Microcosm Evaluation of TCE Degradation in Fractured Rock in Response to Amendments

Hao Wang (hao3@g.clemson.edu) and David L. Freedman (Clemson University, Clemson, South Carolina, USA)
Rong Yu (Synterra, Greenville, South Carolina, USA)
Ramona Iery (CIV NAVFAC, EXWC EV31)

Background/Objectives. Persistent groundwater contamination caused by back diffusion of trichloroethene (TCE) from complex geologic formations such as fractured rock is a challenging remediation problem. The extent of the problem is dependent on the magnitude of degradation that occurs within the rock matrix. The presence of iron minerals serves to catalyze abiotic degradation of TCE. However, the reductive capacity of these minerals is limited. After decades of exposure to TCE, the capacity may be exhausted. Addition of an electron donor may permit restoration of the abiotic degradation capacity and also enhance biotic degradation. The objective of this study was to evaluate the interplay between biotic and abiotic degradation processes for TCE in fractured rock in response to amendments with lactate and sulfate.

Approach/Activities. Novel intact rock core microcosms were prepared and operated with samples collected from four sites where back diffusion of TCE contributes to groundwater contamination. The microcosms consisted of rock cylinders (6.03-6.35 cm in diameter and 7.52-7.92 cm in length). The cores were sandwiched between stainless steel end caps. The cores were then wrapped in Teflon® tape and heat shrinkable Teflon® tubing. This assembly was slid into a stainless steel pipe that was welded to the end caps to ensure a leak-proof microcosm. One of the end caps was hollowed out and simulated a fracture surface in contact with flowing groundwater. The cores were infused under pressure with groundwater containing TCE (~42-141 mg/L), bromide (1-5 mM; conservative tracer), and resazurin (1 mg/L; redox indicator). The hollowed out end that simulated a fracture surface was filled with uncontaminated groundwater and was subject to back diffusion. Once per week, 2 mL of uncontaminated groundwater was injected into the simulated fracture and the displaced groundwater was collected and analyzed for volatile organics, bromide, sulfate, and volatile fatty acids. One of the treatments received only unamended groundwater. Another set was amended with lactate (1.3-5.0 mM). For three of the four sites, another set of microcosms received lactate plus sulfate (5-10 mM). The microcosms were monitored for 9-21 months.

Results/Lessons Learned. For all four sites, amending the groundwater with lactate enhanced biotic and abiotic degradation of TCE. Degradation rate constants were 2.2-5.5 fold higher with the addition of lactate compared to the unamended treatment. For two of the four sites, lactate stimulated complete reductive dechlorination of TCE to *cis*-1,2-dichloroethene (cDCE). This is consequential because cDCE has a lower retardation coefficient than TCE and therefore diffuses out of the rock matrix at a faster rate. For all but one lactate-amended microcosm, there was no further reduction of cDCE to VC, indicative of an absence of *Dehalococcoides* or *Dehalogenimonas*. For the three sites with microcosms amended with lactate and sulfate, the presence of sulfate limited the extent of biotic reductive dechlorination of TCE in favor of sulfate reduction (and presumptively the formation of iron sulfide minerals). Numerical modeling of the rock cores indicated that degradation of TCE occurred within the rock, not just at the fracture surface. This was corroborated by detection of acetate and lactate within the rock cores at the end of the incubation period, when the cores were cut into pucks and analyzed for volatile fatty acids. Acetate is the main product from incomplete oxidation of lactate. These results confirm

the potential for bioremediation to enhance biotic and abiotic degradation of TCE within fractured rock at sites with complex geological formations.