

SELECTING REMEDIATION GOALS BY ASSESSING THE NATURAL ATTENUATION CAPACITY OF GROUND-WATER SYSTEMS

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ABSTRACT

Remediation goals for the source areas of a chlorinated ethene-contaminated ground-water plume in Kings Bay, GA were identified by assessing the natural attenuation capacity of the aquifer system. The redox chemistry of the site indicates that sulfate-reducing ($H_2 \sim 2$ nanomoles per liter, (nM)) conditions near the contaminant source grades to Fe(III)-reducing conditions ($H_2 \sim 0.5$ nM) downgradient of the source. Sulfate-reducing conditions facilitate the initial reduction of perchloroethene (PCE) to trichloroethene (TCE), cis-dichloroethene (cis-DCE), and vinyl chloride (VC). Subsequently, the Fe(III)-reducing conditions drive the oxidation of cis-DCE and VC to carbon dioxide and chloride. This sequence of redox conditions gives the aquifer a substantial capacity for biodegrading chlorinated ethenes. Natural attenuation capacity, defined as the slope of the steady-state contaminant concentration profile along a ground-water flowpath, is a function of biodegradation rates, aquifer dispersive characteristics, and ground-water flow velocity.

Natural attenuation capacity at the Kings Bay site was assessed by estimating ground-water flow rates ($\sim 0.23 \pm 0.12$ m/d) and aquifer dispersivity (~ 1 m) from hydrologic and scale considerations. Apparent biodegradation rate constants (PCE and TCE $\sim 0.01 d^{-1}$; cis-DCE and VC $\sim 0.025 d^{-1}$) were estimated from observed contaminant concentration changes along aquifer flowpaths. Given estimates for these parameters, a boundary-value problem approach was used to estimate levels to which contaminant concentrations in the source-areas must be lowered (by engineered removal), or ground-water flow velocities lowered (by pumping) in order for the natural attenuation capacity to achieve maximum concentration limits (MCLs) prior to reaching a predetermined regulatory point of compliance.

INTRODUCTION

Chlorinated ethenes are subject to natural attenuation processes such as dilution, adsorption, and biodegradation in all ground-water systems (Wiedemeier et al., 1997). However, the efficiency of biodegradation, the process that causes the actual destruction of contaminants, varies widely. In many ground-water systems, biodegradation and other natural attenuation processes are not sufficient to protect downgradient receptors from contamination. For this reason, U.S. Environmental Protection Agency (EPA) guidance has stressed that natural attenuation is most often appropriate when used in conjunction with engineered reduction of contaminant sources:

“In the majority of cases where monitored natural attenuation is proposed as a remedy, its use may be appropriate as one component of the total remedy, that is, either in conjunction with active remediation or as a follow-up measure” (U.S. EPA, 1997, p.1).

The manner in which natural attenuation and active remediation measures (such as source removal, pump-and-treat, chemical oxidation, or enhanced bioremediation) are combined depends on the natural attenuation capacity of a system. If the natural attenuation capacity is small, for example, then active remediation measures will need to remove or immobilize a high proportion of the contaminant source in order to protect

downgradient receptors from contamination. Conversely, if the natural attenuation capacity is large, then less source removal may be required in order to protect downgradient receptors. In either case, it is necessary to quantify the natural attenuation capacity of a system in order to effectively combine contaminant source-removal methods with natural attenuation. The purpose of this paper is to assess the natural attenuation capacity of a chlorinated ethene-contaminated aquifer in Kings Bay, GA, and to use this assessment for selecting engineered source-reduction goals at the site.

Natural Attenuation Capacity

The concept of “assimilative capacity” is well-known in soil science (Charbeneau and Daniel, 1993, p. 15.1) and surface water hydrology (Chapra, 1996, p. 11) and refers to the capacity of a system to absorb and/or transform pollutants. By analogy, a “natural attenuation capacity” can be defined for ground-water systems as being the ability to lower contaminant concentrations along aquifer flowpaths.

In surface-water systems, assimilative capacity depends upon hydrologic (stream flow, mixing, and hydrodynamic dispersion), and biological (biological oxygen demand) factors and is assessed using analytical or digital water-quality models. Similarly, the natural attenuation capacity of ground-water systems depends upon hydrologic (dispersion and advection) and biological (biodegradation rates) factors that can also be assessed using quantitative models. The sum of dispersive, advective, sorptive, and biodegradative processes acting on a solute in a one-dimensional flow system is given by the solute-transport equation:

$$\frac{C}{t} = D \frac{d^2C}{dx^2} - v \frac{dC}{dx} - \frac{\rho_b K_d}{n} \frac{dC}{dx} - kC \quad (1)$$

where D is the coefficient of hydrodynamic dispersion (m²/d), v is the velocity of ground-water flow (M/d), ρ_b is bulk density, K_d is a linear

sorption distribution coefficient, n is porosity, and k is a first-order biodegradation rate constant (d⁻¹) (Freeze and Cherry, 1979, p. 402 and p. 552). The coefficient of hydrodynamic dispersion, in turn, is proportional to ground-water velocity and scale-dependent aquifer dispersivity D* (m):

