

## Chlorine Isotope Investigation of Natural Attenuation of Trichloroethene in an Aerobic Aquifer

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Natural attenuation of chlorinated aliphatic hydrocarbons (CAHs) can be an important mechanism for groundwater remediation. It is difficult to determine the effectiveness of natural CAH attenuation from chemical analyses of groundwater samples because mixing, dispersion, and secondary reactions can mask the chemical evidence of attenuation. In this paper, we explore the application of stable chlorine isotope ratio measurements as a new tool for evaluating natural attenuation of CAHs. We report stable isotope ratios of chlorine in both trichloroethene (TCE) and inorganic chloride in groundwater from an aerobic aquifer beneath an extensively contaminated industrial site, the Paducah Gaseous Diffusion Plant in western Kentucky. Variations in the concentrations and chlorine isotope ratios of TCE and chloride in the groundwater are consistent with those expected from natural attenuation. These data support a model in which partial TCE degradation occurred in relatively impermeable, clay-rich sediments above the aquifer, and little or no further degradation of TCE occurred within the aquifer. A record of changing conditions within the TCE source area can be inferred from the spatial variation of chlorine isotope ratios for TCE and chloride within the plume.

### Introduction

Chlorinated aliphatic hydrocarbons (CAHs), including the common solvents tetrachloroethene (PCE), trichloroethene (TCE), tetrachloromethane (CCl<sub>4</sub>), trichloromethane (CHCl<sub>3</sub>), and trichloroethane (TCA), are the most frequently detected groundwater contaminants in the United States (1, 2). These compounds are designated as priority pollutants by the U.S. Environmental Protection Agency (EPA) (3) and are known or suspected to be carcinogenic or mutagenic in humans. A promising means for mitigating CAH contamination in soils and groundwaters is in situ bioremediation, in which microbes convert CAHs to environmentally benign products

such as carbon dioxide (CO<sub>2</sub>), chloride (Cl<sup>-</sup>), and biomass. When in situ bioremediation occurs naturally by indigenous microbial populations, it is termed intrinsic bioremediation or natural attenuation. Natural attenuation can be a remedial alternative for many sites.

One of the most severe limitations of in situ bioremediation is the difficulty of proving that it works (4–6). Demonstration of natural attenuation for the volatile CAHs is particularly difficult due to their slow biodegradation rates. The use of isotope ratio measurements of carbon and chlorine in residual CAHs and their degradation products to evaluate in situ bioremediation is a powerful complement to the conventional approach of monitoring of CAH concentrations and other chemical parameters such as terminal electron acceptors. The concentrations of CAHs and their biodegradation products in contaminated groundwater plumes may be difficult to relate to the efficiency of the bioremediation process because of changes caused by physical processes such as adsorption, mixing, and dispersion as well as secondary reactions that consume biodegradation products (e.g., iron sulfide precipitation). Because biodegradation causes significant isotopic fractionation between residual CAHs and their degradation products, isotope ratios can provide evidence that in situ bioremediation is occurring in situations where chemical measurements alone may provide insufficient or ambiguous data.

Measurement of chlorine stable isotope ratios in natural materials such as rocks and waters has become routine (7–9), but relatively few measurements of chlorine isotopes in CAHs have been reported. A chlorine isotope effect was found in *tert*-butyl chloride (10), demonstrating that <sup>37</sup>Cl is more strongly bound to carbon than is <sup>35</sup>Cl. Significant differences in the δ<sup>37</sup>Cl values of some atmospheric chlorinated organic compounds were measured (11). More recently, δ<sup>37</sup>Cl and δ<sup>13</sup>C values of CAHs obtained from various manufacturers were measured (12–14). Each measured CAH showed a significant range in δ<sup>37</sup>Cl and δ<sup>13</sup>C values.

The present study explores the use of Cl isotope ratios for investigation of natural attenuation of trichloroethene (TCE) at a well-characterized field site, the Paducah Gaseous Diffusion Plant (PGDP) in western Kentucky. The amount of dissolved TCE in the plume is estimated at 3200–4700 kg, with larger amounts present as DNAPL in the source area (25). Using the conventional geochemical criteria for evaluating natural attenuation of CAHs in groundwater (15, 16), the PGDP site ranks low in terms of its potential for anaerobic biodegradation of TCE (17).

