Hydrochemical Facies Analysis of 1,1,1-Trichloroethane and its Degradation Products in Fractured Bedrock

H. Jean Cho, R. Joseph Fiacco, Jr., Matthew H. Daly and John W. McTigue
(Environmental Resources Management, Boston, MA)

Abstract

A release of 1,1,1-trichloroethane (TCA) has resulted in a groundwater plume located in a fractured crystalline bedrock. TCA's three degradation products—1,1-dichloroethane (DCA), 1,1-dichloroethene (DCE) and acetic acid—are also present in groundwater. Significant chloride concentrations exist in and down-gradient of the source area. The distribution and relative concentrations of these five constituents—TCA, DCA, DCE, acetic acid and chloride—have been used to evaluate natural attenuation pathways and to estimate transport velocities.

The source area is adjacent to a surface water divide and is at the top of a groundwater recharge area. Therefore, one would not expect to encounter significant chloride in the groundwater samples. Nevertheless, in the source area, chloride concentrations exceeding 500 milligrams per liter (mg/L) have been measured. These elevated chloride concentrations are attributed to dechlorination of TCA via abiotic and biological mechanisms.

Acetic acid is created during the destruction of TCA via hydrolysis, an abiotic degradation pathway. DCE is produced from TCA abiotically via the elimination of chloride. DCA is produced by the biological reductive dechlorination of TCA. Abiotic degradation of TCA via hydrolysis and elimination is the primary degradation pathway at the site. Biodegradation is not a key transformation pathway of TCA at the site.

The degree of degradation can be easily visualized using ternary diagrams, following the technique used by Lipson and Siegel (*Ground Water*, 38:106-113, 2000) for petroleum hydrocarbons. The mole percentage of DCE relative to the sum of TCA, DCA and DCE increases from less than 10% in the source area to 40% in bedrock beneath an overburden aquifer, which serves as the discharge area for the fractured bedrock system.

The half-life of the two abiotic degradation pathways (hydrolysis to acetic acid and elimination to DCE) has been measured by numerous studies, both in the laboratory and in the field. Therefore, the observed increase in DCE mole percentage with distance from the source area can be used to estimate groundwater velocities in fractured bedrock. Furthermore, the relative enrichment in chloride of source area groundwater compared to un-impacted groundwater can be used to assess the residence time of groundwater in the source area. The hydrochemical data suggests a source area residence time of up to six years, followed by a down-gradient travel time to the groundwater discharge area of approximately one to three years.

Introduction

The hydrochemical facies analysis (HFA) technique was developed in the 1960s as a tool for categorizing waters based on their major ion composition (see discussion of early history in Freeze and Cherry, 1979). One form of HFA is the Piper Diagram, in which major cations and major anions are plotted on ternary diagrams in order to illustrate which cations and anions dominate. When plotted in this fashion, the data can be used to illustrate the evolution of water quality as it migrates through the ground (typically from bicarbonate-rich water to chloride-rich water) or as it mixes with water of a different composition. In recent years, the HFA concept has been expanded to include minor constituents of groundwater, such as petroleum hydrocarbons (e.g., Lipson and Siegel, 2000).

The HFA technique was applied at a fractured crystalline bedrock site where groundwater has been impacted by 1,1,1-trichloroethane (TCA) and its degradation products, 1,1-dichloroethane (DCA) and 1,1-dichloroethene (DCE). HFA was used in combination with bedrock fracture orientation and groundwater elevation data to identify the primary groundwater migration pathway within the fractured bedrock aquifer. In addition, chemical composition data were used to evaluate groundwater residence time within the source area and travel time along the plume axis down-gradient of the source area.

Basic Principals

The basic theory governing the HFA is that a series of predictable natural processes (e.g., sorption, volatilization or degradation) can affect groundwater quality over time at a single location or along a groundwater flow path. By understanding these processes, it is possible to evaluate which one(s) affect the fate of groundwater as it migrates through an aquifer. For instance, to evaluate processes affecting the fate of TCA in groundwater, it is important to gather data regarding the physical and chemical properties of TCA and its degradation products, DCA and DCE (Table 1).

Table 1. Physical and Chemical Properties

Chemical of Interest	Maximum Solubility (mg/L)	Log K_{OC}	Henry's Law Const. (atm m^3/mol)	Vapor Pressure (mm Hf @20°C)	Anaerobic Biodegradation Half Life (Days)	Abiotic Degradation Half Life (Years)
1,1,1-Trichoroethane	1,255	2.45	$1.08x10^{-3}$	123	231 (to DCA)	2 (to DCE)
1,1-Dichloroethane	5,500	1.48	$5.87x10^{-3}$	182	60	43
1,1-Dichloroethene	5,000	1.81	$2.55x10^{-2}$	495	173	$1.2x10^{8}$

References: Groundwater Chemicals Desk Reference by J.H. Montgomery and L.M. Welkom (1989)
Fate of Chlorinated Aliphatic Hydrocarbons in the Vadose Zone and Ground Water by Barbee (1994)
Dense Chlorinated Solvents by Pankow and Cherry (1996)

Table 1 shows that TCA has the highest octanol-water partition coefficient and that DCA has the lowest. Therefore, if sorption is the most important reaction pathway, then over time (or along a groundwater flow path), the groundwater will become enriched in DCA as more and more TCA sorbs to aquifer material. This is illustrated in Figure 1. In Figure 1, it is assumed that the groundwater at the source (or at time 0) is 90.5% TCA, 3.3% DCA and 6.2% DCE. All percentages are mole percentages. Over time, or along a groundwater flow path, the groundwater composition will change in a manner illustrated by the red line if sorption is the primary fate mechanism, with a final composition that is almost entirely DCA. The HFA predicts not only the endpoint, which could be achieved by a simple comparison of partition coefficients, but also the intermediate stages of the sorption attenuation pathway.

