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STABLE ISOTOPE INVESTIGATIONS
OF CHLORINATED ALIPHATIC HYDROCARBONS

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ABSTRACT

Stable isotope ratio measurements for carbon (C) and chlorine (Cl) can be used to elucidate the processes affecting transformation and transportation of chlorinated aliphatic hydrocarbons (CAHs) in the environment. Methods recently developed in our laboratory for isotopic analysis of CAHs have been applied to laboratory measurements of the kinetic isotope effects associated with aerobic degradation of dichloromethane (DCM) and with both anaerobic and aerobic cometabolic degradation of trichloroethene (TCE) in batch and column microbial cultures. These experimental determinations of fractionation factors are crucial for understanding the behavior of CAHs in complex natural systems, where the extent of biotransformation can be masked by dispersion and volatilization. We have also performed laboratory investigations of kinetic isotope effects accompanying evaporation of CAHs, as well as field investigations of natural attenuation and *in situ* remediation of CAHs in a number of contaminated shallow aquifers at sites operated by the federal government and the private sector.

INTRODUCTION

The basis for the isotopic approach to *in situ* monitoring of bioremediation is that isotopic fractionation of chlorine and carbon occurs between reactants and products as CAHs are biologically degraded in the environment. For example, as chlorine atoms are removed from CAHs, the likely statistical bias is toward removing the ^{35}Cl atoms faster than the ^{37}Cl atoms, because the $^{35}Cl–C$ bond is weaker than the $^{37}Cl–C$ bond, and therefore the reaction rate is faster for the $^{35}Cl–C$ bond. This kinetic isotope effect will change the $^{37}Cl/^{35}Cl$ ratio of the CAH relative to that of the derivative chloride. The shift in the ratio can be defined by an isotopic fractionation factor, α, where

$$\alpha = (^{37}Cl/^{35}Cl)_{VOC}/(^{37}Cl/^{35}Cl)_{chloride} \cdot \qquad (1)$$

The residual CAH will generally have higher $^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$ ratios than the initial CAH. However, little is currently known about the magnitude of either carbon or chlorine isotopic

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fractionation during biotransformation of a CAH. One of our highest priorities is to establish the values of the fractionation factors for CAHs under controlled laboratory conditions.

As dechlorination of a CAH proceeds, the $^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$ ratios of the residual CAH will change if α is significantly different from unity. This process can be described in terms of a Rayleigh-type fractionation,

$$R = R_oF^{(\alpha-1)} , \tag{2}$$

where R and R_0 are the $^{13}C/^{12}C$ or $^{37}Cl/^{35}Cl$ ratio at times t and zero, respectively, and F is the residual fraction of CAH at time t. It follows that with knowledge of the appropriate α, determined from laboratory measurements, and the measured values of R and R_0, the value of F can be estimated. Figure 1 shows the change in isotopic δ values as a function of the fraction of CAH consumed by biodegradation for reasonable values of α ranging from 0.999 to 0.990. This plot demonstrates that the residual fraction of CAH can be determined with considerable accuracy, given the typical analytical uncertainty of our $\delta^{37}Cl$ and $\delta^{13}C$ measurements. Isotope ratios are usually reported in δ notation relative to ratios measured in a standard reference material, where $\delta = 1000 \times [(R_{sample}/R_{standard}) - 1]$, and R is the isotope ratio being measured. The δ values are reported in units of per mil (‰) or parts per thousand deviation relative to the absolute isotope ratio in the standard reference material. The generally accepted standard reference material for chlorine isotope ratios is Standard Mean Ocean Chloride (SMOC), and that for carbon isotope ratios is PeeDee Belemnite (PDB), the calcareous shell of a fossil marine organism.

METHODS

We recently developed a new and improved method for isotopic analysis of chlorine and carbon in chlorinated organic compounds (Holt et al. 1997). In our method, the chlorinated solvent is sealed in a Pyrex tube with CuO and combusted for 2 hr at 550°C to produce CuCl, CO_2, H_2O, and Cu_2O. The tube is opened for removal of CO_2, H_2O, and CuO. The CO_2 amount
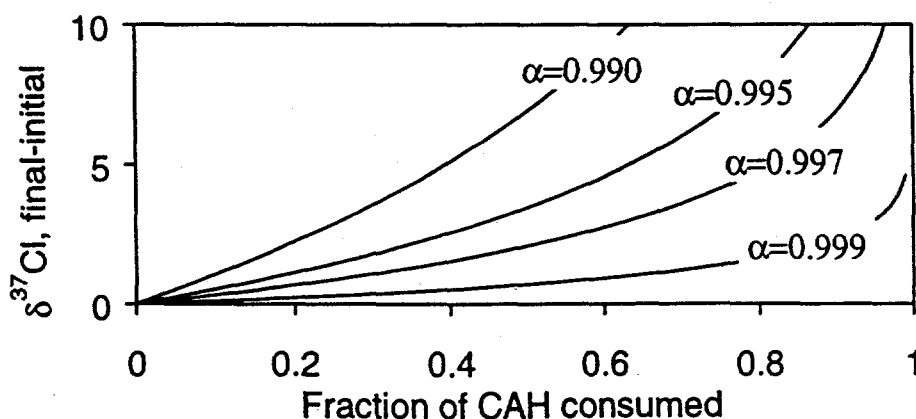

FIGURE 1 Change in Isotopic δ Values as a Function of the Fraction of CAH Consumed in a Biodegradation Reaction Having a Kinetic Fractionation Factor α Ranging from 0.999 to 0.990

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is measured, and the gas is stored for determination of $\delta^{13}C$. Excess CH_3I is added to the combustion tube containing CuCl, and the tube is resealed for reaction of CH_3I with CuCl for 2 hr at 300°C to produce CH_3Cl and CuI. The CH_3Cl is purified cryogenically for mass spectrometric analysis. The precision of the method in laboratory measurements of reagent solvents is better than ±0.1‰ for both $\delta^{37}Cl$ and $\delta^{13}C$.