### Site Hydrogeology

The stratigraphy at PGDP consists of Pleistocene sediments that uniformly overlie older bedrock (Figure 2). The Pleistocene sediments are divided into three main units: (a) Upper Continental Recharge System (UCRS), (b) Regional Gravel Aquifer (RGA), and (c) McNairy Formation. The UCRS consists of clay-rich silt interspersed with discrete lenses of sand and gravel extending from the ground surface to a depth of approximately 18 m. The unit underlying the UCRS is the RGA, from approximately 18 to 31 m below ground surface (bgs), which comprises the main zone of groundwater contamination. The RGA consists of chert gravel in a matrix of poorly sorted sand and silt. Beneath these two units is the McNairy Formation that varies from clay to sand and extends from the base of the RGA to bedrock at approximately 92 m bgs.

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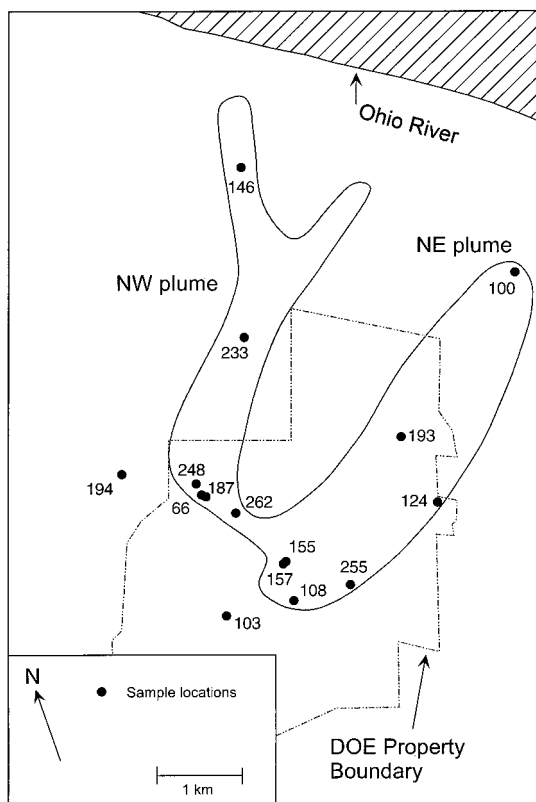


FIGURE 1. Map showing locations of TCE plume and sampled groundwater monitoring wells in and near the Paducah Gaseous Diffusion Plant (PGDP) in Kevil, KY. The principal source area for the TCE plume is near monitoring wells 155 and 157.

The hydraulic conductivity of the sand lenses in the UCRS is at least 2 orders of magnitude larger than that of the interbedded clays and silts (18). The UCRS has a vertical profile of alternating hydraulic conductivity, and within each layer there is lateral heterogeneity. The sand lenses decrease in frequency toward the Ohio River. The hydraulic conductivity of the RGA is 3–5 orders of magnitude greater than that of the sand lenses in the UCRS (18). Groundwater flow through the UCRS to the RGA is primarily vertical due to extreme differences in the hydraulic conductivities of these two units.

The Ohio River is the base level for the RGA, so groundwater flow is generally from south to north, but local flow directions are variable and dependent on both river stage and precipitation events. Pumping tests show that the RGA behaves as a semi-confined aquifer. Measured hydraulic conductivity of the RGA ranges from 0.19 to 2420 m/day and appears to be scale dependent (19–22). The average hydraulic gradient for the RGA ranges from 0.0002 to 0.001 and is spatially specific (23). Effective porosity values of 0.2–0.3 are assumed to be representative of the RGA based on a measurement of 0.25 (24). The thickness of the RGA ranges from 1.5 to 15 m (18). On the basis of an average thickness of 9 m, estimated flow velocities range from 0.05 to 5 m/day with a mean of 0.4 m/day (25).

## Methods

**Sampling.** The sampling locations included six wells in the NW plume, five wells in the NE plume, two wells in the principal source area of both plumes (one each in the UCRS and RGA), and two background wells (Figure 1). Thirteen of the wells are completed in the aquifer of interest (the RGA) and two wells are completed in the UCRS. The selection of well sampling locations was patterned after the recom-

mended approach in ref 16. All of the monitoring wells are constructed of 2-in. diameter stainless steel and are equipped with dedicated Well Wizard bladder pumps and packers, and most have a 1.5-m screen. Each well is packed off just above the screen to avoid unnecessary purging of water. The packed-off volume was purged three times prior to sampling, at pumping rates less than 200 mL/min.

