



Project Summary

Natural Bioattenuation of Trichloroethene at the St. Joseph, Michigan Superfund Site

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Data from the St. Joseph, Michigan, Superfund Site were used in a peer-reviewed video entitled "Natural Bioattenuation of Trichloroethene at the St. Joseph, Michigan Superfund Site." Computer visualizations of the data set show how trichloroethene, or TCE, can degrade under natural conditions. The purpose of the tape is to present sampling results from the site to a technical audience. Although the visualizations show the general distribution of chemicals at the site, it is not possible to determine the precise concentrations from the tape. Thus the data set itself is available in a companion document. The following text is an amplified version of the narration on the video.

This Project Summary was developed by the National Risk Management Research Laboratory's Subsurface Protection and Remediation Division, Ada, OK, to announce key findings of the research project that is documented in a video of the same title (see video ordering information at back).

Site History

The site is located four miles south of St. Joseph and one-half mile east of Lake Michigan (Figure 1). Since the 1940s, the site has supported auto-parts manufacturing, including a foundry, as well as machining and painting operations. Because of past activities, ground water at the site is contaminated with industrial wastes that include trichloroethene (TCE). A plume of contamination reaches

from its source near the industry, toward Lake Michigan to the west (*Tiedeman and Gorelick, 1993*).

The aquifer is primarily composed of medium, fine, and very fine sands that are of glacial origin. The base of the aquifer is defined by a clay layer that lies between 21 and 29 meters below the ground surface. Since the ground water flows toward Lake Michigan, the contamination underlies residential and shoreline property. This water eventually discharges directly into the lake.

Although the TCE contamination is moving toward the lake, evidence indicates that the contaminants are degrading naturally along the way (*McCarty and Wilson, 1992*). Reduction in concentration alone does not necessarily indicate bioattenuation, because concentrations can decline from the effects of advection, dispersion and sorption. Rather, bioattenuation of TCE is indicated here by the presence of daughter products and certain geochemical conditions.

Degradation of TCE

Chlorinated organic compounds such as TCE can be biodegraded in the subsurface, but not because the microorganisms oxidize these compounds as a food source. On the contrary, the degradation of TCE under anaerobic conditions occurs through a reductive transformation where the TCE molecule serves as an electron acceptor. In a loose analogy, we could say that the microorganisms "breathe" TCE. For this type of degradation to occur, another organic

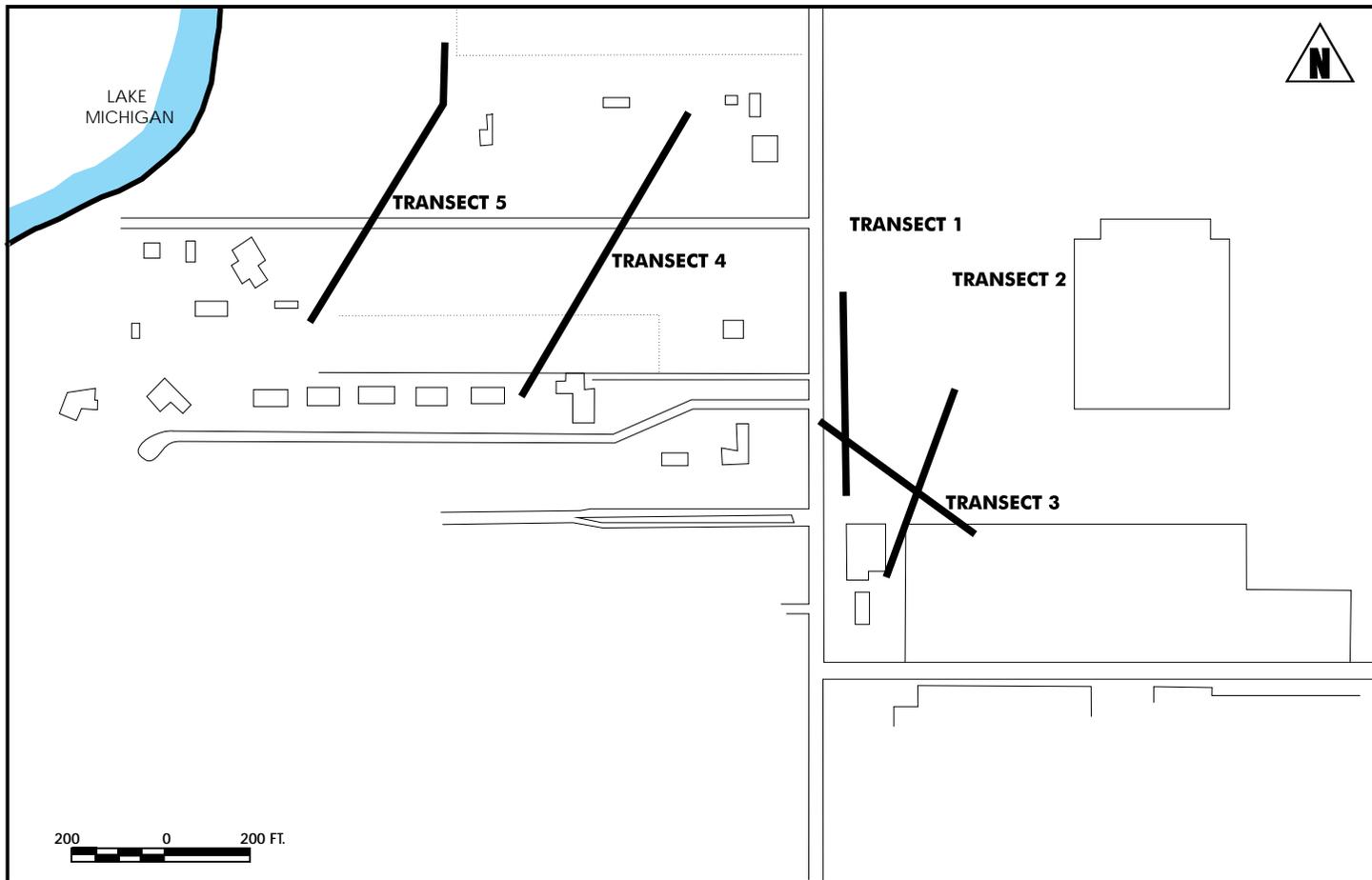
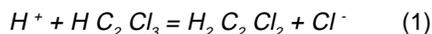


