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Anaerobic transformation of chlorinated aliphatic hydrocarbons in a sand aquifer based on spatial chemical distributions

Lewis Semprini
Department of Civil Engineering, Oregon State University, Corvallis

Peter K. Kitanidis
Department of Civil Engineering, Stanford University, Stanford, California

Don H. Kampbell and John T. Wilson
U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma

Abstract. We estimated the distribution of chlorinated aliphatic hydrocarbons (CAHs) from groundwater samples collected along three transects in a sand aquifer. Trichloroethylene (TCE) leaked and contaminated the aquifer probably more than a decade before we collected the measurements. The data show significant concentrations of TCE, cis-1,2-dichloroethylene (c-DCE), vinyl chloride (VC), and ethene. We attributed DCE, VC, and ethene to the reductive dehalogenation of TCE. The CAH concentrations varied significantly with depth and correlate with sulfate and methane concentrations. Anoxic aquifer conditions exist with methane present at relatively high concentrations at depth. High concentrations of TCE correspond with the absence of methane or low methane concentrations, whereas products of TCE dehalogenation are associated with higher methane concentrations and low sulfate concentrations. Indications are that the dechlorination of TCE and DCE to VC and ethene is associated with sulfate reduction and active methanogenesis. TCE dechlorination to DCE is likely occurring under the less reducing conditions of sulfate reduction, with further reductions to VC and ethene occurring under methanogenic conditions. We estimated that about 20% of TCE has dechlorinated to ethene. The analysis of the data enhanced our knowledge of natural in situ transformation and transport processes of CAHs.

Introduction

A sand aquifer near the town of St. Joseph, Michigan, was contaminated with trichloroethylene (TCE), 1,2-cis-dichloroethylene (c-DCE), 1,2-trans-dichloroethylene (t-DCE), 1-1-dichloroethylene (1,1-DCE), and vinyl chloride (VC). In August–September 1991, 155 groundwater samples were collected along three transects located near the areas of highest concentration. The original motivation for this study was to evaluate the potential of in situ treatment of the chlorinated aliphatic hydrocarbons (CAHs) by stimulating the growth of a native population of aerobic methanotrophic bacteria. We also undertook an analysis of these measurements to define the distribution of CAHs several years after the contamination and to obtain information on the natural mixing and transformation processes under anoxic conditions. This paper summarizes the methodology and the results of the study.

The geologic formation of interest is an unconfined aquifer consisting of a layer of unconsolidated fine sand with some silt. The water table in the study area is 7–16 m below the ground surface. The aquifer is relatively homogeneous, having been formed by eolian sorting of glacial deposits, with a hydraulic conductivity of about 10^{-4} m/s. The thickness of the sand layer is variable, ranging from 12 to 32 m, as is the elevation of the base of the aquifer that undulates over a range of about 16 m. The aquifer overlays a lacustrine clay unit, and at some points the transition from sand to clay is gradual [*Keck Consulting Services, Inc.*, 1986].

The site is bounded by Lake Michigan to the northwest and Hickory Creek to the east. The hydrology of the sandy aquifer is relatively simple: A high recharge rate (about 55 cm/yr) replenishes the aquifer, and the groundwater drains into the lake and the creek, which act as constant-head boundaries, at a nearly steady rate. A groundwater flow divide separates the part of the aquifer that drains into the lake from the part that drains into the creek.

To date, the actual source of contamination at the site has not been identified. An automotive brake manufacturer disposed of wastewater into unlined lagoons from the mid-1950s through the mid-1970s. It has not been confirmed whether TCE was directly discharged to the lagoons.

Regional groundwater flow modeling studies of *Tiedeman and Gorelick* [1993] indicated that disposal lagoons were a possible source of contamination. In their simulations, the contamination source was disposal lagoons situated above the groundwater divide. The simulated spatial distributions of contaminants were consistent with previous field observations, with plumes migrating toward both Lake Michigan and Hickory Creek. Using particle-tracking methods, they also found

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that vertical recharge would cause a downward migration of contaminants as the groundwater flows toward Lake Michigan.

Figure 1 shows the location of the three transects and the groundwater elevation contours. The groundwater flow in the vicinity of the transects is directed toward Lake Michigan, with an advective velocity of the order of 40 m/yr, which more than doubles in the proximity of the lake. However, the advective velocity near the assumed source is of the order of 5 m/yr.

Background

Anaerobic Transformations of CAHs

Bouwer et al. [1981] demonstrated the potential for anaerobic biological transformations of halogenated aliphatic compounds (HACs) in the subsurface. Subsequently, several investigators confirmed that HACs can transform anaerobically under a variety of environmental conditions. Some transformations are abiotic, while others are biotic, i.e., they are biologically mediated through the action of microorganisms [*Vogel et al.*, 1987].

Redox conditions often determine the pathways for the transformation of HACs. Common anaerobic electron acceptors and the associated microbial process, in the order of their redox potential, are nitrate (denitrification); Mn(IV) (manganese reduction); Fe(III) (iron reduction); sulfate (sulfate reduction); and carbon dioxide (methanogenesis). Many of the HACs are highly oxidized and, consequently, are potential electron acceptors [*Vogel et al.*, 1987].

In practice, biotic reductive processes of HACs occur mostly through cometabolism. That is, the HACs do not furnish the microorganisms with energy or growth, but are transformed by microorganism populations that are supported by other electron donors and acceptors. Thus cometabolism requires that additional chemicals be present that can be used for energy and growth. Under anaerobic conditions the HACs act as electron acceptors.

Vogel et al. [1987] reviewed degradation mechanisms of C1 and C2 halogenated solvents, including biotic and abiotic steps. The sequential reduction of chlorinated ethylenes including PCE and TCE is shown in Figure 2. Several investigators have observed these transformations under methanogenic conditions [*Vogel and McCarty*, 1985; *Parsons et al.*, 1984; *Barrio-Lage et al.*, 1986; *Fathepure and Boyd*, 1988]. In the subsurface these transformations have been of particular concern due to the production of VC, a known carcinogen. VC can be further reduced biologically to ethene [*Freedman and Gossett*, 1989; *DiStefano et al.*, 1991] and ethane [*Belay and Daniels*, 1987], both of which are essentially harmless.

Additionally, *Kaster* [1991] observed the partial transformation of PCE and TCE to c-DCE in cultures in the transition from aerobic to anaerobic conditions, accompanied by the release of sulfide and a decrease in the redox potential from 0 to −150 mV, without methane production. Thus there is some evidence that the highly chlorinated PCE and TCE can transform under conditions less strongly reducing than methanogenic, but the transformation appears to go only as far as DCE.

Vogel et al. [1987] reviewed the role of redox conditions on the degree and rates of dehalogenation. The general trend is that as the number of halogen atoms decreases, further dehalogenation by reduction becomes energetically and kinetically more difficult. *Vogel* [1988] found VC to be transformed at a rate over 2 orders of magnitude lower than TCE. This trend has also been observed in cell-free reactions using vitamin B_{12}, coenzyme F430, and hematin; there the rates of reactions of PCE → TCE → DCE → VC → ethene were correlated with the standard reduction potentials. In these enzyme studies, PCE was reduced 10,000 times faster than VC [*Gantzer and Wackett*, 1991]. *Vogel et al.* [1987] and *Criddle and McCarty* [1991] also point out that the reduction reaction rates are faster the lower the redox state of the solution.