If the primary transformation pathway is the physical process of volatilization, then the Henry's Law constant would determine the evolution in groundwater composition. For the three compounds selected, the groundwater

would become increasingly enriched in TCA (see Figure 1). If, rather than sorption or volatilization, biodegradation is the primary reaction pathway, then the HFA predicts the behavior shown in red in Figure 2, with the mixture becoming increasingly enriched in DCA. If abiotic degradation is the primary pathway, then the mixture will become increasingly enriched in DCE, as shown in Figure 2.

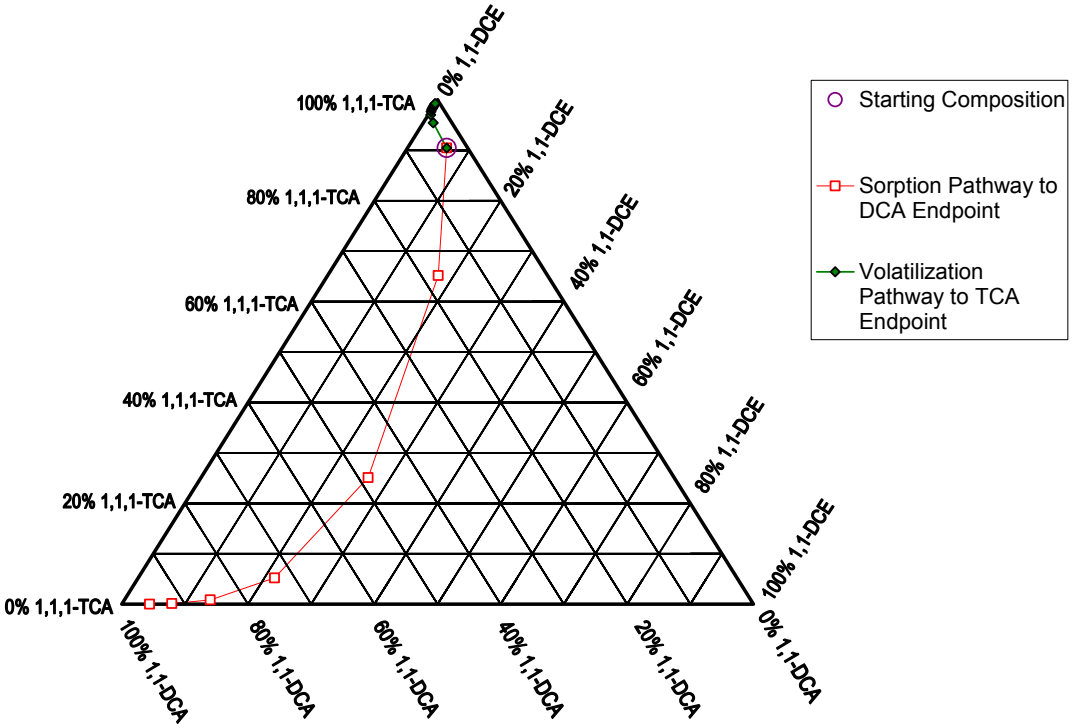

Figure 1. Trilinear Diagram Showing Sorption and Volatilization Pathways

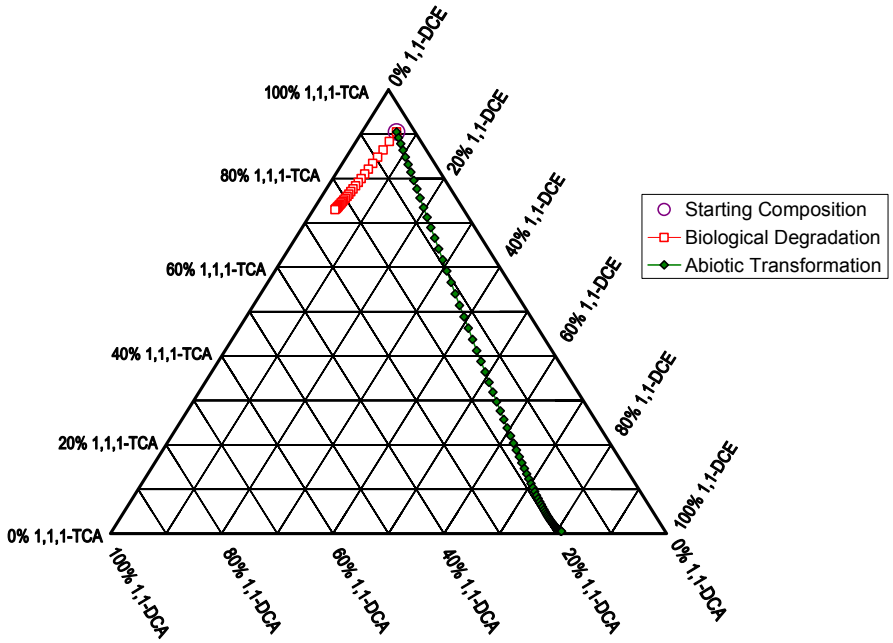

Figure 2. Trilinear Diagram Showing Biodegradation and Abiotic Degradation Pathways

Methods

An HFA analysis is conducted by plotting mole fraction data on a ternary diagram. The ternary diagram is uniquely suited to this analysis because three compounds, TCA, DCA and DCE, are consistently found in site wells. The ternary diagrams used in the HFA were plotted using the following steps:

- three compounds were selected (i.e., TCA, DCA and DCE);
- mass concentrations (e.g., milligrams per liter (mg/L)) were converted to molar concentrations (e.g., micromolar (μM));
- mole fractions were computed for the three compounds; and
- the mole fractions were plotted on the ternary diagram.

If a compound was not detected in a sample, half of the detection limit was used to denote the actual concentration. If, however, a compound that was not detected was computed to have a mole percentage (based on half the detection limit) greater than 5%, that sample was excluded from the ternary diagram.

Because much of the TCA plume is present at some depth below the water table, volatilization was not expected to be a significant transport or fate pathway. The rock has negligible organic matter, so sorption was not expected to be a major pathway. Therefore, the HFA was primarily used to distinguish between biological and non-biological degradation pathways (illustrated in Figure 2).