$$D = v D^* \quad (2)$$

Appropriate procedures for solving equation (1) depend on the ground-water system in question, and the specific problems being addressed. When a contaminant plume has reached approximate steady-state conditions (that is, the plume is not expanding or contracting with time and $C/t=0$), the sorption term becomes small relative to the other three terms, and the solute-transport equation simplifies to the ordinary differential equation:

$$D \frac{d^2C}{dx^2} - v \frac{dC}{dx} - kC = 0 \quad (3)$$

For boundary conditions of $C = C_0$ at $x=0$, and $C=0$ as $x \rightarrow \infty$, equation 3 has the particular solution:

$$C(x) = C_0 \exp \left[-\frac{v + \sqrt{v^2 + 4Dk}}{2D} x \right] \quad (4)$$

Equation (4) indicates that the steady-state solute concentration decrease away from a constant source is dependent on hydrodynamic dispersion (D), the biodegradation rate constant (k), and ground-water velocity (v). With this usage, a positive value of k indicates contaminant loss. The slope of the solute concentration profile along a flowpath is proportional to the value of:

$$\left[-\frac{v + \sqrt{v^2 + 4Dk}}{2D} \right] \quad (5)$$

The term *natural attenuation capacity* (NAC), as used in this paper refers to the quantity given in

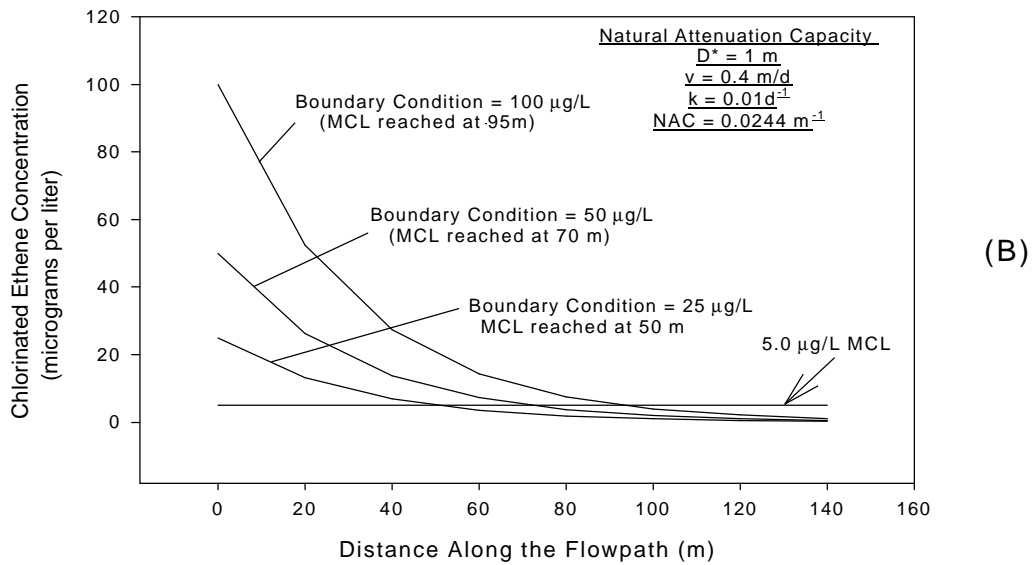
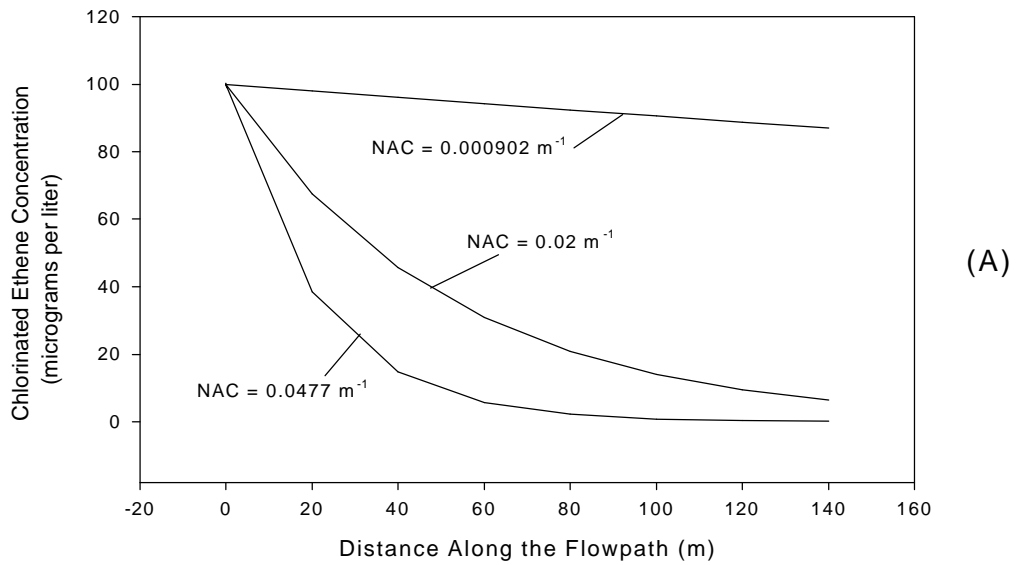


Figure 1.--Schematic diagram showing (A) the affect of natural attenuation capacity and (B) the affect of source-area concentrations on the distance required to decrease contaminant concentrations below MCLs.

equation 5, which has units of m^{-1} . Conceptually, it may be thought of as the contaminant-lowering capacity of an aquifer per meter of flowpath.

