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## Isotopic and hydrochemical studies of groundwater flow and salinity in the Southern Upper Rhine Graben

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**Abstract** In order to determine the origin and the propagation mechanisms of highly concentrated chloride brines within the Quaternary aquifer system in the southern part of the Upper Rhine Graben, a combined isotope (H, O, C) and hydrochemical analysis was carried out. Groundwater recharge in this area is a complex system, consisting of local precipitation, river bank filtration, lateral flow from the Graben borders and, to a minor extent, an old Pleistocene component. In some areas, groundwater consists of up to 90% of recent bank filtrate, reaching depths down to at least 100 m. The isotopic and hydrochemical results show, that the elevated chloride concentrations in the Quaternary aquifer mainly result from leaky settling basins charged by the

French potash mines until the mid 1970s. Input of natural brines coming from tertiary salt diapirs is of only minor importance. While infiltrating, the anthropogenic brines were strongly diluted by local river bank filtrate of the Rhine. Nevertheless, maximum chloride concentrations nowadays still reach some 10,000 mg/l at the base of the aquifer at a depth of more than 100 m below surface. The main volume of the brines is stored in the less permeable lower part of the quaternary sediments (Breisgau-Formation) whereas only a minor part is transported northwards with the rapid convective groundwater flow. Brines undergoing only dilution preserve their hydrochemical characteristics (NaCl-type). In contrast, brines recirculated from the Breisgau-Formation show a northwards increasing alteration through ion exchange processes. Potassium and sodium may be fixed in the fine grained aquifer material while calcium is set free into the groundwater. After a flow distance of about 12 km, complex hydraulic interactions between groundwater and surface waters lead to the rise of strongly diluted and hydrochemically altered brines with chloride contents up to maximum 700 mg/l. The presented case study is an example for a detailed analysis of a multi-component groundwater mixing system using combined isotope and hydrochemical methods. Furthermore, cation exchange is shown as a major process affecting the hydrochemical evolution of the young groundwater in the southern Upper Rhine Graben which is locally strongly polluted by chloride as a consequence of former potash mining.

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### Introduction

The Quaternary sediments of the Upper Rhine Graben (URG) constitute the largest European alluvial aquifer

system. They extend over 9,000 km<sup>2</sup> (Fig. 1), reach 240 m thickness in the southern part of the URG and host a major groundwater resource shared by three countries, Switzerland, Germany (Baden) and France (Alsace). The Rhine aquifer represents about 80% of the regional water supply. This strategic importance of the mainly unconfined alluvial aquifer contrasts with its high vulnerability. The whole Upper Rhine Graben (URG) is densely populated and concentrates industry, built up areas and intensive agriculture. Human impact on the quality of the groundwater resource ranges from industrial and urban point pollution to diffuse inputs from agriculture (Région Alsace 2000). This paper addresses groundwater recharge components, residence time and salinity as important aspects of groundwater quality degradation in the southern part of the Upper Rhine Graben.

The first indications of an increasing salinity of parts of the alluvial aquifer were observed in the 1960s (Sauer 1978). The increase in chloride concentrations was attributed to the impact of mine dumps and residual brines from the potash mining industry (Fig. 2). Mining of Oligocene potash deposits in the southernmost part of the URG started in 1910 in Alsace and ended in 2002.

On the German side, potash mining lasted from 1927 to 1973. The dissolution of salt-bearing mining dumps by rainfall and the direct infiltration of residual brines from storage basins constitute point sources of highly concentrated salt brines. Due to their high density, these brines sink straight to the aquifer basis and then spread laterally according to the morphology of the base of the aquifer to form brine pools. The salinity problem in the URG is further complicated by the existence of salt diapirs rooting in the Tertiary strata and locally penetrating the overlying Quaternary sediments (Fig. 2). These diapirs can be a source of natural brines in the deep parts of the alluvial aquifer. Therefore, it had to be

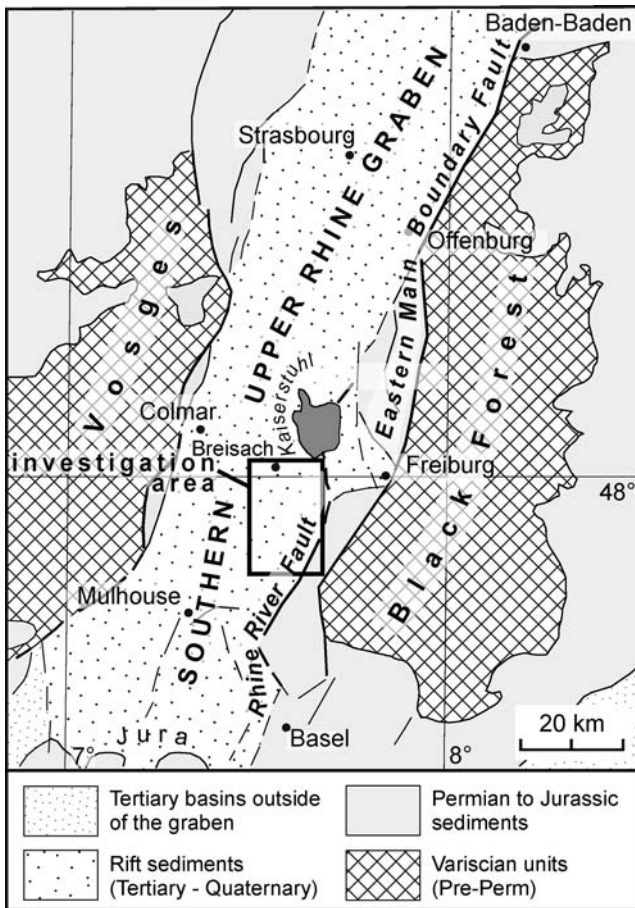


Fig. 1 Location of the investigation area in the Upper Rhine Graben (Pflug 1982, modified)

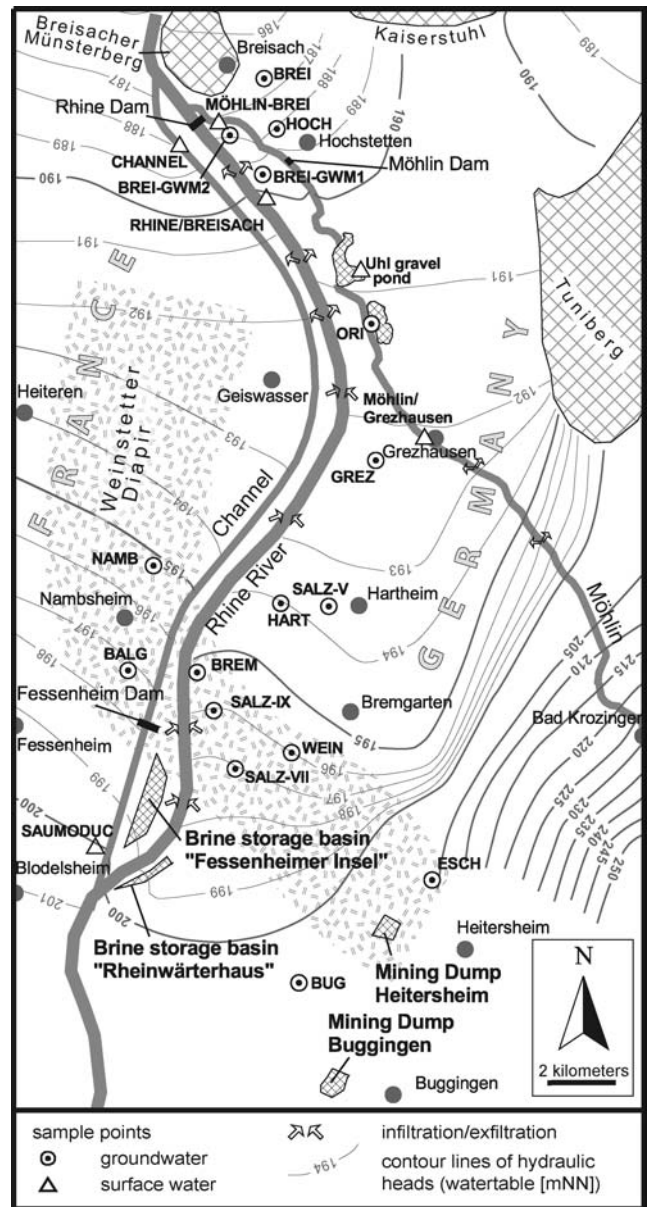


Fig. 2 Location map with sites of anthropogenic chloride input and sample points of groundwater and surface water in the study area. The position of the so called Weinstetter Diapir in the subsurface is indicated by the dotted area

tested, if at certain points, a superposition of natural and human induced groundwater salinisation occurs.

Starting in 1965, a salinity monitoring program was initiated in the German part of the study area between Fessenheim on the French and Breisach on the German side of the Rhine river (Fig. 2). After an increase of the chloride content in the drinking water supply wells of Breisach was first observed, the investigations were intensified in the beginning of the 1990s. New observation wells were drilled and a first synthetic report was published in 1997 (GLA 1997).

The present hydrogeochemical and isotopic cross-border study of the alluvial aquifer between Fessenheim and Breisach was undertaken in the framework of the European INTERREG II program, under the coordination of the German local authority in Freiburg. The aims were: - a better constraint of groundwater recharge and flow in this sector, - improvement of the knowledge about the interaction between groundwater and surface waters - and to investigate the possibility of differentiating sources of salinity by means of isotopic tracers. These data were used as input parameters for a 3D groundwater model, which was built up within the same project (Lang et al. this volume).