Results

Source Area

Residual DNAPL in bedrock fractures was delineated by coupling the results of geophysical imaging logs with data collected using immiscible-fluid absorbent liners (i.e., NAPL FLUTe liners). TCA concentrations in groundwater from fractures containing residual DNAPL ranged from 410 milligrams per liter (mg/L) to 640 mg/L (i.e., 32 percent to 49 percent of solubility), with an average source area concentration of 360 mg/L (i.e., greater than 100 □M). Figure 3 shows the layout of the 12 source area wells on the left. On the right side of Figure 3, the mole percentages of TCA, DCA and DCE in these wells are plotted for three sampling rounds. The data collected in 1999 showed that the groundwater in the source area was dominated by TCA, with TCA mole percentages ranging from 80% to 96%. This is attributed to the on-going dissolution of residual TCA DNAPL, which would have resulted in high mole fractions of the parent compound in source area wells.

The molar fractions of TCA remained above 80% in these wells until the August 2002 sampling round, shown in Figure 3. By this time, the average TCA concentration had decreased as a result of remedial activities in the source area. In conjunction with decreasing TCA concentrations, the mole percentages of TCA's degradation products began to increase. By August 2002, the mole percentage of DCE ranged from 9% in wells where DNAPL was inferred to be present to 28% at wells where significant concentration decreases had been observed.

In May 2003, the average TCA concentration in source area wells had dropped to 46 mg/L. The range of TCA mole percentages had increased; the range was now 40% to 97%. The maximum DCE mole percentage was 42%. The mole percentage of DCA had also increased to a maximum of 19% in two wells.

Therefore, the HFA demonstrated that as the amount of residual DNAPL has been reduced, the source area wells have shown that abiotic transformation of TCA to DCE is the preferred fate pathway. Some biodegradation to DCA is evident, but at a significantly lower rate.

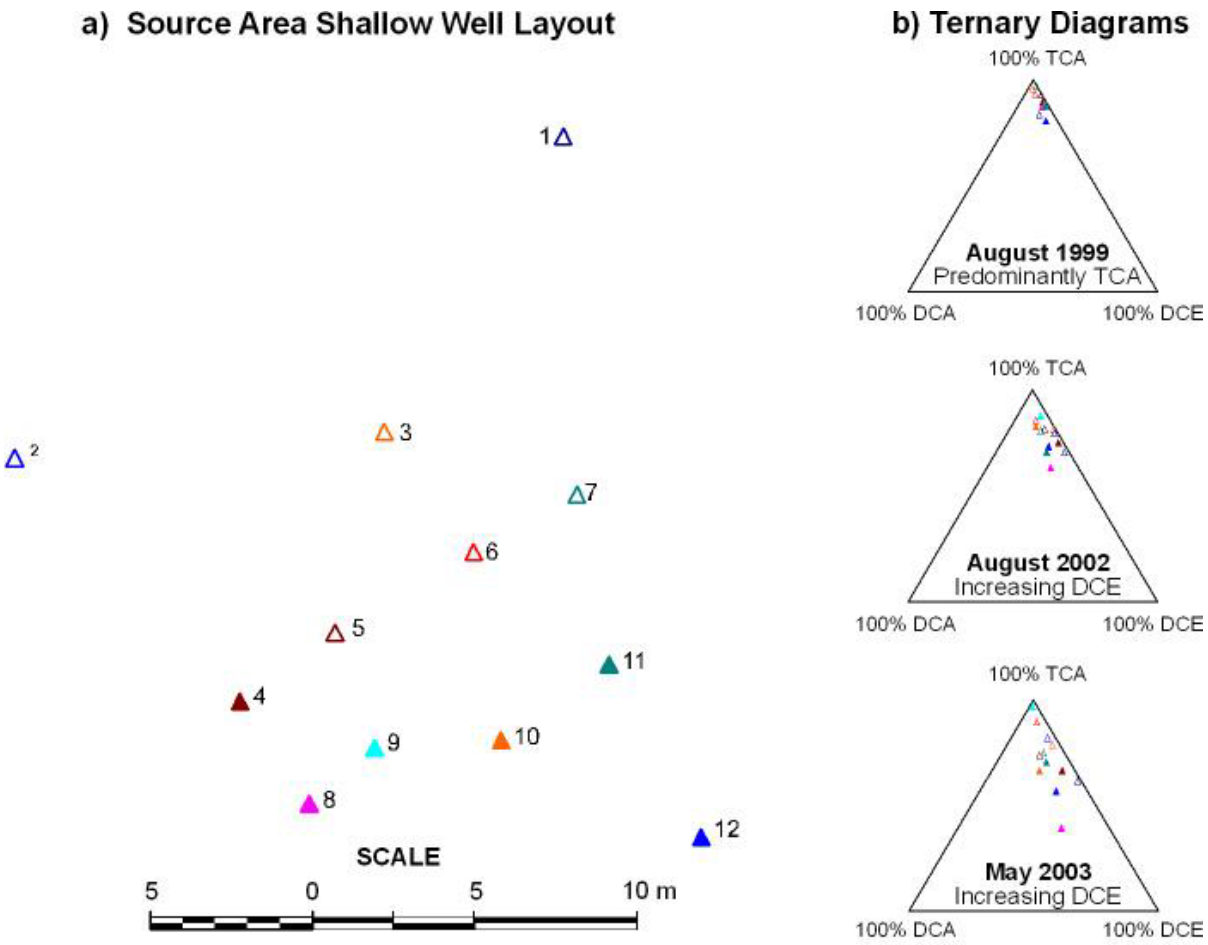

Figure 3. Source Area Data

Identification of Plume Axis

The HFA was applied to wells from across the site in May 2003 (Figure 4). The area shaded in yellow in Figure 4 comprises the source area and the centerline of the plume. As shown, the total TCA+DCA+DCE concentrations in the majority of these wells exceeded 100 µM. These wells were also characterized by groundwater solutions where the dominant volatile organic compound (VOC) was TCA, as indicated in the ternary diagram on the left side of Figure 4.