Untreated water samples for anion and alkalinity analyses were collected in 500-mL polyethylene bottles. Volatile organic analytes for analysis by gas chromatography were collected in pre-acidified 40-mL amber glass vials having septum top lids. Samples for isotopic analysis of dissolved inorganic carbon (DIC) were collected in 10-mL vacutainers. Samples for chlorine isotopic analysis of TCE were collected in pre-evacuated 350-mL Schlenk tubes having glass valve barrels sealed with inert O-rings. All samples were placed in a cooler with ice packs for transport and then stored in a refrigerator at 4 °C prior to analysis.

Field measurements included depth to water, temperature, pH, dissolved oxygen, specific conductance,  $E_h$ , hydrogen sulfide, ammonia, and total and ferrous iron. Temperature, pH, and specific conductance were measured with a Hydrolab flow-through sampling device. Hydrogen sulfide, ammonia, and total and ferrous iron concentrations were analyzed within minutes of sample collection using colorimetric test kits.

**Chemical and Isotopic Analysis.** Nitrate, chloride, and sulfate were analyzed by ion chromatography. Dissolved  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and Ar were measured by ultrasonic vacuum extraction and mass spectrometry (26). Volatile organic compounds (VOCs), including CAHs, were analyzed using a purge-and-trap extraction method coupled with either a gas chromatograph (EPA method 8010) or a gas chromatograph/mass spectrometer (EPA method 8260).

Carbon isotope ratios in DIC were measured after  $\text{CO}_2$  liberation using phosphoric acid (26). Oxygen isotope ratios in water were measured by  $\text{CO}_2$  equilibration (27). Chlorine isotope ratios were measured in two Cl species: (a) dissolved inorganic chloride ( $\text{Cl}^-$ ) precipitated as AgCl and (b) dissolved organic chloride from CAHs (comprising  $\geq 99\%$  TCE in all but one of the samples) extracted from water by using a combination of vacuum extraction, He purging, and cryo-distillation techniques (26). Carbon isotope ratios of TCE were not measured because the sampling procedure used for this study resulted in a large excess of background  $\text{CO}_2$  in the extracted CAH fractions. Chlorine from the AgCl precipitates and CAH extracts was converted to methyl chloride ( $\text{CH}_3\text{Cl}$ ) for mass spectrometric analysis (13). Carbon isotope ratios of  $\text{CO}_2$  were measured at masses 44, 45, and 46 (as  $\text{CO}_2^+$ ), and chlorine isotope ratios of  $\text{CH}_3\text{Cl}$  were measured at masses 50 and 52 (as  $\text{CH}_3\text{Cl}^+$ ) on a modified VG Prism II dual-inlet gas-source isotope ratio mass spectrometer. Isotopic compositions are reported in per mil (‰) deviation from isotopic standard reference materials using the conventional  $\delta$  notation:

$$\delta = ((R_{\text{sample}}/R_{\text{standard}}) - 1) \times 1000 \quad (1)$$

where  $R = {}^{13}\text{C}/{}^{12}\text{C}$ ,  ${}^{18}\text{O}/{}^{16}\text{O}$ , or  ${}^{37}\text{Cl}/{}^{35}\text{Cl}$ . The isotopic standard reference materials are Vienna Pee Dee Belemnite (V-PDB) (28) for carbon, Vienna Standard Mean Ocean Water (V-SMOW) for oxygen (29), and Standard Mean Ocean Chloride (SMOC) for chlorine (7). Analytical precisions of the isotope ratios are  $\pm 0.1$ – $0.2\%$ .

## Results and Discussion

An important factor in studies of this type is the heterogeneity and complexity of the system being sampled. The distribution of contaminants and microbes is heterogeneous at the pore scale, where complex DNAPL–water mass transfer and

biodegradation mechanisms operate (30). This heterogeneity is orders of magnitude smaller than the screened interval being sampled in each monitoring well, and the plume is orders of magnitude larger still. Therefore the data generated for each groundwater sample must be viewed as representing an average of many, much smaller microenvironments, and in this sense interpretations must be made with caution. The interpretation of stable chlorine isotope ratios in this context requires a thorough understanding of the potential causes of isotopic variability in TCE, whether primary (intrinsic to the source) or secondary (effected by biotic and abiotic processes).