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## Geological and hydrogeological framework

The study area is situated in the southern Upper Rhine Graben, south of the Kaiserstuhl (Fig. 1). The Upper Rhine Graben started to evolve during the Eocene (Illies 1977; Pflug 1982; Geyer and Gwinner 1986). During the Plio-Quaternary, it was filled with coarse grained sands and gravels, deposited by the Rhine river and its tributaries from the Vosges and the Black Forest.

The Tertiary basement consists of clays and marlstones of Oligocene age. The Plio-Quaternary sediments above can be subdivided into four hydrogeological units. The Iffezheim-Formation at the bottom is considered, together with the Tertiary sediments, as the substratum of the aquifer. The Iffezheim-Formation is made up of densely packed clayey and silty sands, silts and clays and completely weathered gravels of local (Vosges and Black Forest) origin. Its hydraulic conductivity is low. The unit reaches its maximum thickness of about 40 m in the central part of the Graben.

The Iffezheim-Formation is overlain by the Breisgau-Formation which forms the basal part of the Quaternary porous aquifer of the southern Upper Rhine Graben. It consists of more or less densely packed sandy to silty gravels that are partly altered. On the basis of lithology, the Breisgau-Formation can be subdivided vertically into two subunits: the Lower Breisgau-Schichten show moderate to low hydraulic conductivities, the Upper Breisgau-Schichten moderate to high conductivities. In the so-called Geiswasser Basin, the Breisgau-Formation reaches its maximum thickness of about 200 m.

The upper part of the Quaternary aquifer is made up of the Neuenburg-Formation, gravels with variable sand

content and intercalated coarse grained (pebble) layers. The maximum thickness of the Neuenburg-Formation is about 70 m. Its hydraulic conductivity is high to very high. Both the Breisgau-Formation and the Neuenburg-Formation show a lithological differentiation from the central area close to the Rhine river toward the foothills of the Vosges and the Black Forest respectively. Whereas in the central part, calcareous alpine material dominates the composition of the sediments, material derived from the foothills increases toward the western and the eastern borders of the aquifer. This change in lithofacies comes along with a decrease in hydraulic conductivity toward the border area.

Generally speaking, the base of the aquifer dips from the foothills of the Vosges and the Black Forest respectively, toward the central part of the Graben. Its deepest point in the study area is located in the so-called Geiswasser Basin south of Neuf-Breisach (F) at about 240 m below surface. From the Geiswasser Basin northward, the base of the aquifer ascends, bifurcating into two channel-like branches. One channel goes to the north-northwest, the other one runs in a northeasterly direction, passing the narrowing between the Münsterberg at Breisach (Germany) and the Kaiserstuhl (Fig. 2). This overall picture is complicated by a number of faults, which not only affect the base of the aquifer but also locally influence the thickness of the overlying hydrogeological units.

One important structure, probably caused by salt-induced uplift of the Tertiary basement, is the so called Weinstetter Diapir (Esslinger 1968). It runs from the area of Eschbach-Heitersheim (D) toward the northwest (Fig. 2). At Nambshheim (F), it bends into a northerly direction (Lutz and Cleintuar 1999). At the "Dome of Balgau" (east of the village of Balgau, France), which is part of the Weinstetter Diapir, the base of the aquifer lies about 70 m higher than in its surroundings. It plays an important role in the present-day observed distribution of the highly concentrated salt brines, which infiltrate into the subsurface on the so called "Fessenheimer Insel", situated only 1.5 km south-southeast.

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## Groundwater flow

On a regional scale, groundwater flow is directed from the foothills of the Black Forest and the Vosges towards the Rhine river. From Zienken (south of Heitersheim) to Grezhausen, the groundwater flow regime is mainly directed toward the Rhine (see Fig. 2). Variations in local recharge and water level fluctuations of the Rhine river affect only temporarily some parts of the aquifer close to the river (Königer et al. 2001).

From Grezhausen northward, groundwater flow is dominated by bank infiltration because of the damming of the Rhine river southwest of Breisach (Kulturwehr). North of that dam, the groundwater flow follows two

paths. One part exfiltrates downstream of the Breisach dam, the other flowpath runs northward through the valley between the Münsterberg (Breisach) and the Kaiserstuhl.

South of Hochstetten, the river Möhlin passes through the Uhl gravel pond. To avoid massive groundwater drawdown as a consequence of the Breisach dam and incised bed of the Möhlin, another dam was established on the Möhlin river. Infiltration upstream of this dam leads to local modifications in groundwater flow which only concern the shallow part of the aquifer.

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## Methods

### Sampling

Four sampling campaigns were performed. During a first campaign in 1998, pumped samples were taken from several selected piezometers and wells (Kloppmann 1999; Kloppmann 2000; Région Alsace 2000). The second campaign was undertaken between May and July 2000 on a total of 71 sampling points of surface water (Rhine river, Möhlin river, Rhine Channel (Grand Canal d'Alsace), Uhl gravel pond) and groundwater (observation wells and pumping wells). At 20 selected points in the Breisach area in the third campaign, a chemical and isotopic monitoring program was carried out from September 2000 to the end of August 2001. Sampling was done twice a month in order to investigate variations in the recharge components and fluctuations of salinity during the year.

In a final campaign in September 2001, 25 mostly shallow observation and irrigation wells, drinking water wells and the deep observation well "Balgau" on the French side of the Rhine were sampled for a general survey of superficial salinity in this area and to study the extension of bank infiltration. All sampling points referred to in the text are shown in Fig. 2.

Groundwater sampling in 1998 was carried out with pumps, extracting groundwater over the whole active screen. Thenceforward in the campaign in 2,000 special scoops were used, which allow sampling at different depths (without pumping). This method avoids vertical groundwater circulation and mixing effects caused by pumping in wells with long screen sections. Due to generally high aquifer permeabilities and therefore no stagnant groundwater in the observation wells of the study area, this is an adequate method of sampling. In some of the wells, multiple sampling at different depths was carried out. Wells for drinking water supply were repeatedly sampled at the installed pump after different pumping durations.

All sampling localities and analyzed data are documented in Regierungspräsidium Freiburg (2002). Table 3 abstracts the data from several selected localities, mostly with deep multi-level-piezometers (see Fig. 2).

### Analysis

The analytical program includes the physico-chemical parameters measured in the field (pH, specific electric conductivity) and further parameters, analyzed in the laboratories. A minimum program (spec. el. conductivity, major ions and  $\delta^{18}\text{O}$ ) was conducted on all samples. The complete program was only carried out on a selection of samples chosen on the base of the results of the first survey.

For the determination of the contents of anions and cations as well as for the isotopes  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $^3\text{H}$  (as well as  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  analyzed in the survey in 1998), standard analytical techniques were applied.

The  $^{14}\text{C}$  activity of samples from the campaign in 2000 was measured by accelerator mass spectrometry (AMS) by BETA Analytic Inc. (FL, USA). After pretreatment of the water sample by acid attack and reduction of  $\text{CO}_2$  to C under hydrogen flux with Co, AMS results are derived from the reduction of sample carbon to graphite (100%C), along with standards and backgrounds.

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## Results and discussion

### Groundwater recharge components

#### *Identification of different recharge components*

The groundwater in the Rhine Graben aquifer is a multiple component mixing system with a contribution from different recharge components. Hydrogen carbonate and nitrate concentrations in combination with the  $\delta^{18}\text{O}$  values were used to discriminate and quantify the recharge components of groundwater. Table 1 gives an overview on the contents of  $\text{HCO}_3$ , nitrates and  $\delta^{18}\text{O}$  values in the main groundwater components as well as in some groundwaters of mixed origin.

Three principal recharge components of the alluvial aquifer can be distinguished (Regierungspräsidium Freiburg 2002). Tributaries of the Rhine river coming from the Black Forest (e.g. river Möhlin) have low contents in solutes and relatively low  $\delta^{18}\text{O}$  values due to an altitude effect (e.g. Herdeg 1993). The Rhine river and its filtrate show moderate contents of hydrogen carbonate and low contents of nitrate (Table 3). The stable isotope values of the Rhine river and of the Rhine Channel, which is diverted from the Rhine river at Huningue (F) north of Basle, are similar and clearly depleted in  $^{18}\text{O}$  (by about 2–3‰) and in  $^2\text{H}$  with respect to the local recharge component (see below). This depletion in  $^{18}\text{O}$  is due to a typical altitude effect. The mean altitude of the catchment area of the Rhine river comprises part of the Swiss Alps and is relatively high compared to the URG and the surrounding lower mountain ranges (Black Forest, Vosges). The range of –11‰ to –12‰ observed for  $\delta^{18}\text{O}$  corresponds to mean altitudes of about 1,000–1,500 m taking into account

**Table 1** Mean values for hydrochemical constituents ( $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ) and  $\delta^{18}\text{O}$  of the main surface and groundwater types in the study area (Regierungspräsidium Freiburg 2002)

Component	$\delta^{18}\text{O}$ , ‰ VSMOW (mean)	Hydrogen carbonate, mg/l (mean)	Nitrate, mg/l (mean)
Precipitation in the Rhine valley (Station Freiburg <sup>a</sup> )	-8.3		
Rhine/Breisach	-10.9	150–200	Mostly < 10
Möhlín (at inflow to the gravel pond Uhl)	-9.6	About 50–80	< 10
Groundwater, Upper Breisgau and Neuenburg Formation (depth < 100 m), recharged from local precipitation	-8.5 (-8.0 to -8.6)	About 270	up to 80
Groundwater, mainly recharged from Rhine infiltration	≤ 10.3	About 150–200	< 15
Groundwater, mainly recharged from Möhlín infiltration near Hausen	About -8.5 to -9.5	About 260	About 50

<sup>a</sup>Mass-weighted mean value for 1999–2000 (personal communication Hydroisotop/Bundesamt für Strahlenschutz, Freiburg, 17.5.02)

relationships established for South Germany and North Switzerland (Balderer et al. 1991). The third recharge component is derived from local precipitation with a mean of  $-8.5\text{‰}$  for  $\delta^{18}\text{O}$ . It shows increased hydrogen carbonate concentrations and in consequence of agricultural fertilizer washout mostly high nitrate contents.

