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## Identifying Abiotic Chlorinated Ethene Degradation: Characteristic Isotope Patterns in Reaction Products with Nanoscale Zero-Valent Iron

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Carbon isotope fractionation is of great interest to assess chlorinated ethene transformation by nanoscale zero-valent iron at contaminated sites, in particular to distinguish the effectiveness of an implemented abiotic degradation remediation scheme from biotic degradation intrinsic to a site. In a laboratory study, transformation of trichloroethylene (TCE), *cis*-dichloroethylene (*cis*-DCE) and vinyl chloride (VC) with two types of nanoscale iron materials showed different reactivity trends, but consistent carbon isotope enrichment factors ( $\varepsilon$ ) of 19.4 per mill  $\pm$  1.8 per mill (VC), -21.7 per mill  $\pm$  1.8 per mill (*cis*-DCE), 23.5 per mill  $\pm$  2.8 per mill (TCE) with one type of iron (Fe<sup>BH</sup>), and from -20.9 per mill  $\pm$  1.1 per mill to 26.5 per mill  $\pm$  1.5 per mill (TCE) with the other (Fe<sup>H2</sup>). Products of the dichloroelimination pathway (ethene, ethane, acetylene) were consistently by 10 per mill more isotopically depleted than those produced by the hydrogenolysis pathway (*cis*-DCE from TCE, VC from *cis*-DCE) displaying a characteristic pattern that may serve as a robust indicator of abiotic dehalogenation of chlorinated ethenes.

In a second part, this characteristic carbon isotope pattern was tested as a way to delineate abiotic dehalogenation associated with nanoparticulate zero-valent iron (Fe<sup>BH</sup>) treatment at a field site contaminated by TCE. In contrast to information from compound concentrations alone, carbon stable isotope ratios of TCE could unequivocally prove that transformation occurred at some of the monitoring wells. Isotope analysis of the reaction products ethene and ethane gave additional insight that made it possible to identify the contribution from abiotic transformation by  $Fe^{BH}$  as opposed to natural biodegradation that was already going on at the site. Such additional information of product isotope ratios may be an important diagnostic parameter in future studies that aim at distinguishing biotic and abiotic transformations which occur by different pathways.