Up- and cross-gradient of the source area, TCA has been degraded by abiotic and biological pathways to DCE and DCA, respectively. Down-gradient of the plume core, progressive degradation of TCA to DCE, and to some extent DCA, is evident.

In summary, groundwater in the source area, where residual DNAPL was present, is characterized by a TCA-rich chemical signature. In the immediate area down-gradient of the source, TCA levels continue to be elevated as the migration of TCA-rich groundwater from the source area compensates for any degradation that occurs. Up-gradient and cross-gradient of the source area, the chemical signature becomes more degraded indicating that abiotic and biotic degradation was not balanced by residual DNAPL dissolution. Similarly, down-gradient of the plume core, natural attenuation via abiotic and biological pathways has resulted in groundwater with significant proportions of DCE and DCA relative to TCA.

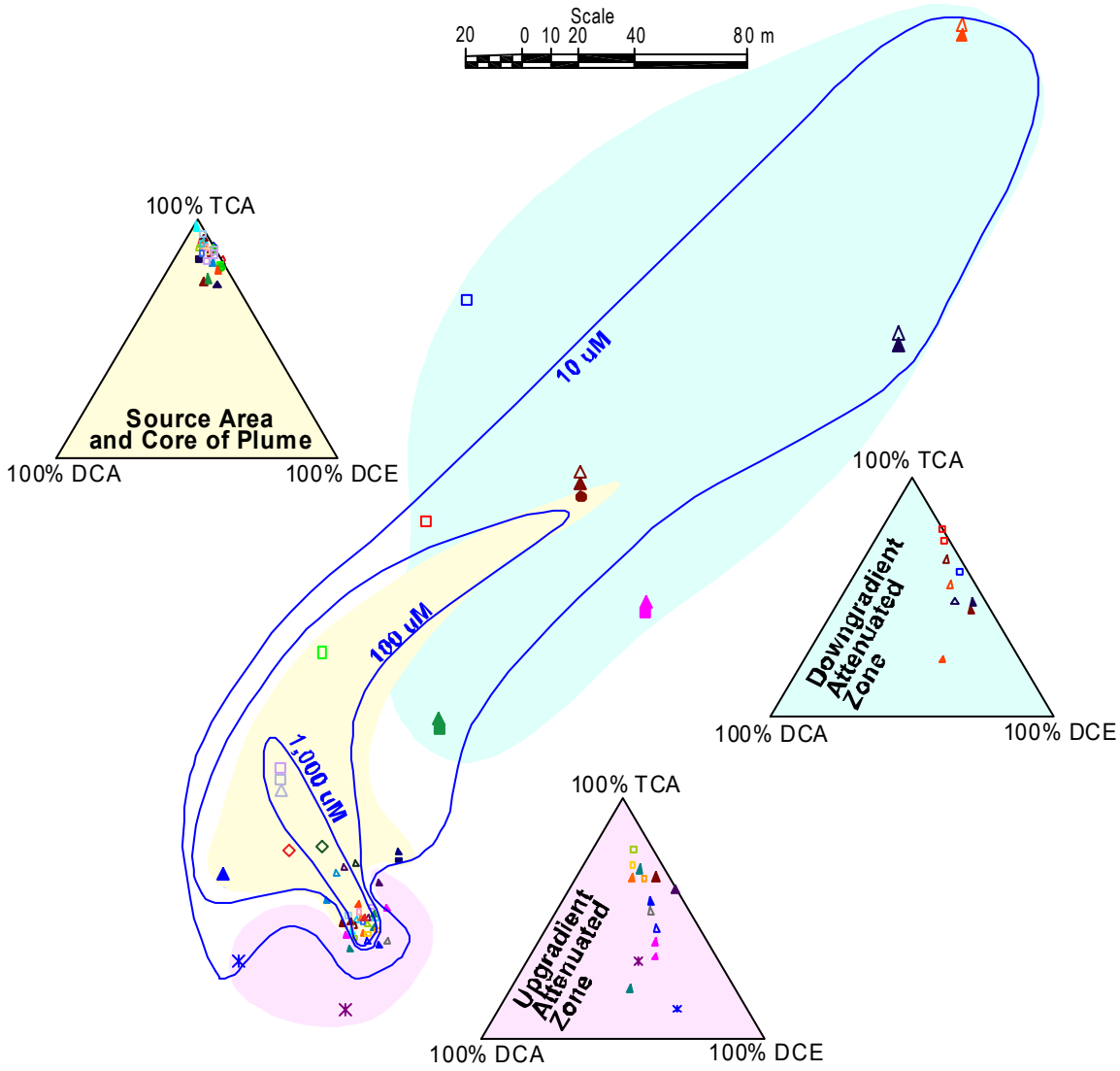

Figure 4. Plume Data Schematic, May 2003

Chloride Concentrations

The source area is located beneath a building on the top of a hill immediately down-gradient of a groundwater flow divide. Very limited groundwater recharge occurs between the groundwater flow divide and the suspected source area. Because there are no up-gradient sources of chloride, chloride concentrations in groundwater should be relatively low. However, chloride concentrations in the crystalline bedrock source area exceed 500 mg/L, as shown in Figure 5. The highest chloride concentrations coincide with wells that are located within the residual DNAPL source area. As noted above, TCA concentrations have decreased significantly within the source area and enhanced degradation of TCA has occurred since 1999. The chloride, which is a conservative ion, is therefore assumed to come from the dechlorination of TCA.

Significant downward vertical hydraulic gradients have been measured in the source area, resulting in groundwater migration that is both vertically downward and in the down-gradient horizontal direction. This is evidenced in Figure 5 by the similar shape and location of the highest chloride concentrations in both the shallow and deep bedrock source area wells. Conversely, an elongated chloride plume is present in the deep bedrock wells only, indicating down-gradient migration of source area groundwater in deeper bedrock. Further down-gradient of the source area, chloride concentrations range from 170 mg/L to 310 mg/L (Figure 6).

