

Extraction of Degradation Rate Constants from the St. Joseph, Michigan Trichloroethene Site

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1 Background

Anaerobic biodegradation of TCE occurs through successive dechlorination from trichloroethene to dichloroethene, vinyl chloride and ethene [2]. The process produces three isomers of DCE (1,1-DCE, cis-1,2-DCE, and trans-1,2-DCE). Although TCE was commonly used in industry, the DCEs were not; and ethene would not be expected in most ground waters. Thus the presence of these compounds are indicative of degradation when found in anaerobic ground waters. Implicit in the work of [1] and [3] is the fact that degradation of TCE at the St. Joseph site was not predicted from theoretical considerations; rather degradation of TCE was established from the field data as described in this proceedings [9]. The purpose of this paper is to present estimates of averaged concentrations, mass flux and degradation rate constants.

2 Ground Water Flow

Ground water flows at the St. Joseph site from the contaminant source toward Lake Michigan. The average hydraulic conductivity at the site was estimated at 7.5 m/d from a calibrated ground water flow model [6]. The estimated travel time for TCE between the source and the lake is approximately 18 years (Table 1). If the contamination was released only in the aqueous phase, one would expect that contaminants released 18 years or longer ago would by now have discharged into the lake. The observed contaminant distribution suggests a continuing source, most likely a DNAPL.

3 Averaged Concentrations

Data were collected from the site from sets of borings that formed four on-shore and one off-shore transects that crossed the plume (see Figure 1 of [9]). These range from 130 m to 855 m from the suspected source of contamination. From the borings, a three-dimensional view of the contamination was developed. A field gas chromatograph was used to determine the boundaries of

Distance from source (m)	Transport Time (y)	Transect Width (m)	Average Concentration ($\mu\text{g/L}$)		
			TCE	cis DCE	Vinyl Chloride
130	3.2	108	6,500	8,100	930
			<i>68,000</i>	<i>128,000</i>	<i>4,400</i>
390	9.7	150	520	830	450
			<i>8,700</i>	<i>9,800</i>	<i>1,660</i>
550	12.5	192	15	18	106
			<i>56</i>	<i>870</i>	<i>205</i>
855	17.9	395	< 1	< 1	< 1
			<i>1.4</i>	<i>0.8</i>	<i>0.5</i>

Table 1: Attenuation of the chlorinated ethenes along the length of the plume

the plume. Sampling continued until the entire width of the plume was crossed at each transect. By following this procedure the transects are known to have contained the entire plume. This approach allows calculation of total mass that crosses each transect, and thus gives an estimate of flux of each contaminant as a function of distance from the lake.

Transect-averaged concentration estimates were developed by using the SITE-3D graphics package [7]. The data were represented as sets of blocks that are centered around each boring. The blocks were each 5 ft high, corresponding to the length of the slotted auger. At each transect, the average concentration was calculated by summing over the blocks and dividing by the area of the transects.

In Table 2, concentration estimates are presented for the perpendicular transects ordered from furthest up gradient (transect 2) to furthest down gradient (transect 5). The concentration estimates are based only upon blocks from the anaerobic portion of the aquifer (and thus differ from the averages in Table 1). All of the chlorinated ethenes show decreasing concentration with distance down gradient. Thus, all of the rate coefficients developed below reflect a net loss of the species. The chloride concentrations increase down gradient as expected from the dechlorination of the ethenes. However, on a molar basis the increase in average chloride concentration is greater than which would result from dechlorination alone.

4 Mass Flux

The concentration results (Table 2) show that by the time the contaminants reach the lake their concentrations are reduced to very low levels. It is equally important to determine the mass of chemicals released to the lake per year. Given the approximate ground water velocities and the contaminant concentrations in the transects, an estimate of the mass flux of chemicals can also be estimated. Advective mass fluxes of each chemical were estimated per transect by multiplying the seepage velocity by concentration in each block formed by SITE-3D. The results are given in Table 3 which shows a decline in mass flux of each chlorinated ethene. The reduction in flux ranged from

Chemical	Transect 2	Transect 4	Transect 5	Lake Transect
TCE	7411	864	30.1	(1.4)
c-DCE	9117	1453	281	(0.80)
t-DCE	716	31.4	5.39	(1.1)
1,1-DCE	339	24.3	2.99	<i>blq</i>
VC	998	473	97.7	(0.16)
Ethene	480	297	24.2	no data
Sum of the Ethenes	19100	3150	442	(3.5)
Chloride	65073	78505	92023	44418

Table 2: Transect-averaged concentrations ($\mu\text{g/L}$) from the anaerobic zone. Values in parenthesis were based upon one or more estimated values and *blq* indicates no detection above the limit of quantitation

