Microbial Degradation of Chlorinated Aliphatic Hydrocarbons: Field Investigations Using Stable Carbon and Chlorine Isotopes

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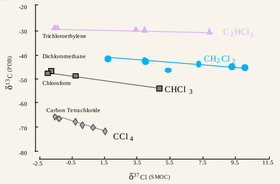
Introduction

The application of stable-isotope-ratio measurements of C and Cl to investigate the environmental behavior and fate of anthropogenic chlorinated aliphatic hydrocarbons (CAHs) is a relatively new approach. We have developed new methods for the sampling and isotopic analysis of CAHs and applied these to measure isotopic fractionation of C and Cl during vapor-liquid partitioning and microbial degradation in liquid cultures in the laboratory. We have also performed several field studies of C and Cl isotopes in contaminated aquifers in which either natural or engineered degradation of CAHs has occurred. Data for two field sites, both contaminated with trichloroethene (TCE) but undergoing different remediation regimes are shown here.

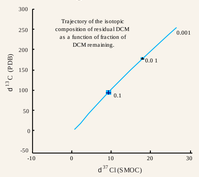
Background: Bench Scale Experiments

Evaporation of Pure Phase CAHs



Evaporation experiments were performed by sampling the residual compound at several points during evaporation of neat solvents. Further tests are currently underway to measure the isotopic trajectories of both the chloroethenes and chloroethanes during evaporation from pure phase and from solution in water. See:Huang, L., Sturchio, N., Abrajano, T., Heraty, L., Holt, B., 1999. Carbon and chlorine isotope fractionation of chlorinated aliphatic hydrocarbons by evaporation,Organic Geochemistry(30)8a, pp. 777-785.

Dichloromethane Biodegradation

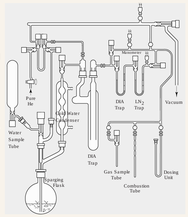


Batch culture biodegradation experiments were performed at 22°C using MC8b, a gram negative methylotrophic organism related to Methylobacterium/Ochrobactrum. Above data represents three separate experiments. Isotopic determinations were performed on headspace gas. See: Heraty, L. J.,Fuller, M. E., Huang, L., Abrajano, T., and Sturchio, N. C., 1999. Isotopic Fractionation of Carbon and Chlorine by Microbial Degradation of Dichloromethane. Organic Geochemistry. (30)8a, pp. 793-799.

Background: Methods

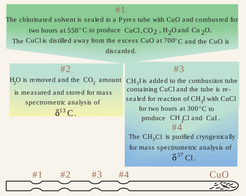
VOC Extraction

Diagram of extraction line used to remove VOCs from water samples. Groundwater samples are aspirated into Water Sample Tube, pre evacuated and loaded with NaOH. In the lab the sample is then transferred into the Sparging Flask under vacuum. The VOCs are stripped out of solution using a stream of Helium through a quadruple-trap system. The purified VOCs are then measured and transferred into a Combustion Tube for the conversion to CO_2 and CH_3Cl.



See: Holt, B., Heraty, L., and Sturchio, N., 1999. Extraction of Chlorinated Aliphatic Hydrocarbons from Groundwater for Isotopic Analysis of Chlorine and Carbon ACS National Meeting, New Orleans LA.

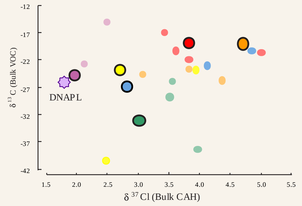
Combustion and Cryogenic Separation Procedure



The combustion of VOCs and subsequent cryogenic separation following the above steps, produces CO_2 and CH_3Cl from the same sample. Each step corresponds to a constriction of the combustion tube, shown in cartoon. See: Holt, B,D., Sturchio, N.C., Abrajano, T.A. and Heraty, L.J., 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.

