

Where is the Vinyl Chloride? Alternative Natural and Enhanced Degradation Pathways for Chlorinated Solvents

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Background/Objectives. Monitored natural attenuation (MNA) and enhanced in situ biodegradation (EISB) are two of the most common strategies for remediating chlorinated solvent compounds. With both strategies, sequential reductive dechlorination of the chlorinated compound, most commonly trichloroethene (TCE) and/or perchloroethene (PCE), is the presumptive contaminant degradation pathway. This degradation pathway transforms PCE to TCE, TCE to *cis*- or *trans*-dichloroethene (cDCE or tDCE), cDCE/tDCE to vinyl chloride, and vinyl chloride to ethene, the terminal dechlorination product. Consequently, a sequential increase/decrease in the concentration of each of these compounds is expected following EISB implementation, and some level of cDCE/tDCE and vinyl chloride detections are generally expected at sites undergoing MNA via reductive dechlorination. However, at many sites, particularly those with naturally aerobic, oxidative aquifer conditions, this is not the case. At these sites EISB has been shown to reduce PCE and TCE to cDCE/tDCE, but the subsequent reduction in cDCE/tDCE concentrations is not followed by increases or even detections of vinyl chloride or ethene. While the absence of vinyl chloride is favorable given its toxicity, the lack of degradation products can be problematic when there is a need to demonstrate that complete reductive dechlorination (to ethene) is occurring, as part of an EISB or MNA strategy. Analytical tools and data interpretation methods developed in recent years can be used to provide multiple lines of evidence for alternative degradation pathways for PCE and TCE degradation products, thereby providing a means to understanding and demonstrating the fate of these compounds during EISB and MNA applications.

Approach/Activities. PCE and TCE degradation products generated during reductive dechlorination (i.e., hydrogenolysis) may degrade by alternative pathways including reductive dichloroelimination (β -elimination), aerobic cometabolism and abiotic oxidation. These pathways may be facilitated by multiple reactants, microbial species and enzymes, further complicating the process of identifying and characterizing specific degradation pathway(s). Innovative analytical strategies were employed on multiple chlorinated solvent sites and the results were interpreted to assess the presence and importance of potential alternative degradation pathways. The specific analytical methods used included magnetic susceptibility, carbon-14 (C-14) TCE assays, compound-specific isotope analysis (CSIA), acetylene analysis, quantitative polymerase chain reaction (qPCR)-based microbial analysis, and various geochemical analyses. The results of these analyses were used, within the context of the conceptual site model, to conduct direct, temporal and geospatial evaluations to assess the presence and prevalence of alternative degradation pathways under site-specific conditions. These evaluations were then used to assess the viability of EISB and MNA remediation strategies.

Results/Lessons Learned. Analytical results and data interpretations for multiple sites will be presented to demonstrate the evaluation of specific alternative degradation pathways for TCE and cDCE. For one of the sites, multiple lines of evidence were used to show that while reductive dechlorination of PCE is occurring to some degree, aerobic cometabolism is the dominant TCE degradation pathway, with both TCE and cDCE also degrading through β -elimination and abiotic oxidation pathways. Results of a C-14 TCE cometabolism assay, combined with qPCR functional gene analysis, were particularly helpful in identifying and

quantifying aerobic cometabolic degradation. The use of this information in developing and evaluating in situ remedial alternatives for the site will also be presented.