



## Anatomy of contaminated aquifers of an industrial site: insights from the stable isotope compositions of waters and dissolved inorganic carbon

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The hydrogen and oxygen isotopes of water and the carbon isotope composition of dissolved inorganic carbon (DIC) from different aquifers at an industrial site, highly contaminated by organic pollutants representing residues of the former gas production, have been used as natural tracers to characterize the hydrologic system. On the basis of their stable isotope compositions as well as the seasonal variations, different groups of waters (precipitation, surface waters, groundwaters and mineral waters) as well as seasonably variable processes of mixing between these waters can clearly be distinguished. In addition, reservoir effects and infiltration rates can be estimated. In the northern part of the site an influence of uprising mineral waters within the Quaternary aquifers, presumably along a fault zone, can be recognized. Marginal infiltration from the Neckar River in the east and surface water infiltration adjacent to a steep hill on the western edge of the site with an infiltration rate of about one month can also be resolved through the seasonal variation. Quaternary aquifers closer to the centre of the site show no seasonal variations, except for one borehole close to a former mill channel and another borehole adjacent to a rain water channel. Distinct carbon isotope compositions and concentrations of DIC for these different groups of waters reflect variable influence of different components of the natural carbon cycle: dissolution of marine carbonates in the mineral waters, biogenic, soil-derived CO<sub>2</sub> in ground- and surface waters, as well as additional influence of atmospheric CO<sub>2</sub> for the surface waters. Many Quaternary aquifer waters have, however, distinctly lower <sup>13</sup>C<sub>DIC</sub> values and higher DIC concentrations compared to those expected for natural waters. Given the location of contaminated groundwaters at this site but also in the industrially well-developed valley outside of this site, the most likely source for the low <sup>13</sup>C<sub>DIC</sub> values is a biodegradation of anthropogenic organic substances, in particular the tar oils at the site.

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### INTRODUCTION

Contamination of soil and groundwater by organic pollutants is a serious environmental problem common to many urban areas and industrial sites. In particular, former industrial sites may pose special problems because many industrial processes use or produce highly toxic pollutants (e.g., heavy metals, aggressive chemicals and organic compounds) that may accidentally find their way into the natural hydrologic cycle. In such cases it is of particular importance to characterize the hydrological situation in order to be able to assess the dispersion of the organic contamination. Groundwater pollution and the hydrologic situation is commonly evaluated in terms of measurements of the concentrations of anions, heavy metals or organic substances in water, via time-sequence analyses of chemical tracers, and/or via pump-experiments. Many of these measurements of chemical tracers may be influenced by

sorption processes or chemical reactions within the aquifer and can, therefore, give a distorted picture of the contamination. In contrast, stable isotope studies of hydrogen, oxygen, and dissolved organic and inorganic carbon in water can potentially be used as natural tracers that directly reflect the hydrologic situation and are less influenced by extraneous sorption processes. Furthermore, for low temperature conditions the H and O isotope composition of water is not influenced by chemical reactions within the aquifer (e.g., Clarke and Fritz, 1997). It has been known from numerous studies, that the analyses of hydrogen and oxygen isotopes of water provide information on recharge areas and mixing processes of different water bodies (e.g., Clayton *et al.*, 1966; Moser and Rauert, 1980; Kharaka and Carothers, 1986; Clarke and Fritz, 1997). Seasonal variations of the isotopic composition of precipitation and groundwater Rozanski *et al.* (1993) can give additional information on infiltration times, flow paths and flow velocities. In addition, the carbon isotope composi-

tion of dissolved inorganic carbon (DIC) can provide a tracer for anthropogenic contamination, given that the natural system can also be characterized (e.g., Nachtwey *et al.*, 1991; Flintrop *et al.*, 1996; Clarke and Fritz, 1997).

The use of stable isotope studies of hydrogen, oxygen, and carbon in groundwaters as natural tracers for the hydrogeologic system is exemplified here on the basis of a case study from a former gas production plant in Southern Germany. Extensive destruction of this site during the Second World War caused severe damage to the plant that, in addition to production-specific leaks, has led to extensive contamination of sediments and groundwater by organic residues of the gas production. The pollution, mainly tar and its distillates, was recognized in 1970 during excavation for a liquefied natural gas storage tank and the site has since been under investigation for eventual remediation.

### GEOLOGICAL AND HYDROGEOLOGICAL SETTING OF THE SITE

The site is located in the south-west of Germany, in the valley of the Neckar River (Fig. 1). The river passes through a graben forming part of an extensive fault system that strikes NW–SE. A Quaternary fluvial gravel aquifer forms the first and main aquifer of three aquifers in the region. These aquifers are overlain by silty-clayey, organic matter-bearing alluvium. Above it, artificial fillings made up of building rubble and gravel have been deposited in the site of interest (Figs. 2 and 3). The Quaternary gravel deposit consists of marine carbonate pebbles derived from regionally abundant Jurassic rocks. Tar-oil contamination is located within this aquifer. The flow direction of groundwater is parallel to the adjacent river with a flow of about 2.5 m/d (Herfort, 2000). Water in the Quaternary aquifer is generally confined. Underneath the Quaternary aquifer are two further aquifers. The second “Gipskeuper” aquifer is a dolomitic, gypsum-bearing clay- and siltstone of marine origin. Within the heavily tectonized river valley, the original gypsum has nearly all been dissolved by upwelling mineral waters from the third aquifer, the “Upper Muschelkalk” (Ufrecht, 1998a, b). This latter is a marine carbonate unit and the most important aquifer in this area for mineral waters. Chemical compositions of the mineral waters differ substantially though because of variable admixing of Gipskeuper groundwaters and deeper brines (Ufrecht, 1998b). The mineral waters are artesisally confined. Owing to extensive faulting, the mineral waters infiltrate locally into the overlying Quaternary aquifer and also drain into the Neckar River.

On the basis of a number of reports and evaluations (e.g. Geologisches..., 1989, 1992; Zamfirescu, 2000; Herfort, 2000), it is known that the organic contamination at the site consists of