The concept of natural attenuation capacity as defined in equation 5 is useful because it illustrates those characteristics of a hydrologic system that affect the efficiency of natural attenuation. For example, if the biodegradation rate constant is small ($\sim 0.001 d^{-1}$) relative to the ground-water velocity ($\sim 1 m/d$) and aquifer dispersivity (10 m), the NAC of the system will also be small ($0.009902 m^{-1}$). Because of this small NAC, contaminants will be transported relatively long distances downgradient of a source area (Fig. 1A). Conversely, if the biodegradation rate constant is high ($0.01 d^{-1}$) relative to ground-water velocity ($0.2 m/d$) and aquifer dispersivity (1 m), the NAC will be proportionally higher ($0.0477 m^{-1}$) and the transport of contaminants will be restricted closer to the source area (Fig. 1A).

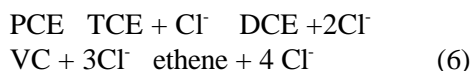
In addition to natural attenuation capacity, the distance that contaminants are transported in a ground-water system depends on contaminant concentrations at the source area (C_0 in equation 4). If contaminant concentrations at the source are relatively high, a longer ground-water flowpath will be required for a given NAC to reach MCLs than if source-area concentrations are lower (Fig. 1B).

This reasoning identifies two ways in which the natural attenuation capacity of a ground-water system can be integrated with engineered methods to achieve overall site remediation. The first way is to use engineering methods (excavation, in-situ chemical oxidation, in-situ bioremediation, etc.) to lower source area concentrations to levels that the NAC present in the aquifer can lower contaminant concentrations to MCLs at a given point of compliance. The second way is to decrease the velocity of ground-water flow away from a contaminant source area, which in turn increases NAC (Fig. 1A). This can be accomplished using conventional pump-and-treat technology.

Biodegradation of Chlorinated Ethenes

The biodegradation of chlorinated ethenes

is complex because these compounds are subject to reductive (Vogel et al., 1987; McCarty and Semprini, 1994; Bouwer, 1994), oxidative (Bradley and Chapelle, 1996), and cometabolic (Vogel et al., 1987; McCarty and Semprini, 1994) biodegradation processes. Under anoxic conditions, chlorinated ethenes such as perchloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE) and vinyl chloride (VC) are subject to reductive dechlorination according to the sequence:



However, the efficiency of dechlorination differs for methanogenic, sulfate-reducing, or Fe(III)-reducing conditions (Smatlak et al., 1996). Under methanogenic and sulfate-reducing conditions, dechlorination of PCE and TCE is rapid and efficient. Dechlorination is less efficient under Fe(III)-reducing conditions, and dechlorination does not occur under oxygen-reducing conditions. Thus, the distribution of redox conditions affects the rate and extent of reductive dechlorination of chlorinated ethenes in ground-water systems.

Highly chlorinated ethenes such as PCE and TCE are not generally subject to oxidative biodegradation processes. Lightly chlorinated ethenes such as DCE and VC, however, can be oxidized to carbon dioxide (CO_2) under oxic or Fe(III)-reducing conditions. It is not yet clear, however, whether DCE oxidation under Fe(III) reducing conditions is first preceded by reductive dechlorination to VC (Bradley and Chapelle, 1996). Cometabolic processes, in which chlorinated ethenes are gratuitously degraded by enzymatic processes designed to metabolize organic compounds other than chlorinated ethenes, have been widely documented (Vogel et al., 1987; McCarty and Semprini, 1994) and can be an important component of natural attenuation in some systems.

It is observed that sequential reduction of PCE and TCE followed by oxidation of DCE and VC is the most efficient combination of mechanisms for completely degrading chlorinated ethenes (Cox and others, 1995). Thus, the efficiency of natural attenuation, and thus the

natural attenuation capacity of ground-water systems, is directly related to the distribution of ambient redox processes (Chapelle, 1996).

Estimating Natural Attenuation Capacity

The natural attenuation capacity at individual field sites can be estimated by obtaining estimates of k , v , and D (equation 5). Values of v can be estimated using standard field hydrologic methods, and D can be estimated from v (equation 2) and the scale of the plume (Gelhar and others, 1992). Similarly, the kinetics of biodegradation can be estimated using field methods (Buscheck and Alcantar, 1995; Chapelle and others, 1996; Weaver and others, 1996). If v and D can be reliably estimated, and if concentration changes of contaminants can be documented with field data, k can be estimated by curve-fitting solutions of equation 4 to field data. This can be done by coding equation 4 as a transform in a spreadsheet, or can be done using an established computer code such as Bioscreen (Newell and others, 1996). Site-specific D , v , and k values, in turn, can be used to quantitatively describe the natural attenuation capacity (equation 5) of particular ground-water systems.