#### Balance of groundwater components

From the analysis of  $\delta^{18}\text{O}$  it is possible to set up a balance for the different components of the groundwater in the study area. This balance was mapped within a band a few kilometers wide parallel to the Rhine river, which corresponds to the area where groundwater salinity is studied in more detail.

The calculations were done on the basis of  $\delta^{18}\text{O}$  values with the simplifying assumption of a two-component system (bank infiltration from the Rhine river, recharge from local precipitation). The following mixing equation was used:

$$\%_{\text{comp.1}} = \frac{\delta^{18}\text{O}_{\text{sample}} - \delta^{18}\text{O}_{\text{comp.2}}}{\delta^{18}\text{O}_{\text{comp.1}} - \delta^{18}\text{O}_{\text{comp.2}}} \times 100$$

with  $\%_{\text{comp.1}}$ , percentage of groundwater component 1;  $\delta^{18}\text{O}_{\text{sample}}$ ,  $\delta^{18}\text{O}$  value of the sample;  $\delta^{18}\text{O}_{\text{comp.2}}$ ,  $\delta^{18}\text{O}$  value of groundwater component 2;  $\delta^{18}\text{O}_{\text{comp.1}}$ ,  $\delta^{18}\text{O}$  value of groundwater component 1.

Additional calculations with results of tritium and hydrochemical analysis were used to verify whether the

samples can be described properly with the two-component system. This was not the case for some samples in the surrounding of Hochstetten, where groundwater can be strongly influenced by bank infiltration from the Möhlín river. This tributary drains the foothills and highly elevated parts of the Black Forest and shows relatively low  $\delta^{18}\text{O}$  values similar to those of the Rhine river (Herdeg 1993). The groundwater balance in this region therefore shows a major uncertainty. The results from the calculation are summarized in Table 2.

#### Spatial distribution of bank infiltration from the Rhine river

The spatial distribution of  $\delta^{18}\text{O}$  values confirms the results from piezometric groundwater measurements and groundwater flow direction and gives further information on the origin of the groundwater (Fig. 3).

East of the Rhine river, groundwater in the southern part of the study area is predominantly composed of local precipitation, of bank infiltration from river Möhlín and, to a minor extent, of bank infiltration derived from the Rhine river.

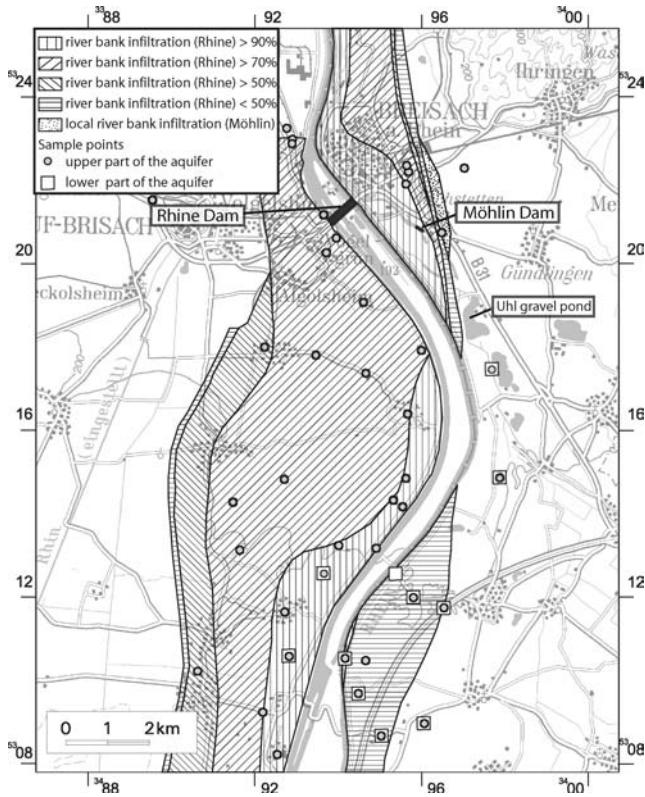
Bank infiltration of river Möhlín occurs in the area of Hausen and continues east of Breisach to the north. Between gravel pond Uhl and Möhlín dam there is some increased infiltration of the Möhlín only concerning the upper part of the aquifer while below 30 m depth bank infiltrate from river Rhine dominates.

A considerable contribution of bank infiltration from the Rhine river only was detected west of Bremgarten and south of Breisach. In the Fessenheim-Bremgarten area, the Fessenheim dam may lead to some bank infiltration from the Rhine Channel. Interpretation of the results of the time series of  $\delta^{18}\text{O}$  clearly shows that the Breisach dam enhances bank infiltration on its upstream side, beginning at the Uhl gravel pond.

In several wells sampling at distinct depths was possible (Table 3). In general  $\delta^{18}\text{O}$  values do not vary with respect to aquifer depth. Only in the Hochstetten area the amount of bank infiltration from the Rhine river increases with depth. This is due to the enhanced local infiltration of the river Möhlín upstream the dam, which only contributes to the upper part of the aquifer. The

**Table 2** Evaluation of the amount of bank infiltrate of the Rhine river in the groundwater (see also Table 1 for  $\delta^{18}\text{O}$  values of local recharge and Rhine infiltration)

	$\delta^{18}\text{O}$ value, ‰ VSMOW
<i>Groundwater component</i>	
Recharge from local rainfall	-8.60 to -8.00
Bank infiltration from river Rhine	About -11.00
<i>Evaluation of the amount of bank infiltration from river Rhine</i>	
Amount of bank infiltration < 50%	> -9.80
Amount of bank infiltration ≥ 50%	≤ -9.80
Amount of bank infiltration > 70%	< -10.20
Amount of bank infiltration > 90%	< -10.70



**Fig. 3** Distribution of bank infiltrate within the Quaternary aquifer of the study area

shallow groundwater in this sector therefore has to be considered as a ternary mixing system, consisting of recharge from local precipitation as well as bank infiltration from the Rhine river and the Möhlin.

The  $\delta^{18}\text{O}$  values indicate that bank infiltration from the Rhine river is present throughout the aquifer down to its base to a depth of more than 100 m below surface. This was also proved by the results of tritium measurements and time series analysis.

For the small tributary Möhlin an important decrease in the  $\delta^{18}\text{O}$  values from the upstream part (inflow Uhl gravel pond:  $-9.45\text{‰}$ ) to the downstream part (Möhlin/Breisach:  $-10.01\text{‰}$ ) was observed (mean values). This is the result of a progressive admixture of groundwater with a high portion of infiltrated Rhine water into the Möhlin river. The Uhl gravel pond is not influenced by water from the Rhine, as indicated by the results of the isotope studies.

West of the Rhine river, groundwater flow is mainly directed from southwest to north and northeast (Fig. 2). There is only a small contribution from bank infiltration from the Rhine river, mainly coming from the south (perhaps due to the Fessenheim dam). There is no significant bank infiltration from the sealed Channel. The high proportion of bank infiltration from the river Rhine into the groundwater west of the Channel originates from the infiltration of numerous small irrigation channels which are flooded with Rhine water.

## Groundwater residence time

### Tritium

Tritium ( $^3\text{H}$ ) contents in modern precipitation in Western Europe steadily approaches the natural background values which were observed before the atmospheric nuclear tests in the 1950s and 1960s. Simultaneously the thermonuclear signal in the groundwater bodies is attenuated through the low half-life period of tritium with respect to the thermonuclear signals.

Lumped parameter models (Maloszewski and Zuber 1996) that fit with the potential flow patterns in an unconfined aquifer like the alluvial Rhine aquifer (Exponential Model MEX and combined Piston Flow Exponential Model PFE) show that the maximum tritium content in groundwater which can be expected today lies around 25 TU for the MEX and in the range of 45 TU for the PFE (Fig. 4).

On the basis of their tritium content it is possible to classify groundwater samples according to their mean residence time in the aquifer. However, mixing of a tritium-bearing and a tritium-free component as well as the influence of Rhine bank infiltration with its strong variations in the  $^3\text{H}$  content coming from nuclear power plants has to be considered.

Most analyzed samples yielded tritium contents between 3.6 TU and 41.2 TU for groundwater and 13.5 TU and 63.7 TU for river Rhine and Channel water respectively. The tritium content was below the detection limit only in the multi level observation well ORI below 133 m depth ( $^3\text{H} < 0.6 \text{ TU}$ ). Based on the tritium values, groundwaters in the study area can be classified into three groups.

- Groundwater without detectable tritium (ORI below 133 m); post-bomb groundwater components from the last 50 years are missing.
- Groundwater with tritium content equal to or even lower than in present-day precipitation. This indicates that young components are mixed with old,  $^3\text{H}$ -free components (ORI, screen 100–122, ESCH below 46 m, WEIN below 103 m).
- Groundwater with tritium values in the range or above prevailing values of precipitation. This type can be found in most of the sampled wells. Part of these groundwaters (Fig. 4, Table 3) is rich in tritium ( $> 30 \text{ TU}$ ) and depleted in  $^{18}\text{O}$  and  $^2\text{H}$ , which indicates a predominance of Rhine bank infiltration.

