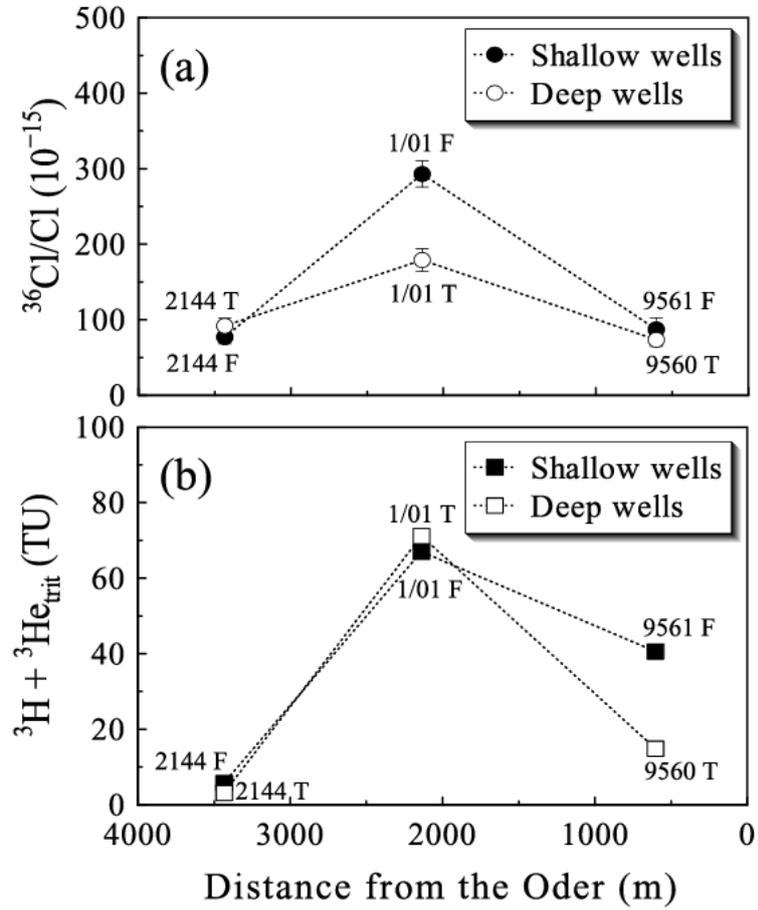


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Fig. 3. Sample preparation scheme for ³⁶Cl AMS (accelerator mass spectrometry).

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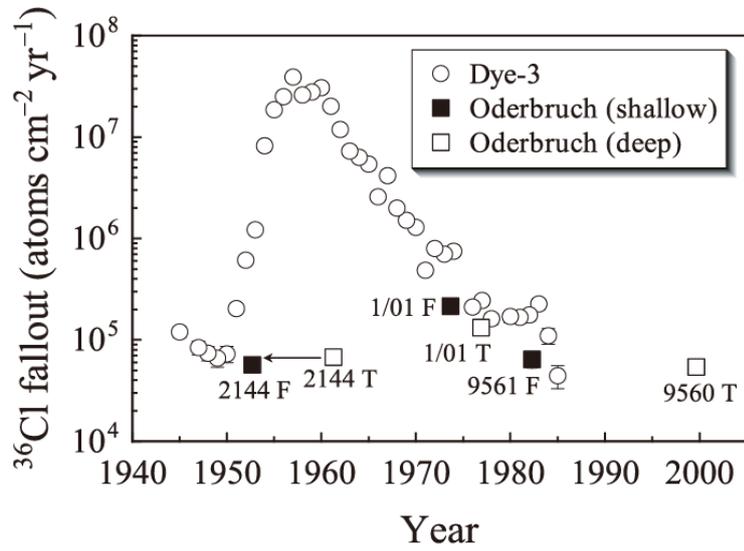
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5 Fig. 4. $^{36}\text{Cl}/\text{Cl}$ ratios and initial tritium concentrations [18,21] for the Oderbruch samples as a
6 function of the distance from the Oder. (a) $^{36}\text{Cl}/\text{Cl}$ ratio. (b) Initial tritium concentration.

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Fig. 5. Comparison of measured ^{36}Cl fallout values from Dye-3 ice core [12] and the estimated fallout values from the Oderbruch groundwater samples. The estimated fallout values were calculated using Eq. (2) and presented as annual fluxes (atoms $\text{cm}^{-2} \text{yr}^{-1}$). The ages assigned to the Oderbruch samples are from the $^3\text{H}/^3\text{He}$ ages (Table 1) using 2003 as year zero. The age of 2144 T sample should be older as indicated by the arrow; the sample has low initial tritium concentration (3.2 TU; Table 1).

Table 1

Measured Cl^- concentrations, $^{36}\text{Cl}/\text{Cl}$ ratios and ^{36}Cl concentrations for the Oderbruch samples

Sample	Distance* (m)	Screen depth (masl)†	Cl^- (mg/l)	$^{36}\text{Cl}/\text{Cl}$ (10^{-15})	^{36}Cl (10^6 atoms/l)	^3H (TU)	$^3\text{He}_{\text{trit}}‡$ (TU)	$^3\text{H}/^3\text{He}$ age (a)
9561 F	604	-2.4	104.9	87 ± 15	156 ± 27	12.8	27.8	21
1/01 F	2139	-3.5	61.9	293 ± 17	308 ± 18	13.0	54.0	29
2144 F	3434	-4.3	22.7	77 ± 9	30 ± 3	0.4	5.5	50
9560 T	604	-16.8	94.6	73 ± 9	118 ± 14	12.3	2.5	3
1/01 T	2139	-17.0	76.4	179 ± 15	233 ± 19	16.6	54.6	26
2144 T	3434	-17.9	25.4	92 ± 11	40 ± 5	0.3	2.9	42

Concentrations of ^3H and $^3\text{He}_{\text{trit}}$, and $^3\text{H}/^3\text{He}$ ages are from Massmann [18] and Sültenfuß and Massmann [21].

*Distance from the Oder.

†m above sea level.

‡Tritogenic ^3He .