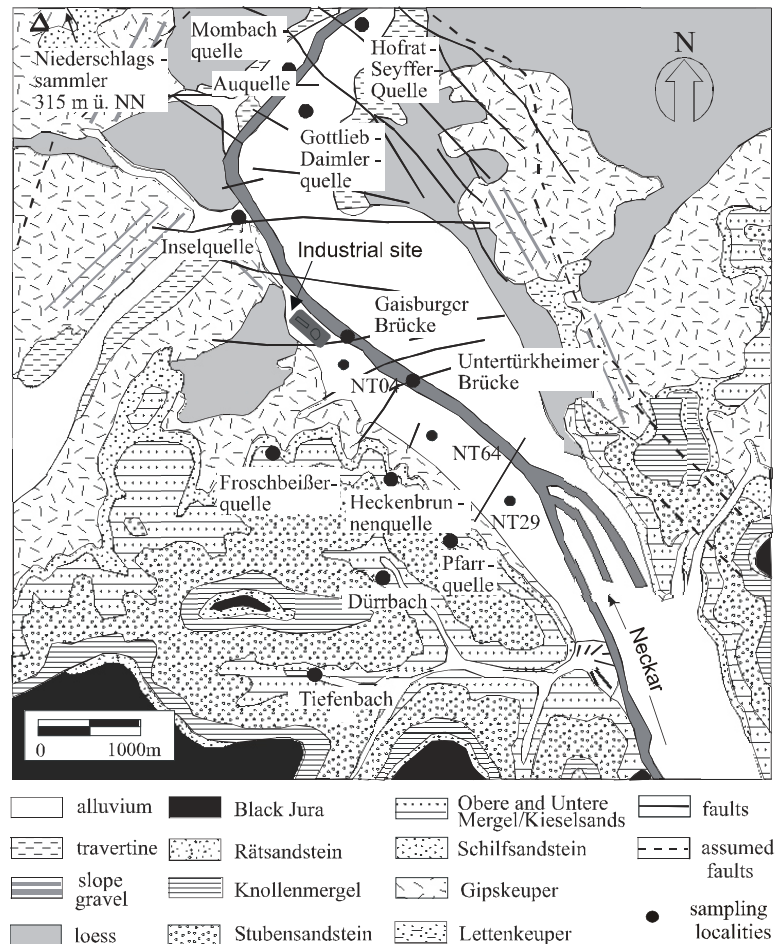


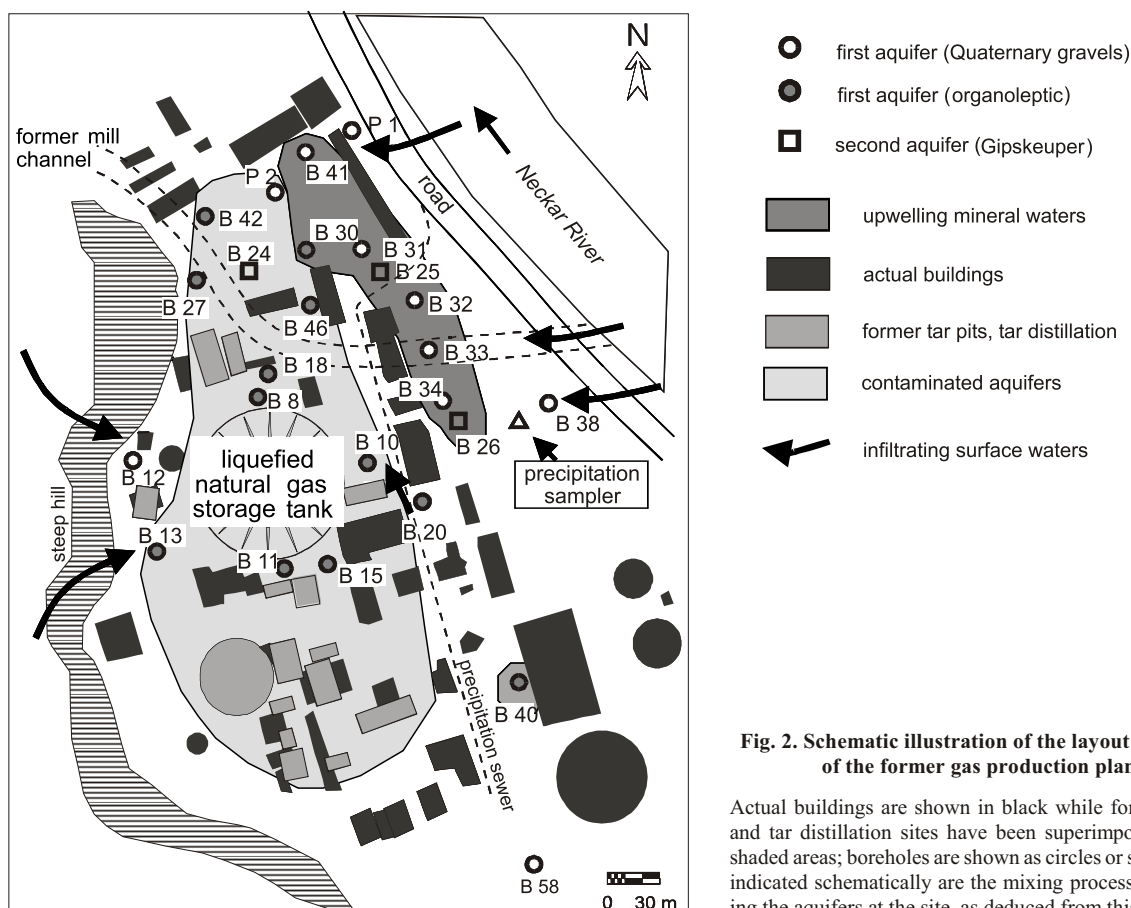
Fig. 1. Geological background and sampling localities for the area around the industrial site

Geology after Vollrath (1959); Quaternary aquifer boreholes outside of the industrial site are prefixed NT; for additional information on sampling localities see Figure 2 and Table 1

about 32 mg/l of suspended and dissolved hydrocarbons, with up to 79 mg/l of BTEX's (benzene, toluene, ethylbenzene, xylene), polyaromatic hydrocarbons with values up to 1.0 mg/l (3.2 mg/l for naphthalene), and up to 0.02 mg/l of chlorinated hydrocarbons. However, under the present conditions of the aquifer these extreme concentrations reach acceptable background values over the scale of 10's of metres.

### ANALYTICAL METHODS

Water samples were taken on a monthly basis for 18 months from a number of boreholes accessing the Quaternary and Gipskeuper aquifers on the site. Several boreholes were clearly organoleptic. In addition, boreholes in the Quaternary aquifer up-stream of the site, several sources of mineral water from the Muschelkalk aquifer, as well as samples from the adjacent Neckar River and a number of smaller brooks and springs in the area were sampled regularly (Fig. 1). Two precipitation samplers (stationed at the site at 220 m AMSL and at the weather station of Stuttgart, 315 m amsl) (Figs. 1 and 3) were also sampled regularly. Samples from the boreholes were



first taken with an insertion pump with a large pumping capacity, which was pumped long enough to remove the standing water column and/or until constant values were measured for the conductivity, temperature and pH of the water. Subsequently this system was replaced with a smaller volume peristaltic pump connected to a tube permanently suspended in the borehole by a metal weight with the tube being open at the depths where the borehole tapped the aquifer, that is, in-line with the natural flow of the system. Comparisons of samples taken with both systems showed no differences in chemical and isotopic composition (Angloher-Reichel, 2001).

For oxygen and hydrogen isotope analyses 50 ml glass bottles with conical plastic insets were filled completely after several rinse cycles with the sample water. For DIC (dissolved inorganic carbon) samples, 20 ml samples were taken in crimp-top vials to which about three to five drops of a saturated solution of mercury chloride were added. All samples were stored at 4°C in a refrigerator until analyses.

Samples of solids (carbonates and natural organic matter) were taken from sediment drill cores, while atmospheric and soil CO<sub>2</sub> were sampled using a previously evacuated glass flask. The flask was opened to air via a filter or attached to appropriate steel access tubes that were part of a soil gas monitoring system already installed at the site by another research group. Organic contaminants were sampled directly with a heavy spoon attached to a line and submersed into contaminated boreholes accessing the tar/oil residues.

Hydrogen isotope analyses followed the Zn-based method modified after Vennemann and O'Neil (1993), with 3 l of water taken up into a small capillary tube and dropped into an Ar-flushed, Zn-containing glass tube (100 mg of Zn purchased from the University of Indiana). The water was then frozen at liquid nitrogen temperatures and after evacuation of the Ar and air, the tube was sealed under vacuum. Water was quantitatively reacted in the tube with the Zn at 480°C for 10 min to produce H<sub>2</sub>. For the oxygen isotope analysis standard automated, on-line CO<sub>2</sub>-H<sub>2</sub>O equilibration techniques at 25°C adapted after Epstein and Mayeda (1953) were used on 4 ml-sized water samples. CO<sub>2</sub> from DIC was obtained by injecting about 0.5 to 5 ml of water via a septum into an evacuated vessel containing about 5 drops of 100% orthophosphoric acid produced according to the recipe of Coplen *et al.* (1983). The extracted CO<sub>2</sub> was then cryogenically purified and transferred and sealed under vacuum into a glass tube for subsequent isotopic analysis on the mass spectrometer. By weighing the injection syringe before and after injection and measuring the amount of CO<sub>2</sub> produced on a calibrated manometer, the concentration of DIC was also determined. Carbonates were measured using the conventional acid-digestion adapted after McCrea (1950). Samples of organic matter and the tars and oils were decarbonated using 10% HCl and subsequently washed with water and dried at 70°C for 12 hours. About 2 to 4 mg of organic matter was oxidized at 1050°C to produce CO<sub>2</sub> with an elemental analyzer (*Heraeus CHN-O-Rapid*) attached directly