Sources of Uncertainty

Estimating biodegradation rate constants using field data is subject to numerous sources of uncertainty which need to be explicitly considered in any application. These uncertainties include (1) variation of ground-water flow rates, (2) uncertainty in adequately sampling contaminant concentrations within the plume, and (3) deviations from steady-state conditions within the plume. Variation of ground-water flow rates in time and space due to heterogeneity of hydraulic conductivity and hydraulic gradient changes due to recharge events occurs in all shallow aquifers. This is an important source of uncertainty in estimating biodegradation rate constants because an n -fold error in groundwater flow velocity (v) results in an n -fold error in calculated biodegradation rate constant (k) (equation 3). Because of this inherent error, which can vary in time, it is appropriate to use ranges of v in

estimating k , and reporting k values as \pm the range of variation. This is the procedure used in this paper. If variations in ground-water flow with time are large, then the steady-state assumption inherent in equation 3 is not appropriate and time-dependent solutions of equation 1 must be used (Rifai and others, 1995). Furthermore, if transverse dispersion is significant in a system, then a 2-D or 3-D treatment of the problem is more appropriate (Weaver and others, 1996).

Adequate sampling of contaminant concentrations in a plume can be a significant source of uncertainty in evaluating the behavior of chlorinated ethene concentrations (Cherry, 1996). Contaminant concentrations are observed to vary significantly between the "core" and "fringes" of plumes. These variations can significantly effect natural attenuation capacity estimates and calculated biodegradation rates.

Field methods for estimating biodegradation rate constants were first applied to petroleum hydrocarbon contaminants (Buscheck and Alcantar, 1995; Chapelle and others, 1996) in ground water. For chlorinated ethenes, this procedure is complicated by the fact that TCE, DCE, and VC are produced as daughter products from PCE as well as being degraded. TCE, DCE, and VC concentration changes along a flowpath segment reflect the difference between production and degradation. Thus, for TCE, cis-DCE, and VC, this procedure yields overall degradation rate constants which *underestimate* actual degradation rate constants.

Clearly there are numerous sources of uncertainty inherent in quantifying biodegradation rate constants using field data. Furthermore, many of these uncertainties are difficult or impossible to quantify. While uncertainty can be reduced by extensive data collection, they cannot be eliminated entirely. For these reasons, biodegradation rate constants, and estimates of natural attenuation capacity, obtained using these methods should be regarded as estimates.

RESULTS AND DISCUSSION

Geology, Hydrology, and Site History

The site used for this study is an

abandoned landfill known as the Old Camden Road Landfill located at the Naval Submarine Base (NSB) Kings Bay, Georgia. A map of the landfill and the orientation of the contaminant plume, as determined by monitoring wells and direct-push data is shown in Figure 2. This site is underlain by sediments of back-barrier island and

barrier island origin. The most permeable sands underlying the site are present between depths of 10 and 11 m below land surface, and record the sedimentation of a prograding barrier island. This permeable zone is referred to informally as the “11 meter” aquifer in this report. This permeable zone is underlain and overlain by finer-grained sands

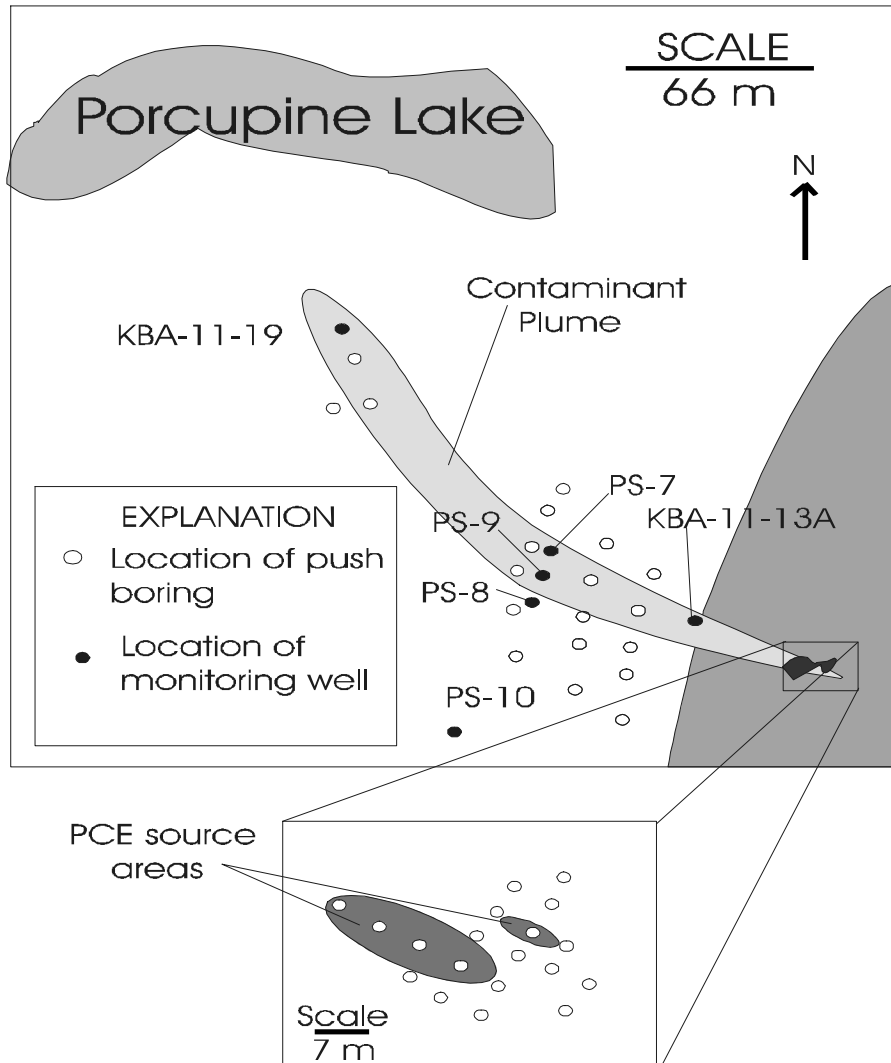


Figure 2.--Location of PCE source areas and orientation of chlorinated ethene contaminant plume.

