

Chemical Distributions and Anaerobic Transformation of Chlorinated Aliphatic Hydrocarbons in a Sand Aquifer

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INTRODUCTION

A sand aquifer near the town of St. Joseph, Michigan, was contaminated with trichloroethylene (TCE). Monitoring well data, indicated dichloroethylene (DCE), and vinyl chloride (VC), were present as transformation products. A detailed chemical characterization of the subsurface was performed that demonstrated the anaerobic transformation of TCE to DCE, VC, and ethene. The characterization permitted zones to be identified where transformations are occurring, and permitted flux estimates of the contaminants and transformation products.

The potential for anaerobic biological transformations of chlorinated aliphatic hydrocarbons (CAHs) in the subsurface was demonstrated in 1981 (1). Subsequently, CAHs in general have been found to be transformed under a variety of environmental conditions in the absence of oxygen. Redox conditions in the subsurface are often regulated by microbial processes. 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 CAHs are highly oxidized and have redox potentials above these common electron acceptors (2), and therefore can be reduced. The sequential reduction of the double-bonded CAHs, including tetrachloroethylene (PCE) and trichloroethylene (TCE), is of concern since these compounds are frequently observed at contamination sites, and there is potential for the formation and accumulation of vinyl chloride (VC), a known carcinogen. Recently there has been renewed interest in anaerobic transformation of chlorinated ethenes, with the observations that VC can be further reduced biologically to ethene (3,4).

Reductive dehalogenation depends on the availability of electron donors (5,6,3). At contamination sites, along with CAHs, other co-contaminants such as fuels, alcohols, ketones, organic acids, and unidentified forms of Chemical Oxygen Demand (COD), are often present that can serve as electron donors to drive the anaerobic transformations.

The geologic formation of interest at the St. Joseph site is an unconfined aquifer consisting of a layer of unconsolidated fine sand with some silt. 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 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/year) replenishes the aquifer and the groundwater drains into the lake and the creek, which act as constant-head boundaries, at a nearly steady rate.

An automotive brake manufacturer disposed of wastewater into unlined lagoons from the mid-1950's through the mid-1970's. It has not been confirmed whether TCE was directly discharged to the lagoons. Regional groundwater flow modeling studies indicated that the lagoons were a possible source of contamination (7).

METHODS

In August-September, 1991, 155 groundwater samples were collected along three transects located near the areas of highest concentration. Two transects (1 and 2) were nearly perpendicular to the groundwater flow and Transect 3 was nearly parallel. The three transects included a total of 17 borings within the saturated zone. Groundwater samples were collected at five foot intervals between the water table, located within 35 to 40 feet from the ground surface, and the underlying clay confining bed, located 65 to 90 feet below the ground surface. The groundwater samples were collected through a five foot long, 4.25 inch ID. stainless steel drive-point that was slotted with 0.01 inch openings. The drive point was driven ahead of the drilling augers.

Real-time gas chromatography analyses were performed in the field to aid in selecting the location of the borings. Water samples were analyzed in the laboratory for TCE and its anaerobic transformation products using purge and trap with gas chromatography (8). Methane, ethene, and ethane were determined by a headspace procedure (9). Ammonium ion was measured as Total Kjeldahl Nitrogen (TKN), and chloride and sulfate were measured by ion chromatography (8)

RESULTS

The characterization showed some pockets of very high contaminant concentration. The maximum TCE concentration was 133 mg/L. Elevated methane concentrations were present at greater depth (maximum, 11.3 mg/L). 1,2-cis-dichloroethylene(c-DCE) was the dominant DCE isomer present. The maximum concentrations of the DCE isomers were as follows: c-DCE, 133 mg/L; trans-DCE, 3.9 mg/L; and 1,1-DCE, 5.3 mg/L. VC and ethene (maximum, 56 mg/L; 6.6 mg/L, respectively) were associated with the areas of elevated methane concentrations, and depressed sulfate concentrations. The high methane concentrations indicated methanogenic conditions existed, and the presence of ethene indicated some of the TCE had been completely dechlorinated. Ethane, however, was not detected.

