



Organic solvent contamination of a complex industrial site: Insights from compound specific isotope analysis combined with classical isotopic tools

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Introduction and setting

Isotope techniques are gaining increasing importance for the assessment of polluted groundwater bodies below and downstream of industrial sites. Where classical isotopic tracers help to understand flowpaths, groundwater residence times, communications between aquifers and bio-geochemical reactions, Compound Specific Isotope Analysis (CSIA) is an emerging tool to discriminate organic pollutant sources, and to identify and quantify biological and abiotic degradation of organic compounds. In the last few years, considerable efforts have been made to overcome the major drawback of CSIA by gas chromatography-isotope ratio mass spectrometry (GC-IRMS), its lack of analytical sensitivity, by adapting preconcentration and injection techniques (Zwank *et al.*, 2003). Method detection limits for isotope analyses of organic compounds have now reached a concentration range typically encountered in groundwater bodies influenced by industrial point pollution (down to low $\mu\text{g/l}$ range) so that field studies of organic contaminant plumes become possible (e.g. Hunkeler *et al.*, 2004).

The present study addresses a urban industrial site near the center of Strasbourg (F), the Plaine des Bouchers site and the underlying alluvial aquifer of the Rhine valley, contaminated at present mainly by chlorinated organic solvents (tetrachloroethylene PCE, trichloroethylene, TCE, 1,2 cis-dichloroethylene, c-DCE, 1,1 dichloroethane and 1,1,1 trichloroethane) and heavy metals.

The “Plaine des Bouchers” is the oldest industrial area of Strasbourg created and sys-

tematically planned around 1910. The sector is about 2 km long and 1 km wide and concentrated industrial activity (about a hundred factories in 1966), with a complex evolution linked to changes following the last World War and recent economical mutations. The area has now shifted to tertiary activities but several industrial sites are still active. It is situated on highly permeable alluvial deposits of the Rhine valley, which build up an aquifer of major importance for the regional water supply.

Carbon isotope analyses were performed on PCE, TCE and c-DCE as well as on DIC ($\delta^{13}\text{C}$ and A^{14}C) in the aim to discriminate sources of chlorinated solvents in the contaminant plume under and downstream of the industrial area. They were combined with stable isotope (^{18}O , ^2H) and tritium analyses to better constrain the local flow conditions. Two sampling campaigns (2000, 2003) allowed assessing the medium term evolution of concentrations and isotope signatures.

Results and discussion

Stable isotope ratios of water were used to elucidate interaction between surface waters (Rhine channel, gravel pits) and groundwater. All values fall in the typical range for shallow alluvial groundwaters derived from local rainfall without contribution of Rhine water or signs of evaporation in the gravel pits. Tritium values indicate recent groundwaters with residence times less than 10 years.

$\delta^{13}\text{C}$ values of dissolved PCE for the potential source areas as well as for most downstream wells are situated in a narrow range of -24.5 ± 0.48 per mille vs. PDB for most wells and show no significant variations from 2000 to 2003 in spite of a general decrease of concentrations. Concentration patterns and isotopic variations allow identifying two main source areas for the main PCE plume. A distinct isotope signature was encountered for two wells downstream of the contaminated sectors where PCE is clearly depleted in ^{13}C with $\delta^{13}\text{C}$ values between -29.9 and -30.1 per mille. One of these wells is a decontamination well for the industrial area. A distinct PCE source has to be postulated, as isotope fractionation due to biodegradation would lead to ^{13}C enrichment in residual PCE and not to depletion. On the whole, the $\delta^{13}\text{C}_{\text{PCE}}$ values show no sign for biodegradation of PCE in coherence with the mainly aerobic conditions in the aquifer.

Most measured TCE and c-DCE samples are enriched in $\delta^{13}\text{C}$ with respect to PCE and compared to the ranges measured for unaltered industrial products (Beneteau *et al.*, 1999, Jendrzewski *et al.*, 2001). For one well, a significant ^{13}C enrichment of TCE in the 2003 sample with respect to the 2000 sample was observed accompanied by decreasing concentrations. The overall observed range for TCE is quite large and extends from -27.6 to -8.54 per mille. c-DCE ranges from -14.7 to -13.5 per mille (these data is not comparable to unaltered industrial products) The enriched signa-

tures can be explained by biodegradation of TCE and of c-DCE to less chlorinated compounds. Both anaerobic (e.g. Slater *et al.*, 2001) and aerobic (Barth *et al.*, 2002) biodegradation of TCE lead to isotopic enrichment of the residual compound. Given that the concentrations of vinyl chloride and ethene are below detection limit it can be postulated that the TCE and c-DCE have been partly mineralised.

$\delta^{13}\text{C}$ values of DIC decrease from -11 to -15 ‰ with increasing alkalinity and increasing Ca+Mg and nitrate concentrations. ^{14}C activities decrease from 89.6 to 66 pmc indicating a radiocarbon-free old DIC source. It is probable that nitrates are derived from the nitrification of an ammonium pollution that would decrease pH and allow further dissolution of the carbonate matrix. Both carbonate dissolution and oxidation of organic matter seem to contribute to the overall DIC budget. Biodegradation of chlorinated ethenes alone would require too high initial concentrations to explain the observed decrease of $\delta^{13}\text{C}_{\text{DIC}}$ values but it can be postulated that in the past other organic pollutants were present in the site.

Conclusions

Combination of classical isotope tools with CSIA allow to analyse flow patterns, geochemical reactions pollution sources and biodegradation of chlorinate ethenes in a shallow alluvial aquifer concerned by point source pollution under a historical industrial complex. CSIA on PCE, TCE and c-DCE shows a diversity of sources and evidences of ongoing biodegradation of TCE and DCE. Major ion chemistry, stable carbon isotopes and radiocarbon demonstrate the contribution of both mineral dissolution and oxidation of organic matter to DIC.

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