In the study area, no general correlation between tritium and depth exists (Fig. 4). Very high tritium contents in deep wells (e.g. multi-level piezometers BREM, BALG) in the direct vicinity of the Rhine river show the effect of deep bank infiltration leading to high tritium values in the aquifer down to a depth of at least 150 m. This is also confirmed by the results of the  $\delta^{18}\text{O}$  study. Only a few wells show groundwater stratification and an increasing age of groundwater with depth.

## Oxygen-18

$\delta^{18}\text{O}$  time-series analyses were carried out for 1 year in the area south of Breisach. The data were used for the estimation of the residence time of young groundwater by comparing  $\delta^{18}\text{O}$  time-series analysis with the amplitude of  $\delta^{18}\text{O}$  variations in the Rhine.

In comparison with the Rhine river the level of  $\delta^{18}\text{O}$  in the nearby groundwater shows only little variation. However, decreasing amplitudes during the 1 year observation time were observed with increasing distance to the river bank.

Using the dispersion model (Maloszewski and Zuber 1996) with the amplitude of  $\delta^{18}\text{O}$  values of the Rhine river as an input-function (amplitude of  $\delta^{18}\text{O}$  in the Rhine water  $\approx 1.5\%$ ) and the range of the  $\delta^{18}\text{O}$  values in the groundwater as an output signal, the mean residence time of Rhine bank infiltration water was calculated (for:  $D/vx = 0.1 - 0.5$ ;  $D$  = dispersion coefficient,  $v$  = mean flow velocity of water,  $x$  = length of the system measured along the streamlines; Maloszewski and Zuber 1996). For the shallow, about 10 m deep piezometers 140/019 (BRE-GWM2) and 136/019 (BRE-GWM1, see Fig. 2) in orthogonal distances of 0.2–0.3 km to the river bank the estimated mean residence time ranges from about 5–8 months. For further shallow and deep observation wells at larger distances (up to 1.5 km) the observed amplitudes were lower than the accuracy of measurement, so the dispersion model gives mean residence times of at least 1 year.

Using the dispersion model, the amount of young local bank infiltrate with an age of less than 6 months was estimated. In the direct vicinity of the Rhine it amounts theoretically to about 20–50%, and decreases with distance to the Rhine.

## Old groundwater components

Carbon isotope analyses ( $\delta^{13}\text{C}_{\text{DIC}}$ ,  $^{14}\text{C}_{\text{DIC}}$ ) were carried out on 23 samples during the sampling campaigns in 1998 (pumped samples) and 2000 (scooped samples).

*Evaluation of  $\delta^{13}\text{C}$  data* Carbon-13 analyses were used to obtain information about isotope exchange processes which may influence the  $^{14}\text{C}$  activities. The results cover a wide range between  $-9.0\%$  and  $-15.4\%$  VPDB. Only two samples are lower than  $9.0\%$  VPDB (see below).

Natural waters in contact with carbonate rocks generally show values between  $-12\%$  and  $-17\%$  VPDB depending on the  $\delta^{13}\text{C}$  of the gas phase, the partial  $\text{CO}_2$  pressure in soil, open or closed system conditions with respect to soil  $\text{CO}_2$  and the pH of groundwater. In relation to this range the analyzed samples show a shift toward slightly increased values, reflecting isotope exchange processes which can lead to  $^{13}\text{C}$  enrichment in the liquid phase. This may be the case for rock–water interactions as well as interactions between water and

atmospheric  $\text{CO}_2$  (Moser and Rauert 1980; Eichinger 1982; Clark and Fritz 1997).

In the study area, groundwater is strongly influenced by bank infiltration from the Rhine (Herdeg 1993; Regierungspräsidium Freiburg 2002). Because of the striking  $\delta^{18}\text{O}$  signatures of the Rhine bank infiltration water the relationship between  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}$  was examined in more detail (Fig. 5). Both parameters show an overall tendency of  $\delta^{13}\text{C}$  increase in  $^{18}\text{O}$ -depleted groundwaters, expressing that increased bank infiltration from the Rhine leads to increasing  $\delta^{13}\text{C}$  values. This may be caused mainly by isotope exchange of the river water with atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2/\text{Air}}$ :  $-8\%$ ). For Rhine water  $\delta^{13}\text{C}$  values range between  $-9\%$  and  $-11\%$  VPDB (Mook 1970).

Due to comparable exchange processes for  $\delta^{13}\text{C}$  and  $^{14}\text{C}$ , the isotope exchange processes documented in elevated  $\delta^{13}\text{C}$  values should lead to an enrichment in  $^{14}\text{C}$  activities. While young groundwaters in the Rhine valley aquifer show  $^{14}\text{C}$  activities of at least 65 pmc, exchange with air  $\text{CO}_2$  will lead to relatively high starting values for  $^{14}\text{C}$  ranging up to about 100 percent modern carbon (pmc) or even higher.

For two samples (BREM below 105 m; BALG below 85 m) clearly elevated  $\delta^{13}\text{C}$  values were found ( $-5.7\%$  VPDB;  $-8.7\%$  VPDB). This is interpreted as the result of isotope exchange with the carbonate matrix leading to a strong  $^{13}\text{C}$ -enrichment ( $\delta^{13}\text{C}$  of carbonates:  $0 \pm 3\%$  PDB). Such processes are well known from very old groundwaters, for example in the South German Molasse Basin (Bertleff 1986; Prestel 1990).

*Results of  $^{14}\text{C}$  analysis*  $^{14}\text{C}_{\text{DIC}}$  activities in the study area show values between 5.8 pmc and 110 pmc. Samples were obtained from wells with depths of up to 150 m by pumping (sampling campaign in 1998) or scooping (sampling campaign in 2000).

The lowest values (confirmed by the results of repeated sampling) were found for the piezometer ORI below 133 m (pumped sample: 5.8 pmc; scooped sample: 10.4 pmc). These samples with very low  $^{14}\text{C}$  indicate a high age of groundwater, perhaps even of Pleistocene recharge conditions. This is confirmed by their  $\delta^{18}\text{O}$  values and tritium content below the detection limit.

Ten samples show  $^{14}\text{C}_{\text{DIC}}$  activities below 65 pmc (see Table 3): the wells GREZ (below 110 m), WEIN (below 120 m; samples from pumping and scooping), BREM (below 105 m), SALZ IX (scooped at a depth of 125 m), ORI (below 133 m), ESCH (below 33 m). All other 13 samples show  $^{14}\text{C}$  activities up to 110 pmc.

The samples with slightly lower  $^{14}\text{C}$  activities between 34.3 pmc and 55.1 pmc are difficult to interpret because in all these samples tritium was detected even in high concentrations. Beyond this, some of these samples show slightly elevated  $\delta^{13}\text{C}$  values which could indicate additional effects from isotope exchange with the atmosphere. These samples must be described as resulting from multi-component systems, containing a

