

Chlorine and Hydrogen Isotope Fractionations during Physical Processes

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Background/Objectives. Chlorinated ethenes are the widespread source of groundwater contamination, which mostly originate from industrial and dry-cleaning facilities. Once these contaminants are released to the subsurface, they move under the water table, accumulate on low permeability zones, and form sources of groundwater contamination. The contaminant plumes, which develop from the contaminant sources, undergo different processes such as advection, dispersion, diffusion, sorption and biodegradation. The knowledge of the processes affecting the movement of contaminant plume is beneficial to develop effective remediation strategies. There is a general acceptance that physical processes have negligible effect on stable isotope fractionations. However, most of the studies on the effect of physical processes on stable isotope fractionations of chlorinated ethenes focused only on carbon stable isotope fractionations.

Approach/Activities. A series of laboratory batch and column experiments has been conducted to study the effect of sorption, desorption, diffusion and back-diffusion processes on C, Cl, and H isotope fractionations of trichloroethene (TCE) and cis-dichloroethene (cis-DCE) in controlled conditions.

Results/Lessons Learned. All three stable isotopes (C, Cl, H) showed fractionations during the aforementioned processes. The extent of fractionations for C and Cl stable isotopes were small and can be neglected when compared with the isotope fractionations during degradation processes. Nonetheless, H isotope fractionations was significant during the physical processes. Sorption experiment results showed that C and Cl isotopic ratios of TCE and cis-DCE in the aqueous phase shifted toward enrichment, indicating that TCE and cis-DCE molecules with lighter isotopes are adsorbed as expected. The shift in H isotopic ratios of TCE and cis-DCE was toward depletion of the solution in heavier isotopologues during sorption process, which is a counter-intuitive phenomenon. Results from back-diffusion experiments showed that for all three stable isotopes, the lighter isotopes back-diffused first as expected. The results from the current study showed that the effect of physical processes such as sorption, diffusion, and back-diffusion on C and Cl isotope fractionations are small and can be neglected when compared with degradation processes. However, H isotope fractionations of TCE and *cis*-DCE was significant. The reported values for H isotope fractionations of TCE due to biodegradation are small compared to H isotope fractionation values obtained in this study for physical processes. Therefore, compound-specific hydrogen isotope analysis can be a promising tool to identify physical processes that affect the movement of chlorinated ethenes in the subsurface.