Reductive dehalogenation relies on the availability of electron donors [*Baek and Jaffe*, 1989; *Freedman and Gossett*, 1989; *Fathepure and Boyd*, 1988]. At contamination sites, along with HACs, other cocontaminants (such as fuels, alcohols, ketones, organic acids, and unidentified forms of chemical oxygen demand (COD)) are often present and can serve as electron donors to drive anaerobic transformations. *McCarty and Wilson* [1992] present the amount of COD decrease associated with the sequential reduction TCE → DCE → VC → ethene as well as the production of methane. The greatest amount of COD decrease is associated with the production of methane.

DiStefano et al. [1991] found that an anaerobic mixed culture fed with methanol degraded 55 mg/L of PCE to VC and ethene. Approximately 70% of the methanol was converted to acetate, while about 30% was used up in dechlorination reactions. Methanogenesis, which consumes large amounts of COD, was suppressed under these conditions. Thus a large fraction of the electron donor participated in the dechlorination reactions.

Field Observations of Anaerobic Transformations

Transformations of chlorinated ethenes have been observed in several field studies. *Major et al.* [1991] presented field and laboratory evidence for the in situ biotransformation of PCE to ethene and ethane at a chemical transfer facility site in north Toronto. They indicated that cocontamination with methanol and acetate created methanogenic conditions. *Wilson et al.* [1991] and *Ehlke et al.* [1991] demonstrated through field and laboratory microcosm studies that TCE was being transformed to c-DCE and VC in an aquifer at the Picatinny Arsenal, New Jersey. *McCarty and Wilson* [1992] indicated that the reductions of TCE to DCE and VC were associated with a decrease in COD at the St. Joseph, Michigan, NPL site. Anaerobic transformation of PCE to TCE and c-DCE was also indicated at the U.S. Coast Guard Air Station at Traverse City, Michigan [*Sewell et al.*, 1990], where there is cocontamination of PCE with gasoline. Microcosm studies showed toluene could serve as an electron donor to drive the reduction of PCE [*Sewell and Gibson*, 1991]. *Kaster* [1991] indicated that in contaminated aquifers in Europe, transformation of PCE and TCE to c-DCE was observed in aquifers that were anaerobic, but not methanogenic. He indicated that further reduction to VC was probably limited to aquifers where the low reduction potentials associated with methanogenesis were achieved.

The detailed chemical characterization of the St. Joseph site supported these previous findings. The characterization permitted identification of zones where transformations were occurring and permitted flux estimates of the contaminants and transformation products.

Methods

Sampling Program

The characterization was a joint effort of Allied-Signal Corporation, Engineering Science, U.S. Environmental Protection Agency (EPA) Region 5, U.S. EPA Kerr Laboratory, and

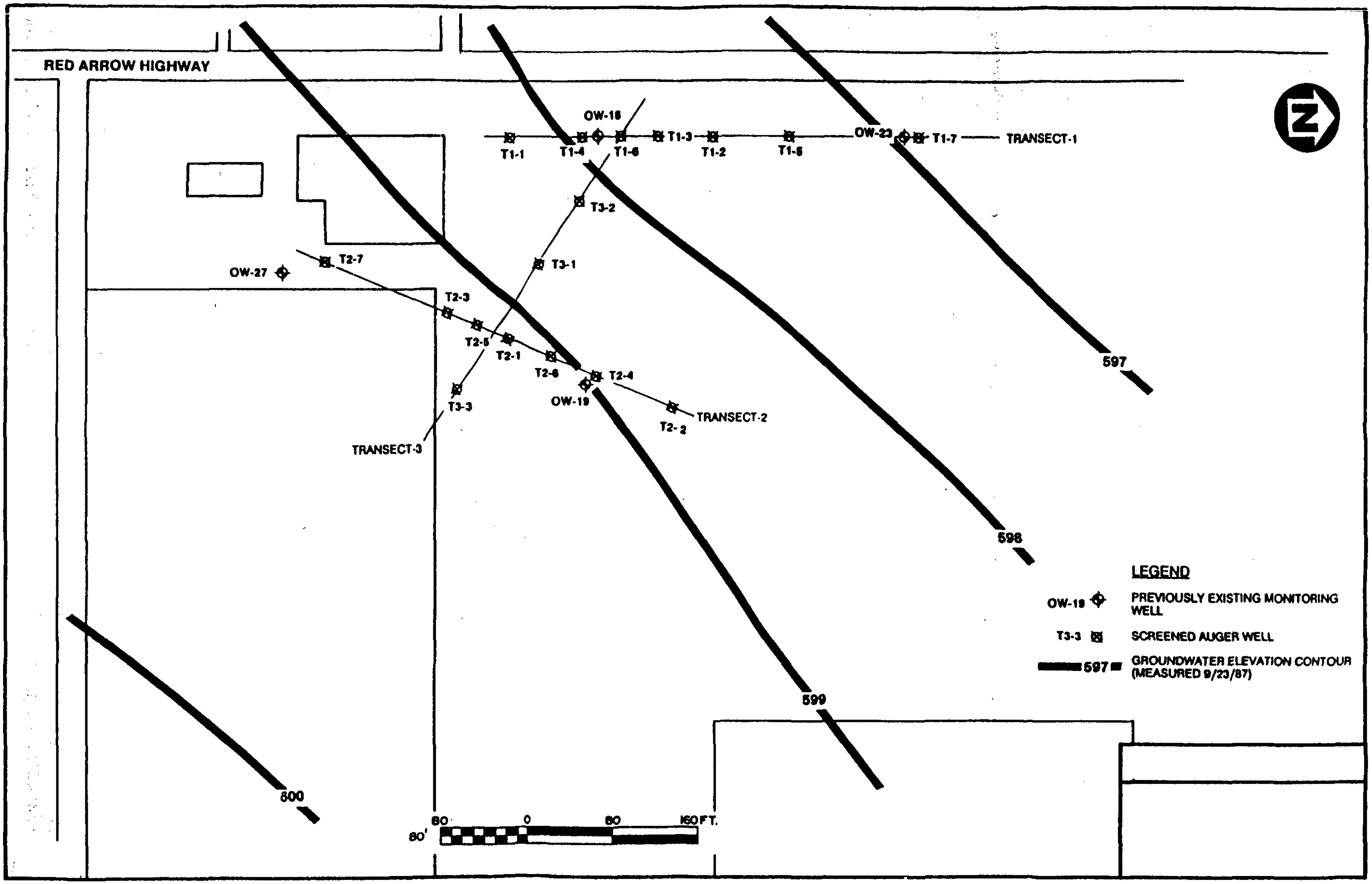

Figure 1. Location of the three transects and groundwater elevation contours at the St. Joseph, Michigan, NPL site. (1 foot equals 0.3048 m.)

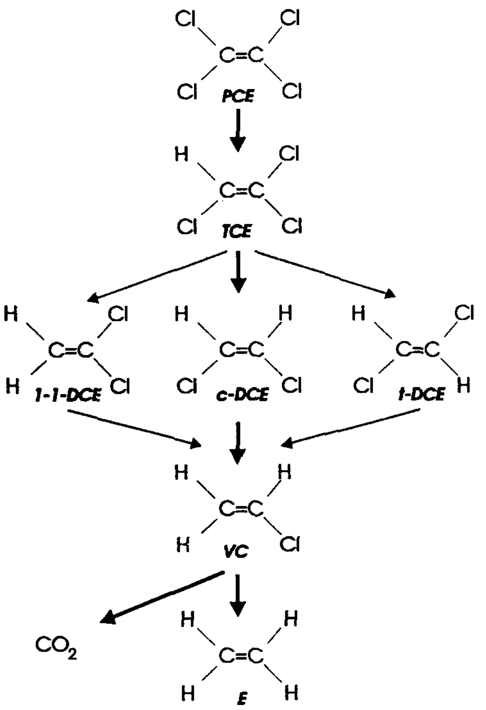

Figure 2. Sequential anaerobic transformation of PCE and TCE.