The transects showed general spatial trends in concentrations of CAHs, ethene, methane, sulfate, and ammonium ion. The high contaminant concentrations (>10,000 mg/L) of TCE and c-DCE tend to be at shallower depths (65 to 75 ft), compared to VC (65 to 85 ft) as well as methane and ethene (65 to 85 ft). The high values of VC and ethene were usually associated with high values of methane.

Figure 1 shows a typical distribution of the CAHs, ethene, and methane that was observed in the borings. The methane concentration increases with depth. The low methane was associated with high TCE concentrations. The TCE concentration decreased as the methane concentration increased with depth. The c-DCE profile was similar to that of TCE but shifted to a greater depth. The VC and ethene increased with depth, consistent with methane. The ethene profile was a subdued version of methane's. The results show the sequential transformation of TCE, with complete dechlorination to ethene at depth associated with higher methane concentrations.

Figure 2 shows the distribution of ammonia, chloride, and sulfate in the same boring. The sulfate concentration decreases with depth as methane concentrations increase. This indicates the preferential 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. The chloride profiles shows no trend with depth, due to high background levels in the groundwater.

2-D contour analysis showed similar spatial trends. TCE was present in zones of low methane concentration. c-DCE was found between areas of low and high methane concentrations. t-DCE and 1,1-DCE show contours that are similar to c-DCE, but reduced in concentration, indicating similar processes produced and transformed the DCE isomers. VC and ethene were associated with the zones of high methane and low sulfate concentrations. The contaminant contours indicate VC production and complete dechlorination to ethene was associated with zones of methanogenesis. The abrupt decrease in TCE concentration in the highly methanogenic zones indicates reductive transformation in the zone surrounding the methanogenic zone, in areas associated with sulfate reduction. 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.

Table 1 presents estimates of mole fluxes of the CAHs, ethene, and methane across Transects 1 and 2. The mole flux of CAHs plus ethene (Total Ethenes) at Transect 2 (upgradient) was 1.9 times greater than at Transect 1 (downgradient). The flux of methane is approximately four times greater through Transect 2 than through Transect 1. Thus, more highly anaerobic conditions may exist upgradient. c-DCE represents the greatest mole flux in both transects, indicating significant anaerobic transformations are taking place. Ethene represents a greater mole flux out of Transect 1 than VC, possibly indicating more complete dehalogenation with transport downgradient. Ethene represents 8 to 22 percent of the total mole flux. Thus, a significant amount of the CAHs is being completely dehalogenated to a non-toxic endproduct.

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Table 1. CAH, Ethene, and Methane Flux Estimates for Transects 1 and 2

	TCE	c-DCE	VC	Ethene	Total Ethenes	Methane
Transect 1						
Mole Flux (g mole/yr)	470	730	180	380	1760	3280
Mole Flux (percent)	27	41	10	22	100	-
Transect 2						
Mole Flux (g mole/yr)	1120	1580	360	280	3340	11750
Mole Flux (percent)	34	47	11	8	100	-