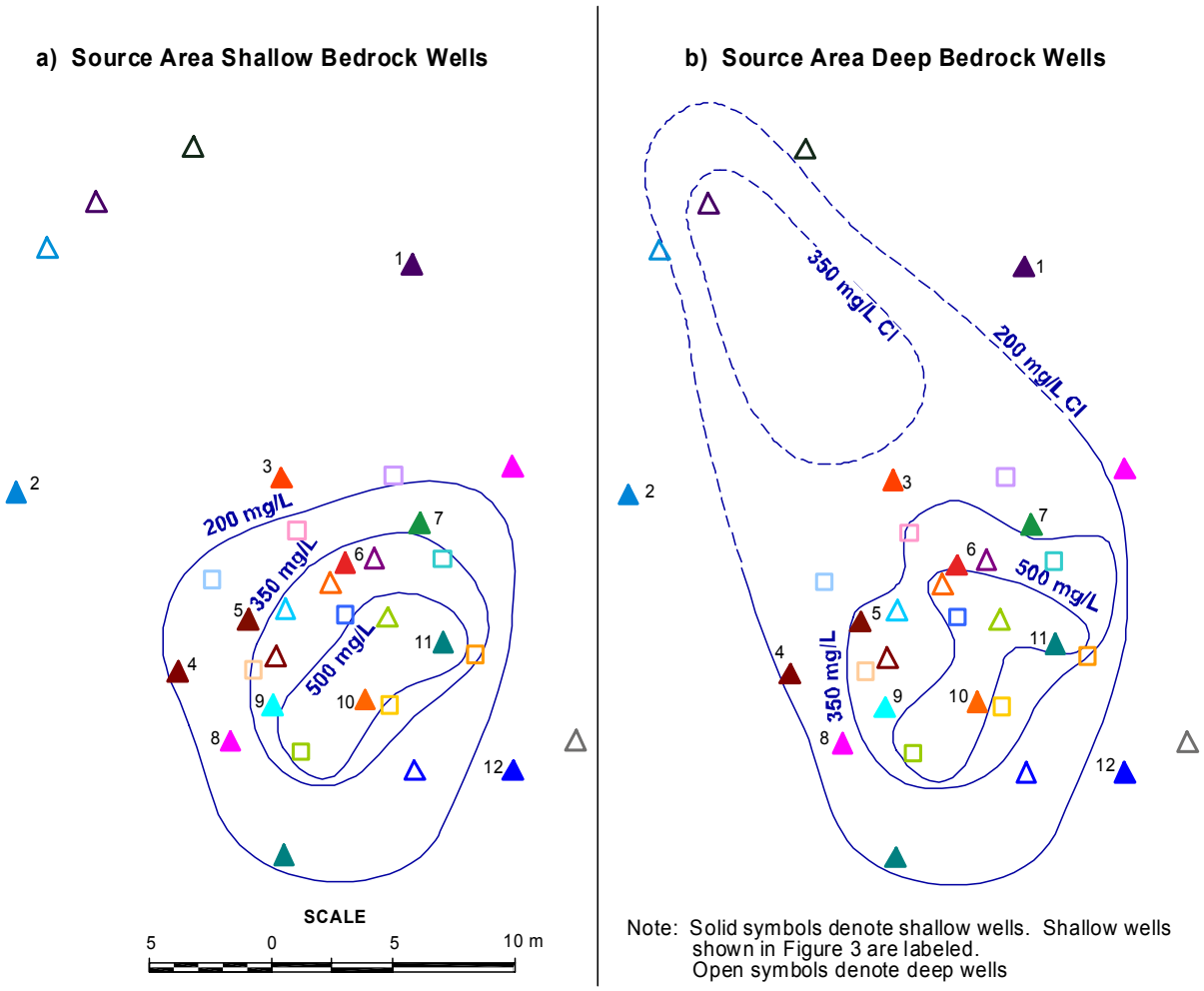

Figure 5. Source Area Chloride Concentrations

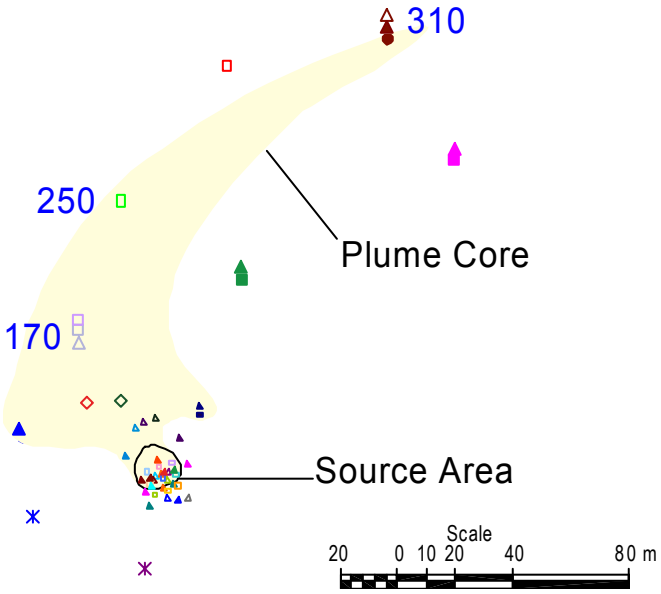

Figure 6. Down-gradient Chloride Concentrations

Acetic Acid and DCE Concentrations

The scientific literature on the abiotic degradation of TCA reports that both DCE and acetic acid are produced (Gerkens and Franklin, 1989). The literature also suggests that the hydrolysis pathway to acetic acid is slightly favored relative to elimination to DCE. Acetic acid is a byproduct of TCA transformation via hydrolysis (TCA + $2H_2O \rightarrow CH_3COOH + 3H^+ + 3Cl^-$). Unlike chloride, acetic acid is a reactive compound that is readily used as a substrate by microorganisms. The presence of acetic acid in groundwater is a function of both the degradation rate and the rate of biological activity. Therefore, the acetic acid concentration is temporally variable. Nevertheless, acetic acid can be used as an indicator of degradation and, in some cases, as a tracer. Acetic acid has been detected at concentrations up to 190 mg/L in 14 site wells. A contour plot of acetic acid detections is shown in Figure 7. The distribution of acetic acid in source area wells is similar to that of chloride. However, the zone of detectable acetic acid is narrower, due to the reactive nature of this compound.