Stanford University. The groundwater sampling consisted of 17 slotted auger borings along three transects. Personnel from the Kerr Laboratory of EPA performed real-time gas chromatography (GC) analyses in the field as a guide in selecting the location of the borings. Groundwater samples were collected at 5-foot (1.5 m) intervals between the water table, located within 35–40 feet (11–12 m) from the ground surface, and the underlying clay confining bed, located 65 to 90 feet (20–27 m) below the ground surface. The groundwater samples were collected through a 5-foot-long (1.5 m long), 4.25-inch-ID (10.8 cm ID) steel drive point that was slotted with 0.01-inch (0.25 mm) openings. The drive point was driven ahead of the drilling augers. Groundwater was pumped to the surface through black HDPE tubing using a submersible pump. The sampling cell at the surface consisted of a flow valve, Tygon tubing, a glass monitoring port, and a glass monitoring port at the end of the cell. The probe devices included a redox probe and a combination of dissolved oxygen (DO), conductivity, and temperature probe.

At each 5-foot (1.5 m) interval, 30–40 gallons (110–150 L) of groundwater were purged through the system. To prevent excessive mixing of the groundwater from the shallower or deeper depth the flow rate was restricted to 5 gallons/min (19 L/min) on intervals capable of sustaining a well yield greater than 5 gallons/min (19 L/min). The entire sampling apparatus was decontaminated between groundwater samples by first purging with Alconox and tap water, followed by a second purge with tap water, followed by a final purge with deionized water. The sampling cell, Tygon tubing, and the glass flasks were decontaminated separately with the same procedure. Between boreholes the augers were steam cleaned and new HDPE tubing was installed. The boreholes were grouted upon the completion of the sampling.

The well yield, or maximum pumping rate that could be maintained at each level, hinted at the presence of zones of variable conductivity. Two zones of high yield are evident in transect 1, with thicknesses restricted to 10–15 feet (3.0–4.6 m). Their depth below the ground surface varies within the transects. A shallow high-yield zone is located within 30 feet (9.1 m) of the groundwater table. A second high-yield zone is about 15 feet (4.6 m) above the clay layer. In transect 2 there is also evidence of two zones of high conductivity. The shallower high-yield zone is within 10–15 feet (3.0–4.6 m) of the groundwater water table, and occurred at a slightly shallower depth than the first zone of transect 1. The second, deeper zone was within 5–20 feet (1.5–6.1 m) of the clay surface at about the same level as in transect 1. The most upgradient well of transect 3 (T3-3) had only a shallow zone of high yield. Clay was encountered in this boring at a depth of less than 65 feet (19.8 m). The two borings of transect 3 between transects 1 and 2 (T3-1 and T3-2) also penetrated two zones of high yield. The shallow zone was 10–15 feet (3.0–4.6 m) below the groundwater table, and the deeper zone was at the top of the clay layer.

The oxidation-reduction (redox) potential, temperature, and dissolved oxygen (DO) were monitored prior to the sampling. The samples were collected after the redox potential stabilized and the DO decreased to steady state levels. The groundwater samples were collected from the end of the Tygon tubing or from the side spout of the glass flask after the probes were removed. Samples were collected for volatile organic compounds (VOCs) from each sampling location. With the exception of a few sampling depths where well yields were low, samples were collected for methane, ethene, and ethane analysis, conventional inorganic compounds, and metals.

A total of three transects were completed with a total of 17 slotted auger borings (Figure 1). Transect 1 and 2 span the width of the plume and contain seven boreholes each. Transect 3 was completed between transects 1 and 2 and was located roughly in the center of the plume.

The field personnel conducted on-site GC analysis for TCE and its anaerobic transformation products. The purpose of the on-site analysis was to guide the selection of the next boring location, so that the width of the plume and the center of highest concentration could be found using a succession of boreholes. The progression of the boreholes is indicated by the borehole numbers along each transect. Samples for VOC analysis were shipped on ice to the EPA Kerr Laboratory. No attempt was made to collect samples for soil analysis due to the volatile nature of the contaminants.

Laboratory Analytical Methods

Water samples were analyzed in the laboratory for TCE and its anaerobic transformation products using purge and trap with gas chromatography [*American Public Health Association* (*APHA*), 1992]. The detection limit for chlorinated ethenes by this purge and trap method was 0.5 μg/L. Methane, ethene, and ethane were determined following the headspace procedure described by *Kampbell et al.* [1989]. The headspace concentrations were analyzed using a Hewlett-Packard HP 5840A GC with a flame ionization detector.

A total of 155 samples were collected during the 2-week study period. Of these, three samples were field blanks, three were duplicate samples, and one was a lab duplicate. The field blanks showed the methods used for purging between samples were effective. The two blanks taken between high-concentration samples showed some residual concentrations with blank concentrations representing 0.4–0.9% of the previous concentration measurement. The measurements were all below the detection limit for the blank taken between low-concentration values. The laboratory duplicate differed by 1–11%, with an average value of 4%, for the compounds of interest. Variations in the field duplicates ranged from 1.4 to 40%, with an average value of 8.8%.

Data Interpolation

The data from the water samples were analyzed statistically to construct contour lines of equal concentration and to estimate mass flux rates. This contouring and averaging require the interpolation from the data of the concentration of the solutes on a fine regular mesh. Univariate statistical methods of data analysis, which treat the data independently of their location in space, are not applicable. For example, to compute the total mass, it would not be reasonable to assign equal weights to all measurements because it is common to have more measurements near the center of the plume than elsewhere; instead, one should assign weights that are representative of the area of influence of each measurement and account for the shape of the concentration surface.

Linear geostatistical methods use only the mean and mean square value of the estimation errors. They are practical tools and can account for spatial correlation as a function of distance and direction. However, we found that the estimation errors may vary over orders of magnitude, depending on the proximity of measurements to "hot spots," and are highly skewed (i.e., asymmetrically distributed). Thus the mean and mean square values do not represent adequately the distribution of the estimation errors.

The methodology that we used (K. F. Shen and P. K. Kitanidis, Department of Engineering, Stanford University, Geostatistical analysis of concentration measurements in the field, unpublished report, 1993) produced point estimates, i.e., representative values, as well as confidence intervals, i.e., error bars that indicate the range of possible values. This way, we may evaluate the accuracy of estimated concentrations and masses. The approach accounted for the skewness in the distribution of estimation errors by adding only one parameter to those used in linear geostatistics (variograms or generalized covariances). We determine this parameter from the analysis of the data. The resulting nonlinear estimation method is not substantially more difficult to apply than linear geostatistics.

Results

Contaminant Characterization

One result of this study was how significantly the concentration of the CAHs varied with depth. Previous to this study, the measurements from monitoring wells at this site were not sufficient to establish a relation between the distribution of the contaminants and aquifer depth. The maximum concentrations of the contaminants and the depths at which they occurred in the transects are presented in Table 1.

