

Characterization of MTBE Biodegradation Using Multiple Lines of Evidence: Equilibrium Partitioning, CSIA, and Microbial Analysis

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Background/Objectives. Failure of a storage tank suction fill line resulted in multiple releases containing pure phase MTBE and gasoline range hydrocarbons. Current dissolved MTBE concentrations range from nearly 2,500,000 µg/L in the plume core to 100,000 µg/L on the plume core periphery. A biodegradation study was conducted to evaluate the magnitude and extent of MTBE biodegradation and understand whether elevated concentrations in the plume core may be inhibiting microbial activity. The objectives of the study consisted of using multiple lines of evidence including an equilibrium partitioning method, microbial analysis, and compound specific isotope analysis (CSIA) to evaluate the presence of TBA as it relates to MTBE, identify MTBE degradation pathways, characterize the makeup of the microbial community, and estimate MTBE degradation rates in different representative areas of the site.

Approach/Activities. Assessment of the occurrence and rate of degradation were evaluated using historical site concentration data. Fuel-water partitioning coefficients, volume ratios of fuel in groundwater, and concentrations of TBA in MTBE from technical literature were used to calculate an equilibrium partitioning curve of TBA in groundwater as a function of MTBE concentrations. MTBE and TBA concentrations at the site were plotted against the curve to determine whether the presence of TBA was due to dissolution or biotransformation of MTBE. Soil samples were collected from three soil borings targeting the capillary fringe and saturated zone and 15 groundwater samples were collected from site monitoring wells. Samples were sent to the laboratory for analysis of volatile organic compounds including MTBE and TBA, phospholipid fatty acid (PLFA) analysis, and quantitative polymerase chain reaction (qPCR) analysis. In addition, groundwater samples were also analyzed for geochemical constituents and ratios of heavy to light carbon and hydrogen isotopes using CSIA. Five advanced Bio-Trap® samplers loaded with ¹³C-labeled MTBE were installed in groundwater monitoring wells for 31 days and sent to the laboratory for qPCR, PLFA, and stable isotope probing (SIP) analysis.

Results/Lessons Learned. Increasing TBA/MTBE ratios and concentration plots against equilibrium partitioning curves suggest the presence of TBA in the plume core periphery and downgradient areas is primarily a result of MTBE biotransformation whereas TBA in the plume core is more likely due to dissolution from MTBE product. Plots of isotopic enrichment as a function of distance from the source zone and a comparison to equilibrium partitioning of TBA and MTBE illustrates higher magnitudes of biodegradation as distance from the plume core increases. A 2-D comparison of heavy-to-light isotopic ratios of carbon and hydrogen suggests MTBE degradation follows anaerobic pathways and PLFA analysis confirmed the presence of moderate populations of anaerobic bacteria. Overall, multiple lines of evidence including TBA/MTBE ratios, equilibrium partitioning, quantification of microbial biomass and genetic material, and isotopic enrichment demonstrate MTBE biodegradation on the periphery of the plume core where concentrations are moderate, and little to no biodegradation in the plume core where elevated MTBE concentrations may be toxic to native bacteria or terminal electron acceptors have been depleted and are inhibiting microbial activity. Results of the study suggest active remediation of the source area will be required to reduce MTBE concentrations and replenish terminal electron acceptors to stimulate and enhance the intrinsic biodegradation.