**Table 3** Results of selected hydrochemical and isotop analysis (for sample locations see Fig. 2)

Location (Fig. 2)	Screen m below surface	geol.	Date of sampling	Sampling method	Conduct. ( $\mu\text{S/cm}$ )	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	$\text{HCO}_3$ (mg/l)	Cl (mg/l)	$\text{SO}_4$ (mg/l)	$\text{NO}_3$ (mg/l)	B (mg/l)	$\delta^{18}\text{O}$ , ‰ VSMOW	$^3\text{HUT}$	$\delta^{13}\text{C}$ , ‰ VPDB	$^{14}\text{C}$ (pmc)	(Na+K)/Cl (mol/mol)	Na/K (mol/mol)
ESCH	33-36	Q	26.08.1998	P		114.0	16.9	11.1	1.9	335	38.1	26.6	60.2		-8.74	15.7	-12.3	(30.9)	0.49	9.9
ESCH	46-51	Q	26.08.1998	P		340.0	62.7	410.0	2.9	276	758.0	857.5	14.6	55.0	-9.53	7.4	-13.5	36.5	0.84	240.3
ESCH	64-92	T	26.08.1998	P		997.0	172.0	1110.0	5.8	209	3184.0	1410.0	4.8	152.0	-10.23	6.0	-14.5		0.54	325.3
ORI	70-90	Q	25.08.1998	P		72.1	6.9	8.4	1.4	2,147	31.5	22.7	27.0		-9.35	18.3	-13.9	81.5	0.45	10.2
ORI	100-122	Q	21.06.2000	S 80 m	494	86.0	7.2	13.7	1.5	178	49.6	27.6	32.0		-9.21	23.1			0.45	15.5
ORI	100-122	Q	25.08.1998	P		237.0	25.1	103.0	3.1	157	590.6	4.4			-9.56	4.3	-13.7	73.4	0.27	56.5
ORI	100-122	Q	21.06.2000	S 110 m	1,242	146.0	24.3	63.7	2.4	156	317.0	20.0	8.4		-9.60	3.6			0.32	45.1
ORI	133-171	Q	25.08.1998	P		101.0	33.7	101.0	5.2	377	150.9	115.2	2.2		-11.37	<0.6	-10.4	5.8	1.06	33.0
ORI	133-171	Q	21.06.2000	S 140 m	1,234	105.0	34.9	106.0	5.7	378	152.0	116.0	1.9		-11.39	<0.6			1.11	31.6
ORI	133-171	Q	21.06.2000	S 165 m	1,235	113.0	34.3	106.0	5.7	388	160.0	117.0	0.7	37.0	-11.43	<0.6	-9.0	10.4	1.05	31.6
WEIN	84-99	Q	20.08.1998	P	2,820	206.4	37.1	226.0	5.2	224	705.8	28.1	47.3		-8.74	20.5	-14.5	84.4	0.50	73.9
WEIN	84-99	Q	16.06.2000	S 92 m	2,650	240.0	42.5	245.0	5.7	347	672.0	35.6	48.5	18.0	-8.81	20.2	-10.8	71.6	0.57	73.1
WEIN	103-109	Q	20.08.1998	P	2,760	97.6	19.4	432.0	3.9	375	573.0	220.0			-9.28	16.2	-12.5	64.4	1.17	188.3
WEIN	103-109	Q	16.06.2000	S 105 m	3,840	178.0	34.5	616.0	5.2	355	932.0	305.0	26.6		-9.49	8.0			1.03	201.4
WEIN	120-150	T	20.08.1998	P	7,660	714.0	231.0	4060.0	12.2	223	7804.0	504.1	2.2		-9.62	13.8	-12.4	39.3	0.80	565.7
WEIN	120-150	T	20.06.2000	S 135 m	24,900	803.0	376.0	5480.0	20.0	192	10500.0	797.0	5.6	976.0	-10.22	7.7	-9.6	34.3	0.81	465.8
BREM	30-40	Q	19.08.1998	P	967	78.2	10.8	89.6	8.1	225	163.4	37.4	19.9		-10.94	40.5			0.89	18.8
BREM	30-40	Q	16.06.2000	S 35 m	1,041	81.0	16.4	94.5	8.2	227	163.0	44.7	21.9		-10.86	35.8	-10.9	86.7	0.94	19.6
BREM	50-100	Q	19.08.1998	P	1,067	77.9	10.8	115.0	8.6	235	194.0	33.1	18.1	35.0	-10.91	40.1			0.96	22.7
BREM	50-100	Q	16.06.2000	S 60 m	1,081	86.0	10.7	126.0	8.7	228	199.0	48.6	22.4		-10.93	39.2			1.02	24.6
BREM	105-158	Q	19.08.1998	P	20,800	316.0	43.2	4330.0	109.0	260	6795.0	145.6	0.0	52.0	-10.78	30.5	-5.7	42.9	1.00	67.5
BREM	105-158	Q	16.06.2000	S 110 m	7,150	25.7	2.7	1550.0	70.9	293	2170.0	91.4	23.8	99.0	-10.92	37.2			1.13	37.2
BREM	105-158	Q	25.07.2000	S 150 m	58,400	1230.0	157.0	13600.0	338.0	187	22900.0	430.0	22.2	<20	-10.55	17.7			0.93	68.4
SALZ VII	8-115	Q	20.06.2000	S 15 m	413	72.0	8.3	10.1	2.2	206	14.2	34.2	12.5		-8.83	14.9			1.24	7.8
SALZ VII	8-115	Q	20.06.2000	S 70 m	1,653	73.0	9.0	286.0	4.6	361	312.0	55.0	65.2	30.0	-9.07	33.6			1.43	105.7
SALZ VII	8-115	Q	20.06.2000	S 90 m	1,777	72.2	8.8	308.0	4.7	370	337.0	53.5	66.9	30.0	-9.03	36.4			1.42	111.4
SALZ VII	8-115	Q	29.06.2000	S 105 m	12,860	299.0	31.0	2600.0	20.8	353	4260.0	141.0	68.2	11.0	-9.26	41.2			0.95	212.5
SALZ IX	0-132	Q	20.06.2000	S 15 m	608	91.0	10.4	30.7	4.8	250	47.9	35.0	39.9		-9.05	21.3			1.08	10.9
SALZ IX	0-132	Q	20.06.2000	S 75 m	860	71.2	8.9	95.6	8.8	255	112.0	36.8	38.7	32.0	-9.35	22.4			1.39	18.5
SALZ IX	0-132	Q	25.07.2000	S 125 m		745.0	102.0	10200.0	261.0	272	17200.0	468.0	18.4	79.0	-10.58	15.2	-12.3	55.1	0.93	66.4
BALG	5-11	Q	02.11.1998	P	590	80.0	11.0	8.4	1.8	203	43.2	30.0	17.2		-11.00	32.0			0.34	7.9
BALG	28-42	Q	02.11.1998	P	590	96.0	14.1	17.0	1.8	203	96.0	29.5	16.7		-11.10	37.0			0.29	16.1
BALG	55-69	Q	02.11.1998	P	1,220	147.0	24.4	97.7	7.3	170	369.0	31.9	12.9		-11.10	38.0			0.43	22.8
BALG	85-105	Q	02.11.1998	P	15,707	1207.0	150.5	1804.0	19.8	35	5490.0	18.0	9.0		-10.90	14.0			0.51	154.9
BALG	85-105	Q	04.09.2001	S 104 m	32,700	2310.0	328.0	4730.0	35.0	38	12100.0	150.0	25.2		-10.76				0.61	229.7
BALG	85-105	Q	04.09.2001	S 95 m	13,500	871.0	103.0	2070.0	17.8	141	4890.0	27.4	12.0						0.66	197.7
GREZ	26-32	Q	19.08.1998	P	644	96.6	10.7	10.0	1.8	220	45.2	33.0	66.8		-8.50	30.7	-14.1	79.8	0.38	9.4
GREZ	26-32	Q	16.06.2000	S 29 m	628	102.0	12.2	8.9	2.0	217	49.6	35.4	63.6		-8.53	32.1			0.31	7.6
GREZ	110-122	Q	16.03.1999	P	491										-9.31	24.9	-13.5	43.2		
GREZ	110-122	Q	21.06.2000	S 116 m	492	80.7	13.4	9.2	1.5	197	35.5	34.7	32.5		-9.39	28.5			0.44	10.4
HOCH	63-70	Q	21.08.1998	P	528	66.6	8.6	24.7	1.8	189	52.7	33.1	8.4		-11.06	27.2	-10.2	109.8	0.75	23.3
HOCH	63-70	Q	10.06.2000	S 67 m	610	84.0	9.9	27.6	2.2	189	81.5	39.7	9.7		-10.82	27.5			0.55	21.3
HOCH	84-97	Q	21.08.1998	P	899	109.0	13.8	38.1	2.5	199	168.5	33.7	9.7		-10.79	27.6	-10.2	95.1	0.36	25.9
HOCH	84-97	Q	16.06.2000	S 90 m		140.0	17.0	46.4	3.1	183	238.0	39.7	10.2	28.0	-10.85	22.0			0.31	25.4
BREI	63-68	Q	26.08.1998	P	2,224	279.0	31.1	93.6	4.4	202	637.0	33.7	10.6	21.0	-10.64	20.8	-13.5	86.6	0.23	36.2
BREI	63-68	Q	10.06.2000	S 66 m	2,500	304.0	31.8	120.0	4.9	175	688.0	31.9	10.4		-10.78	21.4			0.28	41.6
HART	27-33	Q	19.08.1998	P	834	87.3	10.9	63.5	3.0	248	97.1	39.9	45.1		-9.06	21.8	-10.6		1.04	36.0
HART	27-33	Q	16.06.2000	S 30 m		91.0	10.1	74.6	3.3	285	105.0	39.1	34.6	24.0	-9.10	18.9			1.13	38.4



HART	108-120	Q	19.08.1998	P	3,040	101.0	14.1	505.0	5.3	312	791.0	43.5	51.3	-9.10	35.0	-12.7	86.8	0.99	162.0
HART	108-120	Q	20.06.2000	S 114 m	2,220	98.0	15.2	367.0	5.2	323	511.0	44.0	65.5	-9.07	27.9			1.12	120.0
SAZ V	8-169	Q	19.06.2000	S 35 m	1,221	144.0	22.5	96.3	4.0	364	184.0	48.8	88.3	-8.62	21.1			0.83	40.9
SAZ V	8-169	Q	19.06.2000	S 75 m	1,545	127.0	17.1	171.0	4.9	365	255.0	44.0	70.6	-8.71	23.6			1.05	59.3
SAZ V	8-169	Q	19.06.2000	S 135 m	1,716	143.0	19.0	207.0	5.2	373	347.0	40.1	66.9	-8.65	21.5	-10.5	88.6	0.93	67.7
BUG	24-30	Q	19.08.1998	P	1,550	71.8	17.6	110.0	112.0	294	223.9	51.9		-8.59	22.7			1.21	1.7
BUG	41-57	Q	19.08.1998	P	2,250	104.0	18.2	224.0	144.0	429	434.8	60.0		-8.66	23.1	-15.4	97.6	1.10	2.6
RHINE/ BREISACH		Q	10.05.2000	S	402	58.6	7.6	15.5	2.2	183	21.3	31.9	4.0	-11.23	40.4			1.22	12.0
Mhlm/ Grezhausen		Q	09.05.2000	S	186	25.6	3.2	8.3	1.5	74	10.6	19.2	3.7	-9.57	13.4				
SAUMOBUC		Q	17.05.2001	S		1070.0	57.4	30900.0	1320.0	37	50200.0	2000.0	22.5	-7.70				0.97	39.8
SAUMOBUC		Q	10.05.2000	S	98,000	1160.0	52.9	25600.0	1060.0	41	41100.0	1980.0	46.5	-8.25	18.8			0.98	41.1
NAMB	120-173	Q	14.11.2001	S 165 m		99	5.6	333.0	52.4	122	747.0	22.9	7.6					0.75	10.8
Schliengen	60-150	T	20.03.1998	S 116 m	14,170	423.0	194.0	3057.0	34.5	378	1400.0	6180.0	<0.1	-8.79	<0.5			3.30	150.0

S = extraction by scooping, sampling depth; P = extraction by pumping; pmc = percent modern carbon; Q = Quaternary alluvial sediments; T = Tertiary rock; sw = surface water; () = value questionable

young component ( $^{14}\text{C}$  activity: 65–100 pmc; tritium clearly detectable) and an old component ( $^{14}\text{C}$  activity low or even not detectable; tritium not detectable). It is assumed that in the surroundings of these wells deep aquifer layers contain noticeable amounts of stagnant groundwater which is not connected to recent flow processes and therefore shows high age.