Relatively high concentrations (several milligrams per liter) of TCE, c-DCE, and VC exist at all locations within 20 m of the center of the plume. The maximum concentrations of CAHs are 2 orders of magnitude higher than the maximum concentrations observed in the previously available monitoring wells [*McCarty et al.*, 1991]. Since c-DCE is the dominant DCE isomer present, it is the only isomer included in Table 1. The maximum concentrations of the DCE isomers were as follows: c-DCE, 133 mg/L; t-DCE, 3.9 mg/L; and 1,1-DCE, 5.3 mg/L. The maximum concentrations of the DCE isomers occurred at the same locations. Methane and ethene were also observed, with maximum concentrations of 12.3 and 6.6 mg/L, respectively. The high methane concentrations indicated that methanogenic conditions existed at the field site, and the presence of ethene indicated some of the TCE had been completely dechlorinated. Ethane, however, was not detected.

The maximum concentrations of the contaminants were also found at different locations and depths in the transects. The high contaminant concentrations ($>10{,}000$ μg/L) of TCE and c-DCE tend to be at shallower depths (65–75 feet (19.8–22.9 m)) compared to VC (65–85 feet (19.8–25.9 m)) as well as methane and ethene (65–85 feet (19.8–25.9 m)). The high values of VC and ethene were usually associated with high values of methane.

The distribution of CAHs, methane, and ethene, versus depth in bore T1-6 are shown in Figure 3, on a molar basis for comparison purposes. The methane concentration was the lowest at a depth of 60 feet (18.3 m) and increased with depth reaching a maximum concentration at 75 feet (22.9 m). The low methane was directly related to high TCE concentrations. The maximum TCE concentration was observed at 65 feet (19.8 m) and decreased as methane increased with depth. The c-DCE profile was similar to that of TCE but shifted to a greater depth. The maximum c-DCE concentration was observed at 70 feet (21.3 m) at a depth where TCE concentration decreased and methane concentration increased. The VC and ethene increased with depth consistent with methane. The ethene profile was a subdued version of methane's.

Figure 4 shows the concentration depth profiles in bore T2-3, which was directly upgradient of T1-6. The profiles are similar to that of T1-6, but the maximum TCE and c-DCE concentration occurred at the same depth location where methane concentrations were increasing, but have not reached their maximum concentration. VC and ethene profiles are similar to methane's. Similar trends as those shown in Figure 3 and 4 appear in most bores having high contaminant concentrations (Table 1). The profiles indicate sequential dechlorination of TCE with the greater extents of VC and ethene occurring at depth in the zone of high methane concentrations. Also c-DCE is present in zones where the methane concentration was increasing and is greatly reduced in the zones of the highest methane concentration.

The inorganic profiles of sulfate (SO_4), chloride (Cl), and ammonium (NH_4), measured as total Kjeldahl nitrogen (TKN), in bore T1-6 are shown in Figure 5. Sulfate is higher in the zone of low methane concentrations and decreases with depth as methane concentrations increase. This indicates the sequential use of sulfate as an electron acceptor at shallower depths. The ammonium profile is similar to that of sulfate. The decrease in both sulfate and ammonium with depth and the increase in methane indicates an increase in anaerobic activity. The decrease in ammonium could be associated with cell synthesis. TCE rapidly decreases in this zone, while c-DCE increases to a maximum and then decreases as sulfate and ammonium decreases and methane increases.

The inorganic profile in bore T2-3 (Figure 6) differs somewhat from T1-6. Sulfate does not show as drastic a decrease with depth as ammonium. It is interesting to note that TCE did not decrease as abruptly with depth as in the T1-6 transect. The

Table 1. Values and Depths of Maximum and Minimum Concentrations Measured in Bores

	TCE		c-DCE		VC		Ethene		Methane	
Bore	Concentration, μg/L	Depth, feet	Concentration, μg/L	Depth, feet	Concentration, μg/L	Depth, feet	Concentration, μg/L	Depth, feet	Concentration, μg/L	Depth, feet
T-1-1										
High	542	60	317	60	161	70	261	85	8,120	85
Low	7.4	85	<5	85	8	60	<1	45	303	45
T-1-2										
High	9,870	60	4,800	60	4,430	65	6,620	70	6,660	80
Low	11.4	45	76	45	9.0	45	3	45	11	45
T-1-3										
High	16,100	70	16,900	75	56,400	75	2,686	80	7,700	85
Low	<5	40	<5	40	<5	40	<1	40	<6	40
T-1-4										
High	21,300	70	31,300	80	11,000	80	1,689	85	6,480	85
Low	12	45	31	45	<5	65	<1	45	<6	45
T-1-5										
High	939	70	1,670	65	769	60	280	60	2,530	75
Low	33	40	21	40	<5	40	<1	40	<6	40
T-1-6										
High	67,700	65	51,100	70	778	75	3,101	75	8,560	75
Low	42	50	13	50	<5	70	13	55	175	60
T-1-7										
High	14	55	89	65	<5	55	2	75	9,630	70
Low	<5	70	<5	55	<5	55	<1	55	<6	55
T-2-1										
High	58,300	65	35,400	65	6,290	45	3,152	75	1,430	75
Low	435	75	327	80	321	80	<1	45	<1	45
T-2-2										
High	2,240	60	339	55	8	55	96	70	8,500	70
Low	38	70	11	80	<5	40	<1	40	73	40
T-2-3										
High	68,000	80	55,500	80	2,020	85	1,512	85	5,640	85
Low	8	45	113	45	<5	15	2	45	199	45
T-2-4										
High	993	60	613	50	250	75	303	70	5,200	70
Low	19	75	6	70	10	45	<1	45	<6	45
T-2-5										
High	55,400	65	128,000	75	4,430	85	2,871	80	8,560	80
Low	84	45	26	45	<5	45	20	60	2,290	65
T-2-6										
High	2,660	60	4,890	60	2,660	60	4,266	65	11,720	65
Low	310	45	414	45	148	45	18	45	743	45
T-2-7										
High	56	45	114	45	35	45	219	85	4,770	55
Low	<5	75	<5	55	8	55	1	50	76	70
T-3-1										
High	133,000	75	54,600	75	2,610	80	2,810	80	10,950	80
Low	38	45	154	45	<5	50	26	60	2,010	60
T-3-2										
High	78,200	70	82,400	75	2,350	75	4,894	85	11,590	80
Low	213	50	79	50	<5	50	4	60	178	60
T-3-3										
High	89,300	60	78,800	65	7,590	50	3,722	70	12,310	70
Low	2,680	80	4,840	80	<5	55	868	55	3,700	50

1 foot equals 0.3048 m.

decrease in NH_4 is associated with methane increase with depth, possibly indicating enhanced microbial activity.

The chloride profiles show no trend with depth. The chloride concentrations, however, are a factor of 2 greater on a molar basis than can be attributed to the complete dechlorination of maximum TCE concentrations. The high background chloride makes it difficult to identify chloride generated from CAH transformation.

The contaminant profiles indicated production of VC and complete dechlorination to ethene is associated with zones of methanogenesis. The abrupt decrease in TCE concentration in the highly methanogenic zones indicates it has been reductively transformed in the zone surrounding the methanogenic zone, in areas associated with sulfate reduction. The highest concentration of c-DCE occurs in zones where TCE is decreasing with depth, in a transition zone from sulfate-reducing to methanogenic conditions. The increase in methane, VC, and ethene is associated with decreases in sulfate and ammonium, indicating enhanced anaerobic activity at greater depth.

