

## **Flow paths, mixing processes and exchange reactions in organic contaminated groundwaters of industrial sites: insights from the H and O stable isotope composition of water and that of dissolved organic and inorganic C**

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### *Introduction*

Contamination of soil and groundwater by organic pollutants is a serious environmental problem. In particular, former industrial sites may pose special problems because of the high toxicity of their pollutants. Because of the high toxicity of the pollutants it is important to characterize the hydrological situation in order to be able to assess the dispersion of the organic contamination. Groundwater pollution is commonly evaluated in terms of analyses of anions, heavy metals and/or organic substances as well as adding chemical tracers to the groundwater and evaluating the hydrologic situation via time-sequence analyses of the tracers and/or via pump-experiments. Many of these measurements of chemical tracers may be influenced by sorption processes or chemical reactions and can, therefore, give a distorted picture of the contamination. In contrast, stable isotope studies of hydrogen, oxygen, and carbon in water can potentially be used as natural tracers that are not influenced by sorption processes. Furthermore, under most low temperature conditions the H and O isotope composition of water is also not influenced by chemical reactions within the aquifer. It is known from several studies, that the analyses of hydrogen and oxygen isotopes of water provide information on recharge areas and mixing processes of different water bodies. Seasonal variations of the isotopic composition of precipitation and groundwater can give additional information on infiltration times, flow paths and flow velocities. In addition, the carbon isotope composition of dissolved inorganic carbon (DIC) can provide a tracer for anthropogenic contamination, given that the natural system can be characterized too.

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 is presently under investigation for remediation.

### *Geological and hydrogeological setting*

The site is located in the south-west of Germany, in the valley of the Neckar river, a tectonically defined graben forming part of an extensive fault system that strikes NW-SE. The main aquifer is a Quaternary fluvial gravel deposit overlain by silty-clayey, organic matter-bearing alluvium. Above it, artificial fillings made up of building rubble and gravel have been deposited. The Quaternary gravel deposit consists of Jurassic marine carbonate pebbles and it is the first of three aquifers. 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. Water in the Quaternary aquifer is generally confined. Underneath the Quaternary aquifer are two further aquifers that complicate the hydrogeologic situation. 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". This latter is a marine carbonate unit and the most important aquifer in this area for mineral waters of different chemical composition, depending on admixing of Gipskeuper groundwaters and deeper brines (Ufrecht, 1997). The mineral waters are artesisally confined. Owing to extensive faulting, the mineral waters infiltrate locally into the overlying aquifers and the river.

### *Results and Discussion*

The different surface waters, groundwaters, and mineral waters can be characterized and clearly differentiated on the basis of their O and H isotope composition (Fig. 1). Variations in the O and H isotope compositions can detect the locally variable influence of surface infiltration to the main aquifer. Furthermore, small-scale mixing processes between the different groups of waters can be recognized. In combination with the carbon isotope

compositions of DIC the following influences can be distinguished within the Quarternary aquifer at the former gas production site: 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, and local infiltration by artesisally confined mineral waters in the northern part of the site.