exhibiting lower hydraulic conductivity. Aquifer tests and slug tests at this site indicate that hydraulic conductivities of the sands range from 0.6 to 3 m/d. The lithology of these sands suggest that the 11-meter aquifer is characterized by higher hydraulic conductivities ($K \sim 10$ m/d) relative to overlying and underlying sands. Because of its relative permeability, the 11-meter aquifer is a preferential pathway for horizontal ground-water flow and contaminant transport in this system.

Overlying the 11-meter aquifer at depths of approximately 3-5 meters below land surface is

a layer of organic-rich sands. This organic-rich layer has the important effect of removing dissolved oxygen from recharging water and producing uniformly anoxic conditions in the 11-meter aquifer. In addition, organic matter that was disposed of in the landfill contributes to highly reducing conditions. Ground-water flow in the 11-meter aquifer is predominantly to the west, and can be easily traced by methane-bearing water originating from the landfill.

The Old Camden Road landfill was used to dispose of municipal waste between 1974 and 1981. Trenches were excavated to a

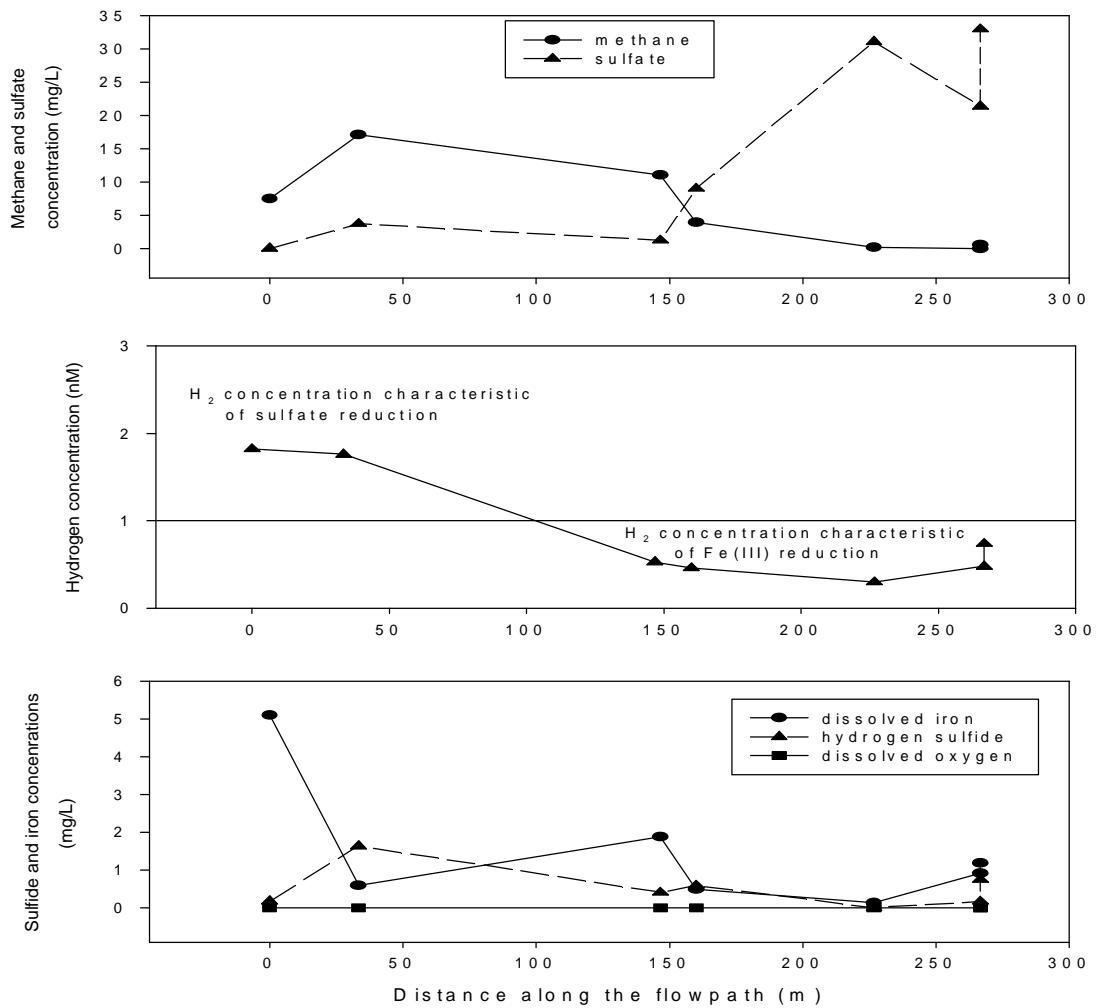


Figure 3.--Redox chemistry of ground water in the contaminant plume.

depth of between 2 and 4 meters, filled with waste, and covered with fill. At some time during waste-disposal operations, PCE was released at the landfill. Two discrete PCE sources were identified by direct-push sampling of ground water and aquifer sediments (Fig. 2) as part of this study. These sources are highly localized suggesting that the contamination events occurred at two discrete times. Emanating from these sources is a discrete plume of chlorinated ethene-contaminated ground water that flows toward Porcupine Lake located adjacent to the landfill (Fig. 2). The geometry and extent of the contaminant plume was previously delineated by direct push methods (ABB Environmental Services, Inc., 1997).