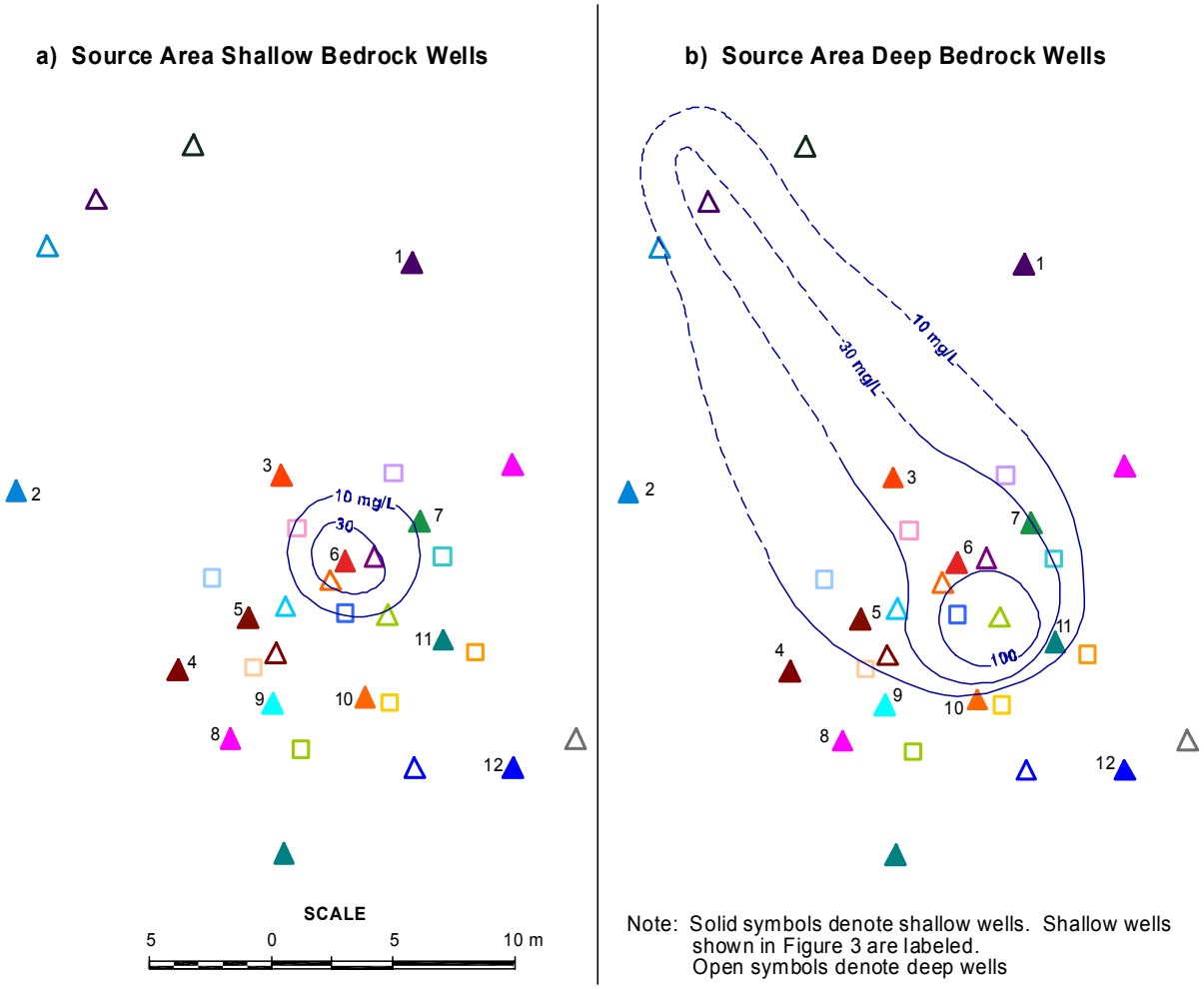

Figure 7. Source Area Acetic Acid Concentrations

TCA is degraded abiotically via an elimination reaction to DCE (TCA $\rightarrow$ DCE + H^+ + Cl^-). Figure 8 shows the relationship between DCE concentration and acetic acid concentration for all samples for which acetic acid was analyzed. For samples in which acetic acid was not detected, half of the detection limit of 5 mg/L was used. The green lines in Figure 8 have a unit slope. If half of the abiotic degradation of TCA occurred by the hydrolysis pathway and half occurred by the elimination pathway, then data would plot on the green lines. It is

evident that in some wells, particularly deep bedrock wells, significantly more acetic acid is produced, on a molar basis, than DCE. This enrichment in acetic acid occurs in spite of the high reactivity of acetic acid. Approximately half of the data plot above the green line and half plot below the green line, suggesting that the hydrolysis reaction is at least as favored as the elimination reaction.