Considering isotope effects due to hydrochemical reactions in carbonate aquifers (such as the Rhine valley aquifer)  $^{14}\text{C}$  activities exceeding 65 pmc can be assigned to modern groundwater with young age (Clark and Fritz 1997).

The interpretation of the carbon isotope results clearly documents that recent groundwater circulation affects the Rhine valley aquifer down to great depth. In the deepest part of the aquifer, however, groundwater with a very old age was also found in basal Quaternary layers without recent circulation. Groundwater exclusively from the stagnant layer was found in the observation well ORI below 133 m. All other samples with lower  $^{14}\text{C}$  activities result from mixing with young components.

A synoptic view of  $\delta^{18}\text{O}$  data and  $^{14}\text{C}$  data with a classification into 4 groups is given in Fig. 6. Group Ia contains wells with young groundwater near the Rhine (clear influence of isotope exchange with the atmosphere) as well as at some distance eastwards (group Ib). Group II is exclusively old groundwater, probably of Pleistocene origin. The wells belonging to groups III and

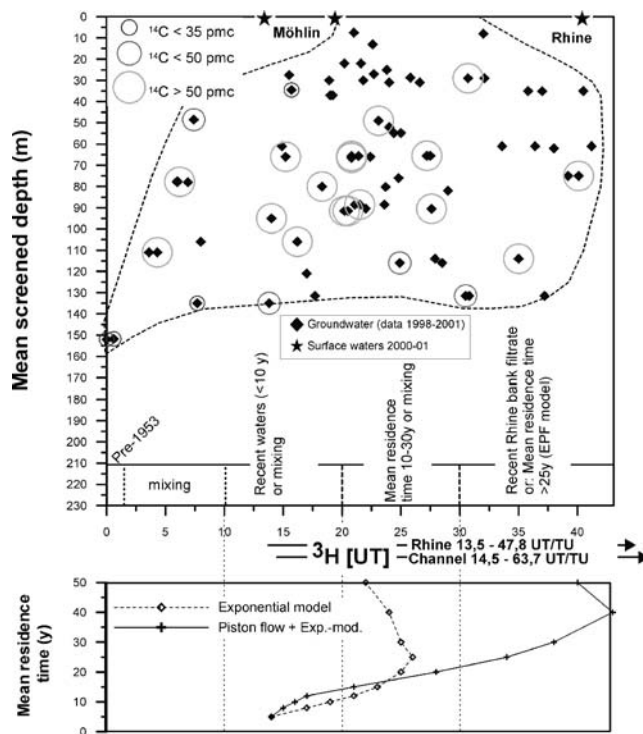


Fig. 4 Correlation of tritium content of the groundwater with depth and mean residence time of the groundwater (PFE: Piston Flow Exponential Model)

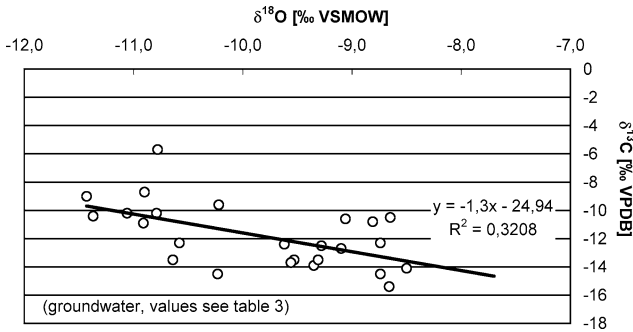


Fig. 5 Correlation of  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$

IV show mixing between young (groups Ia and Ib) and old (group II) groundwater, the difference between both groups depending on the proportion of bank infiltration from the Rhine.

Extent of groundwater salinity

Results of hydrochemical analyses

The results of selected hydrochemical and isotope analyses are documented in Table 3.

Chloride

In the study area, the regional background of chloride concentrations in groundwater due to anthropogenic diffuse pollution by sources such as agricultural input or thawing salts can reach up to 60 mg/l. However, most of the shallow and deep wells in a narrow sector parallel to the Rhine river on its eastern bank between Bremgarten and Breisach (Fig. 7) show chloride concentrations that are significantly higher. The highest chloride concentrations were detected in the wells SALZ IX (17,200 mg/l) and BREM (22,900 mg/l; scooped sample from 150 m depth).

High chloride concentrations of 10,500 mg/l were also found in the 150 m deep well WEIN, screened in Tertiary marls and siltstones. Tritium values between

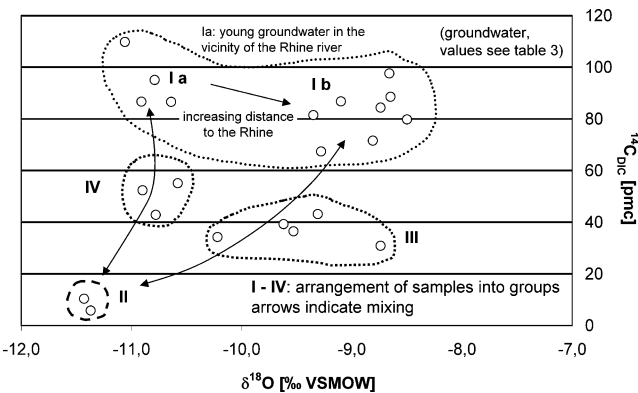


Fig. 6 Correlation of  $^{14}\text{C}$  vs.  $\delta^{18}\text{O}$

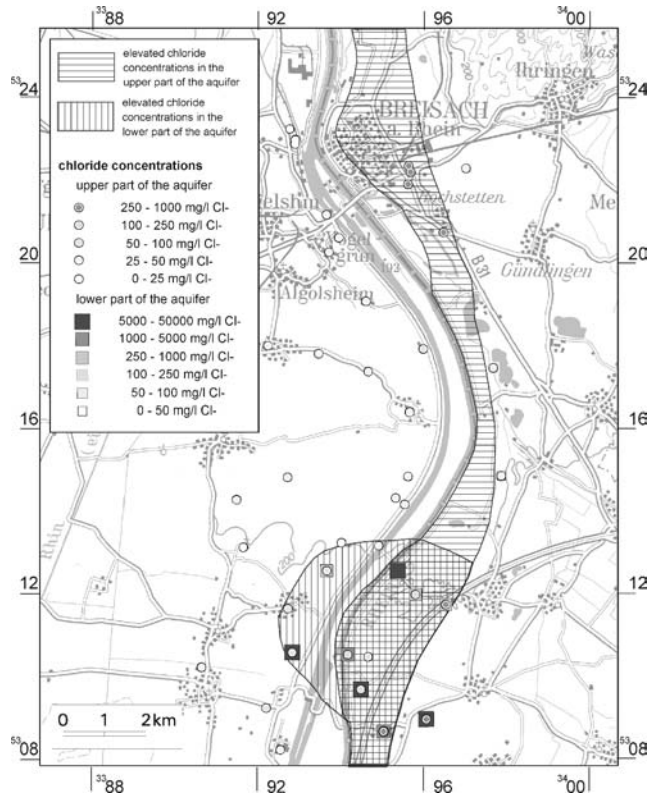


Fig. 7 Distribution of elevated chloride concentrations within the Quaternary aquifer of the study area

8 TU and 14 TU indicate that this groundwater is composed of a mixture of an old component derived from Tertiary sediments and a younger component coming from the Quaternary sediments (multi-component system).

In the vertical profiles of multi-level observation wells east of the Rhine salinity generally increases with depth. At the present state of knowledge, the concentrations in deep sections of the aquifer are comparatively lower in the north (Hochstetten, Breisach) than in the southern region (Bremgarten) but there are only a few deep observation wells in the north.

On the western bank of the Rhine, between Fessenheim and Neuf-Breisach this only applies to the deep observation well BALG (below 85 m) while in shallow wells chloride concentrations are mostly below 60 mg/l. Enhanced chloride concentrations were confirmed by the new piezometer NAMB, for which so far only few data are available (see Fig. 2, Table 3; Regierungspräsidium Freiburg 2002).

In the catchment area of the pumping station of Breisach, groundwater is strongly influenced by bank infiltration from the Rhine (Fig. 3). The chloride content in the wells increases from 80 mg/l at 10 m depth to 700 mg/l at 70 m. In the drinking water taken from depths between 5 m and 18 m, the chloride content permanently reaches about 150 mg/l. This is in clear contrast with the low values observed for Rhine river

water (around 20 mg/l). Concentrations in the Rhine Channel are slightly higher (40 mg/l) as a consequence of the discharge from a disposal channel, the “Saumoduc”, bringing to the Rhine highly concentrated brines from the french potash mining area (chloride content above 40,000 mg/l).