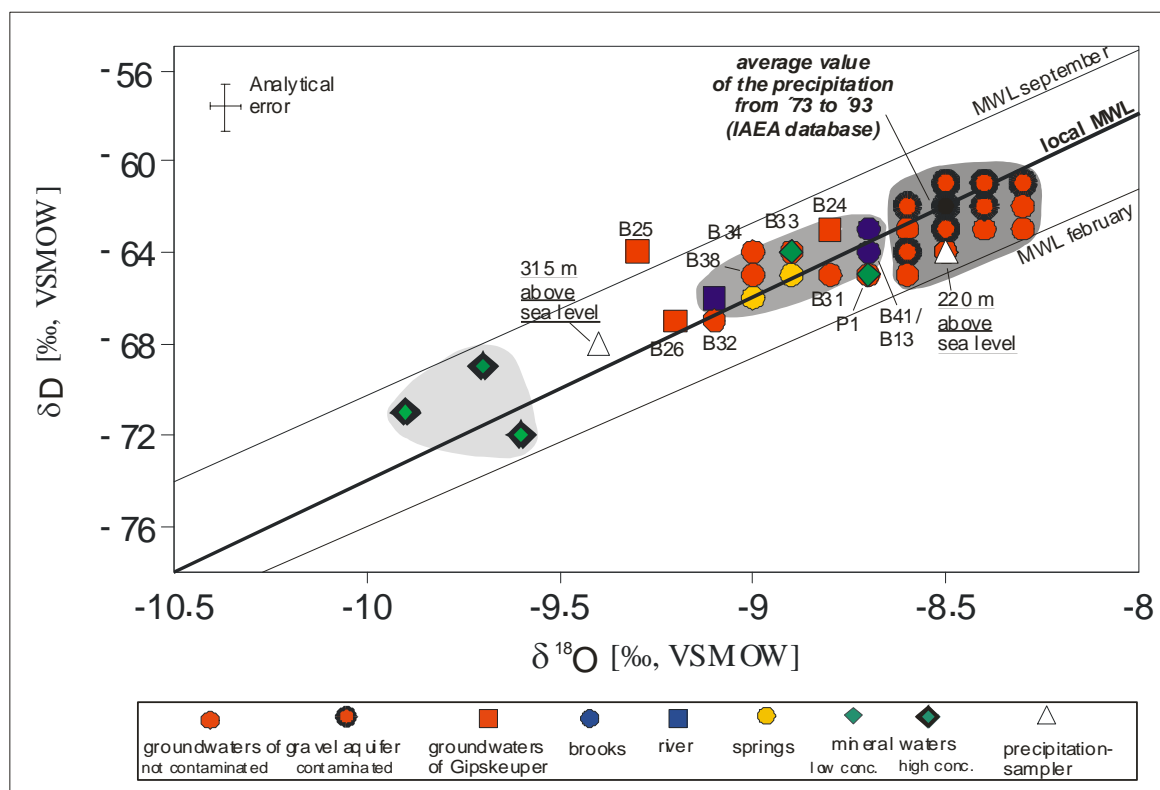


Fig. 1. Summary of the H- and O-isotope composition of the different ground- and surface waters sampled at the site.

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 C<sub>DIC</sub>, allowing for a calculation of the mixing proportions within individual boreholes. Quite surprisingly, the proportions of different waters in the boreholes vary considerably both in terms of space and time, depending on the flow regime of the adjacent Neckar 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 penetrating the aquifer. A comparison of the isotopic compositions of waters sampled on a monthly basis over the course of two years indicates similar trends throughout each year, which

reflects that there were no drastic changes in the weather pattern over the sampling period. However, 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. Seasonal variations in the isotopic composition of the different waters are related to seasonal variations in temperature and seasonably changing air masses in the recharge area. The magnitude of variation decreases significantly from precipitation via surface waters and down to groundwaters. The 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 Quarternary gravel aquifer reflect the seasonal isotopic variations in precipitation but with a delay of about one month, indicating fairly rapid infiltration. Such seasonal variation is not recognizable in the central areas of the site owing to longer flow paths and residence times.

Interpretation of the carbon isotope compositions of the dissolved inorganic carbon (DIC) have been made in the context of different natural and anthropogenic carbon components making up the background ( $\text{CO}_2$ , carbonates, organic substances). The different components have significant differences in their carbon isotope composition: marine carbonates of the sediments as well as atmospheric and possible mantle-derived  $\text{CO}_2$  are clearly enriched in  $^{13}\text{C}$  compared to the natural and anthropogenic organic substances and the soil  $\text{CO}_2$ . The concentration and isotopic composition of DIC in most waters can be interpreted within the framework of the natural biogenic and geogenic carbon system (Fig. 2). DIC of small fluvial surface waters and local spring water sampled distant from anthropogenic carbon sources is predominantly influenced by soil  $\text{CO}_2$ , while DIC of the large river is, in addition, 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 but generally do not correlate with the photosynthesis-respiration-cycle of natural plants. 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 Quarternary aquifer is characterized by significant depletion of  $^{13}\text{C}$  with values lower than those expected to be in equilibrium with natural soil  $\text{CO}_2$ . The remarkably low  $\delta^{13}\text{C}_{\text{DIC}}$  values, especially in the polluted aquifers can not be explained by variations in the natural organic substances measured. Oxidative decomposition products from biodegradation of