Transect	Mass flux kg/y						
	TCE	c-DCE	VC	Ethene	Total Ethenes	Methane	Chloride
<i>2 (Aug-Sept, 1991)</i>	117	133	16.8	7.60	283	65.7	1456
<i>1 (Aug-Sept, 1991)</i>	50.0	45.2	16.8	7.95	125	49.2	545
<i>4 (Mar. 1992)</i>	30.9	41.7	3.87	10.8	88.4	101	4610
<i>5 (Apr. 1992)</i>	0.95	10.0	1.68	0.164	13.1	46.7	5290
Reduction Ratio	123	13	10	46	22		

Table 3: Flux Estimates for Transects 1, 2, 4 and 5. The reduction ratio is the ratio of mass flux at transect 2 to that at transect 5.

a factor of 10 to 123. The flux of methane showed no consistent pattern. Chloride flux increased beyond Transect 1.

5 Degradation Rates

The transport of each chemical is parametrized by the ground water flow velocity, the retardation coefficient, the dispersivities, and the decay constant. Specifically, two-dimensional solute transport with first order decay obeys

$$R \frac{\partial c}{\partial t} = \underbrace{D_{xx} \frac{\partial^2 c}{\partial x^2} + D_{yy} \frac{\partial^2 c}{\partial y^2}}_{\text{Dispersion}} - \underbrace{v \frac{\partial c}{\partial x}}_{\text{Advection}} - \underbrace{\lambda^* c}_{\text{Decay}} \quad (1)$$

where R is the retardation coefficient, c is the concentration, t is time, D_{xx} and D_{yy} are the longitudinal and transverse dispersion coefficients, respectively, x is longitudinal distance, y is the distance transverse to the plume centerline in the horizontal plane, v is the seepage velocity, and

λ^* is the first order decay constant. First order decay is assumed for this analysis, because it is the usual way to report degradation rates of chlorinated hydrocarbons [4]. This form of the transport equation assumes that the ground water flow is uniform and aligned with the axis of the plume as observed for the plume. This assumption also allows application of analytic solutions as described in the appendix.

The concentration of dissolved chemicals can change because of the effect of the terms on the right hand side of equation 1. Dispersion is used to characterize apparent physical dilution in aquifers. Dispersion is currently understood to result primarily from ground water flow through heterogeneous materials. In multi-dimensional flow, advection can cause concentrations to decrease because of divergence of flow lines. Advection does not directly change concentrations in one-dimensional flow, but influences the contribution of dispersion. Decay changes concentration through removal of mass from the aquifer.

The significance of these observations is that when presented with a set of contaminant concentrations, the distribution of contamination may depend upon physiochemical and biological processes. Observed concentrations in themselves do not indicate the contribution of each process to the plume shape. Extraction of apparent rates from the field data needs to account for the multiple processes. In Table 5 estimated rate constants are given for St. Joseph. These constants were determined from the solution of the transport equation presented in the appendix. The solution included advection, retardation, longitudinal and transverse dispersion, and first order loss. Inclusion of transverse dispersion is important because this characterizes down-gradient spreading of the plume. The observed widths of the plume at St. Joseph are given in Table 1 and were used to estimate the transverse dispersivity according to the procedure given in the appendix. The effect of transverse dispersivity on the estimated rate constants, however, decreases as the plume widens and the centerline concentrations decrease. Longitudinal dispersivity has been shown to have a minor impact on the estimated rate constants at distances between transects on the order of 100 meters [8].

The rates given in Table 4 are called net rates, because, for the daughter products, the observed concentrations are a result of production of the daughter from decay of the parent *and* decay of the daughter itself. The gross rate of decay of the daughter (Table 5) that does not include its production was determined by the procedure given in the appendix. The two rates are the same for TCE, since no production of TCE occurred. The gross rates are, as expected, higher than the net rates, because production of a compound must be balanced by high gross rates to attain the observed net rate.

Chemical	Transect 2 to 4	Transect 4 to 5	Transect 5 to Lake
TCE	0.30	1.7	1.7
cDCE	0.26	0.58	3.3
VC	0.15	0.78	2.6

Table 4: Net apparent degradation rate constants (1/y) from the two-dimensional model (equation 3)

Chemical	Transect 2 to 4	Transect 4 to 5	Transect 5 to Lake
TCE	0.30	1.7	1.7
cDCE	0.54	1.1	4.0
VC	2.6	3.1	20

Table 5: Apparent degradation rate constants (1/y) from the two-dimensional model equation 3 and the gross rate correction given by equation 7

6 Conclusions

The western TCE plume at St. Joseph, Michigan showed a decrease of maximum TCE concentration by a factor of 50,000 from the furthest up-gradient transect to the lake transect. Concentrations of each contaminant declined to values below the respective MCLs when sampled from the lake sediments. Mass fluxes decrease by factors of 10 to 123 from the source to the last on-shore transect (number 5). Thus, not only do the concentrations decline, so does the loading in the ground water. The reduction in loading is attributed to degradation, because of the geochemical evidence presented by [9]. Further, when site-specific estimates of the transport parameters are used in solutions of the transport equations the apparent reduction in concentration is only accounted for by loss of mass. These apparent degradation rate constants were calculated from the St. Joseph, Michigan data set through application of a two-dimensional analytical solution of the transport equation. Since transverse spreading of the plume reduces the contaminant concentrations, the effect of transverse dispersivity was included in the analysis.

