Case Study of Natural Attenuation of Trichloroethene at St. Joseph, Michigan

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Introduction

Trichloroethene (TCE) was found in ground water at the St. Joseph, Michigan, Superfund site in 1982. The site, located 4 miles south of St. Joseph and 0.5 mile east of Lake Michigan, has been used for auto parts manufacturing since 1942. The aquifer is primarily composed of medium, fine, and very fine glacial sands. The base of the aquifer is defined by a clay layer that lies between 21 and 29 meters below the ground surface, with elevation of the clay layer increasing toward Lake Michigan. Investigation at the site included an exhaustive study of 41 possible contaminant sources but did not definitively identify the source.

The source was apparently situated over a groundwater divide, however, as the contamination was divided into eastern and western plumes. Both plumes were found to contain TCE, cis- and trans-1,2-dichloroethene (cis-DCE and t-DCE), 1,1-dichloroethene (1,1-DCE), and vinyl chloride (VC). Initial investigation indicated that natural anaerobic degradation of the TCE was occurring in the western plume, because of the presence of transformation products and significant levels of ethene and methane (1, 2).

This paper describes the investigation at the site and presents the field evidence for natural attenuation of TCE. Since degradation of TCE is known to occur anaerobically under differing redox conditions and to produce specific daughter products, the relationships between measured concentrations of chlorinated ethenes and various redox indicators are emphasized.

Sampling Strategy

Water samples were taken in October 1991 and March 1992 from a 5-foot long slotted auger (3). Seventeen boreholes were completed near the source of the western plume (1), which formed three transect crossing the contaminant plume. Data from these first three transect were analyzed by Semprini et al. (4).

In 1992, two additional transect (4 and 5 on Figure 1) consisting of nine additional slotted auger borings were completed. These two transect were chosen to sample the plume in the vicinity of Lake Michigan. In each boring, water samples were taken in 5-foot intervals from the water table to the base of the aquifer. Onsite gas chromatography was used to determine the width of the plume and the point of highest concentration in each transect. The onsite gas chromatography ensured that the entire width of the contaminant plume was captured within each transect. In August 1994, data were collected from a transect located about 100 meters offshore that was roughly parallel to the shore line and contained four borings. Water samples were taken with a barge-mounted geoprobe (3). Data from the lake transect showed the location of the plume by the observed reduction in dissolved oxygen concentrations and the measured redox potentials.

Results

Figures 2 through 5 show the data from all the boreholes separated by transect, which in effect also separates them by sample date. By compositing the data set, sitewide trends can be seen. These figures are supplemented by Figures 6 through 9, which show contaminant distribution with depth in single boreholes from representative locations. Significant methane concentrations occurred where dissolved oxygen concentrations were low (Figure 2). Variation in concentration occurring on a scale smaller than the length of the auger is not accurately represented, as waters of differing chemistry may mix upon sampling. This may explain why a few data points simultaneously have high methane and high oxygen concentrations. Most importantly, the figure indicates that a large number of sample locations at the site had the necessary strong reducing conditions for reductive dechlorination to occur.
Figure 1. St. Joseph Superfund site plan.

Figure 2. Scatter plot of methane and oxygen data.

Figure 3. Scatter plot of sulfate and oxygen data.

Figure 3 shows the distribution of sulfate and oxygen. Many of the points cluster near the sulfate axis, which generally corresponds to the regions of high methane concentration. Generally the sulfate concentrations around the site are high, and completely clear patterns of sulfate depletion are not found in the composited data set. The trends that exist in the data are best illustrated by the contaminant distribution in individual boreholes. These data suggest that transformation of TCE to DCE occurred where the sulfate concentration showed some sign of decline. Clustering of the sulfate data occurred at sulfate concentrations of 300 micromolar (mM) or less and oxygen concentrations of 50 mM or less.

Many of these points occurred in the transition between the aerobic and methanogenic region. Compared with higher sulfate concentrations at other locations, these points tentatively indicate sulfate reduction zones, which may be concurrent with methanogenesis (5). In particular, in Transect 4 and 5 the uppermost sample locations
were devoid of contaminants and were oxygenated. Sulfate concentrations in the range of 300 to 500 μM at these points indicate background sulfate levels.