Hydrogen and oxygen isotope compositions ( $\delta D$ ,

Borehole/Locality	1997												1998			
	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.								
Quaternary aquifer on-site																
B 8	-62	-8.6	-63	-8.5	-64	-8.5	-66	-8.7	-63	-8.6	-64	-8.5	-63	-8.5	-62	-8.3
B 10	-62	-8.7	-62	-8.7	-59	-8.6	-61	-8.6	-63	-8.7	-67	-8.5	-60	-8.7	-65	-8.4
B 11					-63	-8.6			-65	-8.6					-61	-8.5
B 12	-66	-8.6	-65	-8.5	-66	-8.4	-63	-8.5	-64	-8.3	-62	-8.4	-60	-8.5	-65	-8.3
B 13	-63	-8.5			-62	-8.4	-64	-8.5	-64	-8.2	-61	-8.2	-63	-9.2	-68	-9.0
B 15	-66	-8.6	-63	-8.5	-60	-8.4	-63	-8.4	-63	-8.1	-63	-8.3	-63	-8.1	-59	-8.1
B 18					-61	-8.5			-63	-8.4					-60	-8.4
B 20					-61	-8.5			-63	-8.4					-62	-8.5
B 27	-63	-8.7	-61	-8.6	-60	-8.7	-64	-8.6	-64	-8.5	-65	-8.7	-65	-8.6	-66	-8.6
B 30	-64	-8.7	-61	-8.6	-63	-8.7	-64	-8.6	-67	-8.5	-65	-8.6	-66	-8.5	-60	-8.5
B 31					-64	-8.8			-63	-8.8					-68	-8.8
B 32	-65	-9.2	-65	-9.1	-67	-9.2	-66	-9.2	-70	-9.2	-67	-9.3	-67	-9.2	-66	-8.8
B 33					-62	-8.8			-64	-8.8					-65	-9.0
B 34					-63	-9.0			-65	-9.0					-62	-8.9
B 38	-65	-9.1	-68	-9.0	-64	-9.0	-62	-9.1	-63	-8.7	-63	-8.8	-66	-8.9	-66	-8.9
B 40					-59	-8.5			-62	-8.5					-62	-8.4
B 41	-59	-8.5	-62	-8.7	-62	-8.7	-62	-8.7	-64	-8.6	-65	-8.6	-63	-8.6	-65	-8.6
B 42					-63	-8.4			-64	-8.4					-66	-8.5
B 46					-66	-8.6	-64	-8.6	-61	-8.4	-62	-8.6	-62	-8.5	-62	-8.5
B 58	-64	-8.6	-64	-8.6	-64	-8.6	-67	-8.6	-63	-8.6	-66	-8.5	-64	-8.6	-68	-8.5
P 1					-62	-8.7			-64	-8.7					-68	-8.6
P 2	-65	-8.3	-62	-8.4	-61	-8.5	-62	-8.2	-65	-8.4	-60	-8.3	-59	-8.2	-64	-8.2
Quaternary aquifer upstream																
NT 04	-62	-8.2	-63	-8.3	-61	-8.4	-61	-8.2	-60	-8.3	-66	-8.2	-64	-8.4	-62	-7.8
NT 29	-62	-8.6	-63	-8.5	-65	-8.5	-60	-8.4	-61	-8.3	-62	-8.6	-65	-8.8	-62	-8.8
NT 64	-64	-8.6	-65	-8.4	-63	-8.4	-64	-8.5	-66	-8.4	-60	-8.5	-61	-8.5	-60	-8.3
Gipskeuper aquifer																
B 24	-62	-8.7	-64	-8.6	-62	-8.7	-63	-8.8	-62	-8.7	-63	-8.8	-67	-8.8	-62	-8.7
B 25					-63	-9.4			-63	-9.1					-64	-9.2
B 26	-67	-9.3	-71	-9.3	-67	-9.3	-68	-9.2	-65	-9.1	-68	-9.2	-65	-9.3	-68	-9.2
Springs																
Froschbeiberquelle	-62	-9.0	-69	-9.1	-67	-9.0	-63	-9.0	-69	-9.0	-67	-9.0	-67	-8.9	-65	-8.8
Heckenbr unnenquelle	-62	-9.0	-67	-9.1	-67	-9.1	-64	-9.1	-68	-8.9	-66	-9.1	-67	-8.9	-65	-8.9
Pfarrquelle	-63	-9.0	-68	-9.1	-64	-9.0	-63	-9.1	-68	-8.8	-66	-8.9	-67	-8.9	-66	-8.8
Local streams																
Dürrbach	-60	-8.6	-65	-8.8	-63	-8.5	-63	-8.7	-64	-8.8	-66	-8.9	-66	-8.9	-63	-8.8
Tiefenbach	-59	-8.6	-63	-8.8	-62	-8.6	-59	-8.3	-65	-8.9	-65	-8.9	-65	-8.9	-65	-8.9
Neckar River																
Neckar -Gaisburg	-65	-9.2	-65	-8.8	-62	-8.9	-61	-8.6	-66	-9.1	-69	-9.5	-65	-9.2	-68	-9.3
Neckar -Untertürkheim	-69	-9.3	-64	-8.7	-65	-8.9	-60	-8.7	-69	-8.9	-70	-9.5	-67	-9.1	-69	-9.3
Mineral waters																
Hofrat -Seyffer -Quelle							-70	-10.1	-73	-9.8	-73	-10.0	-72	-9.9	-71	-9.9
Inselquelle							-70	-9.7	-69	-9.7	-70	-9.7	-69	-9.8	-70	-9.8
Auquelle							-64	-8.9	-63	-8.8	-66	-8.9	-61	-9.0	-64	-8.9
Gottlieb -Daimler - Quelle									-72	-9.5					-73	-9.7
Mombachquelle									-63	-8.5					-66	-8.8
Precipitation samplers																
NS-TWS			-31	-4.6	-52	-6.9	-55	-7.8	-66	-8.3	-120	-15.4	-65	-8.8	-108	-13.8
NS-DWD			-41	-5.5	-37	-6.9	-50	-7.7	-129	-17.1	-103	-14.1	-66	-8.3		



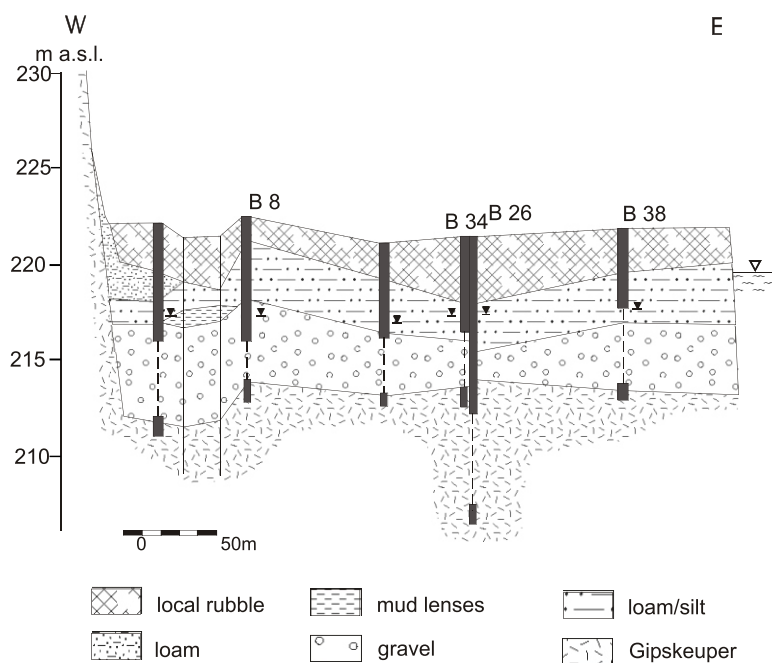


Fig. 3. Schematic geological cross-section of the aquifers at the industrial site

Geology adapted from Geologisches Landesamt Baden-Württemberg (1992)

to the mass spectrometer. All samples were measured for their isotopic compositions on a *Finnigan MAT 252* mass spectrometer at the University of Tübingen.