The average groundwater sampled at PGDP has  $\delta^{18}\text{O}$  values that vary from  $-5.8\text{‰}$  to  $-4.9\text{‰}$ . Dissolved  $\text{O}_2$  concentrations vary from 1.0 to 7.9 mg/L, pH values from 5.7 to 6.8, and  $E_h$  values from 120 to 460 mV (Table 1). Chemical indicators of electrochemical status are generally consistent with conditions favorable to aerobic microbial respiration (e.g.,  $\text{CH}_4 < 0.002$  mg/L;  $\text{NH}_3 \leq 0.1$  mg/L,  $\text{H}_2\text{S} \leq 0.02$  mg/L,  $\text{Fe}^{2+} \leq 0.2$  mg/L). These data indicate that if anaerobic conditions are present within the system they occur within microenvironments that represent only a relatively small fraction of the volume being sampled.

The concentrations of dissolved TCE range from  $<0.001$  to 180 mg/L. Compounds known to be produced by anaerobic biodegradation of TCE [including *cis*-1,2-dichloroethene (*cis*-DCE), vinyl chloride (VC), and ethene] are present at relatively low concentration (*cis*-DCE in some wells) or are undetectable (VC and ethene). The highest *cis*-DCE concentrations were measured in UCRS wells 157 and 187, where conditions favorable to anaerobic TCE degradation are most likely to have existed at some point in the history of the site. The area in which well 187 is located [Solid Waste Management Units (SWMUs) 7 and 30] was the site of a gasoline spill, an incinerator, and a fire training ground, thus there were abundant sources of organic carbon that could sustain anaerobic conditions. In a nearby UCRS well that was not sampled during this study, the VC concentration measured previously was greater than those of *cis*-DCE and TCE. Traces of toluene have also been detected in some UCRS and RGA wells in this area. The presence of *cis*-DCE and VC indicate that anaerobic TCE degradation has occurred within the system.

The concentrations of DIC increase and  $\delta^{13}\text{C}$  values of DIC decrease with decreasing  $\text{O}_2$  in the PGDP groundwater. This indicates  $\text{O}_2$  consumption and  $\text{CO}_2$  production by aerobic microbial respiration. The decrease in C isotope ratio with increasing DIC concentration indicates that microbial respiration involves oxidation of an organic carbon substrate having a  $\delta^{13}\text{C}$  value  $< -20\text{‰}$ . This carbon source could be either natural dissolved organic matter or contaminants (including TCE), but the C isotope data are not uniquely diagnostic of a particular source. Dissolved  $\text{O}_2$  concentrations are always appreciable ( $\geq 1.0$  mg/L), indicating that aerobic respiration is nutrient- or transport-limited, and/or distributed recharge of oxygenated water is occurring throughout the aquifer. The sample having the highest DIC concentration (from UCRS well 187) also has the highest  $\text{Cl}^-$  concentration, the highest *cis*-DCE/TCE ratio, and the lowest  $\text{O}_2$  concentration, indicating that at least some of the DIC may have been produced by anaerobic degradation of TCE within the UCRS.

The  $\delta^{37}\text{Cl}$  values of TCE range from  $-1.0$  to  $+2.0\text{‰}$ . The  $\delta^{37}\text{Cl}$  value increases with decreasing TCE concentration in the aquifer (Figure 2). The lowest measured  $\delta^{37}\text{Cl}$  value for TCE was from a UCRS well (157) in which near-saturated TCE concentrations ( $>900$  mg/L) had been previously measured and which is located adjacent to the major source of TCE contamination on the site ( $\geq 100\,000$  kg of spillage estimated from 1952 to 1993). The relationship of  $\delta^{37}\text{Cl}$  values

with the concentrations of TCE (Figure 2) resembles that of a Rayleigh-type isotopic fractionation model for dechlorination of TCE from a uniform reservoir. An isotopic fractionation factor,  $\alpha$ , can be derived from the analytical data by using the exponential function