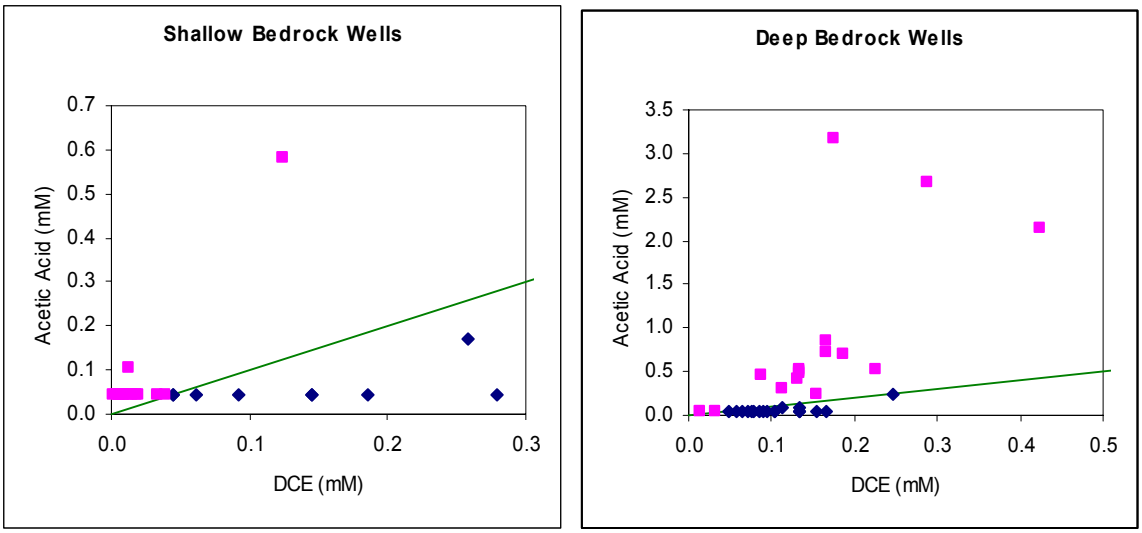

Figure 8. Comparison of DCE and Acetic Acid Concentrations

Estimate of Groundwater Travel Time Using Degradation Half-Lives

It is clear that the primary TCA degradation pathway within site groundwater is via abiotic degradation (see Figure 4). Natural abiotic transformation of TCA results in both DCE and acetic acid, with approximately half of the TCA degrading to acetic acid. The total abiotic half-life of TCA, combining both elimination and hydrolysis pathways, is approximately five years at a temperature of 15°C (McCarty, 1994).

Using this information, an estimated groundwater travel time at the site was computed, building upon the molar ratios of TCA, DCA and DCE and the known half-life of TCA. This analysis makes the following assumptions:

- TCA degradation is a first-order process. The half-life of TCA is 5 years.
- Based on the historical groundwater chemistry data set, the source concentration comprises 300mg/L of TCA, 4 mg/L of DCA, 18 mg/L of DCE, and 0 mg/L of acetic acid.
- TCA degradation occurs by abiotic transformation only. No production of DCA via biological transformation is modeled.
- Half of the TCA degradation results in DCE, and half of the degraded TCA results in acetic acid.
- No further loss of DCE (e.g., by volatilization) or acetic acid occurs.

Table 2 shows the results of this calculation. Over the course of 0.8 half-lives (i.e., four years), the mole percentage of TCA is expected to decrease from 91% to 55%, while the mole percentage of DCE increases from 7% to 43%. Because biotransformation is not modeled, the mole percentage of DCA remains essentially unchanged. The right-hand column of Table 2 identifies the wells located along the plume axis, shown in Figure 9, which have mole percentages consistent with a given degree of degradation.

Table 2. Predicted TCA, DCA and DCE Composition Changes for Site Groundwater

Time	Concentration (mg/L)			Mole Percentage			Modeled Time Based on Half-Life	Well with Similar Chemical Signature
	TCA	DCA	DCE	TCA	DCA	DCE		
Initial	300	4	18	91%	2%	7%	May 2000	D1
0.1 half-life	270	4	30	86%	2%	12%	October 2000	D2
0.2 half-life	250	4	40	81%	2%	17%	May 2001	D3
0.4 half-life	200	4	59	72%	2%	26%	May 2002	D4
0.6 half-life	170	4	80	63%	2%	35%	May 2003	D5
0.8 half-life	140	4	80	55%	2%	43%	April 2004	D6

