



APPLICATION OF COMPOUND SPECIFIC ^{13}C ISOTOPE INVESTIGATIONS OF CHLORINATED HYDROCARBONS IN CONTAMINATED GROUNDWATERS

K. OSENBRÜCK, M. HEIDINGER, A. VOROPAEV, S. ERTL*, L. EICHINGER
Hydroisotop GmbH, Schweitenkirchen, Germany

Chlorinated hydrocarbons are one of the most common pollutants found in groundwater. Due to complex contamination situations with overlapping contamination plumes the assessment of the organic contaminants requires the installation of expensive observation wells and high analytical effort. Here the determination of the stable isotope ratio $^{13}\text{C}/^{12}\text{C}$ of the organic compounds offers a promising and efficient tool to investigate the origin and the biodegradation characteristics of the chlorinated hydrocarbons in groundwater.

The application of the method is based on characteristic isotope fingerprints, differing in chlorinated solvents. This isotope fingerprint is derived from different production pathways and is not influenced by transport or by retardation processes in the underground. Due to the fact, that two different contaminations can easily be distinguished by isotope ratios, an improved distinction of spatially and temporally different contamination plumes might be possible.

In course of biologically mediated degradation processes a shift of the isotope ratios between the precursor and the product can frequently be observed, such as with denitrification or sulfate reduction processes. The isotope fractionation is due to a preferential reaction of the bonds formed by the lighter isotopes and leads to a progressive enrichment of the heavy isotopes in the precursor while the product becomes depleted in the heavy isotopes. Biological degradation of the highly chlorinated hydrocarbons is due to a co-metabolic dechlorinisation. Tetrachloroethene (PCE) for example degrades under anoxic conditions via trichloroethene (TCE) to *cis*-1,2-dichloroethene (cDCE). Subsequent degradation to vinyl chloride (VC) and ethene may appear under aerobic as well as reducing environments depending on the site specific conditions.

In several laboratory studies [1, 2] it has been shown, that biodegradation of the chlorinated hydrocarbons is accompanied by an isotope fractionation of the stable carbon isotopes. The isotope ratios may be used to assess and quantify the degradation of the organic compounds at the field sites. This application has gained great interest for remediation strategies including monitored natural attenuation of contaminations [2, 3].

In contrast to the laboratory studies, many of the field investigation show no evidence for isotope fractionation although biodegradation of the chlorinated hydrocarbons in the groundwater is significant. Here, we present the results of 21 field studies, where compound specific ^{13}C isotope ratios have been applied. Only in some cases isotope fractionation processes of chlorinated hydrocarbons due to biodegradation have been observed. The measured $\delta^{13}\text{C}$ values agree reasonably with a Rayleigh type isotope fractionation model, where the fractionation factors are used as fitting parameters.

The occurrence and the degree of significant isotope fractionation of chlorinated hydrocarbons is still an open question. Major factors that control the extend of measurable ^{13}C isotope

* Also: Institut für Biogeochemie und Meereschemie, Universität Hamburg, Hamburg, Germany.

fractionation of chlorinated hydrocarbons in groundwater most likely include parameters as activity and type of the microbiological species, availability of cosubstrates as well as hydrochemical and hydrogeological conditions.

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