the organic pollutants are expected, however, to have low  $^{13}\text{C}$  content and are likely to be responsible for the low  $\delta^{13}\text{C}$  values of DIC in the Quarternary aquifer. The lowest  $\delta^{13}\text{C}$  values and at the same time the highest DIC concentrations have been measured immediately *downstream* of the known pollution. Further downstream the DIC concentrations decrease and  $\delta^{13}\text{C}_{\text{DIC}}$  values increase again, except for boreholes influenced by mineral waters, which have significantly higher DIC concentrations. Thus dilution and mixing effects can be clearly resolved. Generally low  $\delta^{13}\text{C}$  values *upstream* of the former gas production site are likely to reflect regional anthropogenic contamination in the industrialized Neckar valley but not related to the contamination at the former gas production site.

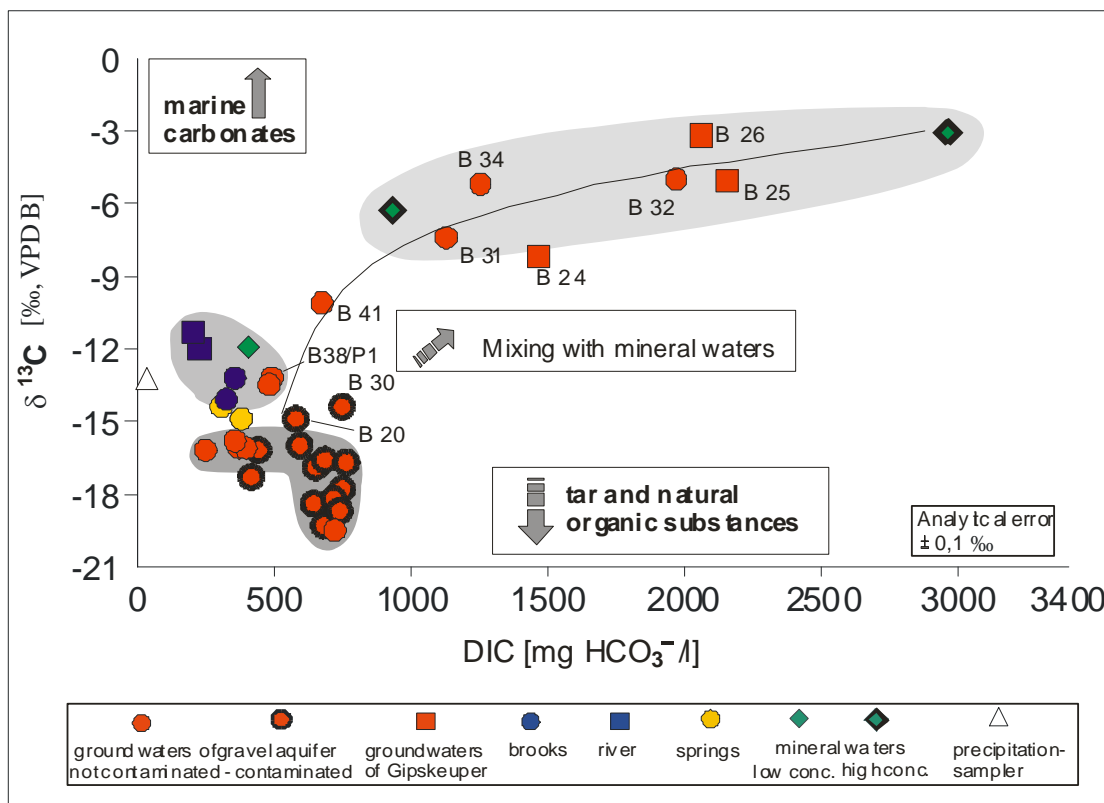


Fig. 2. C-isotope compositions versus bicarbonate ion concentrations of the different ground- and surface waters sampled at the site (from Angloher-Reichel, 2001).

## References

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