7 Disclaimer

This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.

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A Appendix: Extraction of Rate Constants via Two-Dimensional, Steady-State Transport Analysis

The two-dimensional transport equation, subject to the boundary conditions

$$\begin{aligned}
 c(x, y, 0) &= 0 & (2) \\
 c(0, y, t) &= c_o \exp\left(\frac{-y^2}{2\sigma^2}\right) \\
 c(\infty, y, t) = c(x, -\infty, t) = c(x, \infty, t) &= 0
 \end{aligned}$$

has the approximate steady state solution [5]

$$c(x, y) = \frac{c_o \exp \left[\frac{vx}{2D_{xx}} \left(1 - \sqrt{1 + \frac{4\lambda \cdot RD_{xx}}{v^2}} \right) - \frac{\frac{y^2}{\sigma^2}}{\frac{4x D_{yy}}{\sigma^2 v}} \right]}{\sqrt{1 + \frac{\frac{2x D_{yy}}{\sigma^2 v}}{\sqrt{1 + \frac{4\lambda \cdot RD_{xx}}{v^2}}}}} \quad (3)$$

Vertically averaged concentrations and the distances between each borehole were used to develop the boundary condition ($c(0, y, t)$ in equation 2) for application of equation 3. The unknown parameters

are the up-gradient peak concentration, c_o , and the standard deviation, σ , of the distribution. Since the width of the plume, W , was established via the field sampling program, the standard deviation of the distribution can be estimated as $W = 6\sigma$. A mass balance can then be solved for the peak concentration of the gaussian distribution, c_o , from

$$\int n\hat{c}dy = \int nc_o \exp\left(\frac{-y^2}{2\sigma^2}\right) dy = nc_o\sigma\sqrt{2\pi} \quad (4)$$

where n is the porosity, \hat{c} is the vertically averaged concentration, and the y coordinate runs parallel to the transect.

The transverse dispersivity can also be estimated from the measured widths of the transects. The width of a contaminant distribution is related to the transverse dispersivity through

$$D_{yy} = a_{yy}v = \frac{1}{2} \frac{d\sigma^2}{dt} \quad (5)$$

where a_{yy} is the transverse dispersivity. By applying equation 5 in a discrete form and substituting $\Delta t = \Delta x R/v$, an expression for a_{yy} is obtained in terms of the seepage velocity, retardation coefficient, distance between transects (Δx), and change in variance of the gaussian distributions for the transect concentrations ($\Delta\sigma^2$):

$$a_{yy} = \frac{1}{2R} \frac{\Delta\sigma^2}{\Delta x} \quad (6)$$

The only remaining unknown in equation 3 is the decay constant λ^* , which is determined through a bisection search. Table 4 gives the rate constants from the two dimensional model.

A.1 Net and Gross Decay Rates

The rate constants derived from the solution (equation 3 and Table 4) are net rates which include the production and decay of a given daughter product. It is necessary to separate production of the compound from its decay to estimate the gross apparent decay rates for c-DCE, t-DCE, 1,1-DCE and VC. Previous work [8] used a reaction rate model that solved simultaneous ordinary differential equations for this purpose. Here, simplified expressions for the rates were used to estimate the apparent decay rates.

$$\lambda_{j(n)} = f_j\lambda_{j+1(n)}S + \lambda_{j(g)} \quad (7)$$

where $\lambda_{j(n)}$ is the net decay rate determined by equation 3, f_j is the fraction of an isomer (j) produced from the degradation of the parent (j+1), $\lambda_{j+1(n)}$ is the apparent decay rate of the parent defined from equation 3, S is the ratio of molar concentration of parent (j+1) to daughter j, and $\lambda_{j(g)}$ is the gross apparent decay rate of daughter j. For the DCE isomers, f_j is approximated by the average ratio of an isomer j to the sum of the DCEs over the pairs of transects. For VC, f_j is equal to 1.0. The gross apparent decay rates for c-DCE, t-DCE, 1,1-DCE and VC appear in Table 5. Although equation 7 is concentration dependent because of S which was assumed to be the average of the up and down gradient ratios, the results presented in Table 5 are essentially the same as determined from the reaction rate model [8].

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