Chloride concentrations in the groundwater from Tertiary sediments of the “Weinstetter Diapir” (observation well ESCH) amount to about 3,000 mg/l. Due to the geographic position of the well, anthropogenic sources for chloride can be excluded with high certainty. The tritium content of 6 TU in this well indicates a multi-component system with contribution of a young groundwater component leading to a dilution of groundwater within the Tertiary sediments. Groundwater in Tertiary sediments from an observation well near Schliengen (Oligocene, Streifige Mergel Formation) about 15 km south of the Weinstetter Diapir is characterized by a high mineralization with chloride concentrations of about 1,400 mg/l and sulfate concentrations of about 6,000 mg/l (see Table 3; unpublished data from the archive of the LGRB).

### Potassium

Groundwater potassium values in the study area range between 1.4 mg/l and 238 mg/l.

The regional background in shallow groundwater lies between 1 mg/l and 6 mg/l (Fig. 8). In the groundwaters of Tertiary sediments, potassium values are only slightly elevated (e.g. observation well “ESCH”, around 6 mg/l). As documented from the observation well near Schliengen, geogenic values for potassium can rise up to 35 mg/l.

In contrast to these natural values, the potassium content in the mining brines as well as downstream of the mining dumps of Buggingen is strongly elevated (above 1,000 mg/l in the Saumoduc).

The sampling of 70 locations in the study area yielded elevated potassium values above 10 mg/l only in wells in

the vicinity of the former brine sedimentation basins on the “Fessenheimer Insel” and salt heaps near Buggingen. The highest values (100–260 mg/l) were found in the deep wells BREM (below 105 m) and SALZ IX. Strongly elevated values are also recorded from the observation wells near Buggingen (BUG, 110–140 mg/l) downstream of the mining dumps.

Further north of the storage basins, potassium values in groundwater are strongly declining despite of elevated chloride concentrations. From a regional view, this is already documented in low potassium values in observation wells near Hartheim as well in the surrounding of Breisach and Hochstetten. It is assumed that ion exchange processes which also influence the sodium content (see below) are responsible for the lowering of the alkali concentrations. Therefore, a simple northward tracing of the anthropogenic induced brines by means of elevated potassium values is not possible.

### K/Cl ratios

The K/Cl ratio allows to classify the samples into three groups. Combined high chloride and potassium values only occur in samples with a close spatial relationship to the mining dumps (Buggingen) and brine storage basins (Fessenheimer Insel). The salinity in these samples can therefore be related to anthropogenic inputs. This applies to most deep samples from the observation wells near Bremgarten (BREM) as well as from Buggingen (BUG), which show extraordinarily high K/Cl ratios.

Figure 8 shows an attempt to interpret the K/Cl ratios in the study area. Only a few of the observation wells have significantly elevated potassium contents of more than 6 mg/l. This might be the regional maximum background value for potassium beneath which no detailed data interpretation is possible. Using the K/Cl ratio of the “Saumoduc”-samples and a simple model of pure dilution, it can be shown that only a few samples are exclusively influenced by pure dilution. Most of the samples with elevated chloride contents show a stronger decrease in potassium as indicated by the line of pure dilution. This is interpreted as an additional ion exchange process leading to a strong removal of potassium out of the groundwater (the assumed path of development of the K/Cl-ratios is marked in Fig. 8 with a dotted line).

### (Na + K)/Cl equivalent ratios

In the study area between Bremgarten and Breisach, values for the (Na + K)/Cl equivalent ratio lie in a wide range between 0.2 and 1.4. The background values for chloride reach up to 60 mg/l.

The correlation of the equivalent ratio (Na + K)/Cl with the chloride concentration shows a wide spread (Fig. 9). It could be caused by processes of dilution and ion exchange. Assuming a line of pure dilution, also starting at the samples from the “Saumoduc”, the

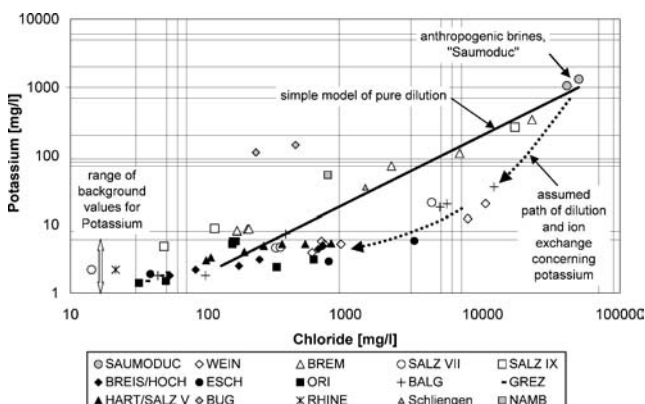
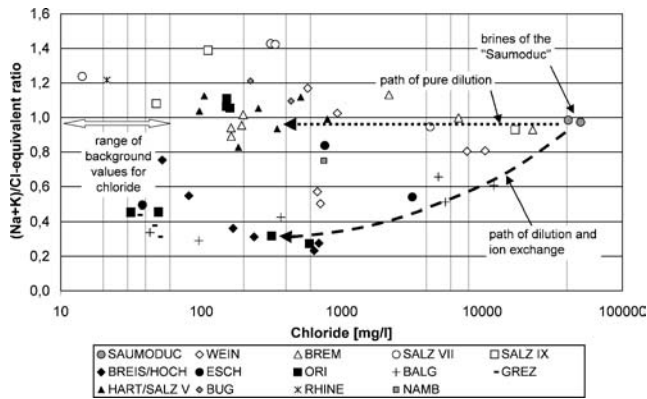


Fig. 8 Correlation of potassium versus chloride; solid line: simple model of pure dilution; dotted line: assumed path of hydrochemical development by dilution and ion exchange



**Fig. 9** Correlation of  $(\text{Na} + \text{K})/\text{Cl}$ -equivalent ratios versus chloride; solid line: simple model of pure dilution; dotted line: assumed path of hydrochemical development by dilution and ion exchange

chloride concentration should decrease, while the ratio  $(\text{Na} + \text{K})/\text{Cl}$  persists at 1. In contrast, combined dilution and ion exchange should lead to values  $< 1$ .

Pure dilution seems to occur in the piezometers BREM, SALZ VII, SALZ IX, HART/SALZ V, ORI 70–90, ORI 100–122, BUG, while in the piezometers BALG, ORI 133–171, HOCH, BREI ion exchange processes increasingly receive importance. For the sample locations WEIN und ESCH a clear classification is not possible. The chemical data show, that alkali deficits are compensated by calcium and magnesium ions leading toward  $\text{CaNaCl}$ - and  $\text{CaCl}$ -type groundwater. This groundwater type is usually found in very old deep groundwater sources (DVWK 1987). In our study, the  $\text{CaNaCl}$ -type groundwater results from the distinctive anthropogenic groundwater salinity and ion exchange processes seem to have taken place since the input of the brines in the last few decades.

### Discussion about the origin and the mechanisms of salinisation

Concerning the origin of the elevated chloride concentrations in the study area between Bremgarten and Breisach, three potential sources can be assumed: (1) infiltration of residual potash-processing brines, mainly from the storage basins on the “Fessenheimer Insel”, (2) leaching of the potash mining dumps at Buggingen and Heitersheim, (3) rise of natural brines into the Quaternary aquifer, derived from the leaching of the “Weinstetter Diapir”.

In the first step, the composition of the geogenic deep groundwater component in the study area was investigated. Due to its geographical position, an influence of anthropogenic salinity can be excluded for the observation well near Eschbach (ESCH). There the high chloride concentrations are interpreted as derived from primary geogenic brines that originated from the leaching of evaporite-bearing Tertiary sediments

(Weinstetter Diapir, see Fig. 2). The main groundwater characteristics at Eschbach (high chloride and sulfate contents, low  $\text{Cl}/\text{SO}_4$  equivalent ratio of about 3, low potassium content, high magnesium content  $> 60 \text{ mg/l}$ ) are confirmed by data from the observation well at Schliengen (about 15 km southwest of Eschbach, not shown in Fig. 2) which is also screened in Tertiary sediments.

However, the low  $^{14}\text{C}$  activities show that the exchange with groundwater from the overlying Quaternary aquifer is very limited. This chloride source can therefore only be of subordinate relevance for the origin of the high chloride concentrations observed in the Quaternary aquifer system. The groundwater from the observation well ORI which is not in close spatial relationship to the “Weinstetter Diapir” shows no tritium, less than 10 pmc for  $^{14}\text{C}$ , and  $\delta^{13}\text{C}$  values between  $-9\text{‰}$  and  $-10.4\text{‰}$  VPDB. These data clearly indicate an old, Pleistocene component. This exclusively old groundwater contains about 150 mg/l chloride which may result from ascending groundwater from Tertiary sediments. Groundwater motion must be very slow (stagnant conditions), in the absence of young groundwater components. The isotope information from the deep wells ESCH and WEIN, screened in Tertiary rocks, shows that deep groundwater is a multi-component system, containing a very old component. Interpreting the chemical data therefore has to take into account that younger groundwater can mix with deeper horizons.

Most of the other sample sites are situated in an area, where anthropogenic salinity may occur. This makes it difficult to differentiate between geogenic brines derived from the leaching of evaporites and anthropogenic input.

In the second step, we tried to identify the composition of the original anthropogenic brine which infiltrated from the storage basins on the Fessenheimer Insel. Unfortunately, no analyses of brines from the period 1957 to 1976 are available. Analyses of the water of the present-day brine channel “Saumoduc” were used, although they may have a different composition due to changes in the production process and increasing input from remediation wells during the last few years. We assume that the former brines were saturated with respect to  $\text{NaCl}$ , leading to chloride concentrations of about 200,000 mg/l. As a consequence of their high density, these infiltrating brines did not follow the main groundwater flow direction but sank straight to the base of the aquifer.

