Stable Carbon and Hydrogen Isotope Ratios for Assessing the Fate and Transport of 1,4-Dioxane

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Background. 1,4-Dioxane (1,4-D) degradation rates at groundwater sites vary significantly. Published half-lives for in situ 1,4-D degradation rates resulting from enhanced aerobic cometabolic bioremediation range from less than a day to approximately a month. In contrast, reported median and mean natural attenuation half-lives for 1,4-D source attenuation rates for California sites are much longer (2.5 and 8.7 years, respectively). In light of recent advances in using compound specific isotope analysis (CSIA) to assess 1,4-D degradation in groundwater, CSIA may be a powerful method to provide additional insights into 1,4-D concentration change in an engineered in situ remediation system or in large, dilute plume subject to natural attenuation. To better understand possible isotopic composition evolution of 1,4-D in a reactive transport system, a study is being conducted to assess the following representative generic conceptual model scenarios: (1) constant, slow biodegradation under homogenous aerobic conditions favoring 1,4-D biodegradation throughout the plume and (2) spatially and/or temporally variable redox conditions, with degradation in spatially distributed aerobic zones, and little to no degradation in other redox zones.

Approach. An analytical model is used to simulate 1,4-D fate and transport and isotopic enrichment for both scenarios; an isotopic mixing model was applied to Scenario 2 to calculate the expected 1,4-D isotope ratios and concentrations in groundwater samples collected in a monitoring well that intercepts groundwater from different redox zones. The following input parameters, based on literature reported values, are used to model the trends of 1,4-D concentration and isotopic composition change for both scenarios: initial 1,4-D concentrations and isotopic compositions, established 1,4-D carbon- and hydrogen-isotope enrichment factors, and potential 1,4-D reaction half-lives in groundwater.

Model results are applied to the 1,4-D CSIA data collected during a field pilot test for aerobic in situ cometabolic biodegradation at the former McClellan Air Force Base (McAFB). The in situ bioreactor established through propane and oxygen addition to recirculated groundwater was able to achieved a >95% treatment efficiency of 1,4-D. To interpret the CISA data, redox conditions, bacterial populations, and functional genes were evaluated based on groundwater samples from several monitoring wells.

Results. The modeling results of these two scenarios are offered as a guide for interpreting CSIA results as applied to the fate and transport of 1,4-D. Modeling results indicate substantial isotopic enrichment in Scenario 1, but isotopic enrichment in Scenario 2 may not be detectable due to masking by 1,4-D from “non-degradation” zones. This finding demonstrates the potential for “false negatives” when applying CSIA towards 1,4-D at field sites represented by Scenario 2. Although counterintuitive, it may be more difficult to detect isotope fractionation for Scenario 2 plumes because degradation rates are higher, highlighting the importance of utilizing multiple lines of evidence when assessing the fate of 1,4-dioxane in groundwater. The CSIA data together with chemical, redox, and microbial data collected during the field pilot test at former McAFB suggest that Scenario 2 is the more appropriate conceptual model to explain observed 1,4-D degradation. The implications of the model results to the management of a 1,4-D dilute plume in an aquifer of mixed redox conditions will also be discussed.