The entire chlorinated ethene (TCE, DCEs, and VC) and ethene data set is plotted in Figures 4 and 5 as a chlorine number, $N_{Cl}$, that is defined by

$$N_{Cl} = \frac{\sum w_i C_i}{\sum C_i}$$

where $w_i$ is the number of chlorine atoms in molecule $i$ and $C_i$ is the molar concentration of each ethene species. The chlorine number composites the ethene concentrations and scales them from 0 to 3. At 0 no chlorinated species are present, and at 3 all of the ethene is in the form of TCE. Generally, the integer chlorine numbers (0, 1, 2, 3) are obtained with non-0 concentration only of the ethene with that number of chlorine atoms. There are fortuitous combinations, however, of positive non-0 concentrations that give integer chloride numbers. None of these combinations occurred in the St. Joseph data set.

High chlorine numbers were associated with many of the high dissolved oxygen concentrations (Figure 4), indicating that most of the chlorine was contained in TCE molecules at these sampling points. Some of these had chlorine numbers of 3, indicating that TCE was the only species present. The majority of locations with chlorine numbers below 3 were anaerobic, which also corresponded to methanogenic locations. The latter condition, in conjunction with the presence of the TCE degradation products (indicated by the low chlorine numbers), indicates degradation of the TCE. When the data set is plotted against the methane concentration (Figure 5), the data appeared scattered over most of the graph. Some of the lowest chloride numbers were associated with the high methane concentrations.

Generally, many of the downgradient locations (squares on Figures 4 and 5) showed chlorine numbers above 2 and lower methane concentrations. These data suggest that in the downgradient transect, TCE degraded to DCE under other than methanogenic conditions.

Data from selected borings represent the general trends with depth in each of the transect (Figures 6 and 7). In Transect 2, located near the presumed source of contamination, dissolved oxygen was depleted below the 60-foot depth (Figure 6). Between 45 and 60 feet, the 45- and 55-foot depths showed significant dissolved oxygen as well as significant methane concentrations. Sulfate showed a weak declining trend with depth to about 70
feet. Significant TCE and cis-DCE concentrations were found only from 75 to 85 feet below the surface (Figure 7). VC was found at concentrations of 40 μM or less over most of the borehole. Ethene was found at highest concentrations at the bottom of the borehole, where methane concentrations also were highest.

Borehole T42 had the highest chlorinated ethene concentrations recorded for Transect 4, and it also represents the general chemical distribution for the downgradient transect (Figures 8 and 9). From the water table to the depth of 60 feet, oxygen concentrations were high but decreasing (Figure 8). This contrasts with the upgradient transects, which showed less consistent depletion of oxygen near the water table. Sulfate concentrations decreased from 60 to 70 feet, roughly the same zone in which oxygen was declining. From 70 to 85 feet, sulfate concentrations remained low but increased from 80 feet to the bottom of the borehole. Methane was not present in the aerobic zone above 65 feet, but it increased sharply in concentration from 70 to 80 feet before decreasing.

Figure 9 shows the distribution of the chlorinated ethenes and ethene in T42. TCE was found from 60 feet downward, with its maximum concentration occurring at the 70-foot depth. The region above the 60-foot depth was free from chlorinated ethenes, so the high sulfate and oxygen concentrations found there correspond with no activity due to TCE degradation.

The cis-DCE concentration was also highest at the 70-foot depth. Methane first appeared at 65 feet, and the peak cis-DCE concentration occurred where sulfate concentrations declined to the minimum. VC was found from 65 feet to the bottom of the borehole. Ethene was found from 70 feet downward, corresponding closely to the most methanogenic part of the borehole.

**Conclusion**

Because of a variety of evidence, the data set from St. Joseph suggest the occurrence of natural attenuation. The composited data set indicate that, with the exception of a few points, the oxygenated and methanogenic zones of the aquifer are clearly separated. The presence of many methanogenic locations in the aquifer show that the strongly reducing conditions required for production of VC existed in the aquifer. The distribution of the chloride number indicate that the majority of sample locations where daughter products were present were also anaerobic. Data from individual boreholes indicate that high cis-DCE concentrations were commonly associated with declines in oxygen and sulfate concentrations and appeared on the upper edge of the methanogenic zone. Generally, ethene was found in the most methanogenic portions of the aquifer and was also associated with relatively high VC concentrations, suggesting that the ethene production was limited to those sample locations.

**References**


