Enhancing Remedial Performance Assessments at Complex Sites Using Compound Specific Isotope Analysis and Molecular Biological Tools

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Background/Objectives. Following a decade of enhanced in situ bioremediation (EISB) in chlorinated solvent dense, non-aqueous phase liquid (DNAPL) source areas in fractured basalt, a comprehensive groundwater monitoring dataset has been collected, including extensive datasets of various biogeochemical parameters, delta carbon-13 ($\delta^{13}C$) compound specific isotope analysis (CSIA) of chlorinated volatile organic compounds (VOCs), and molecular biological tools (MBTs). Given the complexity of the site conditions (multi-component DNAPLs, primary and secondary porosities, potentially inhibitory compounds) and changing conditions in the source areas and plumes as remediation progressed, analysis of the CSIA and MBT datasets was conducted to enhance the evaluation of EISB and monitored natural attenuation (MNA) remedy performance. The objective of this project was to evaluate the extent of degradation, potential degradation mechanisms, degradation rates, and temporal and spatial changes in degradation activity for chlorinated VOCs in both the source areas and downgradient plumes.

Approach/Activities. $\delta^{13}C$ CSIA data for groundwater and DNAPL samples collected from over 50 monitoring wells were used to estimate best-fit site-specific isotopic enrichment factors for seven chlorinated VOCs (1,1,2,2-tetrachloroethane [1,1,2,2-TeCA], 1,1,2-trichloroethane [1,1,2-TCA], 1,2-dichloroethane [1,2-DCA], tetrachloroethene [PCE], trichloroethene [TCE], vinyl chloride [VC] and chloroform [CF]). Enrichment factors were derived using Modified Kuder plots and compared to literature-derived enrichment factors to identify dominant degradation mechanisms. MBT data were compared to the interpreted dominant degradation mechanisms based on enrichment factors as evidence to support the interpreted degradation mechanisms. Further, the site-specific enrichment factors were used to estimate first-order degradation rates across the site, and associated half-lives for the chlorinated VOCs.

Results/Lessons Learned. Site-specific enrichment factors supported dominance of anaerobic biodegradation pathways for PCE, TCE, 1,1,2-TCA, CF and EDC in the areas where electron donor persists. VC appears to be degrading under both aerobic biodegradation and abiotic degradation pathways near a zero-valent iron permeable reactive barrier. Outside of the bioactive zone, there is some evidence for aerobic (co)metabolic degradation of EDC in the downgradient natural attenuation area. Consistently increasing enrichment in the $\delta^{13}C$ signatures of the primary DNAPL components 1,1,2-TCA and EDC confirms that ongoing source treatment is reducing source mass. $\delta^{13}C$ signatures in the plumes downgradient of the EISB area confirm limited natural biological attenuation is ongoing, with the exception of VC, which biodegrades aerobically. Calculated half-lives were typically shorter in the bioactive zone and longer in the downgradient area, consistent with enhancement of bioactivity in the EISB area and natural attenuation downgradient. Several calculated half-lives were less than two years, most often for locations downgradient of the source areas where concentrations are typically lower. The results of the isotopic assessment are being used to streamline future sampling events, targeting key locations to monitor EISB performance and changes in offsite

degradation activity, coupled with microbial analysis at select locations to gain further insight into dominant degradation mechanisms.