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Stable Isotopic Investigations of in-situ Bioremediation of Chlorinated Organic Solvents

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Research Objective

Contamination of soils and groundwaters with chlorinated aliphatic hydrocarbons (CAHs) is one of the most serious environmental problems in the DOE system and in the nation at large. These compounds are designated as priority pollutants by the U.S. Environmental Protection Agency (EPA) and are known or suspected to be carcinogenic or mutagenic in humans. These compounds are readily transported by groundwater and are not reduced to acceptable concentrations for human consumption by most municipal water supply treatments; thus the compounds represent a significant hazard to a large portion of the human population. In situ bioremediation is an emerging technology that shows great promise for mitigation of CAH contamination at many sites.

One of the most severe limitations of in-situ bioremediation is the difficulty of proving when it is working at a given site. The concentrations of CAHs and their degradation products in plumes may be difficult to relate to the efficiency of the remediation process because of dilution effects, but this problem is mitigated to a large extent by measuring isotope ratios. If there is a significant isotopic fractionation between CAHs and derivative chlorine-bearing products, then the fraction of CAH that is dechlorinated can be inferred from the $^{37}\text{Cl}/^{35}\text{Cl}$ and $^{13}\text{C}/^{12}\text{C}$ isotope ratios of the residual CAH. It is important to point out that there is currently no published information available on the magnitude of chlorine and carbon isotopic fractionation associated with biological degradation of CAHs. We plan to help eliminate this important gap in our knowledge with the work being performed here.

This work is relevant to EMSP goals because it will provide a new and cost-effective means of evaluating and monitoring the effectiveness of in-situ bioremediation. It will employ newly developed techniques to characterize isotopic fractionation (of chlorine and carbon) associated with biotic and abiotic degradation of CAHs in laboratory microcosms. These techniques and the data acquired by using them in laboratory studies will form the fundamental basis for quantitative assessment of the mechanisms, rates, and efficiencies of various in-situ bioremediation schemes for CAHs.

Research Progress and Implications

This report summarizes work as of 21 months into a 36-month project. First, we have developed methods for precise measurement of stable carbon and chlorine isotope ratios of micromolar amounts of CAHs. We have also developed methods for quantitative extraction of CAHs from water and air. We have applied these methods in laboratory experiments, to investigate isotopic fractionation caused by microbial degradation and by abiotic processes such as evaporation and chemical reduction. We have also applied these methods to field investigations of contaminated groundwater aquifers at the Paducah Gaseous Diffusion Plant, Kentucky and at several manufacturing plants in the Chicago and Kansas City metropolitan areas. Results of much of this work have already been incorporated into four manuscripts that have been published, accepted for publication, or are in review (see references below).

The microbial degradation of CAHs can cause large isotopic fractionation of carbon and chlorine isotopes. The carbon isotopic fractionation is about 11 times as large as the chlorine isotopic fractionation in the system that we have best characterized to date (aerobic degradation of dichloromethane [DCM]). The carbon isotopic fractionation during aerobic microbial degradation of DCM (42.4 per mil) is about twice as large as that during microbial oxidation of methane, and the chlorine isotopic fractionation is about 3.8 per mil (Heraty et al., 1998), with the residual DCM being enriched in the heavy isotopes. Our preliminary results show that the isotopic fractionation

between CAH liquids and vapors is much smaller than that caused by microbial degradation. The carbon isotopic fractionation between CAH liquids and vapors is such that the vapor is enriched in the heavy isotope, so the residue of evaporation is isotopically depleted in the heavy isotope. This finding allows the isotope effects of microbial degradation to be readily distinguished from those of evaporation, and thus is immediately applicable in the field.

Planned Activities

During the remaining time of this program, we will proceed further with all three of our primary tasks: analytical and sampling methods development, laboratory experiments, and field studies. In the analytical and sampling methods development task, we plan to implement a continuous-flow capability for on-line Cl isotope ratio measurement of very small (i.e., <0.1 micromole) samples of CH₃Cl on our mass spectrometer. The ability to analyze such small samples is necessary for field studies of contaminated aquifers, where concentrations of chlorinated VOCs may be only in the ppb range. This will lead to the eventual ability to perform compound-specific Cl isotope analysis of mixtures of chlorinated VOCs. In the laboratory experiment task, we will continue our ongoing series of liquid culture and soil column experiments with aerobic and anaerobic microbes. We will also continue our investigation of abiotic processes that may fractionate stable isotopes, such as evaporation and adsorption, as well as the potential of Fe-bearing minerals for abiotic degradation of chlorinated VOCs. In the field studies task, we plan to study CAH plumes at several more well characterized sites.

Other Access To Information

- B.D. Holt, N.C. Sturchio, T.A. Abrajano, and L.J. Heraty (1997) Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. *Analytical Chemistry* 69, 2727-2733.
- N.C. Sturchio, J. Clausen, L.J. Heraty, L. Huang, B.D. Holt, and T. Abrajano (1998) Stable chlorine isotope investigation of natural attenuation of trichloroethene in an aerobic aquifer. *Environmental Science and Technology* (in press).
- L.J. Heraty, M.E. Fuller, L. Huang, T. Abrajano, and N.C. Sturchio (1998) Isotopic fractionation of carbon and chlorine by microbial degradation of dichloromethane. *Organic Geochemistry* (in review).
- L. Huang, L.J. Heraty, and N.C. Sturchio (1998) Equilibrium liquid-vapor fractionation factors of chlorinated aliphatic hydrocarbons. *Organic Geochemistry* (in review).