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C-isotope exchange between DIC and organic compounds (TCE)

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Introduction

Carbon isotope fractionation during degradation of organic contaminants (e.g. TCE, BTEX) in aquifers is an important tool to study and model the effectiveness and progress of natural attenuation. Carbon isotope exchange between organic compounds and dissolved inorganic carbon (DIC) has been regarded to be negligible. However, there is no conclusive proof, that the isotopic composition of DIC has no influence on the $\delta^{13}C$ ratio of organic compounds, especially during degredation.. We report preliminary data from laboratory exchange experiments in aqueous solutions between isotopically 13-C labelled DIC with TCE ($\delta^{13}C_{PDB}$ = -22‰.) The concentration of DIC varied between 10 and 1000mg/l, and of TCE between 10 and 100mg/l. Experiments were performed in 100ml glass vials filled with 80ml sample solution at different ratios of DIC/TCE. They started at room temperature and were continued after 90 days at 60˚C. The isotopic composition of TCE was measured periodically with a Finnigan Delta Plus XL GC-IRMS.

Results

Compared to a standard solution without 13-C enriched DIC all TCE samples showed no significant changes in $\delta^{13}C$ ratios for the first three months at room temperature. However, at 60˚C TCE became enriched in 13-C by at least 2‰ after two weeks and the $\delta^{13}C$ ratios continued to increase with experimental time. Shifts were systematically with the lowest found in samples with the lowest DIC/TCE ratio and the highest in those with the highest DIC/TCE ratio. The sample with the highest DIC/TCE ratio (10mg/l TCE and 1000mg/l DIC) showed a $\delta^{13}C_{PDB}$ ratio of +40‰ after five months. Concentration of TCE was constant within a certain error throughout experimental time; in samples with high DIC concentrations a white precipitation became visible (due to reduced carbonate solubility at higher temperatures).

Conclusions

Our data suggest, that the general assumption that organic and inorganic bound C in aquifer components does not exchange is not true. Further research is necessary to assess extend, mechanism, kinetics and processes under which the exchange occurs and whether it has implications for the use of stable isotopes to quantify degradation reactions in the environment.

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Natural attenuation of organic compounds in the unsaturated zone

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Contaminated land poses a serious problem with respect to soil quality and the risk of spreading of pollutants into other compartments of the environment. A major concern at most contaminated sites is the risk of groundwater pollution by organic and inorganic compounds. Since the remediation of all of the contaminated sites is economically not feasible in many countries, groundwater risk assessment procedures are needed for the ranking of sites, decision making on further use and remedial actions. Recently "Natural Attenuation" of organic pollutants received much interest as a remediation strategy in groundwater. Studies on natural attenuation in the unsaturated zone, however, are very limited although processes like aerobic degradation and volatilisation of organic compounds are very likely more efficient than in the water saturated zone. This contribution presents results on scenario-specific modelling of natural attenuation of petroleum hydrocarbons volatilising from complex organic mixtures ("fuels") in the unsaturated zone. The model is validated with data from a unique field experiment conducted at a Airforce base in Denmark.

Hydrocarbons can reach the groundwater by transport with seepage water and by spreading in the soil-gas. Degradation processes can limit the spreading in the unsaturated soil zone and - in the best case - restrict the contamination to the unsaturated zone. The objective of this study was to use numerical simulations to elucidate the processes/parameters which are relevant in contaminant spreading and thus for groundwater risk assessment. The modelling results compare well to data from the well-controlled field test with an emplaced kerosene source. Sensitivity analyses were performed accounting for physical-chemical properties of fuel constituents and soil properties.

Scenario-specific numerical simulations illustrate that the overall biodegradation rates depend mainly on properties of the organic pollutants such as Henry’s Law constant, the soil water content, and less on the individual degradation rate constants or temperature. Low Henry's law constants result in relatively high biodegradation rates whereas compounds with high vapour pressure und low water solubility are lost to the atmosphere. The contaminant transfer rates into groundwater are relatively small, but lead locally to concentrations above the legal limit (in the capillary fringe region). Contaminant transport by seepage water is just minor compared to vapour phase transport of volatile compounds by diffusion.

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