$$R/R_0 = F^{\alpha-1} \quad (2)$$

where  $R$  and  $R_0$  are the  $^{37}\text{Cl}/^{35}\text{Cl}$  ratios of the residual TCE and the initial TCE, respectively, and  $F$  is the fraction of TCE remaining. This function describes the familiar Rayleigh-type isotopic fractionation that accompanies a variety of natural processes. The data shown in Figure 2 yield a best-fit  $\alpha$  value of 0.999475. This  $\alpha$  value is an upper limit, because significant decrease in TCE concentration in the plumes must be attributed to dispersion and mixing with TCE-free water. Experimental  $\alpha$  values for Cl isotopic fractionation by microbial degradation of TCE are not yet available, though an  $\alpha$  value of 0.9962 has been reported for aerobic microbial degradation of dichloromethane (31).

The relation between the  $\delta^{37}\text{Cl}$  values and concentrations of  $\text{Cl}^-$  is shown in Figure 3. All plume samples have higher  $\text{Cl}^-$  concentrations than the background wells (103 and 194), and there is a correlation of increasing  $\text{Cl}^-$  with decreasing TCE (i.e., decreasing values of  $F$ ). This indicates that increases in  $\text{Cl}^-$  concentration could have resulted from TCE degradation. An alternative explanation is that this correlation could have resulted from input of other sources of dissolved  $\text{Cl}^-$ ; however, we are aware of no major sources of groundwater  $\text{Cl}^-$  input, other than TCE degradation, in the study area. Weather conditions requiring use of road salt are rare in Paducah, KY, and other potential major sources (such as salt piles, landfills, evaporite deposits, atmospheric deposition of sea salt, trapped seawater, and saltwater intrusion) are absent. The site is devoid of water softeners and septic systems, and there has been no agricultural activity on the PGDP property since the plant began operations in 1951. The only wells that could be affected by current agricultural activities are 100, 146, and 194. Comparison of the background wells sampled upgradient of the plume, 103 (beneath undeveloped grassland) and 194 (in forested area adjacent to cornfield), shows that only about 18 mg/L  $\text{Cl}^-$  and 6 mg/L  $\text{NO}_3^-$  could be attributed to agricultural input in well 194. The relatively high  $\text{NO}_3^-$  concentrations in wells 66, 248, and 262 may be related to a nitric acid spill that occurred upgradient of well 262.

Simple closed-system models of TCE degradation are generally inconsistent with the data shown in Figures 2 and 3. If we assume the initial TCE concentration and  $\delta^{37}\text{Cl}$  value for TCE are those measured in sample 157 (180 mg/L,  $-1.0\text{‰}$ ), the background  $\text{Cl}^-$  concentration and  $\delta^{37}\text{Cl}$  value are those measured in sample 194 (20 mg/L,  $+1.1\text{‰}$ ), and the  $\alpha$  value for TCE degradation is 0.999475 as estimated from the data in Figure 2, then we can predict the trajectory of a closed-system model labeled "A" in Figure 3. This model cannot explain the data, with the exception of samples 157 and 193, even by accounting for dilution with background water, because the predicted  $\delta^{37}\text{Cl}$  values for  $\text{Cl}^-$  are lower than the measured values. An alternative closed-system model labeled "B" in Figure 3, where the initial  $\delta^{37}\text{Cl}$  value for TCE is  $+1.5\text{‰}$  and the  $\alpha$  value is 0.997375 (five times larger isotopic fractionation than  $\alpha = 0.999475$ ). Model B, when accounting for dilution by background water, is consistent with the data in Figure 3 but is not consistent with the TCE isotopic data because it generally predicts much higher  $\delta^{37}\text{Cl}$  values for TCE than those measured. For example, model B predicts that the  $\delta^{37}\text{Cl}$  values for TCE at  $F = 0.1$  and  $F = 0.01$  are  $+7.6\text{‰}$  and  $+13.6\text{‰}$ , respectively.