Two-Dimensional Contours

The two-dimensional concentration contours of the CAHs, ethene, methane, and sulfate for transect 2 (upgradient) are shown in Plate 1. Methane is distributed over a large area of

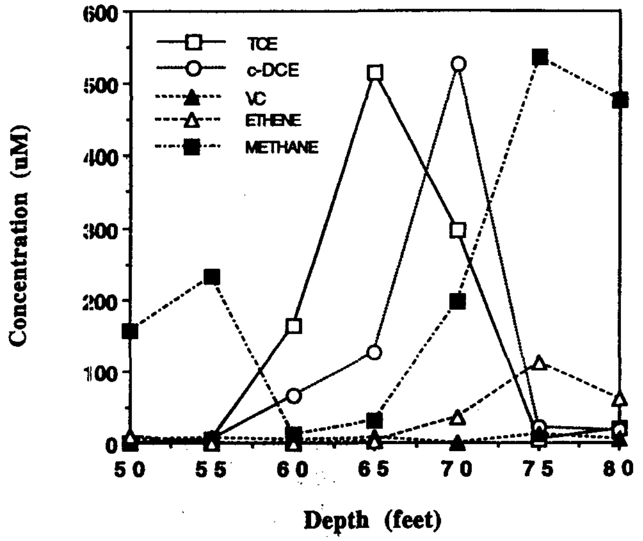

Figure 3. Chlorinated aliphatic hydrocarbons (CAH), ethene, and methane concentration profile versus depth in bore T1-6.

the cross section with highest concentration at depth near the center of the transect. The concentration changes sharply from the center to the left of the transect. The highest methane concentrations are correlated with low sulfate concentrations.

TCE has two high-concentration regions: one shifted to the left at a shallower depth than the methane high and one deeper and to the left at a region where the methane concentration is low. TCE is also shown to be less evenly distributed over the cross section than methane, with very sharp gradients over short distances. The two high–TCE concentration hot spots above 300 μmol/L represent an area of 10–30 m^2. The high TCE concentrations surround the methane plume, with TCE concentration greatly reduced where the methane concentration is high. The areas of high NH_4 (not shown) are associated with high TCE concentrations.

The maximum c-DCE concentration is located between the two TCE highs. The high in c-DCE concentration is in a transition zone of low to high methane concentrations. Note that the c-DCE plume is located between the two regions of very low sulfate concentration. A narrow band of elevated c-DCE exists in the center of the transect at shallower depths. The contours of t-DCE and 1,1-DCE (not shown) are similar to that of c-DCE, but reduced in concentration. The results indicate similar processes are producing and transforming the DCE isomers. The results indicate that the presence of sulfate could inhibit the further reduction of c-DCE, or perhaps indicate zones where the electron donor concentrations were lower and thus biological activity was less.

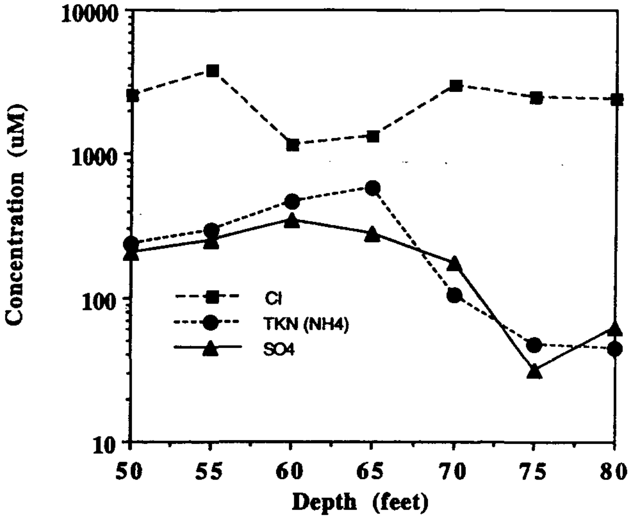

Figure 5. Inorganics concentration profile versus depth in bore T1-6.

The VC contours show a narrow band of high concentration in the center of the transect. The high concentration exists between the methane and the TCE highs, with the deeper VC plume associated with methane. A narrow band of elevated concentrations is found at shallower depths, consistent with the c-DCE data.

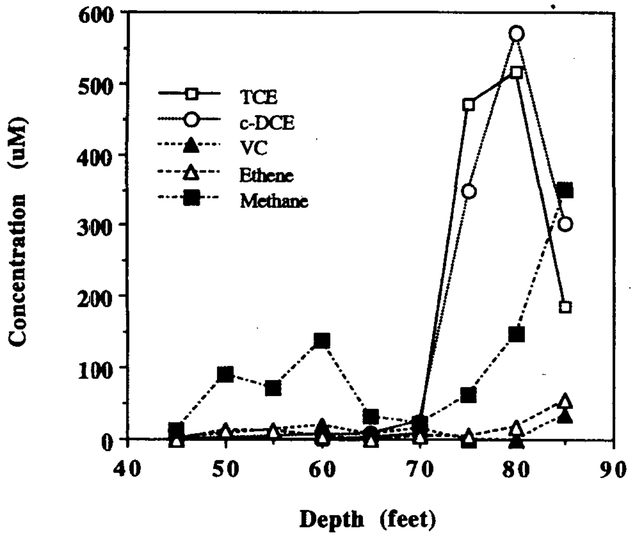

Figure 4. CAH, ethene, and methane concentration profile versus depth in bore T2-3.

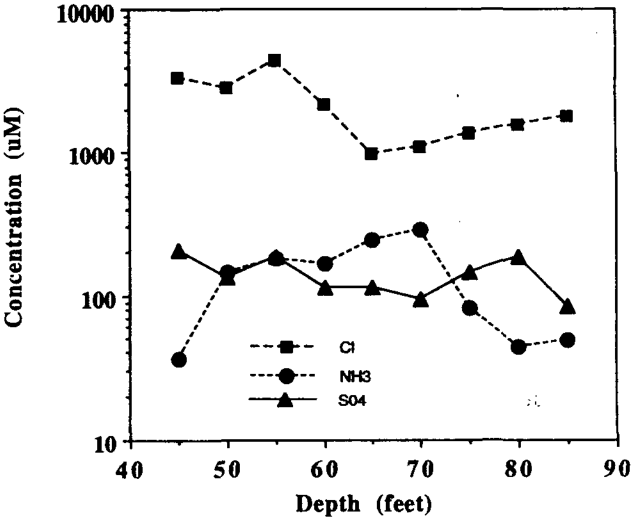

Figure 6. Inorganics concentration profile versus depth in bore T2-3.