To collect water samples for isotopic analysis of CAHs, we use evacuated glass bottles having gas-tight Teflon valves (Holt et al. 1995). For analysis of CAHs in water samples, we use an on-line vacuum extraction/helium-stripping method, with cryogenic trapping procedures to separate the CAHs from the water prior to stable isotope analysis (Holt et al. 1995).

RESULTS

Laboratory Studies

We are performing a series of laboratory studies to measure kinetic isotope effects during microbial degradation of CAHs under different geochemical conditions and during evaporation of CAHs. Figure 2 shows an example of data that we have produced to quantify the kinetic isotope effect accompanying aerobic degradation of DCM by pure microbial strain MC8b. Such data can be applied in field studies of microbial DCM degradation in aerobic environments.

We have shown that evaporation of CAHs results in a distinctly different isotopic fractionation than does biodegradation; therefore, these two processes can be distinguished readily in the field by the isotopic variations they generate in the residual CAH fraction (Huang et al. 1999).
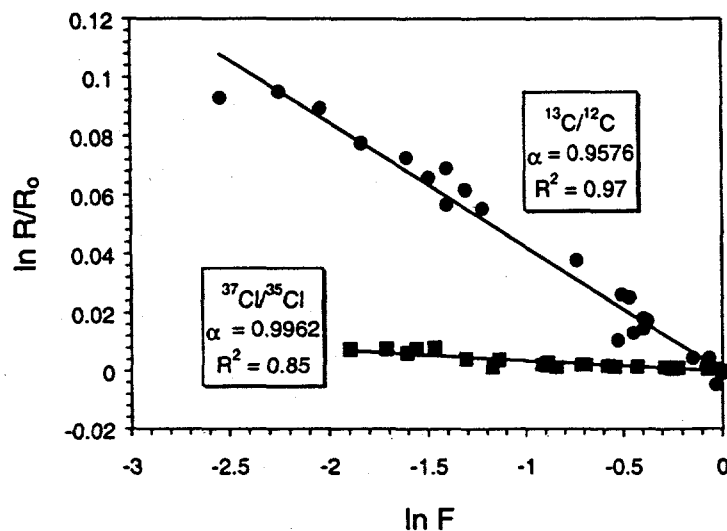

FIGURE 2 Measured Kinetic Isotope Effect for Carbon (circles) and Chlorine (squares) during Aerobic Degradation of DCM by the Pure Microbial Strain MC8b (Heraty et al. 1999)

Field Studies

    We have completed a number of field investigations of stable isotope ratios of CAHs, and others are in progress. Our initial field study was of TCE contamination at the Paducah Gaseous Diffusion Plant in western Kentucky. Stable isotope data for Cl in TCE (Figure 3) and dissolved inorganic chloride showed that although natural attenuation of TCE had occurred in the clays and silts overlying the aerobic gravel aquifer at the site, no further attenuation had occurred within the gravel aquifer (Sturchio et al. 1998).

CONCLUSIONS

    Stable isotope ratio measurements of C and Cl in CAHs have powerful applications in site characterization, both for identifying natural attenuation processes and for monitoring the effectiveness of engineered bioremediation solutions. Further work is needed to build the database of kinetic fractionation factors associated with common microbial ecosystems and pure microbial strains known to have abnormal propensities for CAH degradation. Sufficient knowledge of fractionation factors, along with relevant hydrologic and geochemical parameters, will enable the derivation of quantitative estimates of the extent and rate of *in situ* CAH attenuation in contaminated aquifers, soils, and vadose horizons. This approach can contribute to potentially large cost savings for site remediation.
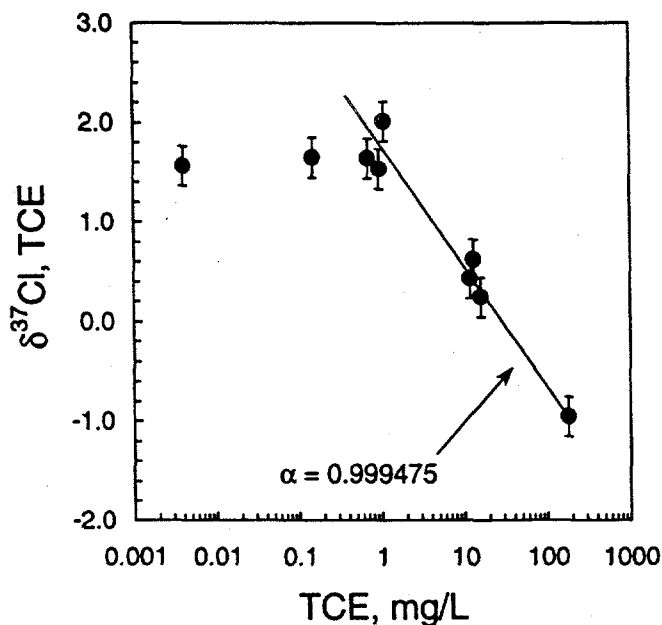

FIGURE 3 Values of $\delta^{37}Cl$ versus TCE Concentration in Water Samples from the Paducah Gaseous Diffusion Plant in Western Kentucky, Showing that Natural Attenuation of TCE Had Occurred at the Site (An apparent α value of 0.999475 was derived by least-squares linear regression of the data [Sturchio et al. 1998].)

ACKNOWLEDGMENT

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