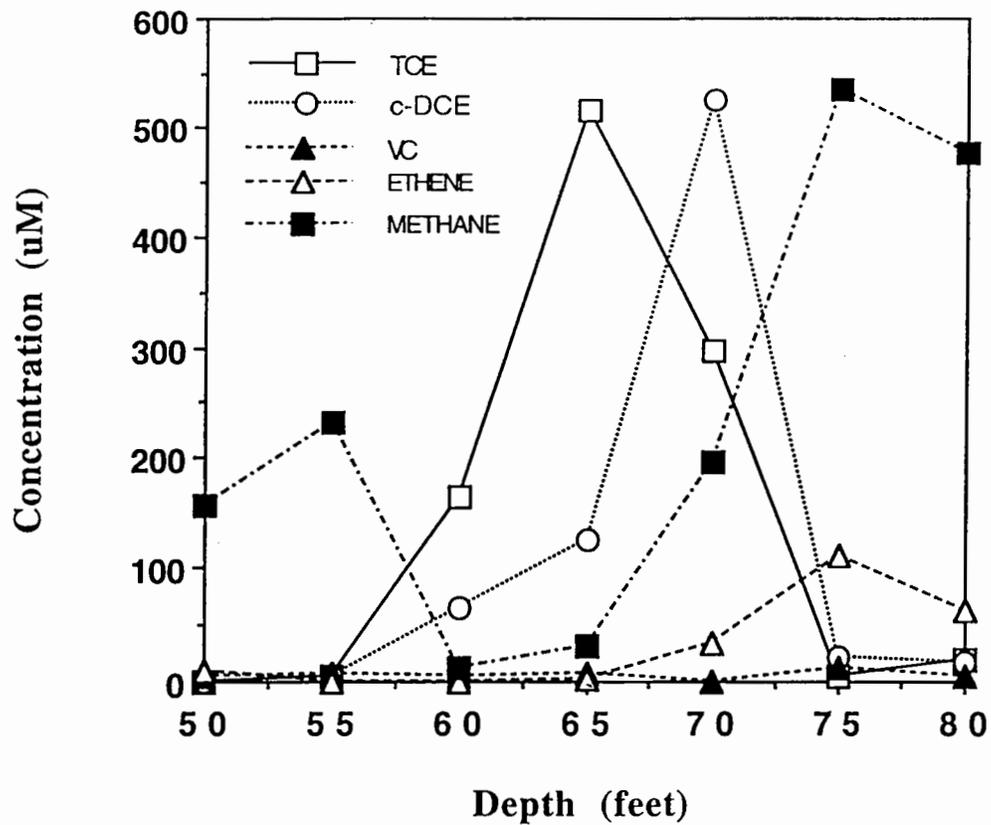


Figure 1. CAH, ethene, and methane concentration profile in bore T1-6.

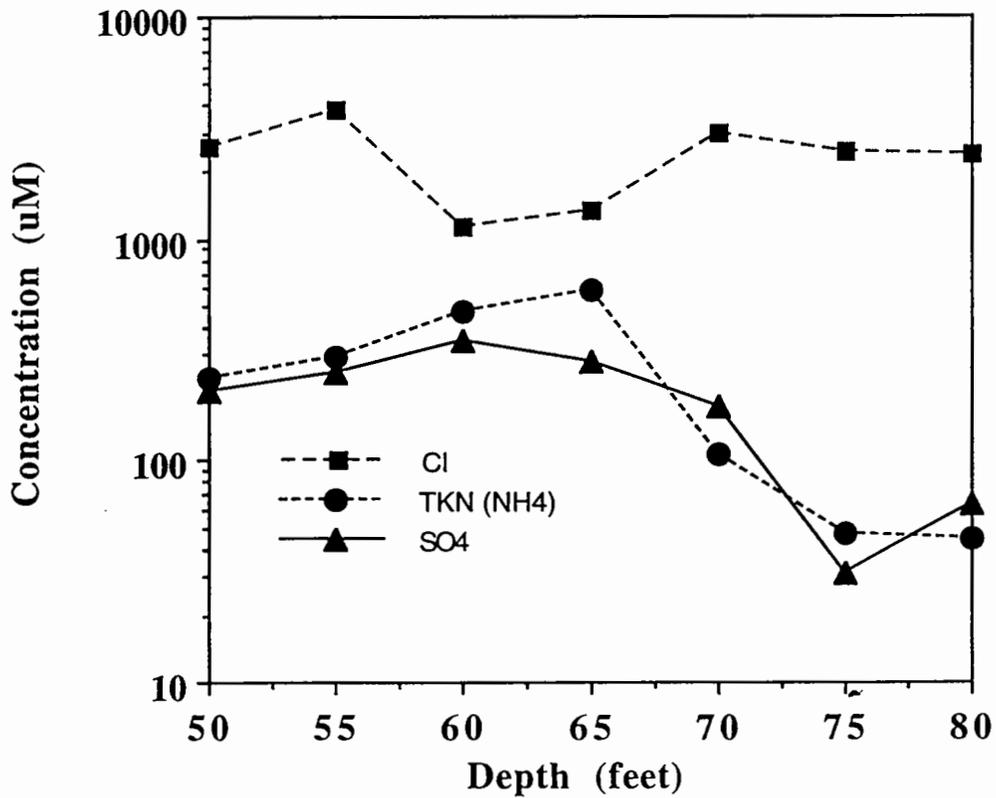


Figure 2. Inorganics concentration profile versus depth in bore T1-6.

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16. 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.			
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