Delineation of Redox Processes

Ground-water chemistry data were used to delineate the distribution of redox processes in the ground-water system underlying and downgradient of the Old Camden Road landfill. The methodology used in this delineation has been described previously (Chapelle, 1996). Concentrations of redox-sensitive parameters dissolved oxygen, methane, sulfate, molecular hydrogen (H_2), sulfide and dissolved iron are plotted versus distance along the flowpath are shown in Figure 3. Sulfate concentrations are relatively low underlying the landfill, while methane concentrations are relatively high. The high methane concentrations indicate the presence of active methanogenesis in the landfill itself. However, measured concentrations of hydrogen (H_2) indicate that sulfate reduction is the predominant redox process in the 11- meter aquifer underlying the landfill, and grades into uniformly Fe(III)-reducing conditions downgradient of the landfill. Concentrations of dissolved sulfide and ferrous iron are consistent with this interpretation, with relatively high concentrations of sulfide underlying the landfill that decrease downgradient. Downgradient of the landfill, concentrations of ferrous iron (1-2 mg/L) are consistent with ongoing Fe(III) reduction. These sequential reducing (sulfate

reducing) to more oxidizing (Fe(III) reduction) conditions are favorable for degrading chlorinated ethenes, and would be expected to confer a substantial natural attenuation capacity to the system.

Concentration Changes of Chlorinated Ethenes

Ground-water chemistry data collected by direct push methods in this study (Fig. 2) indicate that PCE is the principal contaminant in the source area, and that PCE is sequentially dechlorinated along the ground-water flowpath. Additional direct-push data (ABB Environmental Services, Inc., 1997) documents contaminant behavior in the plume. Concentrations of PCE, TCE, cis-DCE, and VC within the plume are plotted versus distance along the flowpath in Figure 4.

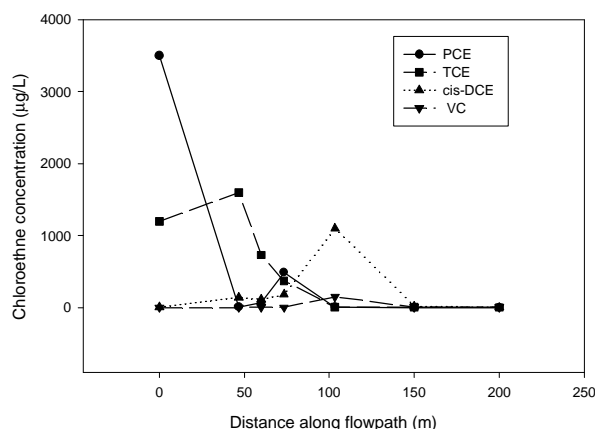


Figure 4. Concentrations of PCE, TCE, cis-DCE, and VC along the flowpath within the contaminant plume.

Near the source areas, PCE and TCE are the only measureable contaminants. By 50 meters downgradient, however, PCE concentrations have decreased to near the detection limit and the principal contaminant is TCE. TCE concentrations decrease along the flowpath and by

100 meters along the flowpath, cis-DCE is the principal contaminant and VC concentrations increase. By 150 meters along the flowpath, VC is the principal contaminant remaining. These data show that daughter products of reductive dechlorination are actively produced in this system, and are direct evidence of reductive dechlorination in this ground-water system. Furthermore, the decrease of cis-DCE and VC along the flowpath suggests continued reductive biodegradation, the

initiation of oxidative biodegradation, or both.

Kinetics of Chlorinated Ethene Biodegradation

The data of Figure 4 can be used to estimate degradation rate constants for individual chlorinated ethenes. Observed decreases in individual chlorinated ethene concentrations with fixed values of v and D^* are shown fitted to the

