Overcoming pH Effects on a "Stalled" In Situ Bioremediation System

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Background/Objectives. A former printing operation along South Carolina's Coastal Plain impacted shallow groundwater with chlorinated ethenes. Groundwater occurs at 6 feet below ground surface (bgs), and was impacted vertically to a confining unit at 24 feet and horizontally across 5 acres. DNAPL was not identified. Redevelopment as a shopping center was sought. No drinking water receptors were identified; however, chlorinated ethenes, sourced from impacted groundwater, were observed in soil gas above risk-based worker protection benchmarks near the proposed 136,000-square foot retail anchor store. The remediation objective was groundwater PCE and TCE reduction to site-specific concentrations calculated using risk-based ground water to soil gas modeling. Using in situ bioremediation, Terracon was able to achieve regulatory site closure with respect to PCE and TCE; however, the approach should have realized daughter product reduction as well. Although not a remedial goal, cis-DCE was observed to continually accumulate while VC and ethene were only observed ephemerally. Subsequent to regulatory site closure, Terracon was tasked with continued remediation in an effort to reduce total CVOC mass at the request of the site owner and tenants.

Approach/Activities. In 2015, Terracon injected a surfactant-enhanced electron donor, a "low-pH" strain of *dehalococcoides spp.* (*Dhc*), and a K_2HPO_4 buffer. In 6 months, source area PCE ground water concentrations fell from 15,200 mg/L to 220 mg/L. Likewise, cis-DCE, previously present in negligible amounts, continually increased in concentration. In contrast, VC, previously not detected, appeared only infrequently in the source zone. Based on the successful PCE & TCE reduction, the State VCP closed the site. Although cis-DCE formation was prolific, cis-DCE reduction was not as vigorous as anticipated. The reductive dechlorination pathway was effectively stalled. CH_4 production was continually observed; however, study of *Dhc* populations indicated low numbers of active organisms. Data analysis indicated *Dhc* organisms were likely limited by low pH. The initial injection pH was approximately 6.0; in the long-term, aquifer pH fell below 5.0. This pH is too low for optimal performance of the *Dhc* organisms. To maintain the *Dhc* bacteria as a viable biodegradation mechanism, pH near 6.0 (or higher) is desired. Terracon hypothesized that organic acid production from native organisms' fermentation of the labile electron donor (evidenced by CH_4 production) induced H^+ production sufficient to overwhelm the K_2HPO_4 buffer and limit long-term *Dhc* viability. To evaluate the buffer capacity necessary to revitalize dormant *Dhc*, a bench-scale $NaHCO_3$ buffer study was completed and subsequently scaled-up for field in situ implementation.

Results/Lessons Learned. Bench study control PCE and TCE concentrations fell by 13% and 8%, respectively. In contrast, $NaHCO_3$-buffered concentrations fell by 99.9%. Control cis-DCE concentrations increased 16%; pH-buffered cis-DCE concentrations increased by 181%. Control VC samples increased by 7%; buffered VC concentrations increased by 3,636%. These results indicate the ability of $NaHCO_3$ to buffer further H^+ production, and *Dhc* could be revived. Based on these encouraging results, 17 $NaHCO_3$ injection points were completed in April 2017. Source zone pH increased from 5.05 to 6.37. PCE and TCE concentrations decreased by 97%; cis-DCE increased 20%; and VC increased 380%. Subsequent sampling is pending. This experience demonstrates that the native microbes' ability to out-compete "designer" organisms should be carefully considered during design. Although site-specific PCE and TCE closure by the State was achieved in 6 months, had DCE been a contaminant of concern for this project, regulatory site closure would only now be plausible nearly two years after the initial injection.