

## Reactive transport modeling of carbon, chlorine, and hydrogen CSIA data to improve monitored natural attenuation for chlorinated ethenes

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Compound-specific stable isotope analysis (CSIA) has been shown to provide an improved insight into the monitored natural attenuation (MNA) of chlorinated solvents. The work presented here focuses on the simulation of carbon (C), hydrogen (H), and chlorine (Cl) isotopes of chlorinated ethenes with a reactive transport model (RTM) calibrated by CSIA data. Such a model allows for the simulation of variations in concentrations and isotope ratios in aquifer systems as result of various degradation pathways and transport processes. The base RTM model was calibrated for C, H, and Cl isotope fractionation observed during complete reductive dechlorination of TCE in a microcosm experiment. Secondly, the Operational Unit 10 at the Hill Air Force Base site (Utah, USA) was intensively sampled. This intricate site presents two plumes of chlorinated solvents (PCE and TCE), which partly mix. Moreover, based on earlier MNA studies, both reductive dechlorination and aerobic oxidation are likely to occur as the aquifer conditions range from oxic to anoxic. The model aids in drawing a better picture of the fate of those plumes, as each transformation process induces distinctive isotope fractionation patterns for the different elements.

### Results/Lessons learned

We present (i) the model background, which includes the highlights provided by the microcosm experiment, discuss (ii) the collection of CSIA data at the complex field site, and illustrate (iii) potential applications of the model, notably for the interpretation of the above-mentioned field data. The use of CSIA data at the field site reveals the complexity of the studied aquifer, where degradation is shown to mostly occur in restricted areas.

## Relevance of mass transfer processes for the interpretation of stable isotope fractionation

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In recent years, compound specific stable isotope analysis (CSIA) has become an established tool for assessing (bio)degradation of organic contaminants within aquifers. The fractionation of stable isotopes during degradation leads to observable shifts in stable isotope ratios which can serve as a qualitative indicator for in situ contaminant degradation. However, to use stable isotope data to obtain quantitative information on in situ biodegradation requires among others knowledge on the influence of mass transfer processes on the observed stable isotope fractionation.

Mass transfer processes in aquifers range from macroscopic transport including dispersion driven mixing processes to microscopic transport processes controlling the microbial availability of the contaminant. These transfer processes may cause itself an additional fractionation of stable isotopes, but even in the absence of such additional fractionation the mass transfer processes need to be considered for a quantitative analysis of stable isotope signatures [1,2].

This presentation will introduce theoretical and reactive transport modeling concepts on combining mass transfer processes into a quantitative analysis of stable isotope fractionation and the determination of degradation pathways using stable isotope signatures of two different elements. Examples for the verification and application of these concepts will be presented showing the relevance of mass transfer processes at different scales for the interpretation of stable isotope fractionation.

[1] Thullner, Centler, Richnow & Fischer (2012), *Organic Geochemistry* 42, 1440-1460. [2] Thullner, Fischer, Richnow & Wick (2013), *Applied Microbiology and Biotechnology* 97, 441-452.