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The use of stable carbon isotope analysis to model enhanced dissolution of tetrachloroethene

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A controlled release of pure phase tetrachloroethene (PCE) within an enclosed area occurred at a field site. Pure phase PCE was also injected into a 2D model aquifer made to simulate the field conditions. The field site and model aquifer were biostimulated with electron donors and subsequently bioaugmented with a reductively dechlorinating microbial consortium, KB-1TM. Stable carbon isotope measurements were collected periodically to determine if isotopic fractionation of parent and daughter products due to degradation (a fractionating process) could be measured during the dissolution of PCE (a non-fractionating process).

A maximum isotope fractionation of 2.3 permil was observed in the dissolved PCE however, close to the source zone the carbon isotopic signature of the dissolved PCE remained largely unchanged. This suggests that the rate of PCE degradation close to the source was not great enough to maintain a significant isotopic shift (>1 permil) overtime due to the dissolution of PCE (whether abiotically and/or biologically enhanced), which provided a constant pool of non-fractionated PCE. Measurable isotopic shifts were observed adjacent to and/or downstream from the source in the degradation products trichloroethene (TCE), 1,2-dichloroethene (cDCE), and vinyl chloride (VC) after bioaugmentation. Therefore, close to the source zone confirmation of PCE degradation is based primarily on the appearance of the lesser chlorinated ethene transformation products and isotopic signatures of those products consistent with degradation. This trend was observed on a small scale in the model aquifer and similar trends are being observed in the field with greater spatial differentiation.

Because isotopic fractionation occurs during the degradation of chlorinated ethenes, stable carbon isotopes can differentiate between destructive and non-destructive processes. This differentiation cannot be made by concentration measurements alone. The combination of stable carbon isotope and concentration measurements can be used to model contaminant sources, migration pathways and mass destructive remediation processes.

4.62.43

Effect of degradation pathway on isotopic fractionation during aerobic biodegradation of 1,2-dichloroethane

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1,2-dichloroethane (1,2-DCA), a widespread groundwater contaminant, is known to biodegrade via enzymatically initiated oxidation or hydrolysis reactions under aerobic conditions. Current literature reports that stable carbon isotope fractionation of 1,2-DCA during aerobic biodegradation is large and reproducible. This study reports on significant variation in the magnitude of stable carbon isotope fractionation observed during aerobic biodegradation. Biodegradation in an extensive set of experiments including microcosms, enrichment cultures and pure microbial cultures produced a consistent bimodal distribution of enrichment factors (epsilon) with one mean epsilon centered on -3.9 ± 0.6 permil and the other on -29.2 ± 1.9 permil. Reevaluation of epsilon in terms of kinetic isotope effects $^{12}k/^{13}k$, gave values of $^{12}k/^{13}k = 1.01$ and 1.06 , typical of oxidation and hydrolysis (S_N2) reactions, respectively. The bimodal distribution is therefore consistent with the existence of two separate enzymatic 1,2-dichloroethane degradation pathways. Experiments in this study with pure strains of *Xanthobacter autotrophicus* GJ10, *Ancylobacter aquaticus* AD20, and *Pseudomonas* sp. Strain DCA1, for which the enzymatic degradation pathways are known, further support this interpretation. These findings suggest that the appropriate enrichment factor must be known before applying compound specific isotope analysis (CSIA) to quantify intrinsic biodegradation of 1,2-DCA in the field. Significantly, the results also indicate that enrichment factors measured in the field might be used to determine which enzymatic pathway is operative at a given field site.