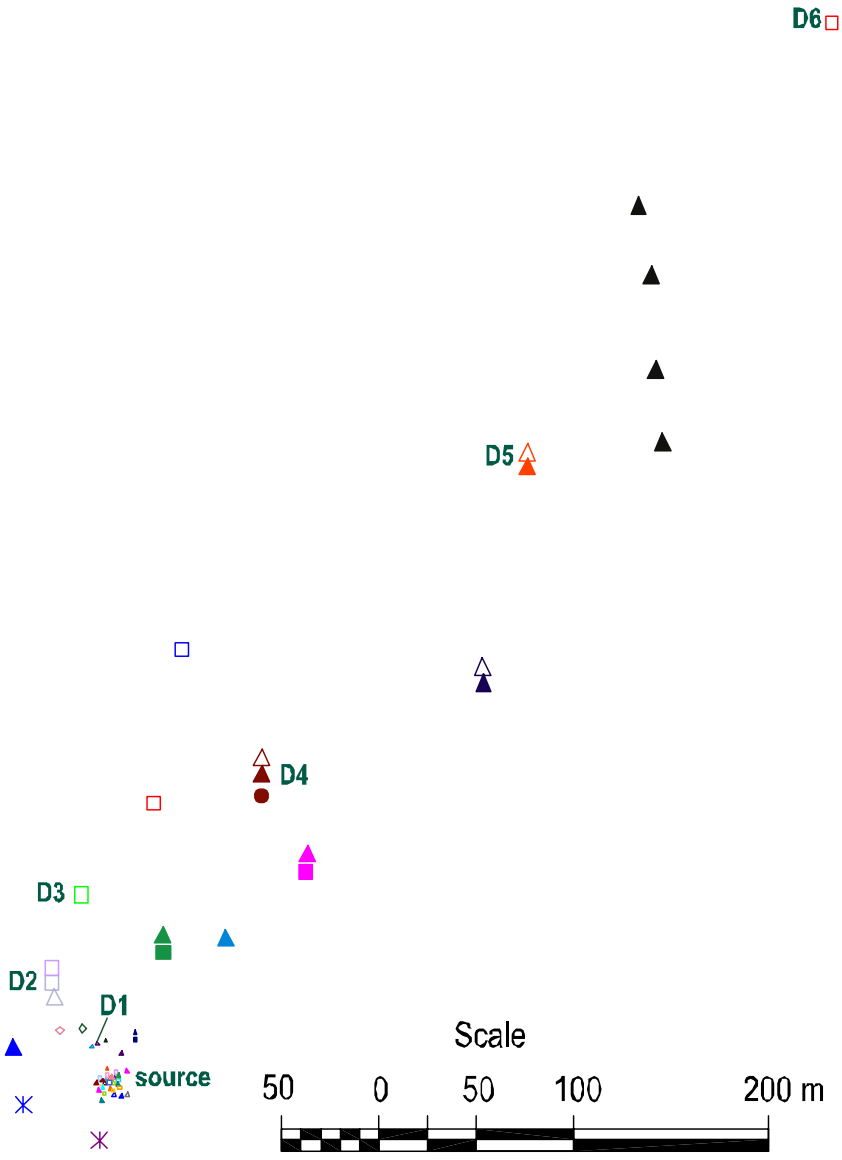

Figure 9. Comparison of DCE and Acetic Acid Concentrations

Table 3 shows the measured concentrations at wells D2 through D6 at dates as close as possible to the predicted travel time from well D1. Based on the measured concentrations, a dilution factor was calculated. This dilution factor was applied to the predicted concentrations from Table 2. The results show that between D1 and D2, relatively minimal plume dilution occurs. There is a significant drop in concentration between D2 and D3 and again between D4 and D5. By the time groundwater has reached D6, the total VOC concentration has dropped by three orders of magnitude. Although all the wells included in Tables 2 and 3 are bedrock wells, D5 is located at the edge of an overburden aquifer, and D6 is located beneath the aquifer. This may explain the significant dilution factors in these wells.

The analysis presented in Tables 2 and 3 implies a groundwater velocity ranging from 0.2 meters per day (m/d) immediately down-gradient of the source to 0.5 m/d at D6.

Table 3. Predicted and Measured Concentrations in Selected Down-gradient Wells Based on a TCA Half-Life of 5 Years

Well ID	Sample Date	Measured Concentration (mg/L)			Dilution Factor	Predicted Concentration (mg/L) with Dilution Factors Incorporated		
		TCA	DCA	DCE		TCA	DCA	DCE
D2	Dec 00	120	<1.9	18	2	136	2	14
D3	Jun 01	12	<0.3	1.4	20	12	0.2	1.9
D4	Aug 02	6.9	0.16	1.1	30	6.7	0.1	1.8
D5	May 03	0.94	0.05	0.30	190	0.87	0.02	0.36
D6	May 04	0.039	0.004	0.021	3,500	0.039	0.001	0.023

Summary and Conclusions

The primary mechanism for natural attenuation at the site is abiotic degradation to DCE and acetic acid. A further attenuation mechanism is dilution, particularly adjacent to and beneath a down-gradient overburden aquifer. A preliminary evaluation of the abiotic degradation data concludes that the plume velocity is on the order of 0.2 m/d to 0.5 m/d.

References

Freeze, R. A. and J. A. Cherry, 1979, *Ground Water*, Prentice-Hall.

Gerkens, R. R. and Franklin, J. A., 1989, "The rate of degradation of 1,1,1-trichloroethane in water by hydrolysis and dehydrochlorination," *Chemosphere*, 19, 12, 1929-1937.

Lipson, D. and D. I. Siegel, 2000, "Using ternary diagrams to characterize transport and attenuation of BTEX", *Ground Water*, 38, 1, 106-113.

McCarty, P., 1994, "An overview of anaerobic transformation of chlorinated solvents," in *Symposium on Natural Attenuation of Groundwater*, EPA/600/R-94/162, pp. 104-108.

Biographical Sketches

H. Jean Cho, Ph.D.
Ms. Cho holds a B.S. in Applied Earth Science from Stanford University and a Ph.D. in Civil Engineering from Princeton University. Her fractured bedrock projects include engineering feasibility studies for proposed open pit mines, closure assessments for open pit and underground mines, and evaluation of the transport and fate of chlorinated hydrocarbons in fractured bedrock groundwater flow systems. ERM, 399 Boylston St., 6th Floor, Boston, MA 02116; (617) 646-7800; (617) 267-6447 (fax); jeancho@alumni.princeton.edu

R. Joseph Fiacco, Jr., P.G.
Mr. Fiacco, Jr. is an Associate at ERM, where he is integrally involved in the assessment and remediation of chlorinated solvents in both fractured bedrock and overburden media. Mr. Fiacco has a B.S. in Earth Sciences from Norwich University and a M.S. in Earth Sciences from the University of New Hampshire. ERM, 399 Boylston St., 6th Floor, Boston, MA 02116; (617) 646-7840; (617) 267-6447 (fax); Joe.Fiacco@erm.com

Matthew H. Daly, P.G.
Mr. Daly is a Project Manager with ERM and his area of expertise focuses on combining chemical and hydrological data to evaluate heterogeneous aquifer systems. Mr. Daly holds a B.S. in Environmental Science from Lehigh University and a M.S. in Geology from West Virginia University. ERM, 399 Boylston St., 6th Floor, Boston, MA 02116; (617) 646-7813; (617) 267-6447 (fax); Matthew.Daly@erm.com

John W. McTigue, P.E., L.S.P.
Mr. McTigue is a Principal with ERM and has over 12 years of experience in environmental site assessment and remediation. He holds a B.A. in Geology from New England College and a M.S. in Geophysics from Boston College. Mr. McTigue has varied technical expertise in federal and state regulations site characterization, subsurface contaminant fate and transport, risk assessment/management and remediation technologies. ERM, 399 Boylston St., 6th Floor, Boston, MA 02116; (617) 646-7842; (617) 267-6447 (fax); John.McTigue@erm.com