Nowadays, the “Saumoduc” brine is characterized by a high potassium content ( $> 1,000 \text{ mg/l}$ ), a low magnesium content ( $< 60 \text{ mg/l}$ ), a  $(\text{Na} + \text{K})/\text{C}$  equivalent ratio of 1, a high  $\text{Cl}/\text{SO}_4$  equivalent ratio (approx. 30) and high  $\delta^{18}\text{O}$  values (about  $-8\text{‰}$  VSMOW) due to the use of groundwater pumped from the Vosges foothill alluvial deposits as process water by the potash mines. It is assumed that the brine was strongly diluted while infiltrating to the base of the aquifer. At the same time the chloride concentrations decreased accordingly and

the  $\delta^{18}\text{O}$  signature of the brine was modified by mixing with Rhine bank infiltration water (around  $-11\text{‰}$  VSMOW).

The comparison of data from the observation wells Eschbach (ESCH), Oberrimsingen (ORI) and Schliengen with the mining brine clearly shows that salinity in the study area primarily originates from anthropogenic inputs. The contribution from geogenic leaching plays a very minor role.

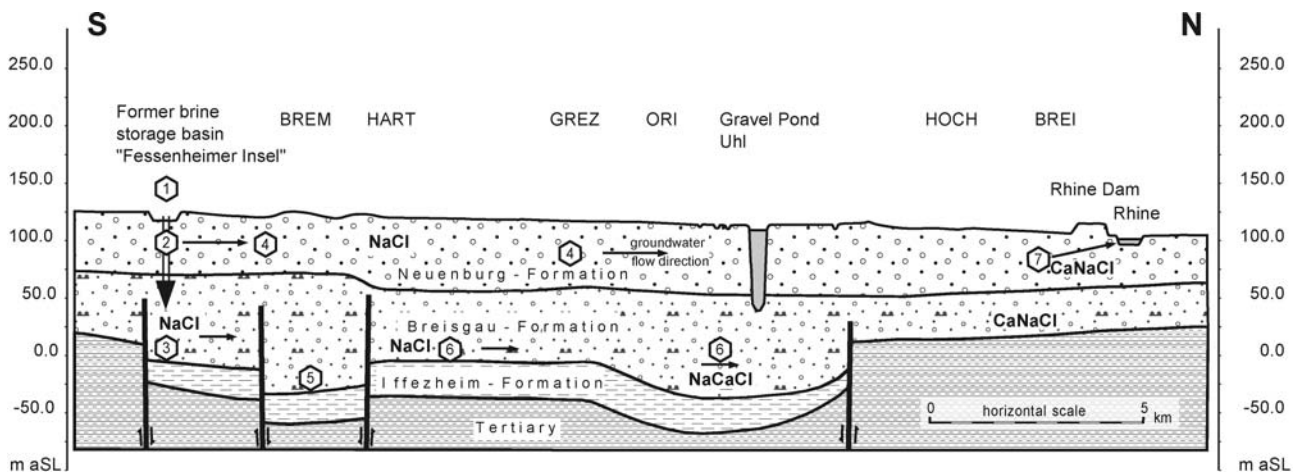
Using isotope and hydrochemical data, different processes affecting the composition and character of the groundwater could be identified in the present study (Figs. 9, 10). The knowledge of these processes helps to further understanding the extent and increase in salinity.

Strong dilution effects in the aquifer are documented by the great amount of Rhine bank infiltration water down to a great depth in the vicinity of the Rhine river and by increasing chloride concentrations toward depth. Additionally hydrochemical data suggest strong ion exchange effects, concerning potassium and sodium. Correlation of the  $(\text{Na}+\text{K})/\text{Cl}$  equivalent ratio versus chloride concentration indicates two different pathways for the extension of salinity (Figs. 9, 10).

On one hand, high chloride concentrations result from the simple dilution of highly concentrated anthropogenic brines. This is demonstrated by the data from the observation wells near the Rhine, from Bremgarten (BREM) and Hartheim (HART) in the south to Oberrimsingen (ORI) in the north. This effect leads to a strong dilution of chloride concentrations in the groundwater flow direction, starting from the “Fessenheimer Insel” as the main source of salinity.

On the other hand, wells with high chloride concentrations group along a line showing ion exchange processes besides dilution (Fig. 9). This line can be traced from Bremgarten (BREM) in the south to Breisach (BREI) in the north. This ion exchange probably occurs preferentially in the strongly altered and less permeable Lower Breisgau-Schichten, where the groundwater comes into contact with clay material.

Later on, the hydrochemically altered brine gets diluted by diffusion and dispersion while moving in the groundwater flow direction. This effect is documented in the south in observation wells Bremgarten (BREM), Weinstetten (WEIN) and Balgau (BALG) which show extremely high chloride concentrations, and in the north



Number	Process	Concentrations	
		Cl (mg/l)	$\delta^{18}\text{O}$ (‰)
1	Infiltration of highly concentrated chloride brine	50 000 - 200 000	-8,5
2	Strong dilution of brine while seeping downwards	20 000 - 50 000?	?
3	Accumulation of diluted brine at the base of the aquifer and spreading by density driven transport	10 000 - 20 000	-10,8
4	Salt transport with convective flow, strong dilution	50-700	-9,5
5	Remobilisation of chloride brine, enhanced by deeply circulating infiltrate of the Rhine River	1 000 - 10 000	-10,8
6	Progressive ion exchange, setting free Ca and fixing K and Na on clay material	500? - 1000	?
7	Increasing chloride concentrations in the upper part of the aquifer as result of ascending groundwater	100 - 800	-11,0

**Fig. 10** (I) Schematic cross-section along the Rhine river with spreading and alternation processes of highly concentrated chloride brines (NaCl, NaCaCl, etc.; groundwater types, BREM, HART, etc.: sample locations); II gives explanations to the processes and resulting concentrations of chloride and values for  $\delta^{18}\text{O}$

in the wells near Hochstetten (HOCH) and Breisach (BREI) with chloride concentrations up to 700 mg/l.

## Summary and conclusions

The combined interpretation of isotope (C, O, H) and hydrochemical data has been applied successfully to differentiate between groundwater recharge components, to understand the groundwater flow pattern, the interaction of surface waters and groundwater and the origin of the salinity of groundwater in the alluvial aquifer south of the Kaiserstuhl between Fessenheim and Breisach.

Three groundwater recharge components have been identified in the study area, mainly on the basis of  $\delta^{18}\text{O}$  values as well as the nitrate and hydrogen carbonate content. The importance of the exchange between the surface waters and groundwater for the flow regime is documented by the complexity of the vertical and lateral distribution of these components within the aquifer. On a quantitative basis, recharge from local precipitation is the most important component throughout the whole study area. The presence of Rhine bank infiltration water in depths down to more than 150 m suggests an intensive vertical exchange within the aquifer close to the river. This is also indicated by the presence of tritium in most of the sampled groundwater at different depths. Only one sample (observation well ORI 133–171m) is free of tritium with a  $^{14}\text{C}$  activity below 10 pmc and  $\delta^{18}\text{O}$  values of  $-11.37\%$  VSMOW indicating a Pleistocene origin of this groundwater. Other samples have tritium contents equal to or lower than those of present-day precipitation, which indicates the mixing of a young component with an old, tritium free component (multi-component system).

Chloride concentrations in the study area, are frequently elevated with respect to natural background values and reach maximum concentrations at the base of the aquifer in the two observation wells SALZ IX (17,200 mg/l) and BREM (150 m: 22,900 mg/l) in the north of the "Fessenheimer Insel". In the upper part of the aquifer, groundwater shows elevated chloride concentrations east of the Rhine river in the whole area between Fessenheim in the south and north of Breisach.

Differentiation between the potential sources of salinity (mining dumps at Buggingen/Heitersheim, storage basins on the Fessenheimer Insel, natural brines by subsosion of the Weinstetter Diapir) is possible on the base of the results of isotope ( $\delta^{13}\text{C}$ ,  $^{14}\text{C}$ ,  $\delta^{18}\text{O}$ ) and hydrochemical data. However, the primary isotopic characteristics may be modified by isotope exchange processes with the carbonate matrix as well as through the influence of surface waters.

The interpretation of the hydrochemical data clearly confirms the view that the highly concentrated (salt saturated) brines from potash ore processing sank to the base of the aquifer and were simultaneously strongly diluted. The brines are stored in the basal layers of the

Quaternary, forming chloride pools that slowly creep northwards due to density driven transport. From these deep pools, salt reaches the circulating groundwater system through diffusion and dispersion processes, undergoing further dilution on its way to the north. This leads to depth profiles with upwards decreasing concentrations due to the effect of strong infiltration from the Rhine and to a decrease in chloride concentration northwards.

The dilution of the mining brines is accompanied by ion exchange processes. Sodium and potassium ions are transferred to the aquifer material which releases alkaline earth ions (mostly calcium and magnesium). As a consequence, the artificial brines change their typical hydrochemical fingerprint from originally high potassium/chloride ratios in the source area to alkaline earth chloride waters northwards. Since the mining brines were introduced into the system only a few decades ago, this ion exchange process seems to occur quite fast in a time span of only a few tenths of years.

A further refinement of the geochemical investigations will be achieved through the interpretation of the signatures of boron, sulfur and oxygen from dissolved boron and sulfates in another publication (Kloppmann, personal communication).

The information gained by the isotope and hydrochemical study was used to constrain the numerical groundwater model which was also constructed within the Interreg II project (Lang et al. this volume).

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