Figure 1. Site plan showing the location of the sampling transects.

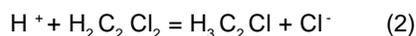
compound must be present to serve as an oxidizable carbon source, or “food” for the microorganisms. Under this condition, and in the absence of oxygen, TCE can be transformed through a series of intermediate chemical compounds to ethene. The intermediates are hazardous, and therefore incomplete degradation of TCE is potentially undesirable.

TCE may undergo a reductive transformation in an anaerobic environment. An enzyme or cofactor catalyzes the reduction of TCE (HC_2Cl_3), resulting in the loss of one chlorine atom:



Three isomers of dichloroethene, or DCE ($\text{H}_2\text{C}_2\text{Cl}_2$), can result: 1,1-DCE; cis-1,2 DCE and trans-1,2 DCE. Of these, cis-DCE is usually produced in the greatest abundance. The presence of the DCE isomers is significant, because these chemicals have rarely been used on a large scale for industrial purposes. Therefore their presence is an indication of transformations occurring in the subsurface.

With the loss of another chlorine atom from a DCE isomer, vinyl chloride ($\text{H}_3\text{C}_2\text{Cl}$) is produced:



The production of vinyl chloride is undesirable because it is a known carcinogen. However, ethene, which is not a compound of regulatory concern, can result from the loss of the chlorine atom from the vinyl chloride:



For further information on TCE biodegradation see McCarty and Semprini, 1994, and Semprini et al. 1995.

Field Evidence for TCE Bioattenuation

At a field site, natural bioattenuation of TCE is indicated

- by the presence and degradation of an oxidizable substrate;

- by the absence of oxygen and the presence of strongly reducing conditions (i.e., the abundance of methane);
- by the presence of the intermediate products (the DCE isomers and vinyl chloride); and,
- by the presence of ethene, the end product.

Specific site conditions determine the rate at which the transformations occur and the likelihood of producing a harmless end product. Each site must be evaluated individually for its potential to degrade TCE. There are sites where TCE either does not degrade or is only partially degraded. Thus the results from St. Joseph show the possibility of degradation of TCE, but do not indicate that degradation will occur at all sites.

Representation of the Data

In the visualizations, each data set is displayed as a set of colored cubes that

surround the borings. Each boring appears as an elongated, colored stack of cubes. This approach was taken so that the data was not smoothed, interpolated, nor extrapolated. The representations of the data, therefore, show the variation in concentration that occurs over small intervals at the site, and the irregularity of the distributions. The top of each set of cubes roughly corresponds to the water table; and the bottom corresponds to the clay layer that forms the base of the aquifer.

Narration on the tape makes it clear that the views have been exaggerated in the vertical direction in order to better illustrate the distribution of the chemicals over the thickness of the aquifer. The lengths of the borings were indicated by noting that each cube in the on-shore borings is 1.5 meters tall, and that the borings contain from five to eleven cubes. Thus the borings represent aquifer thicknesses varying from 7.5 to 16.5 meters. This scale is also noted by the distance (16.5 meters) between the top of the bluff and the shore line. The exaggerated vertical distances contrast with the distance across the site from the industry's parking lot to the shore of Lake Michigan (730 meters); and the width of the contaminant plume (110 meters). These features of the visualizations indicate that the views emphasize vertical variations in the contaminant distribution. In actuality the contaminant plume is a long and thin object.