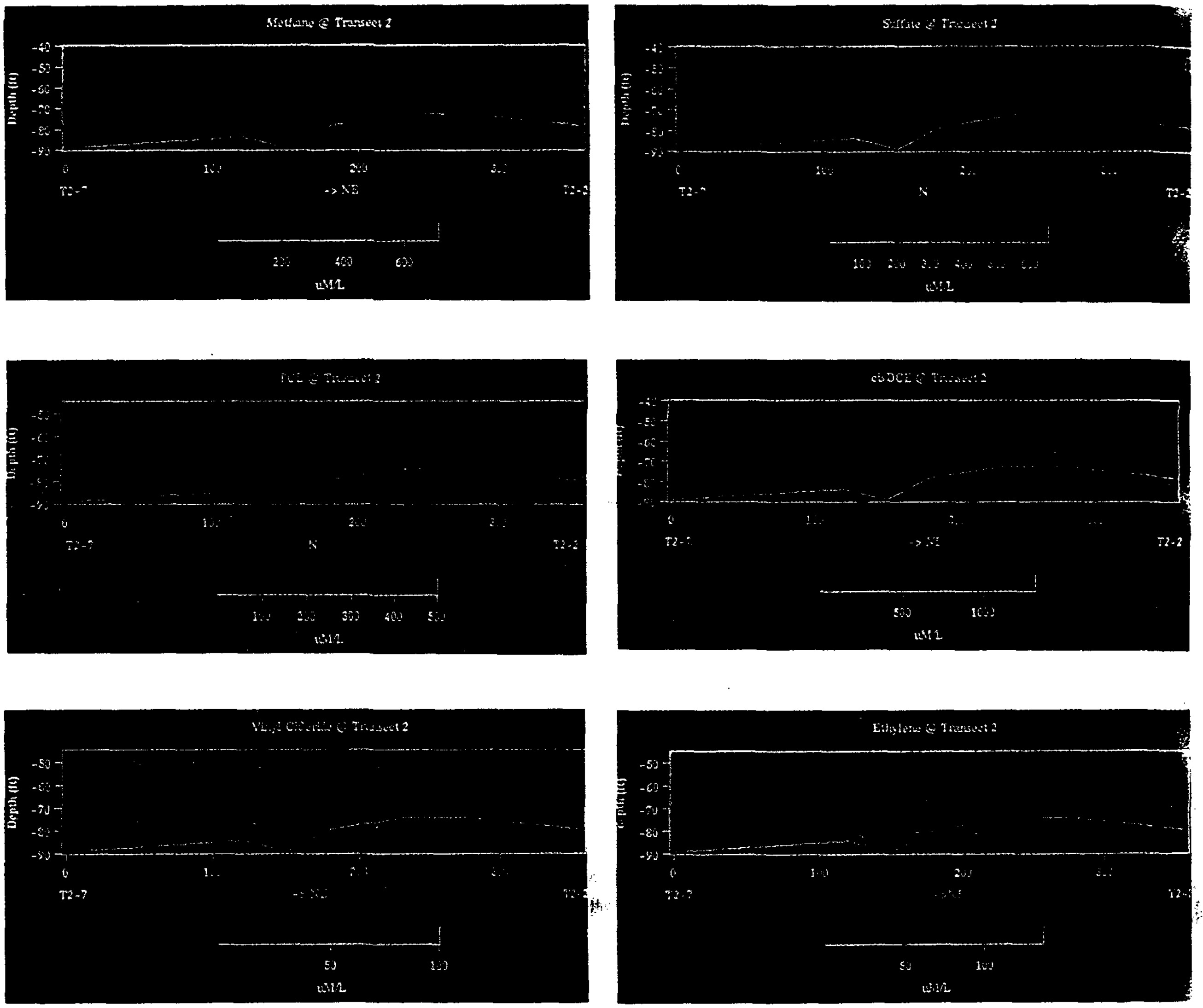

Plate 1. Two-dimensional chemical concentration contours of transect 2 (upgradient). The solid line at depth represents the clay aquitard.

The ethene concentration is positively correlated with the methane concentration, with their high values occurring at the same locations. Ethene is associated with the deeper methanogenic zones, indicating that complete dehalogenation of TCE is associated with methanogenesis. Some ethene is found in the shallower zone where methane is low but some VC exists. However, most of the data indicate that dehalogenation is incomplete in the absence of methanogenic conditions.

The two-dimensional contours along transect 1 (downgradient) are shown in Plate 2. Methane is concentrated left of the center, with the highest concentrations near the bottom of aquifer. A smaller band of high concentration also exists at the far right side of the transect. Here again, low sulfate concentrations are associated with high methane concentrations.

The TCE contours illustrate the sharp gradients in concentration that exist in the vertical direction with 3 order of magnitude changes in concentration occurring over an interval of several meters. It is particularly interesting to note that the zone of high TCE concentration is associated with an area deficient in methane. As in transect 2, TCE surrounds the methane plume but is reduced to very low concentrations in the methane plume. Like transect 2 the areas of high NH_4 (not shown) are associated with high TCE concentrations.

For c-DCE there are also sharp gradients in concentration. Raised DCE levels occur at a greater depth than TCE and in the transition zone from low methane and high methane concentration. This transition is consistent with a trough of elevated c-DCE in the lower left-hand corner of the transect corresponding to the trough of lower methane concentration and the absence of highly active methanogenic conditions. Note that at a depth of 80 feet (24.4 m) and at a distance of 120 feet (36.6 m) the decrease in c-DCE is associated with low sulfate values. Also t-DCE and 1,1-DCE (not shown) show the same profiles as c-DCE. consistent with the transect 2 observations.

In transect 1, elevated VC concentrations are located over a small area near the peak of methane concentration. Ethene has two high concentration regions, within the region of elevated methane concentrations. Also note the elevated levels of ethene at depth are correlated with low values of DCE and sulfate. Both VC and ethene are associated with the region of elevated methane concentrations at depth.

