Naturally-Occurring and Biologically-Mediated Abiotic Transformation of Trichloroethene in Low-Permeability Formations

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Background/Objectives. Naturally-occurring abiotic transformation can be effective in removing trichloroethene (TCE) that is adsorbed to formations with low permeability, where transport is largely controlled by matrix diffusion. Improved methods are needed to quantify the rate of degradation within rock formations. The objective of this work is to develop a protocol that combines multiple lines of evidence and different tools to predict and evaluate transformation of chlorinated ethenes within fractured bedrock under intrinsic or enhanced conditions. Using intact core microcosms, it is possible to conduct a detailed evaluation of degradation processes that are difficult to quantify in the field. Results permit the measurement of biotic and abiotic degradation rates under the influence of matrix diffusion.

Approach/Activities. Department of Defense sites (~20) were screened for potential degradation of chlorinated ethenes within fractured rock. Geochemical, lithologic, hydrologic, and geophysical (magnetic susceptibility and complex electrical resistivity signature) data were considered, along with the potential to force water through intact rock core samples and the presence of acetylene. Geochemical modeling was performed to predict mineral formation. A preliminary test to assess abiotic degradation was performed using a ^{14}C-TCE assay with crushed rock and groundwater. Two sites were identified for further analysis. Groundwater and core samples were collected to construct intact rock microcosms, which were designed to mimic in situ conditions in a fractured bedrock aquifer. TCE and/or ^{14}C-TCE were infused into the rock, along with bromide and resazurin. One end of the core simulated the flow of groundwater over a fracture surface. Treatments included live and unamended; killed and unamended; live and lactate-amended; and live and lactate + sulfate amended. Once per week, 2 mL of groundwater within the fracture zone of the microcosms was displaced with groundwater without TCE or bromide to simulate the flow of uncontaminated water over the contaminated rock matrix. Displaced groundwater was analyzed for TCE, other VOCs, organic acids, anions, and pH. Those amended with ^{14}C-TCE were tested for ^{14}C-labeled CO_2 and soluble products. Evaluation of δ^{13}C was carried out every 3 to 4 months to assess degradation based on enrichment.

Results/Lessons Learned. Microcosms for Site #1 have been operated for approximately eight months and those for Site #2 are in preparation. For Site #1, addition of lactate created low redox conditions and stimulated sulfate reduction. Reductive dechlorination of TCE to *cis*-dichloroethene is ongoing in all the lactate-amended microcosms; this significantly increased the rate at which the total mass of VOCs is removed from the rock matrix. No further biotic reduction to vinyl chloride or ethene occurred. Reductive dechlorination has not occurred in the other treatments. Addition of lactate also stimulated abiotic processes based on increased rates of acetylene + ethene + ethane formation and accumulation of ^{14}C-labeled products. Enrichment of δ^{13}C-TCE in microcosms without reductive dechlorination also suggested the occurrence of abiotic degradation. A 2D model of the microcosms was developed with COMSOL. Higher transformation rates were predicted for lactate amended microcosms, and the lowest rates for

killed controls. Geochemical modeling and geophysical analyses performed thus far are consistent with presence of iron minerals associated with abiotic transformation of chlorinated ethenes.