Isotopic compositions are given in the conventional  $\delta$ -notation in permil, relative to the VSMOW standard (H and O), and the VPDB standard for C. Reference gases used were calibrated against VSMOW/VSLAP for H and O, and against NBS-19 calcite and VSMOW for C and oxygen measured on  $\text{CO}_2$  from carbonates. Accuracy as well as precision were determined by in-house water and carbonate standards extracted and measured in parallel with each batch of 8 to 12 samples. All water samples for H and O isotopic compositions were analyzed in duplicate and the average precision was better than  $\pm 1\%$  for H and  $\pm 0.04\%$  for O. For C-isotope compositions of the DIC, the reproducibility for duplicates was established to be better than  $\pm 0.2\%$  by repeated analyses of the river water, while that for the organic matter and carbonates was  $\pm 0.2$  and  $\pm 0.1\%$ , respectively. Oxygen isotope compositions of the carbonates reproduced to better than  $\pm 0.1\%$ .

## RESULTS AND DISCUSSION

The results for the isotopic measurements as well as the concentrations of DIC or of C in samples of organic matter are given in Tables 1 to 5. Additional information on the pH, is summarized in Angloher-Reichert (2001) but, owing to space limitations are not discussed further here.

### HYDROGEN AND OXYGEN ISOTOPE COMPOSITIONS OF WATERS

The H and O isotope composition of different surface waters, groundwaters, and mineral waters are summarized in Fig-

ure 4. Different groups of waters can clearly be distinguished on the basis of their O and H isotope compositions. These include:

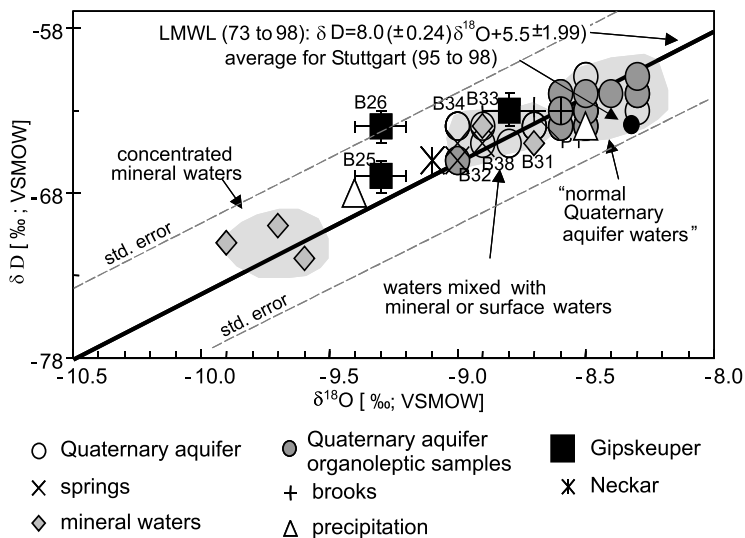
a — mineral waters with a relatively high concentration of dissolved ions (Graf *et al.*, 1994; Ufrecht, 1998a, b) that have a distant, geographically distinct source for water compared to other groundwaters in this area (*cf.* Graf *et al.*, 1994; Ufrecht, 1998a, b);

b — mineral waters with relatively low concentration of dissolved ions, presumably representing variable mixtures of group a) with waters of the Gipskeuper and Quaternary aquifers;

c — waters from the Gipskeuper aquifer that may also have a distinct source but are also variably influenced by admixtures of mineral and Quaternary aquifer waters (*cf.* Ufrecht, 1998a, 1999);

d — waters from the Quaternary aquifer that can be further divided into two groups where one of these has been influenced by upwelling mineral waters and/or infiltrating surface waters while the other group has not (Fig. 4; see also below).

The distinction between which of these types of waters are infiltrating the Quaternary aquifer and where can be made both on the basis of the seasonal variation in isotopic compositions of the different waters (Fig. 5), as well as using the C isotope composition of the DIC (see below). Figure 5 and also Table 1 illustrate that many of the Quaternary aquifer waters, as well as the mineral waters and the Gipskeuper waters, have little or no significant seasonal variation in their H and O isotope compositions. This is to be expected for waters with relatively long flow paths relative to their source and/or for those characterized by slow flow rates because the seasonal differences in isotopic composition, largely reflecting temperature-dependant vapour-liquid fractionation and hence the mean ambient air temperature for the precipitation, get homogenized through advective as well as diffusive mixing (e.g., Clarke and Fritz, 1997). Large seasonal amplitudes in variations of the H and O isotopic compositions are thus common for precipitation in mid-latitude, continental areas but get increasingly dampened for direct surface runoffs relative to larger rivers and finally lakes and deeper groundwaters. Smaller rivers fed by groundwater sources are also expected to have lower seasonal variation. This is observed for the small brooks sampled in the area, which, although they are much smaller in volume of flow, have lower seasonal variation compared to the Neckar (Fig. 5). Even the Neckar River has relatively little seasonal variation (1.3‰ seasonal variation for  $^{18}\text{O}$  compared to about 11‰ for the precipitation), which reflects a relatively long residence time of water in the river (the flow is regulated by several dams upstream of the measurement sites), evaporative effects, as well as a mixture of averaged surface waters and groundwater sources. Of the Quaternary aquifer waters analysed, those closer to the Neckar (B38, P1, P2, NT29) as well as some located close to the steep hill adjacent to the industrial site (B13, B27) clearly show seasonal variation. Compared to the Neckar River, the seasonal variation for these boreholes is, however, somewhat delayed, roughly corresponding to the infiltration time neces-



**Fig. 4.** Average hydrogen and oxygen isotope compositions of different waters shown relative to the local meteoric water line (LMWL) calculated for the results from the IAEA (2004) database for Stuttgart (1973 to 1998)

Shaded dashed lines indicate the standard error for the LMWL; also shown are the average values for precipitation in Stuttgart between 1995 and 1998 (IAEA, 2004); for clarity, the average analytical error is shown for samples from the Gipskeuper aquifer only

sary to cover the distance between the river and the sampling site. On average, the difference in phase between the curves does indicate a delay of approximately two weeks to one month. This is a crude estimate only though, as the sampling was done on a monthly basis only. More surprising are the variations in H and O isotopic composition measured for boreholes B33 and B10 as they are further away from the river but still show weak seasonal variations. As indicated in Figure 2, these boreholes are close to a precipitation sewer and an old mill channel, both of which subsequently discovered on old city maps at the town hall. Hence, on the basis of the H and O isotope compositions alone, mixing between different groups of waters can be recognized on the scale of this industrial site. Mixing between these different waters will certainly also affect the chemical composition of the waters, which may have direct consequences for the monitoring of the contamination and for the remediation of the site itself.

All of the aquifer waters as well as the surface and shallow spring waters sampled in the region cluster well around the local meteoric water line (LMWL) that can be defined on the basis of the database of the IAEA (2004) for the locality of Stuttgart (Fig. 4). The LMWL is thus representative, within error of the variations induced by climatic changes over the course of the past years, for all types of waters in this area. In addition, the average  $\delta D$  and  $\delta^{18}O$  value calculated for the years 1995 to 1998, plots well within the field for the Quaternary aquifer waters (Fig. 4). This is not the case if the average is calculated for the years 1990 to 1998 ( $\delta D = -58.2\text{‰}$ ,  $\delta^{18}O = -8.0\text{‰}$ ), suggesting that the Quaternary aquifer waters reflect the average precipitation over the course of the previous 3 to 4 years, an interpretation that is compatible with flow rates of about 2.5 metres per day (Geologisches ..., 1989, 1992) and the geographic restrictions of the given source area for the Quaternary aquifer in this locality.