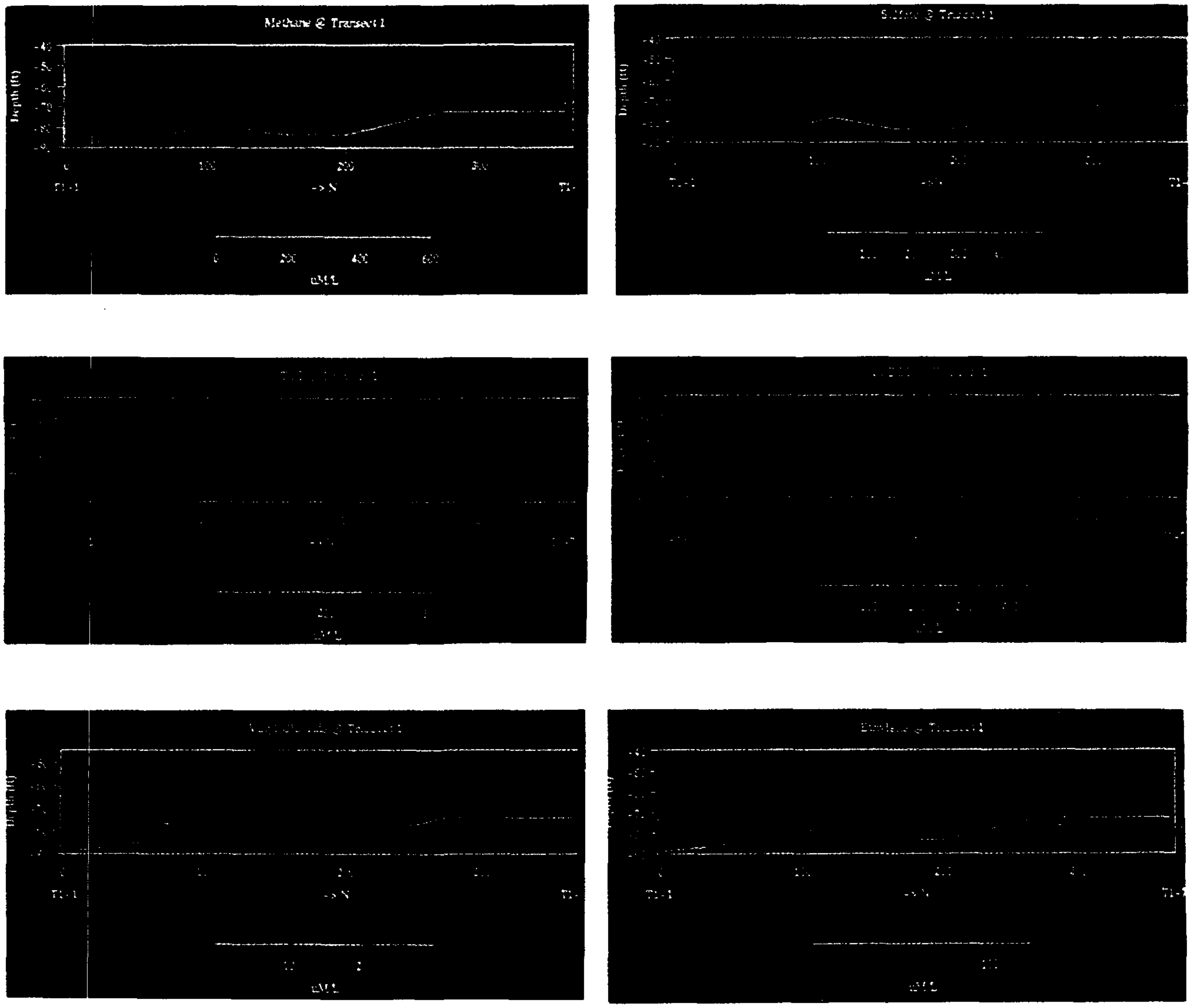

Plate 2. Two-dimensional chemical concentration contours of transect 1 (downgradient). The solid line at depth represents the clay aquitard.

Transect 3, which was performed nearly parallel to the groundwater flow direction, did not yield contours that illustrated the transformations as clearly as those of transects 1 and 2, which were taken approximately parallel to the constant-head contour lines. One of the main reasons is that the transect was not directly centered in the plume and it is not exactly parallel to the direction of the flow, despite our best efforts. Actually, one of the lessons of this study is that one can obtain more information from a transect that is approximately perpendicular to the direction of flow.

Nevertheless, the contours (not shown) from transect 3 showed the highest methane values to be deeper than the highest TCE, consistent with the other transects. The high methane concentrations are located at greater depths downgradient. The elevated DCE values are closer than TCE to the zone of elevated methane, consistent with the other transects. Elevated values of t-DCE and 1,1-DCE also correspond to elevated values of c-DCE. Elevated VC concentrations at depth are associated with the zone of elevated methane concentrations. One shallow area of elevated VC concentrations exists that is not associated with elevated methane values. Ethene is also strongly correlated with the deeper elevated values of methane.

Flux Estimates

Estimates of mass and mole fluxes of the CAHs, ethene, and methane across transects 1 and 2 are presented in Table 2. The estimates assumed that the groundwater flow was perpendicular to the groundwater elevation contours shown in Figure 1. The flux was based on the mean aqueous concentration, the Darcy flow velocity, and the cross-sectional area for flow. To account for the transects not being directly perpendicular to the groundwater flow velocity, the flow velocity vector perpendicular to the cross section was estimated. A Darcy flow velocity of 25 m/yr was estimated based on the hydraulic gradient of 0.008 m/m, a hydraulic conductivity of 1.0×10^{-4} m/s [*McCarty et al.*, 1991]. The velocity vector perpendicular to transects was 17.5 and 23.8 m/yr for transects 1 and 2, respectively. The cross-sectional areas for the flux estimates were 1431 and 1405 m^2 for transects 1 and 2, respectively. These were the areas over which the mean concentration was estimated. We also assumed equilibrium sorption between the aquifer solids and

Table 2. Flux Estimates and COD Reduction Estimates for Transects 1 and 2

	TCE	c-DCE	VC	Ethene	Total Ethenes	Methane
		Transect 1				
Mass flux, kg/yr	61	71	12	11	155	52
Mole flux, g mol/yr	460	730	190	390	1,770	3,250
Mole flux, %	26	41	11	22	100	···
COD consumption, kg/yr	···	11	6	18	35	208
		Transect 2				
Mass flux, kg/yr	147	154	23	8	332	188
Mole flux, g mol/yr	1,120	1,580	360	280	3,340	11,750
Mole flux, %	34	47	11	8	100	···
COD consumption, kg/yr	···	25	12	14	51	750

the aqueous phase. Thus the groundwater flow velocity was used in estimating the flux for all components. The sorbed contaminant was not considered in the flux estimate, since the solid phase was considered immobile. Retardation and sorption estimates, while not needed for the flux estimate, would, however, impact the spatial distribution of the contaminants.

The total mass flux of CAHs plus ethene at transect 2 (upgradient) was 2.1 times greater than transect 1 (downgradient). On a mole flux basis the total fluxes differ by a factor of 1.9, indicating greater amounts of contaminant and products are moving across the upgradient location. The fluxes are in reasonable agreement considering the assumptions made. If the transport conditions were steady state, then the total mole flux into transect 1 should be equal to the mole flux out of the transect 2. Steady state transport conditions, however, are unlikely to exist. A greater mole flux upgradient means that accumulation (increase in storage) in total CAHs and ethene occurs between the two transects.

The flux of methane is approximately 4 times greater through transect 2 than through transect 1, suggesting more highly anaerobic conditions upgradient. Steady state conditions probably do not exist. In the region between the two transects, the mass of methane is likely increasing, since the flux upgradient is much greater. For the methane not to accumulate it must be depleted through some vertical transport mechanism, transformation, or some unknown process.

The greatest mole flux in both transects is represented by c-DCE, followed by TCE. Ethene represents a greater mole flux out of transect 1 than VC, possibly indicating more complete dehalogenation with transport downgradient. The finding that c-DCE has a greater flux than the parent compound TCE indicates that significant anaerobic transformations are taking place. Ethene represents 8–22% of the total mole flux. Thus a significant amount of the CAHs are being completely dehalogenated to a nontoxic end product.

Estimates of the amount of COD reduction required to drive the anaerobic reductions and to produce the methane are also provided in Table 2. The COD estimates were based on the flux estimates and reaction stoichiometry presented in the work by *McCarty and Wilson* [1992]. The COD decrease associated with CAH reduction and methane production was a factor of 3 greater for the upgradient transect 2 compared to transect 1. A decrease of about a metric ton of COD per year is needed to drive the reactions. Most of the estimated COD reduction is associated with methane production. Reduction of the CAHs represents about 6% and 14% of the COD decrease in transect 2 and transect 1, respectively. A significant amount of the estimated COD decrease is therefore associated with reductive dechlorination, which is encouraging considering the fortuitous nature of the reactions.

Discussion of Results

The approach taken for locating the high-concentration zones appears to be very effective. Having an on-site analytical method for CAH analysis to direct the drilling proved to be a valuable aid in locating high-concentration zones of several square meters in extent. The maximum concentrations observed were 1–2 orders of magnitude higher than previously measured in monitoring wells. Multilevel sampling techniques were helpful in revealing the pronounced vertical variability in concentrations and redox conditions. The observations allow us to resolve vertical variations in the concentration of contaminants and inorganic compounds much more accurately than horizontal changes. This is expected in this study since the sampling grid was much finer in the vertical direction than in the horizontal.

