



Chlorine and carbon isotope measurements can help assessing the effectiveness of a zero valent iron barrier

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Chlorinated aliphatic hydrocarbons (CAH's) such as trichloroethene (TCE), cis-dichloroethene (cis-DCE) and vinylchloride (VC) are extensively used in industrial applications. One of the most promising remediation techniques for CAH's in groundwater is their removal via abiotic reductive dechlorination using Zero Valent Iron (ZVI). This is applied for the treatment of contaminated sites by installing permeable reactive barriers (PRB).

In this study, isotope fractionation of chlorinated ethylenes in transformation by cast iron has been investigated, because such types of iron are commonly used in PRBs. Batch experiments have been carried out in closed flasks, containing cast iron with aqueous solutions of TCE, cDCE and VC. These substrates and their respective products have been monitored by headspace samplings for their concentration (by GC-FID) and isotope fractionation of carbon and chlorine (by GC-IRMS).

A decreasing reactivity trend was observed when compounds contain less chlorine atoms, with differences in rate constants of about one order of magnitude between each of the substances $TCE > cDCE > VC$. This resulted in the accumulation of products with fewer chlorine atoms. Therefore a similar observation can be expected if degradation in the field is incomplete, for example in the case of aged or improperly designed PRB.

Pronounced carbon and chlorine isotope fractionation was measured for each of the compounds, and characteristic dual isotope plots (C, Cl) were obtained for TCE and cDCE. These results may serve as an important reference for the interpretation of isotope data from field sites, since stable isotope fractionation is widely recognized as robust indicator for such pollutant transformations.

However, carbon isotope fractionation in a given parent compound may be caused by either abiotic or biotic degradation. In the field, it can therefore be difficult to delineate the contribution of abiotic transformation by PRB in the presence of ongoing biodegradation. This study investigates two different approaches to resolve these concurring modes of transformation: (i) evidence from dual (C, Cl) isotope plots; (ii) evidence from carbon isotope values of degradation products (e.g., cDCE and ethene from TCE, respectively).

The comparison of dual isotope patterns for TCE degradation with cast iron and with *Geobacter lovleyi* exhibited similar slopes for these two types of reaction. This indicates that dual isotope plots may not be able to distinguish biotic and abiotic pathways in this case. However, the information from carbon isotope values in this study confirms earlier results (Elsner et al.), which suggest that isotope values from reaction products can be an expedient way of delineating the occurrence of abiotic transformation, even in the presence of ongoing biodegradation.