#### CARBON ISOTOPE COMPOSITIONS OF DIC IN WATERS

Mixing relationships between different groups of waters are particularly well illustrated through a comparison of the ox-

xygen isotope composition of water and the carbon isotope composition of the DIC (Fig. 6a). Different groups of waters that can clearly be recognized include:

- mineral waters with a relatively high concentration of dissolved ions,
- mineral waters with relatively low concentration of dissolved ions, presumably representing variable mixtures of group a) with waters of the Gipskeuper and Quaternary aquifers,
- waters from the Gipskeuper aquifer that may have a distinct source but are also variably influenced by admixtures of mineral and Quaternary aquifer waters,
- waters from the Quaternary aquifer that can again be further divided into a group influenced by upwelling mineral waters and a second group that is influenced by infiltrating surface waters, in particular infiltration of Neckar River water.

A similar grouping is also evident from a plot of the  $^{13}C_{DIC}$  values and the concentrations of DIC in groundwaters (Fig. 6b). It is possible that for some of the Quaternary groundwaters both mineral and river waters are infiltrating simultaneously. The latter is supported, for example, by borehole B38 both in Figure 6 as well as by the seasonal variation in  $^{13}C_{DIC}$  values for this borehole, which again track those of the Neckar River quite closely (Fig. 7). Other boreholes with monthly variations in the  $^{13}C_{DIC}$  values, such as B31, B32, B34 and B41 (Fig. 6; Table 2), do not necessarily follow the seasonal pattern of the river but instead may reflect variable influence of mineral waters (Fig. 7), perhaps as a function of variable hydrologic gradients superimposed by the hydrologic system.

#### CONTROLS ON CARBON ISOTOPE COMPOSITIONS OF DIC

The controls on  $^{13}C$  values for DIC in the natural system of the present study have been summarized in Figure 8a. The diffusion and uptake of  $CO_2$  in plants is associated with a small enrichment in  $^{13}C$  (about 4‰) while the fixation (carboxylation) as carbohydrate is associated with a strong depletion of  $^{13}C$  in plants (about 23‰). The net result of this fixation is that plants following the Calvin or  $C_3$  cycle of photosynthesis, which is typical for this region, have  $^{13}C$  values of about -24

## Concentrations [mg/l] and carbon isotope compositions

Borehole/Locality	1997												1998			
	July		Aug.		Sept.		Oct.		Nov.		Dec.		Jan.	Feb.		
Quaternary aquifer on-site																
B 8	635	-17.1	712	-17.1	640	-17.2	475	-17.2	653	-17.0	553	-17.0	690	-16.9	812	-16.7
B 10					697	-18.8			662	-18.8					723	-18.5
B 11					749	-17.8										
B 12	251	-16.4	252	-16.2	255	-16.3	240	-16.3	164	-16.9	267	-16.2	259	-16.0	260	-16.1
B 13									595	-15.6					363	-16.6
B 15					606	-17.4			583	-17.9					632	-19.2
B 18					592	-16.0										
B 20									563	-14.8						
B 27																
B 30			840	-13.5	785	-13.3	807	-13.7	763	-14.6	697	-14.5	749	-14.9	695	-14.9
B 31					1295	-7.0			828	-7.5					1311	-7.1
B 32	2222	-4.4	2545	-4.6	2302	-3.8	2557	-4.5	1573	-4.1	2483	-4.4	1537	-5.9	1928	-5.5
B 33									394	-16.6					346	-15.6
B 34																
B 38	440	-13.4	520	-13.3	462	-12.9	667	-14.7	272	-15.2	486	-14.3	517	-13.1	577	-11.7
B 40																
B 41					586	-7.8			381	-11.2					862	-10.1
B 42																
B 46									660	-17.0						
B 58	256	-16.4	398	-15.6	422	-15.9	402	-16.2	382	-14.9	195	-17.0	450	-15.7	484	-16.6
P 1															534	-13.4
P 2																
Quaternary aquifer upstream																
NT 04	750	-18.8													1042	-20.4
NT 29	466	-15.5	378	-15.9	392	-16.1	300	-16.0	346	-15.0	165	-16.9	367	-15.8	377	-15.8
NT 64									252	-18.1					501	-16.4
Gipskeuper aquifer																
B 24	1385	-9.4	1558	-9.0	1602	-9.4	1443	-8.9	1762	-7.5	1734	-7.7	1752	-7.7	1721	-7.6
B 25																
B 26			2187	-3.1					2148	-3.5					2391	-3.5
Springs																
Froschbeißerquelle	319	-14.6	843	-14.7	368	-14.8	312	-14.7	198	-15.0	170	-14.5	234	-13.9	282	-13.7
Pfarrquelle	338	-14.4							214	-15.7					350	-15.0
Local streams																
Dürrbach	317	-13.2	368	-13.0	388	-13.0	368	-12.7	252	-14.2	388	-13.8	369	-13.1	359	-13.1
Tiefenbach									323	-14.2					309	-13.5
Neckar River																
Neckar Gaisburg	221	-13.1	250	-11.7	246	-12.1	151	-12.9	183	-12.7	278	-11.9	236	-12.0	266	-11.4
Neckar Untertürkheim									171	-12.4					268	-11.3
Mineral waters																
Hofrat Seyffer Quelle							966	-6.3	933	-6.5					936	-6.3
Inselquelle							3203	-3.5	3063	-3.2	2979	-3.3	3124	-3.4	2858	-3.3
Auquelle							480	-12.0	374	-12.2					377	-11.4
Precipitation samplers																
NS TWS			11	-4.4			17	-29.1								
NS DWD			65	-13.7			12	-13.9			-11.2					

to  $-30\text{‰}$  (e.g., Vogel, 1993). It is also known that respiration by  $C_3$ -plants and/or natural decomposition of this type of organic matter in the soil produces  $CO_2$  which has very similar  $^{13}C$  values compared to the original vegetation itself, but the diffusion of this  $CO_2$  through the soil again produces an enrichment of about  $4\text{‰}$  (e.g., Cerling *et al.*, 1991). For most natural systems, this  $CO_2$  is the major source of DIC dissolved in deeper groundwaters. At the temperature and pH conditions typical for the soil horizons and aquifers in the present system (about  $15^\circ C$  and  $pH = 7$ ), equilibrium dissolution of soil  $CO_2$  would produce DIC with an average isotopic enrich-

ment factor ( $\epsilon = ( -1) / 1000$ ) of about 9 (Mook *et al.*, 1974), that is  $^{13}C_{DIC}$  values of about  $-15$  to  $-16\text{‰}$ . The Quaternary aquifer waters have  $^{13}C_{DIC}$  values close to those expected for DIC in equilibrium with soil  $CO_2$ , but also a tendency towards lower, sometimes much lower,  $^{13}C_{DIC}$  values (Figs. 6 and 7; Table 2). This suggests that while soil-derived  $CO_2$  is the dominant source of DIC for these groundwaters, other sources may also be possible.