The failure of such simple models to account for the data implies that a model involving additional complexity is

TABLE 1. Chemical and Isotopic Composition of Paducah Groundwater<sup>a</sup>

	regional gravel aquifer wells														
	background wells		UCRS wells		northwest plume						northeast plume				
	well no.														
temp (°C)	103	194	187	157	262	66	248	233	146	155	108	255	124	193	100
E <sub>h</sub> (mV)	17	16	14	17	16	15	15	15	17	18	18	17	16	17	18
pH (units)	191	178	180	380	200	280	160	170	160	200	460	190	120	160	190
DIC <sup>b</sup>	6.2	5.9	6.2	6.8	5.7	5.7	5.7	6.0	6.0	5.9	6.0	6.0	5.8	6.3	5.9
Cl <sup>-</sup>	124	104	351	99	127	106	102	124	125	139	150	223	130	178	125
SO <sub>4</sub> <sup>2-</sup>	3	20	120	30	70	50	50	25	30	85	60	90	70	20	50
NO <sub>3</sub> <sup>-</sup>	5.5	7.0	15	115	10	10	10	15	8.8	10	25	30	10	9.5	7.9
NH <sub>3</sub>	<0.5	6.3	<0.5	<0.5	50	35	30	7.5	15	9.0	9.3	6.8	6.1	0.7	20
H <sub>2</sub> S	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
Fe <sup>2+</sup>	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01
O <sub>2</sub>	0.1	0.1	0.2	<0.1	<0.1	— <sup>c</sup>	<0.1	0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
N <sub>2</sub>	4.4	7.0	1.0	7.6	4.4	7.9	4.7	5.9	5.9	5.6	4.0	1.0	3.3	3.6	5.6
Ar	27.1	26.0	27.5	22.1	25.6	31.0	26.1	25.5	26.1	26.6	25.3	29.3	27.1	26.4	27.6
CH <sub>4</sub>	0.9	0.9	0.9	0.7	0.7	0.9	0.9	0.9	0.9	0.9	0.7	1.1	0.9	0.9	0.9
TCE (μg/L)	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
cis-DCE ((g/L)	<1	<1	490	180 000	16 000	13 000	12 000	150	1	700	950	1300	1100	4	<1
VC (μg/L)	2	<1	84	130	44	58	<1	<1	<1	7	21	10	3	<1	2
ethene (μg/L)	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
δ <sup>18</sup> O, H <sub>2</sub> O (‰)	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
δ <sup>37</sup> Cl, TCE (‰)	-4.9	-5.8	-5.4	-5.3	-5.4	-5.4	-5.6	-5.8	-5.8	-5.5	-5.5	-5.5	-5.3	-5.8	-5.6
δ <sup>37</sup> Cl, Cl <sup>-</sup> (‰)	—	—	—	-1.0	+0.2	+0.6	+0.4	+1.6	—	+1.6	+1.5	—	+2.0	+1.6	—
δ <sup>13</sup> C, DIC (‰)	—	+1.1	+0.7	+0.3	+0.8	+0.9	+0.8	+1.1	+0.8	+1.0	+0.8	—	+1.4	+0.9	+1.1
	-18.4	-16.5	-19.4	-12.0	-18.5	-17.9	-15.4	-16.7	-17.9	-16.8	-17.9	-18.2	-20.0	-19.8	-19.1

<sup>a</sup> Well locations shown in Figure 1. Concentrations are in mg/L unless otherwise indicated. <sup>b</sup> Dissolved inorganic carbon <sup>c</sup> —, not analyzed.



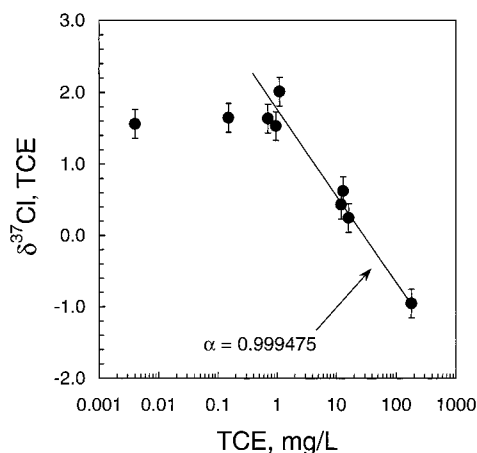


FIGURE 2. Diagram showing  $\delta^{37}\text{Cl}$  value of TCE (‰) vs TCE concentration (mg/L) in water samples. Solid line is exponential best-fit yielding  $\alpha = 0.999475$ .

