Stable Carbon and Hydrogen Isotope Fractionation of Dissolved Organic Groundwater Pollutants by Equilibrium Sorption

Patrick Höhener and Xianjing Yu

Université de Provence-CNRS UMR 6264: Laboratoire Chimie Provence, 3 place Victor Hugo, 13331 Marseille, France.

Shifts in stable isotope ratios in pollutants along flow paths in groundwater are often interpreted as being dominated by kinetic biochemical isotope fractionation, and it is assumed that purely physical processes contribute little to isotope fractionation. The experimental basis for quantifying the isotope fractionation by equilibrium sorption is currently limited to three studies only: two studies performing single step batch sorption experiments (Slater et al, 2000; Schüth et al, 2003) concluded that the isotope fractionation is so small that it can not be measured by isotope mass spectrometry in various pollutants, whereas another study performing laboratory column and multistep batch sorption experiments (Kopinke et al, 2005) found measurable but variable isotope fractionation for 5 organic pollutants, which suggested consequent isotope shifts in hypothetical groundwater plumes.
The objective of this work was to propose a method that is independent of isotope mass spectroscopy to better quantify the fractionation of stable isotopes in groundwater pollutants by equilibrium sorption. To this end, linear free energy relationships (LFERs) were established which relate well known equilibrium vapor-liquid isotope effects to stable carbon and hydrogen isotope enrichment factors for equilibrium sorption. The LFERs were established for normal, cyclic or branched alkanes, monoaromatic hydrocarbons, and chloroethenes. These LFERs predict that isotopic light compounds sorb generally slightly more strongly than their heavy counterparts. Defining fractionation as in classical literature by "heavy divided by light", carbon enrichment factors were estimated which ranged from -0.13 +/- 0.04 ‰ (benzene) to -0.52 +/- 0.19 ‰ (trichloroethene at 5-15 °C). These enrichments are small with respect to enrichments due to biochemical reactions. Hydrogen enrichment factors in 15 different compounds were more significant and lay between -2.4 and -9.2 ‰. For perdeuterated hydrocarbons the enrichment factors ranged from -19 ‰ (benzene) to -65 ‰ (cyclohexane). Laboratory batch sorption experiments were performed with perdeuterated hydrocarbons in aqueous solutions and a humic acid-rich soil as sorbent. The compounds were analysed by gas chromatography. The prediction of D/H enrichment by the LFER agreed well with the measured isotope enrichments or selected perdeuterated compounds.
A reactive transport model incorporating isotope fractionation by sorption (Höhener & Atteia, 2010) was exploited to investigate the effects of equilibrium fractionation in simulated groundwater plumes. These results suggest that isotope enrichments are very small for 13C and 2H at natural abundance and only visible at the forerunning front of expanding plumes. We conclude thus that in most groundwater pollutant studies, the fractionation of isotopes by equilibrium sorption can be neglected.

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