For shallower groundwaters or surface and river waters an additional control on the  $^{13}C$  values of DIC is exchange with or dissolution of atmospheric  $CO_2$  (e.g. Cameron *et al.*, 1995;



Table 2

 $(\delta^{13}\text{C}$  values in permil) of DIC in different waters analyzed

1998										1999							
Mar.	April		May		June		Nov.	Dec.		Jan.	Feb.		Mar.				
732	-18.6	636	-16.6	674	-16.6	655	-16.6	670	-16.7	721	-18.9	694	-18.5	695	-18.6	612	-18.5
				713	-18.5												
253	-15.9	256	-16.1	262	-15.9	246	-16.2			205	-14.3	231	-15.8	253	-15.8	261	-16.1
				362	-16.4					337	-15.3	393	-17.4	391	-17.8	459	-17.1
774	-19.6	707	-17.8	517	-19.2	685	-17.5										
				591	-15.0												
712	-18.0	754	-17.8	700	-18.4	702	-18.7	734	-18.1	725	-18.6	785	-18.5	743	-18.5	759	-18.4
753	-15.1	678	-14.7	699	-14.5	746	-14.4										
				1074	-8.0												
1284	-6.3	1553	-5.7	1966	-5.4	1661	-5.5	783	-8.0	1117	-6.1	1287	-5.8	976	-6.4	1285	-6.0
				1253	-5.2											580	-11.9
532	-12.9	491	-12.6	458	-12.4	459	-12.6	429	-13.8	429	-13.8	505	-12.3	443	-13.0	525	-13.0
				680	-19.3												
826	-10.1			711	-11.1												
				738	-18.7												
				707	-16.2												
466	-16.5	419	-16.0	419	-15.9	444	-16.5	512	-17.3	449	-16.0	491	-17.3	448	-16.7	461	-16.0
528	-13.5	410	-13.2	457	-13.7	466	-13.8	479	-14.2	499	-13.9	499	-14.0	477	-14.4	314	-15.6
		706	-17.9	817	-15.4												
				367	-19.4												
386	-15.7	370	-15.6	346	-15.8	363	-15.6	341	-15.9	349	-15.9	314	-15.7	323	-15.6	314	-15.6
				489	-17.4												
1000	-7.8	1714	-7.4	978	-8.0	938	-7.7										
				2155	-5.1												
2185	-2.9	2169	-3.1	1283	-3.3			1460	-3.2	1510	-3.0	1423	-3.6	1588	-3.5	2039	-3.5
323	-13.3	326	-13.7	375	-14.9	356	-14.7	330	-13.6	336	-14.0	401	-14.2	375	-14.0	436	-15.1
457	-14.7	465	-14.9	451	-14.7												
366	-13.2	359	-13.1	378	-13.0	353	-13.4	277	-15.0	206	-14.3	373	-13.6	350	-13.5	389	-13.6
				339	-14.6												
213	-12.2	226	-11.7	220	-9.9	210	-12.4										
				163	-10.0			184	-12.6	172	-12.8	215	-12.3	179	-12.4	237	-11.9
				901	-6.4												
3045	-3.3	2999	-3.0	2434	-2.0	2947	-3.3									3206	-3.6
				388	-12.1												
15	-10.8	17	-13.8	20	-7.6	142	-18.5					14	-12.0	13	-14.5	25	-17.9
11	-15.8	9	-11.9	16	-7.9												

Hoefs, 2004). This becomes particularly important further downstream in rivers and/or if the rivers are dammed, that is if the exposure to atmospheric  $\text{CO}_2$  is increased. Such processes lead to increasing  $^{13}\text{C}$  content in the DIC (Fig. 8a). An increase in the  $^{13}\text{C}_{\text{DIC}}$  values from ground to surface waters and from smaller to larger river waters is illustrated for the present study by a comparison of the results for the groundwaters relative to the surface waters (Dürrbach and Neckar; Figs. 6 and 7). As a result of variable seasonal biologic and *in situ* photosynthetic activity,  $^{13}\text{C}_{\text{DIC}}$  values may vary seasonally too: commonly

higher values during spring and early summer as a result of preferential  $^{12}\text{C}$  incorporation into organic matter and lower values during autumn/winter because of oxidation of the organic matter (e.g., Telmer and Veizer, 1999; Hoefs, 2004). This pattern is weakly discernable for the Dürrbach and the Neckar, but may be complicated through exchange with atmospheric  $\text{CO}_2$  and temporal damming of the flow (e.g. reduced flow of the Neckar River and hence damming during winter).

In addition, weathering and dissolution of carbonates in aquifers may strongly influence the  $^{13}\text{C}$  values of DIC, com-

Table 3

## Carbon and oxygen isotopic composition of carbonates

Locality	Sample / Grain size [mm]	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$	Carbonate content [%]
		[‰]	[‰]	
Cover sediments				
B 52	I	-6.4	23.5	30
	II	-6.0	23.1	27
B 58	I	-6.6	22.9	32
	II	-6.6	23.3	34
Quaternary aquifer sediment				
B 52	I (20-63)	2.8	26.3	99
	II (20-63)	2.2	26.2	100
	III (20-63)	1.9	26.7	100
	IV (20-63)	1.6	26.4	100
	V (20-63)	1.3	27.5	100
	VI (20-63)	0.1	26.2	97
	VII (1-20)	0.1	25.8	67
	VIII (0.5-1)	-0.6	25.7	31
	IX (0.18-0.50)	-3	24.8	31
	X (0.125-0.18)	-4.9	24	41
	XI (0.063-0.125)	-6	23.5	34
B 58	I (20-63)	2.1	27.2	100
	II (20-63)	1.9	27.6	97
	III (20-63)	1.8	26.1	100
	IV (20-63)	1.8	25.8	98
	V (20-63)	-0.1	25.3	100
	VI (20-63)	-0.1	25.1	100
	VII (1-20)	0.2	25.9	66
	VIII (0.5-1)	-1.3	25.2	26
	IX (0.18-0.50)	-4.7	24.1	36
	X (0.125-0.18)	-5.6	23.8	42
	XI (0.063-0.125)	-5.6	23.8	34
Gipskeuper aquifer				
B 52	I (<1)	-5.8	27.8	29
	II (10-20)	-5.8	27.7	33
B 58	I (<1)	-4.1	26.5	31
	II (10-20)	-4.0	26.5	27
	III (20-30)	-5.8	23.8	38

Table 4

## Carbon isotope compositions of organic matter

Locality (depth in m)	$\delta^{13}\text{C}_{\text{org}}$ [%]	Amount of C [%]
cover sediments		
B 52 (5.0 m)	-28.0	1.2
B 58 (3.7 m)	-27.3	1.4
B 58 (3.9 m)	-27.5	1.3
B 58 (4.0 m)	-27.5	1.3
B 58 woody tissue	-28.8	11.5
Quaternary aquifer		
B 52 (6.6 m)	-27.0	0.3
B 58 (6.4 m)	-26.4	0.2
B 58 Holzfasern	-26.9	4.9
B 60 (3.0 m)	-26.2	0.6
B 60 (3.5 m)	-26.3	0.5
B 61 (3.5 m)	-25.9	0.2
B 61 (4.0 m)	-26.6	0.6
tar and oil residues		
B 10	-27.1	1.7
B 11	-25.2	5.6
B 15	-24.1	91.8
B 23	-24.3	0.5

Table 5

Carbon and oxygen isotopic composition and concentration of CO<sub>2</sub>

Locality	$\delta^{13}\text{C}_{\text{CO}_2}$ [%]	$\delta^{18}\text{O}_{\text{CO}_2}$ [%]	CO <sub>2</sub>
air samples			
Stuttgart, public park	-8.4	28.8	533
on-site, next to road	-13.9	18.6	627
on-site, next to road	-9.3	28.9	869
on-site, next to road	-8.2	40.5	436
Tübingen, public park	-8.8	40.5	437
Tübingen, forest	-9.5	38.2	393
Tübingen, next to road			
soil samples			
B 38 — 40 cm depth (uncontaminated)	-28.3	32.5	1415
B 38 — 40 cm depth (uncontaminated)	-27.4	30.2	3381
B 38 — 40 cm depth (uncontaminated)	-25.7	35.2	8617
B 15 — 100 cm depth (strongly uncontaminated)			
P 2 — 340 cm depth (weakly contaminated)			
mineral waters			
Inselquelle I	-8.6	25.0	12 074
Inselquelle II	-8.2	21.8	15 214