The work demonstrated that detailed characterization of the subsurface provides insight into transformation processes that are occurring in the field. The results of this study indicate the anaerobic transformation of TCE, with the complete dehalogenation to ethene, is associated with methanogenic conditions. Analysis of inorganic contaminants such as sulfate also indicated different redox conditions exist that influence the transformation paths or degrees of completion, and uptake of minor nutrients (NH_4) is likely associated with cell synthesis. The high NH_4 associated with high TCE concentration may indicate cell synthesis is inhibited due to TCE toxicity.

Evidence for methanogenic conditions is based on observations of elevated methane levels in specific areas, simultaneously with reduction in sulfate and ammonium in the same areas. Low sulfate concentrations occur in zones where high methane is also present, and sulfate is somewhat higher in transition zones where methane is increasing and sulfate is decreasing with depth. One plausible explanation is simultaneous sulfate reduction and methanogenesis; it has been demonstrated that sulfate reduction and methanogenesis can occur simultaneously [*Oremland and Taylor*, 1978]. However, sulfate reducers probably will outcompete methanogens in natural habitats where sulfate is not limiting [*Lovley et al.*, 1982; *Robinson and Tiedje*, 1978], which is consistent with the field observations. Another, perhaps less plausible, explanation is spreading of methane from areas of methanogenesis toward areas of sulfate reduction. TCE reduction and c-DCE formation seem to occur in this transition zone. It may be that transformation of TCE to c-DCE is occurring in the zone of sulfate reduction, as discussed by *Kaster* [1991], and further reduction of c-DCE requires more reducing conditions of methanogenesis. Another possibility is that the extent of transformation is associated with the amount of donor consumed, with less sulfate reduction, methane production, and CAH transformation resulting from there being less electron donor present. Here, a more accurate determination of the redox conditions, characterization of microbial activity, and measurements of donor concentration are needed.

It is not known whether methane bubbles are present in the aquifer. The maximum level of methane measured was 11.6 mg/L, representing approximately 45% of the maximum solubility of methane in equilibrium with pure methane gas at the sampling temperature and pressure of 15°C and 1 atm. Other factors, however, could affect the maximum methane solubility, including the presence of other gases, such as nitrogen, carbon dioxide, and ethene. The existence of gas bubbles, therefore, cannot be ruled out.

In these studies the COD of the groundwater was not measured, which would have provided additional confirmation of biological activity, particularly of methanogenesis. The elevated methane values and the decrease of ammonium with depth suggest biological activity. Approximately 0.037 mg NH_4 would be consumed for every milligram of methane produced, based on the stoichiometry presented in the work by *Bailey and Ollis* [1986], with acetate as the electron donor for the anaerobic process. Using bore T1-6 as an example, ammonium decreased by 10 mg/L and methane increased by 8 mg/L over the depth interval of 65–75 feet (19.8–22.9 m), yielding a ratio of 1.25 mg NH_4 decrease per milligram of methane. This ratio is much higher than expected based on stoichiometry. However, it may well be that the approach of focusing on changes in the vertical direction is not valid and that other physical transport and biological processes need to be considered. For example, ammonia could be present at shallower depths due to local application of fertilizer, with depth changes related to recharge conditions.

Although the inorganic parameters such as sulfate and the presence of methane help in evaluating redox conditions, other chemical parameters should be considered. For example, *Lovley and Goodwin* [1988] and *Chapelle and Lovley* [1992] have shown that hydrogen concentrations can be used as an indicator of redox conditions in aquifers. Future studies at this site should include hydrogen measurements for comparison with the CAH distributions and the methane, sulfate, and ammonia distributions.

The description of changes in the chemical parameters has been approached primarily from a microbial process viewpoint. Interpretation of the results should also take into account transport processes. However, this turned out to be a difficult task because (1) neither the source areas of the TCE nor the contamination history are known, and (2) the conductivity is not known with a resolution sufficient for describing the transport of contaminants (of the order of a meter). For these reasons, we must rely basically on the concentration observations.

The different total flux of contaminants across the two transients indicates that steady state transformation conditions do not exist. The flux estimates could be in error due to variations in hydraulic conductivity that exist, but were not considered. Another possibility is that products were formed that were not measured. For example, *Vogel and McCarty* [1985] observed carbon dioxide as a TCE anaerobic transformation product. Carbon dioxide production could not be determined due to its high background level in the native groundwater.

The flux estimates indicated 6–14% of the COD consumption may be associated with dechlorination reactions, which is fairly high if the transformations were fortuitous. *DiStefano* [1991], for example, found under laboratory conditions about 30% of the methanol they added was associated with dehalogenation reactions. The greater estimated COD uptake upgradient is consistent with COD contours reported by *McCarty and Wilson* [1992].

The vertical variations in concentration observed at the St. Joseph site appear to be consistent with our interpretation of the hydrogeology at the site. As previously mentioned, the flow is dominated by recharge. In *Tiedeman and Gorelick*'s [1993] simulations of the groundwater flow and surface recharge at the site, the contamination originating in the lagoon would be pushed downward due to surface recharge as the groundwater flows toward Lake Michigan. If the organic driving the anaerobic processes originated in the lagoon, one would anticipate more anaerobic conditions at greater depths, which is consistent with the observations in the field with methane observed at greater depths.

Transect 3, which is the most parallel to the direction of groundwater flow, shows the methane plume getting deeper with flow toward the lake. It can be hypothesized that the transformations of TCE also follow this track because TCE should also be pushed by recharge toward the bottom and toward more reducing conditions. This may explain why we see more products of transformation and more complete dehalogenation as the depth increases. However, the transport processes are quite complex. For example, one should consider sorption and the resulting retardation for each of the organic compounds.

The other complexity, which cannot be ruled out, is the presence of TCE as a dense nonaqueous phase liquid (DNAPL). The maximum observed TCE concentration of 133 mg/L was observed between transect 2 and transect 1. The maximum concentration is approximately a factor of 10 lower than TCE's solubility limit in water. *Mackay et al.* [1985] indicate that even when DNAPLs are present the observed groundwater concentrations are usually a factor of 10 lower than the solubility limit because of diffusional limitations of dissolution and dilution by dispersion. Modeling studies of the dissolution of DNAPLs of *Anderson et al.* [1992] support this. Thus a TCE NAPL phase, which is slowly dissolving, could be present in the region of the transects.

Despite these difficulties and the complexity that is probably unavoidable in field studies such as this, the picture that emerges from the analysis of the data is quite consistent with the results of laboratory studies. In particular, it is confirmed that (1) the dehalogenation of TCE to VC and ethene is faster and more complete when methanogenic conditions are created due to the presence of an electron donor; (2) ethene and VC are found in areas of high methane concentration and appear to be associated with methanogenesis and low sulfate concentrations; (3) the production of DCE appears to be limited to the transition zone between the zone of methanogenesis and the zone of sulfate reduction, indicating that TCE is being transformed under less reducing conditions, with further reduction of c-DCE occurring under active methanogenic conditions, at low sulfate concentrations; and (4) significant amounts of dechlorination reactions are occurring when compared to the estimated COD uptake driving the reactions.

Detailed studies of subsurface contamination such as those performed here provide a means of investigating transformation reactions that may be slow in nature, occurring over timescales of years. These studies, although complicated due to many unknowns, provide valuable information on the fate of halogenated aliphatic compounds in the subsurface.

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D. Kampbell and J. T. Wilson, U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK 74820.

P. Kitanidis, Department of Civil Engineering, Stanford University, Stanford, CA 94305-4020.

L. Semprini, Department of Civil Engineering, Oregon State University, Corvallis, OR 97331-2302.

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