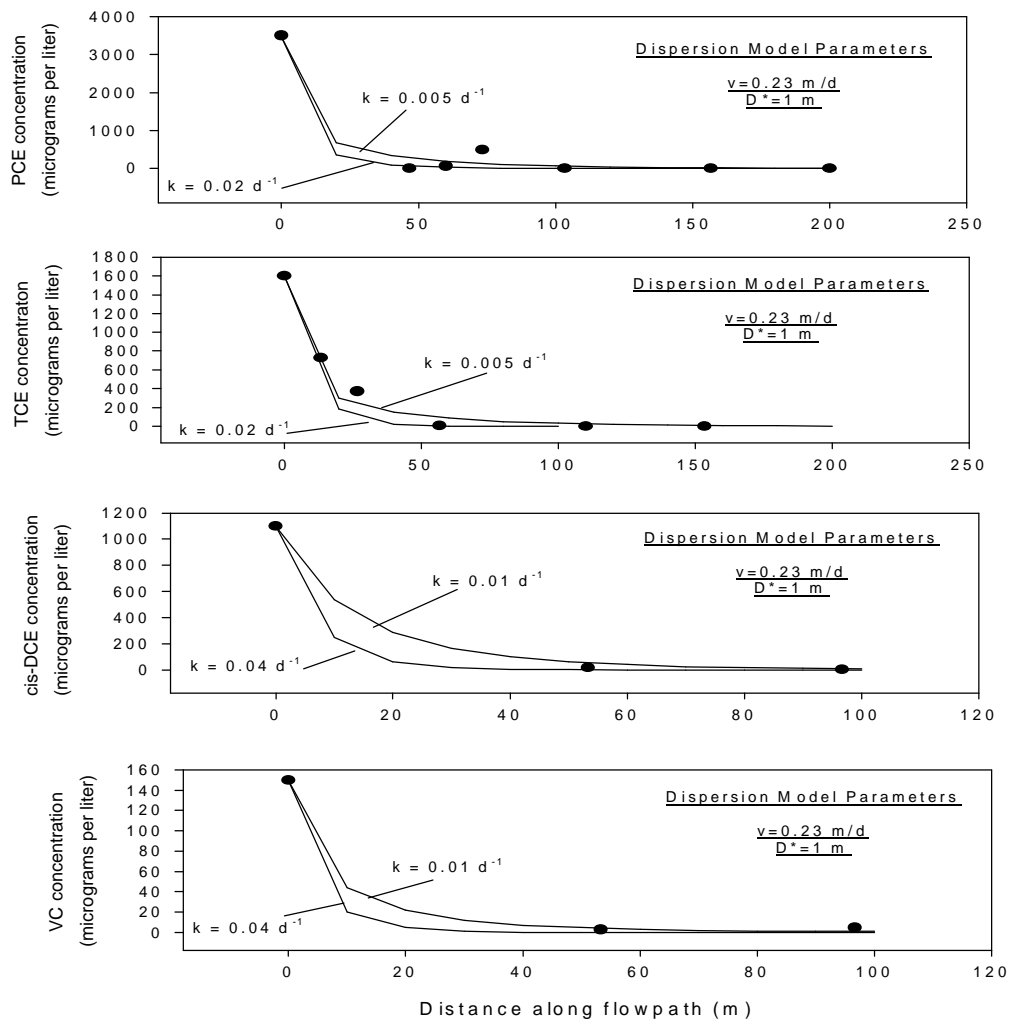


Figure 5.--Estimated values for PCE degradation rate constant and apparent degradation rate constants for TCE, cis-DCE, and VC.

dispersion equation in Figure 5. These individual rate constant estimates were made by curve-fitting only those portions of the concentration profiles where concentrations were declining (Fig. 4). Thus, the PCE curve began at zero distance downgradient, TCE at 50 meters downgradient, and cis-DCE and VC at 100 meters downgradient (Fig. 4). As pointed out previously, this procedure probably underestimates true degradation rate constants. Because ground-water flow velocity estimates have a factor of 2 range (0.23 ± 0.12 m/d), the estimated degradation rate constants also have a range of \pm a factor of 2, in addition to the upper and lower k estimates. Values for estimates of k for the chlorinated ethenes PCE, TCE, cis-DCE, and VC are given in Table 1.

Table 1.--Ranges of estimated values for biodegradation rate constants of chlorinated ethenes.

Chlorinated Ethene	Range of estimated k (d^{-1}) values
PCE	0.02 - 0.005
TCE	0.02 - 0.005
cis-DCE	0.04 - 0.01
VC	0.04 - 0.01

Using the Natural Attenuation Capacity to Estimate Source-Reduction Goals

The kinetic parameters estimated in Table 1, together with estimates of v (0.11-.35 m/d) and D^* (~1 m) can be used to quantify the natural attenuation capacity (NAC) of this ground-water system. The observed NAC can then be used to estimate distances of travel for each chlorinated ethene given an initial concentration. For example, if PCE concentrations in the source area are lowered to 100 $\mu\text{g/L}$ by engineered removal, then contaminant concentrations are predicted to be below the 5 $\mu\text{g/L}$ cleanup standard approximately 70 meters along the flowpath (Figure 6). However, because of the uncertainty associated with the parameter

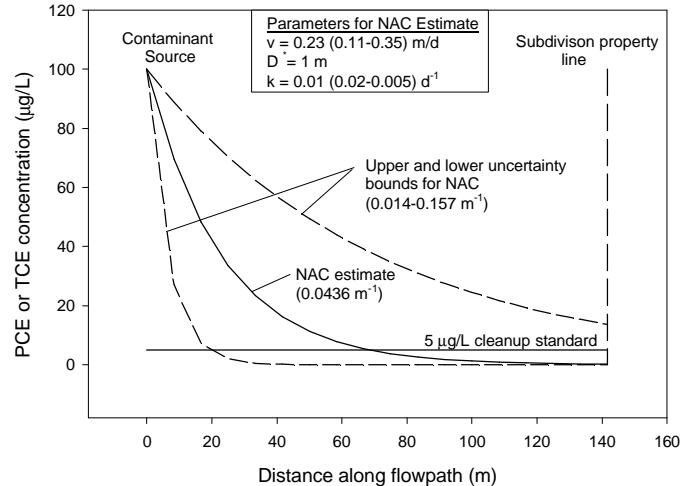


Figure 6.--Estimated distance of transport for PCE and TCE is source area concentrations are lowered to 100 $\mu\text{g/L}$.