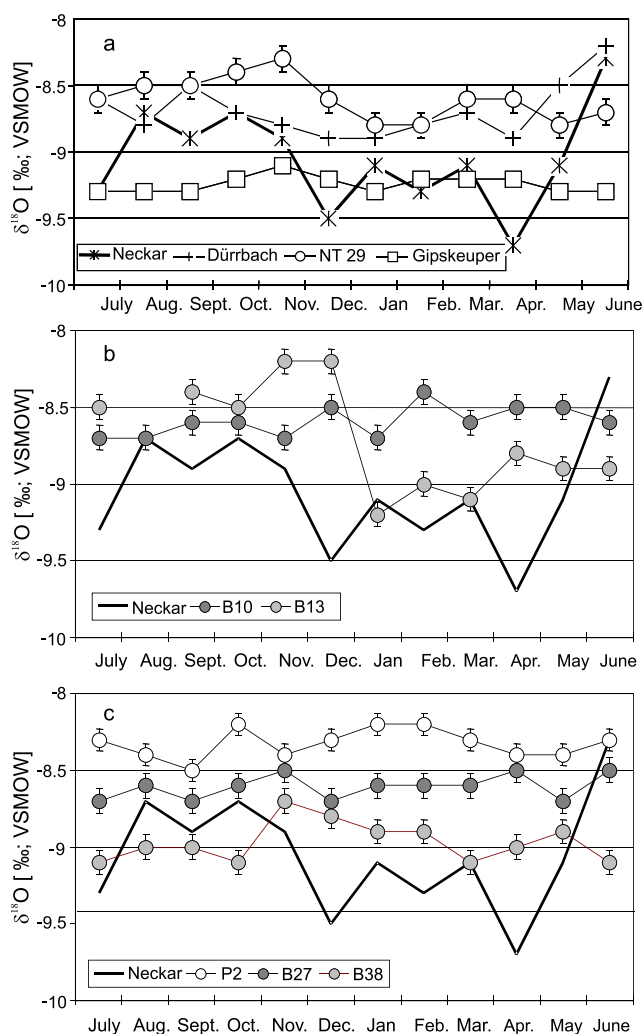
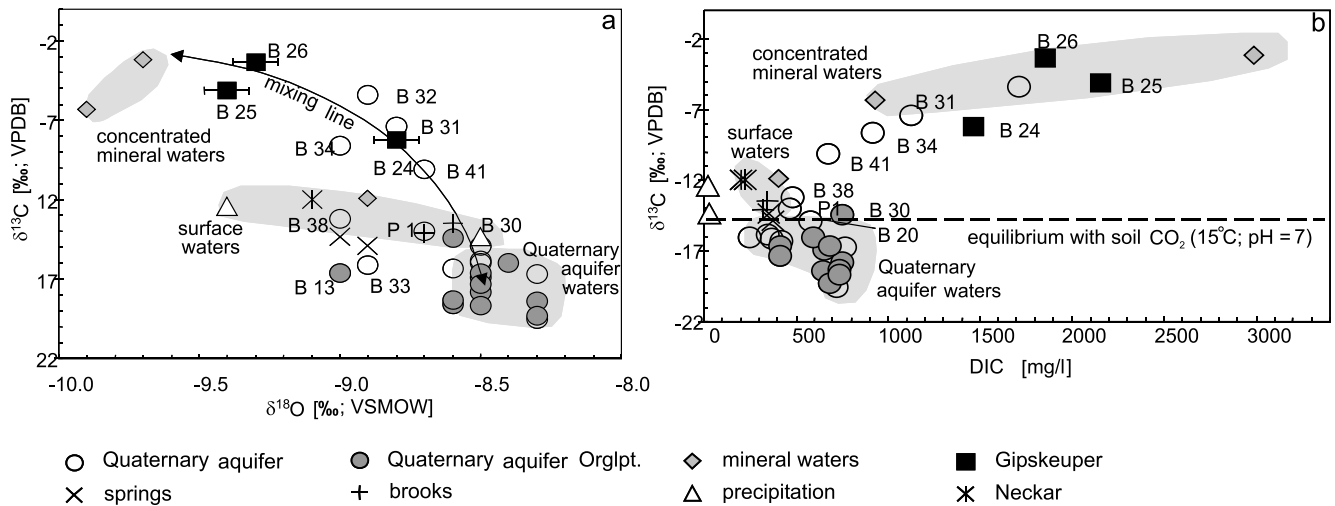
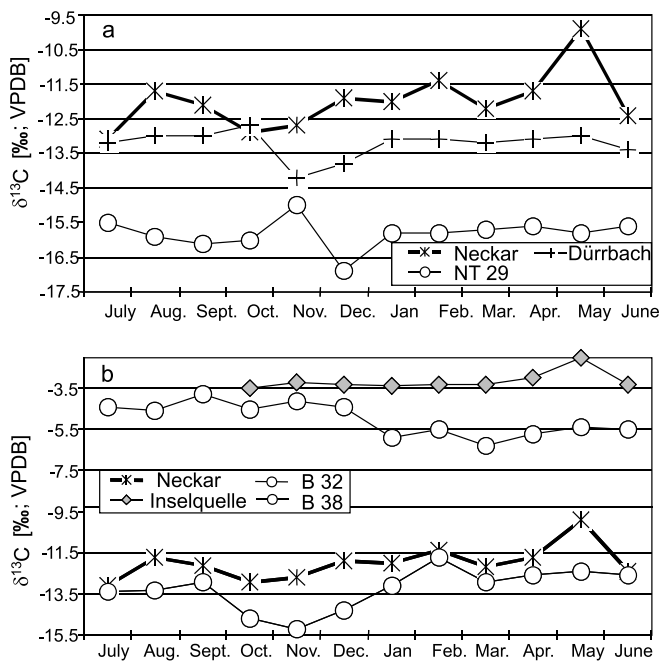


Fig. 5. Seasonal variation of the oxygen isotope compositions of several selected water sources



**Fig. 6. Carbon isotope composition of dissolved inorganic carbon (DIC) relative to the oxygen isotope composition of water (a) and relative to the concentration of DIC (b) for the different waters analyzed in this study**

Errors for the carbon isotope composition and concentrations of DIC are approximatively as large as the symbols; sample names are given only for some of the Quaternary and the Gipskeuper aquifer waters; the mixing line in (a) represents a typical mixing line between two waters of different isotopic compositions and different concentrations of the DIC; a line indicating DIC in carbon isotope equilibrium with soil- $\text{CO}_2$  at average conditions of T and pH is given for comparison



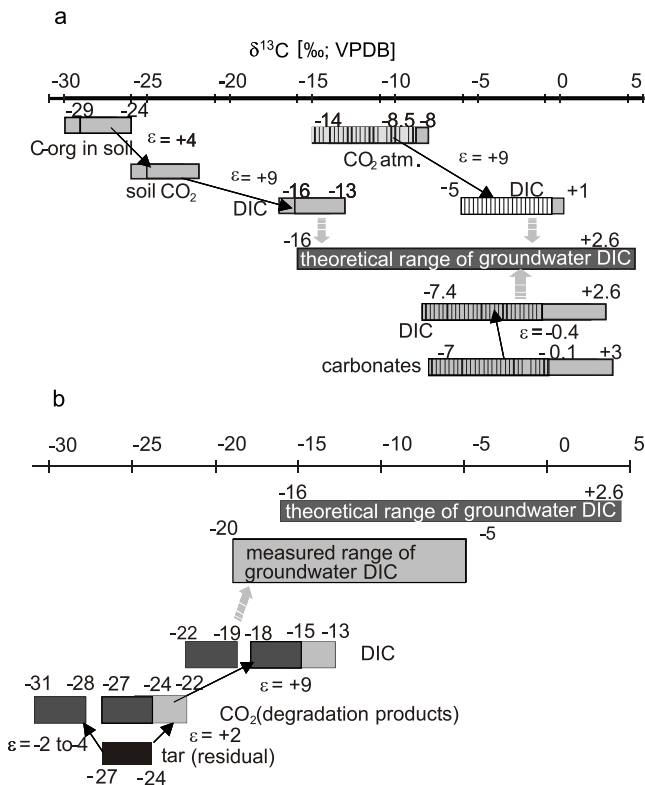
**Fig. 7. Seasonal variation of the carbon isotope compositions of DIC from several selected water sources**

monly leading to an increase in  $^{13}\text{C}$  (e.g., Yang *et al.*, 1996). This is clearly indicated by the  $^{13}\text{C}$  values for DIC from the mineral waters in this study (Figs. 6 and 7; Table 2).

