

Characterization of Contaminant Evolution and Ketones Accumulation in an Aged DNAPL Source Zone within a Sedimentary Bedrock Aquifer

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Background/Objectives. High-resolution hydrogeochemical characterization of a fractured, sedimentary rock aquifer contaminated more than 50 years ago with a dense non-aqueous phase liquid (DNAPL) indicated temporal and vertical contaminant compositional variability in and just downgradient of the source zone. DNAPL samples recovered from wells in 2003 revealed a nearly homogeneous organic mixture composed of chlorinated ethenes, ethanes, methanes, ketones, and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX). In 2003, the contaminant composition was nearly invariant with depth; however, in recent years, depth-discrete sampling in the source zone shows dramatic changes in relative molar composition with depth. This can be attributed to differential degradation processes and rates, as well as variability in groundwater flow and mass fluxes within the fractured bedrock aquifer. The primary objective of this research was to elucidate the relative influence of degradation and mass transfer processes on natural source zone depletion (NSZD).

Approach/Activities. Volatile organic compound (VOC) concentrations derived from high-resolution, depth-discrete rock core samples collected from eight continuous cores were used to quantify the contaminant phase, mass, and composition with depth and to assess NSZD over a 17-year period. Rock core VOC concentrations were converted to equivalent porewater concentrations and compared with effective solubilities to partition the contaminant mass between DNAPL, dissolved, and sorbed phases. Dissolved VOC concentrations of stagnant water in permeable matrix blocks estimated based on rock core data were compared with concentrations of rapidly flowing groundwater in the fractures network along three multilevel monitoring wells. Microbial qPCR and compound specific isotope analysis (CSIA) were also applied to groundwater samples and along with other lines of evidence such as fatty acids and dissolved gas concentrations were used to identify active degradation pathways and mass transfer mechanisms within different hydrogeologic units in the fractured bedrock aquifer.

Results/Lessons Learned. The current contaminant phase and mass distribution estimates in the source zone indicate an 80 to 95% reduction in total mass compared to the 2002 estimate while 38% of the present-day mass persists as residual immobile DNAPL in the source zone. Comparison of rock core VOC data collected in 2003, 2014, 2017, and 2019 shows that ketones are the only contaminant group with increasing concentrations at some depth intervals over this period. In addition, comparison of ketone concentrations in stagnant water within matrix blocks (from rock VOC samples) with flowing groundwater within fractures (from multilevel system groundwater samples) over an 11-year period shows a significant increase in ketone mass fraction in the matrix pore water where appropriate reducing conditions are observed. The distribution of ketones in groundwater with depth is in agreement with the distribution of BTEX and fatty acids (i.e., acetate, propionate, and butyrate) suggesting fermentation of BTEX under strongly reducing conditions in the lower permeability matrix blocks can result in ketone accumulation. Application of qPCR analysis indicated the presence of *Sphaerochaeta* species that probably consume products of BTEX biodegradation and generate H₂ for methanogens as well as ketones and other fermentation byproducts. Higher fractions of generated byproducts resulting from degradation processes can affect interphase mass transfer processes,

contaminant composition, and mass fluxes within different hydrogeologic units that should be considered for the design and implementation of remediation practices.