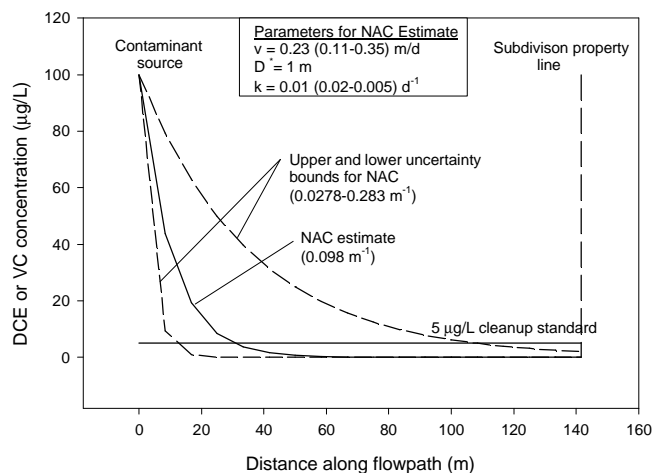


Figure 7.--Estimated distance of transport for DCE and VC from an initial source concentrations of 100 $\mu\text{g/L}$.

estimates, the cleanup standard may be reached in as little as 20 meters, or as much as 160 meters. Similar estimates can be made for TCE (Fig. 6), or DCE and VC (Fig. 7). For DCE and VC, an initial concentration of 100 $\mu\text{g/L}$ would is

estimated to be lowered below the 5 µg/L cleanup standard in 30 meters. Because of the uncertainty, however, this distance may be as little as 10 meters or as much as 110 meters.

Estimating Ground-water Velocity Decrease Goals

Source reduction is not the only engineering option that can be evaluated by considering the natural attenuation capacity. Pump and treat technology is widely used to contain contaminants from offsite migration (NRC, 1997). One effect of pump and treat is to change the rate that contaminated ground water migrates away from a site. This, in turn, can be used to increase the NAC of a site. Given a fixed biodegradation rate constant (0.01 d^{-1}) and a

fixed value of D^* (1 m), decreasing the average velocity of ground water leaving a source area by a factor of two increases the NAC by about the same amount (Fig. 8). Because of this increase in NAC, the 5 µg/L cleanup standard for these individual compounds can be achieved in proportionally less flowpath distance than with unmodified ground-water velocity. Because pump-and-treat is an established technology, increasing the NAC by lowering ground-water velocity may be an appropriate strategy at some sites.

CONCLUSIONS

The ground-water system underlying the Kings Bay site grades from relatively reducing (sulfate-reducing) to more oxidizing (Fe(III)-reducing) conditions. In the zone of sulfate reduction, PCE and TCE are rapidly dechlorinated to cis-DCE and VC. In the Fe(III)-reducing zone, cis-DCE and VC are oxidized to carbon dioxide and chloride. This sequence of redox conditions results in efficient contaminant biodegradation and gives the ground-water system a substantial natural attenuation capacity for chlorinated ethenes. Despite this natural attenuation capacity, ground water containing concentrations of chlorinated ethenes higher than regulatory limits leaves the site and migrates to a nearby point of compliance. This, in turn, necessitates engineered remediation in order to achieve the required site remediation. A kinetic assessment of the natural attenuation capacity indicates that concentrations of PCE and TCE must be lowered below 100 µg/L at least 70 meters from the point of compliance, and that concentrations of DCE and VC must be lowered below 100 µg/L at least 30 meters from the point of compliance. Because the natural attenuation capacity of a system can be increased by decreasing rates of ground-water flow away from a source area, remediation goals can also be accomplished using conventional pump-and-treat technology.

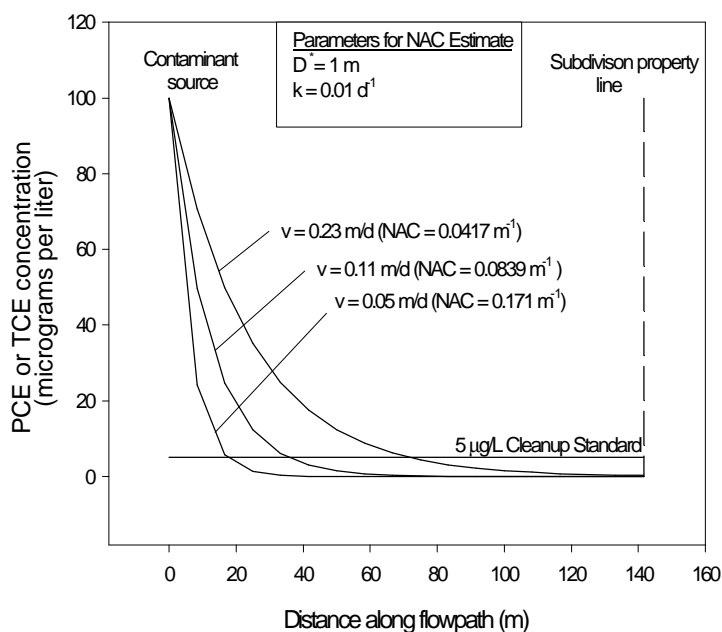


Figure 8.--Estimated distance of transport for PCE and TCE if ground-water velocity away from a source area are decreased from 0.23 to 0.05 m/d.

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