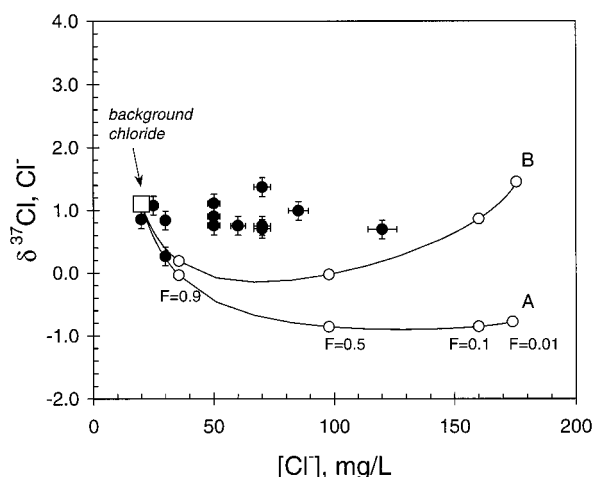


FIGURE 3. Diagram showing  $\delta^{37}\text{Cl}$  values of  $\text{Cl}^-$  (‰) vs  $\text{Cl}^-$  concentration (mg/L) in water samples. Also shown are calculated trajectories for closed-system dechlorination of TCE as a function of fraction remaining ( $F$ ) for different (values and initial values of  $\delta^{37}\text{Cl}$  for TCE (see text for explanation).

required. Complex models could involve: time-dependent changes in the  $\delta^{37}\text{Cl}$  value of TCE and/or of the activity of anaerobes capable of TCE degradation in the source; multiple TCE sources having different isotopic compositions; isotopic fractionation caused by processes other than microbial degradation; differential transport of TCE and  $\text{Cl}^-$ ; or other influences on the concentrations and isotopic compositions of TCE and  $\text{Cl}^-$ . The ability to develop such complex models for TCE and other CAHs will require precise laboratory studies on the magnitude of isotopic fractionation that accompanies such processes as volatilization, solubilization, adsorption, isotope exchange, and biotic and abiotic degradation.

We suggest that TCE degradation may have been more extensive within the UCRS early in the site's history, under conditions favorable to anaerobic degradation (e.g., large amounts of organic co-contaminant), and then conditions changed such that degradation slowed or ceased (e.g., the co-contaminant was consumed). In this case, significant isotopic variations generated near the source area may have propagated outward with time in the aquifer. Volatilization could have been an important process in the vadose zone in the upper part of the UCRS; there is currently a large vadose plume of TCE around the source area near wells 155 and 157. Additionally, vertical transport of DNAPL through the UCRS into the RGA may have resulted in trails of dispersed, residual

TCE that degraded (or volatilized) preferentially relative to that comprising the main, relatively undegraded pools of DNAPL. This form of residual TCE could have an overall  $^{37}\text{Cl}$ -enriched composition (e.g.,  $\delta^{37}\text{Cl}$  values ranging from +1.5‰ to +2.0‰) that could, if quantitatively degraded, yield the relatively  $^{37}\text{Cl}$ -enriched  $\text{Cl}^-$  (e.g.,  $\delta^{37}\text{Cl}$  values ranging from +1.0‰ to +1.5‰) required to explain the data in Figure 3. The occurrence of  $^{37}\text{Cl}$ -depleted TCE in the mid-plume area, but not in the distal areas, could reflect the timing of DNAPL transport from the UCRS in the source area (well 157) to a DNAPL pond at the base of the RGA. Volatilization and microbial degradation processes are not likely to have been important within the RGA; these processes are contradicted by the good correlation between TCE and its nonvolatile co-contaminant tracer  $^{99}\text{Tc}$  throughout the NW plume in the RGA (25).

This study demonstrates that stable Cl isotope ratios provide a powerful tool for evaluating the effectiveness of natural attenuation. At the PGDP site, the isotopic measurements support partial natural attenuation of TCE. This interpretation is consistent with the available hydrogeologic data and the history of activities at the site. In contrast, the conventional approach for evaluating natural attenuation, which does not consider isotopic ratios (e.g., ref 16), indicates inadequate evidence for natural attenuation. On the basis of these findings, which may have significant implications for site remediation, we suggest to incorporate stable chlorine isotope ratio measurements routinely into investigations of sites contaminated with CAHs.

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