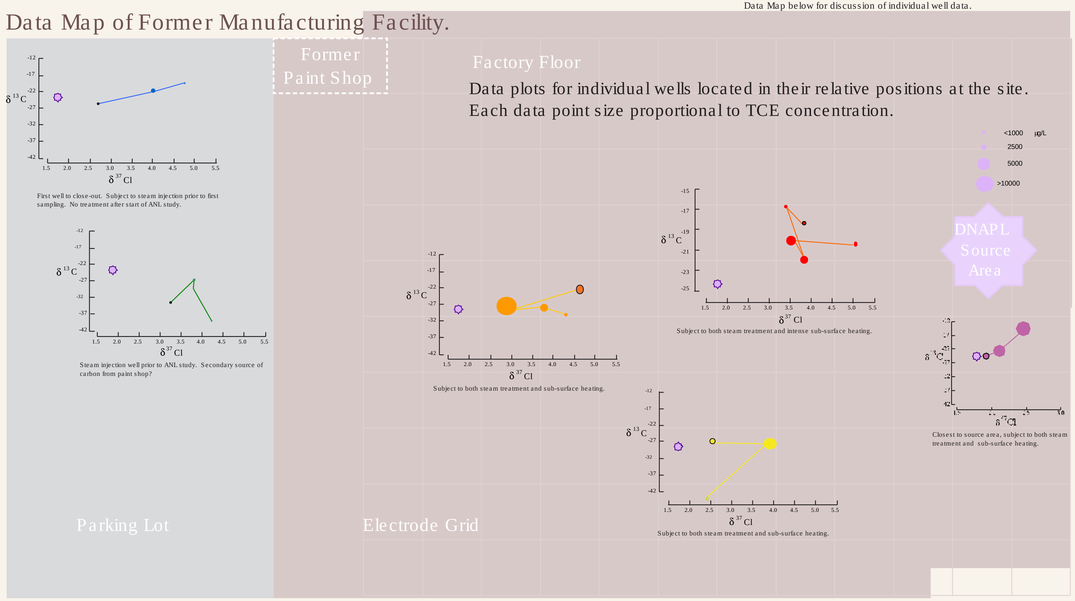
Illinois Site

Isotopic analysis of CAHs collected at a former manufacturing facility started during the last year of an eight year remediation effort, with five sampling events. An estimated 32000 kg of CAHs were released over a 3.5 acre area. Over the course of seven years approximately 27000 kg of hydrocarbons were removed by remediation efforts, primarily steam injection and vapor extraction. During the last year of remediation the site underwent continued vapor extraction combined with six phase electrical resistive heating, which removed an additional 5000 kg of hydrocarbons. The site overlays flat glacial soils, fine sands, silts and clays, with the Tinley ground moraine continuous throughout. Complex plume composition with multiple organic carbon sources (TCE, TCA, hydraulic fluid, paint-shop solvents, petroleum products, and sewage) complicated the interpretation of any site-wide trends. C and Cl isotope ratios indicated processes (evaporation, degradation, and dissolution) consistent with known well histories (proximity to organics, steam injection, heating, etc.). In some wells the observed 13-C and 37-Cl enrichments, more than +3 permil relative to the pure phase DNAPL source, were indicative of significant CAH degradation with time.



Positions of all data for all wells sampled over the course of one year. Heavy black outlines indicate initial value at start of ANL project. See Data Map below for discussion of individual well data.

Data Map of Former Manufacturing Facility.



First well to close-out. Subject to steam injection prior to first sampling. No treatment after start of ANL study.

Steam injection well prior to ANL study. Secondary source of carbon from paint shop?

Subject to both steam treatment and sub-surface heating.

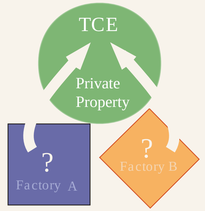
Subject to both steam treatment and intense sub-surface heating.

Subject to both steam treatment and sub-surface heating.

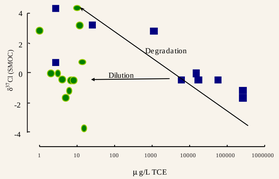
Closest to source area, subject to both steam treatment and sub-surface heating.

South Carolina Site

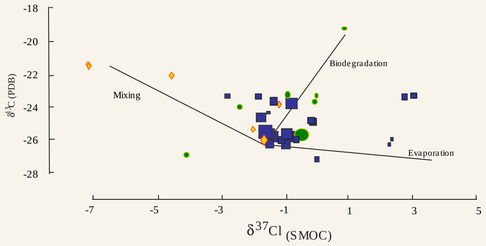
In contrast, at a manufacturing facility where no engineered remediation has been started, evidence for biodegradation and multiple TCE sources was identified. The site is located within the Inner Piedmont Belt of the Piedmont province of South Carolina. Underlain by three saprolitic sub horizons and predominantly gneiss-schist parent rock, groundwater flow and TCE transport are largely fault and fracture controlled. TCE was the predominant source of both organic carbon and chlorine within the plume. The enrichments of both 13-C and 37-Cl within one arm of the plume indicate biodegradation, while other wells indicate that evaporation is the predominant mechanism of natural attenuation, with 37-Cl enrichments up to +4 permil relative to source wells.



Sampling depths at this site vary from surface water to >100m. TCE is found in wells located on three different properties, and the main source was assumed to be from Factory A.



Plot of $\delta^{37}Cl$ vs TCE concentration shows that the effect of dilution/dispersion is very strong.



Plot of $\delta^{13}C$ vs $\delta^{37}Cl$, shows three processes that could affect the isotope ratio of a primary DNAPL contaminant. There appears to be clear evidence for biodegradation as well as a possible separate source of TCE at Factory B, as it is impossible to derive the isotope composition of the most extreme Factory B sample from that of the Factory A source by any known process. Alternatively there may have been variation with time of the isotopic composition of a single source. There appears to be some limited mixing between the Factory A and Factory B TCE, with partial biodegradation of the mixtures. There also may be some evidence of evaporation in the samples from the Factory A site that have anomalous high $\delta^{37}Cl$ values.