



Aerobic biodegradation of chlorinated ethenes in a fractured bedrock aquifer: quantitative assessment by compound-specific isotope analysis

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The industrial application of chlorinated solvents of many years frequently caused severe soil and groundwater contamination. Organic compounds are released into aquifers in various ways, e.g. spills, improper disposal or leaking underground storage tanks; sources of contaminants might be multiple. Fate and behaviour of these compounds in the subsurface depend on a number of physicochemical and biological processes, known as 'natural attenuation'. Compound-specific stable isotope analysis (CSIA) using gas chromatography-isotope ratio mass spectrometry (GC-C-IRMS) has evolved as valuable tool to allocate sources of organic pollutants as well as to study the occurrence and extent of in-situ degradation reactions even at low contaminant concentrations frequently found in the fringe zones of contaminant plumes.

So far, most field applications have been limited to fairly homogeneous aquifers. We have used an integrated approach to study biodegradation of chlorinated ethenes in a heterogeneous bedrock aquifer system. The main contaminants we observed in the plume were perchloroethene (PCE), trichloroethene (TCE) and *cis*-dichloroethene (*cis*-DCE). Compound-specific stable isotope analysis was applied to assess in-situ microbial degradation processes occurring in the contaminated aquifer. Downstream contaminant concentrations decreased but constant $\delta^{13}\text{C}$ signatures indicated that no

degradation of PCE occurred within this part of the plume. In contrast, geochemical site data and isotopic enrichment for TCE and *cis*-DCE demonstrated degradation processes under oxic conditions. Numerical modelling was employed to simulate isotopic enrichment of chlorinated ethenes consistent with reported enrichment factors and to analyse geochemical reactions in the field. For this purpose we integrated existing field information on groundwater flow, non-reactive solute transport, geochemical data, and the compound-specific isotope composition of the chlorinated ethenes into the reactive transport code PHT3D. The integrated approach allowed to verify aerobic degradation processes occurring at the site. As PCE is recalcitrant in aerobic plumes, a conservative tracer approach could be used to estimate the extent of dilution throughout the plume. The calculation of diluted concentrations together with stable carbon isotope data allowed to reliably assess the extent of biodegradation at the site. Plume simulations gave an indication of how isotope signatures are impacted in the field. Dispersion modelling and the conservative tracer approach agreed very well. Our investigation provides a case study illustrating the development and application of quantitative tools to identify source to plume relationships and to verify the specific degradation pathways involved and thus offers a generic approach for assessing and quantifying the natural attenuation of chlorinated ethenes in a heterogeneous flow regime.