The color scale that is used to indicate concentration ranges from blue to red, indicating low to high concentrations, respectively. A logarithmic scale was used to discriminate between concentrations that range over six orders of magnitude.

The St. Joseph Data Set

Data were collected at St. Joseph in sets of borings that form transects across the site. The borings were made with a 1.5 meter long slotted auger from which water samples were taken. A gas chromatograph was used to detect the pollutants as the borings were made. These procedures assured that the transects crossed the entire width of the contaminant plume.

Data were collected from the site in 1991 along transects near the source region, and in 1992 along two transects lying between the source and the lake (*Semprini et al.*, 1994). In August 1994, a set of samples were taken from a barge anchored in Lake Michigan. These samples determined the contaminant concentrations in the ground

water immediately before it discharges into the lake.

Features of the St. Joseph Data Set

In the vicinity of the plume, dissolved oxygen is depleted from the ground water, even though the ground water is oxygen-rich outside the contaminated zone. The ground water is depleted of oxygen near the bottom of the aquifer. Oxygen at intermediate and high concentrations, from two to ten milligrams per liter, is found in some locations near the water table. The methane data show a pattern that is almost exactly opposite that of the dissolved oxygen. Methane concentrations are highest near the bottom of the aquifer and are lowest near the water table. This distribution shows that the aerobic and anaerobic zones in the aquifer are clearly separated.

At St. Joseph, there is a decrease of COD from the source area to the lake. This is indicative of anaerobic degradation of the oxidizable carbon source, which remains to be specifically identified.

The highest TCE concentration at the site is 89,000 micrograms per liter and is found near the source area. The contaminants tend to move toward the lake in the deeper part of the aquifer, as noted by the absence of TCE near the water table. By the time TCE reaches the lake, however, the concentrations are reduced to levels that are mostly undetectable. There are a few TCE concentrations of one to two micrograms per liter in the lake transect. These concentrations are below the EPA drinking water standard of 5 micrograms per liter.

The pattern of declining concentration as the chemicals flow toward the lake is repeated in both the DCE and vinyl chloride data sets. Dechlorination of TCE usually produces the *cis*-DCE isomer in the greatest abundance. At St. Joseph, for example, the *trans*-DCE and the 1,1-DCE concentrations are generally lower than the *cis*-DCE concentrations by at least a factor of 10. The transformation of TCE to DCE may occur under sulfate reducing conditions and sulfate concentrations should be measured.

The maximum *cis*-DCE concentration is 128,000 micrograms per liter, occurring near the bottom of the aquifer in the source region. *cis*-DCE concentrations decline toward the lake and the compound is undetectable in the lake transect. Because the *cis*-DCE is the dominant isomer at St. Joseph, the *trans*-

DCE and 1,1-DCE data sets are not shown in the video tape.

The vinyl chloride distribution follows the general pattern of highest concentrations near the bottom of the aquifer and declining concentrations toward the lake. No vinyl chloride concentrations above the drinking water standard of two micrograms per liter were detected from samples taken in the lake.

The presence of ethene is evidence for the complete dechlorination of the TCE. Ethene is present throughout the contaminant plume; its distribution follows the pattern of the other degradation products.

Summary

In summary, the intermediate products of TCE bioattenuation are found in oxygen depleted portions of the aquifer that are also rich in methane. Ethene is found in significant concentration, indicating some of the TCE is degraded to a compound that is not of regulatory concern. The concentrations of TCE and the degradation products significantly decline toward the lake. The off-shore data show that only minute concentrations of these chemicals exist in the ground water that discharges into the lake.

Analysis of data from the St. Joseph, Michigan Superfund site indicates that natural bioattenuation of TCE is occurring as the contaminants flow toward Lake Michigan. Depletion of oxygen, the presence of methane and the appearance of degradation products indicate that the reduction in TCE concentrations is not solely due to volatilization or dilution. Rather, they are indicative of microbial processes helping to reduce the contaminant concentrations below EPA drinking water standards before the water is discharged into Lake Michigan. Continued monitoring of the site is necessary to demonstrate that contaminant levels remain below accepted standards and that the flux of chemicals into the lake remains low.

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Tiedeman, C., and S. Gorelick, Analysis of uncertainty in optimal groundwater contaminant capture design, *Water Resources Research*, 29(7), 2139-2153, 1993.

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The video, entitled "Natural Bioattenuation of Trichloroethene at the St. Joseph, Michigan Superfund Site" (EPA/600/V-95/001), will be available upon request from:

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