Finally, a number of studies have shown that decomposition of tars and oils as well as other anthropogenic organic components commonly leads to products, including  $\text{CO}_2$ , which are either similar to or depleted in  $^{13}\text{C}$  (by about 2 to 4‰) relative to the isotopic composition of the original and residual

material (Stahl, 1980; Schoell, 1984; Aggarwal and Hinchee, 1991). This is particularly the case if bacterial processes are involved (e.g., Stahl, 1980; Schoell, 1984; Aggarwal and Hinchee, 1991; Conrad *et al.*, 1997; Hammer *et al.*, 1998; Diegor *et al.*, 1999; Hunkeler *et al.*, 1999). Only in the case of degradation of cyclic hydrocarbons, however, has it been observed that the degradation products are slightly enriched in  $^{13}\text{C}$  (by about 2‰; e.g., Stahl, 1980; Schoell, 1984; Suchomel *et al.*, 1990). For the present site a number of studies have shown that bacterially mediated decomposition of the tar-oils does occur (e.g., Meckenstock *et al.*, 1999; Steinbach *et al.*, 2004) and the possible effects of this on the  $^{13}\text{C}_{\text{DIC}}$  values for the site investigated here has been summarized in Figure 8b.

It has been noted above that many Quaternary aquifers, in particular those that are organoleptic but also some that are both upflow as well as downflow of the contamination at the present site, have  $^{13}\text{C}_{\text{DIC}}$  values lower than those expected for DIC in equilibrium with soil  $\text{CO}_2$  in a typical  $\text{C}_3$ -vegetation system (Fig. 6; Table 2). Waters from boreholes with lower  $^{13}\text{C}_{\text{DIC}}$  values generally have higher concentrations of DIC too (Fig. 6; Table 2). Given an equilibrium between soil  $\text{CO}_2$  and DIC and a pH between 6.1 and 8.0, such low  $^{13}\text{C}_{\text{DIC}}$  values are difficult to explain via natural processes in the aquifer (*cf.* Suchomel *et al.*, 1990; Aggarwal and Hinchee, 1991; Nachtweyh *et al.*, 1991; Flintrop *et al.*, 1996; Landmeyer *et al.*, 1996; Clark and Fritz, 1997; Conrad *et al.*, 1997; Angloher *et al.*, 2000). The question can thus be raised, whether this decrease in  $^{13}\text{C}_{\text{DIC}}$  value is related to organic pollutants at this site and/or to other organic pollutants from elsewhere within this industrial valley. As has been explained above, exposure to and exchange with atmospheric  $\text{CO}_2$ , dissolution of the marine carbonate pebbles in the aquifers in a closed system, and/or mixing with the surface or mineral waters can only lead to an increase in the



**Fig. 8.** a — carbon isotope compositions of natural organic matter, carbonates, and soil  $\text{CO}_2$  as well as those of DIC calculated to be in equilibrium with these phases; b — carbon isotope composition of residual taroils, possible  $\text{CO}_2$  degradation products of these, as well as DIC in equilibrium with this  $\text{CO}_2$

For  $\text{CO}_2$  as a degradation product several models have been considered: bacterially mediated decomposition of carbon in the organic phases  $\epsilon = -2$  to  $-4$ ), irreversible reactions with no fractionation during oxidation, and a bacterially mediated production of  $\text{CO}_2$  with enrichment in  $^{13}\text{C}$  as reported for heterocyclic organic phases (see text for discussion); all  $\epsilon$ -values calculated for  $15^\circ\text{C}$ ,  $\text{pH} = 7$

$^{13}\text{C}_{\text{DIC}}$  values (Figs. 6 and 8; Table 2). Hence, it is certainly possible that the relatively low  $^{13}\text{C}_{\text{DIC}}$  values and elevated concentrations of DIC measured for many of the Quaternary groundwaters at the present industrial site are indeed related to anthropogenic contamination. This may also apply to some of the groundwaters sampled outside and well upstream of the former gas production plant but still within the industrial area of the river valley (e.g., NT04 and NT64).

## CONCLUSIONS

The H and O isotope composition of groundwaters, in combination with their carbon isotope composition of DIC clearly separate different types of groundwaters and evaluate the mixing processes within aquifers at a contaminated industrial site. More specifically, the aquifers in the site can be grouped according to the type of infiltration and mixing (Fig. 2):

- infiltration from shallow groundwaters derived from the adjacent steep hill along the western margin of the site,
- river infiltration along the eastern margin of the site,
- local infiltration by artesisally confined mineral waters, presumably along a fault, in the northern part of the site,

— aquifers that are infiltrated by both surface waters as well as mineral waters.

Variable mixtures of these different waters within the gravel aquifers can be presented as mixing lines in terms of their stable isotope composition of O, H, and  $\text{C}_{\text{DIC}}$ , allowing for estimates of the mixing proportions within individual boreholes (Angloher-Reichelt, 2001). Monthly sampling of waters from the boreholes of the site indicate that the proportions of different waters vary both in terms of space and time, depending on the flow regime of the adjacent river, the variable local recharge rates for surface waters, heterogeneities in flow rates owing to local differences in the permeability of the aquifer, and geologic as well as man-made structures at the site. Large deviations in the isotopic compositions of the precipitation for individual months caused by particular precipitation events do allow for evaluation of reservoir effects and influences of man-made and geologic structures on the hydrology of the system. The magnitude of seasonal variation in H and O isotopic composition decreases significantly from precipitation, via surface waters, down to groundwaters. Deep Gipskeuper groundwaters and mineral waters of the Muschelkalk aquifers show no relationship to actual precipitation owing to their distant recharge area and significantly longer flow paths, residence and mixing times within the aquifer. In the marginal areas of the site, groundwaters of the Quaternary gravel aquifer reflect the seasonal isotopic variations of precipitation but with a delay of about one month, indicating fairly rapid infiltration. Except for sites located close to man-made structures (mill channels and rain water sewer), such seasonal variation is not recognizable in the central areas of the site owing to longer flow paths and residence times.

The concentration and C-isotopic composition of DIC in most waters can be interpreted within the framework of the natural biogenic and geogenic carbon system. DIC of small fluvial surface waters and local spring water sampled distant from anthropogenic carbon sources is in equilibrium with soil-derived  $\text{CO}_2$ , while DIC of the river is also influenced by atmospheric  $\text{CO}_2$ . Seasonal variations of the carbon isotope composition and concentrations of DIC in different surface and groundwaters correlate with variable amounts of precipitation and runoff. DIC in deep Gipskeuper and mineral aquifer waters is clearly dominated by marine carbonates, which make up these aquifers. In contrast to waters from uncontaminated sources, the DIC in the contaminated Quaternary aquifer is characterized by depletion of  $^{13}\text{C}$  with values lower than those expected to be in equilibrium with natural soil  $\text{CO}_2$ . The lowest  $^{13}\text{C}$  values and at the same time the highest DIC concentrations have been measured immediately downstream of the known pollution. The low  $^{13}\text{C}_{\text{DIC}}$  values, especially in the polluted aquifers, are best explained by bacterially mediated decomposition of organic contaminants. Further downstream the DIC concentrations decrease and  $^{13}\text{C}_{\text{DIC}}$  values increase again, except for boreholes influenced by mineral waters, which have significantly higher DIC concentrations. Thus dilution and mixing effects can be resolved. Generally low  $^{13}\text{C}$  values upstream of the former gas production site are likely to reflect regional anthropogenic contamination in the industrialized river valley but are not related to the contamination at the former gas production site.

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