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USING TERNARY DIAGRAMS TO CHARACTERIZE BIODEGRADATION AND HYDROPHOBIC SORPTION OF CHLORINATED ETHENES IN GROUNDWATER

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Ternary diagrams are a useful and inexpensive approach to evaluate whether biodegradation, retardation by hydrophobic sorption, or hydrodynamic dispersion causes concentrations of dissolved chlorinated solvents in groundwater to decrease with distance or time along a flow path from a continuous source. The results of a series of analytical, 1-dimensional simulations of chlorinated ethene transport and fate were coupled with case studies to show that the proportions of PCE-TCE-DCE or TCE-DCE-VC concentrations in groundwater will 1) plot at nearly the same location at the source if concentrations only decrease by mixing caused by hydrodynamic dispersion 2) under hydrophobic sorption initially trend with distance from the source position on a ternary diagram to the TCE-DCE or DCE-VC limb, respectively and then move along the limb to the least halogenated member and 3) trend in an arcuate pattern from the source position towards the least halogenated member if biodegradation occurs.

INTRODUCTION

Tetrachloroethene (PCE) and trichloroethene (TCE) are among the top five organic contaminants most common at hazardous waste sites (USEPA, 1991). These chlorinated ethenes commonly degrade in anoxic groundwater by sequential de-chlorination to dichloroethene (DCE), vinyl chloride (VC) and ultimately ethene and carbon dioxide (CO₂). Hydrodynamic dispersion, hydrophobic sorption to organic matter, dechlorination, and volatilization mostly affect the rate and degree to which chlorinated solvent concentrations will be lost from water or attenuated.

The extent to which these processes may occur can be determined by analyzing groundwater for unstable geochemical parameters such as pH, Eh, dissolved oxygen, methane, and select anions and cations, and the aquifer matrix for organic matter content and microbiological parameters. However, in standard regulatory practice, these kinds of data are usually not obtained and it is often unclear which process mainly controls decreasing solvent concentrations over time and distance.

Ternary diagrams have widely been used to evaluate inorganic groundwater geochemistry for over 60 years (Piper, 1944). Ternary diagrams have also been used to characterize source, mobility, and weathering patterns of dissolved gasoline plumes (Luhrs and Pyott, 1992). Recently, ternary diagrams have been used to determine why concentrations of benzene, toluene, and xylene (BTX) decrease with distance and time at places contaminated by hydrocarbons such as gasoline and oil (Lipson, 1996; Lipson and Siegel, 2000). Ternary diagrams show relative proportions as well as total concentrations of the solutes of interest. Therefore, they also can be used to determine if sampling protocols have diluted VOC (volatile organic carbon) concentrations (Robbins and Martin-Hayden, 1991).

In this paper we present the results of theoretical calculations coupled with case studies which indicate that ternary diagrams may be a practical and inexpensive approach to determine why concentrations of chlorinated ethenes may change in contaminated groundwater systems. Our intent in these mathematical experiments was not to create a predictive model for chlorinated ethene mass transfer that applies to all hydrogeologic settings, but rather, to test whether proportions of chlorinated ethenes plotted on ternary diagrams can be useful to identify major attenuation processes.

BACKGROUND

The major processes that cause concentrations of chlorinated ethenes to decrease in groundwater are hydrophobic sorption, dehalogenation, volatilization and hydrodynamic dispersion. Hydrophobic sorption occurs when dissolved organic compounds partition from groundwater into the organic-carbon fraction of aquifer sediments. How chlorinated ethenes partition between water and organic matter is controlled by the chlorinated ethene's distribution coefficient (K_d) (Chapelle, 1993, Olsen and Davis, 1990), which in turn is directly related to its octanol-water coefficient (K_{ow}). The K_{ow} defines how a chlorinated ethene partitions between water and octanol. The more chlorine atoms in the chlorinated ethene, the greater its propensity to sorb to organic matter.

Of the chlorinated ethenes, PCE with four chlorine atoms has the highest K_{ow} , the lowest aqueous solubility, and is more likely to sorb to organic matter than TCE, DCE and VC, which have smaller K_{ow} values and greater aqueous solubilities (Howard, 1991a, 1991b). Along a groundwater flow path from a continuous contaminant source consisting of a chlorinated ethene mixture, pure hydrophobic sorption should produce zones of VOCs, such that PCE should be closest to the

source, TCE further out, DCE further away still, and VC marking the leading edge of the chlorinated plume.

Conceptually, on a ternary diagram for PCE-TCE-DCE (herein called a PTD diagram), data along the flow path would initially plot near the source mixture proportions, move towards the TCE apex and then towards the DCE apex. Subsequently on a TCE-DCE-VC (TDV) diagram, the data would initially plot near the TCE apex and then finally towards the VC apex. In contrast, proportions of chlorinated ethenes at a single well located at a distance sufficiently downgradient along the plume axis to observe the sorption phenomenon, would initially plot at the VC apex on a TDV diagram and then move towards the DCE apex, and finally to the source mixture composition on a PTD diagram.

Microbiologically mediated degradation of chlorinated ethenes sequentially removes chlorine atoms (de-chlorination) and forms chlorinated ethenes with sequentially less chlorine. In this process, the chlorinated ethenes are microbial electron acceptors (DiStefano et al., 1991, De Bruin et al., 1992, Freedman and Gossett, 1989, Vogel and McCarty, 1985). If dechlorination of chlorinated ethenes occurs, their concentrations plotted on a ternary diagram should document increase in proportions of those with a smaller number of chlorine atoms with both distance and time. Data plotted along a flow path from a source would originate near the source area on PTD or TDV diagrams, and then be oriented toward the less chlorinated ethenes' apexes (DCE and VC) as each byproduct undergoes growth and destruction. Concentration plots at a single location over time (e.g. collected during quarterly monitoring) would originate in a region on the diagrams with increased byproduct proportions. Later, the data points would trend towards the proportions of the source. Inflections in the paths the data would proscribe on the diagrams would be caused by differences among rates of decay of parent products to byproducts.

Volatilization of chlorinated ethenes in groundwater refers to the transfer of mass from the dissolved-phase into the vapor-phase of unsaturated soil pores. Volatilization is caused mostly by diffusion of the ethenes from the saturated to the unsaturated zone in the absence of engineered advection, such as induced by air stripping. Natural volatilization primarily occurs near the DNAPL source because plumes of dissolved chlorinated ethenes typically plunge below the water table, limiting diffusive efficiency. Therefore, as a first approximation, we neglected volatilization as a major natural mass transfer process in our study.

Hydrodynamic dispersion dilutes dissolved DNAPL concentrations by mechanically mixing contaminated water with native and uncontaminated groundwater. Data on ternary diagrams would all plot near the same location because dispersion will not appreciably change the proportions of dissolved DNAPL, just the absolute concentrations.

METHODS

Ternary Diagrams

For convenience, we only address the *cis*-1,2-DCE isomer that readily identifies TCE degradation and generally only occurs as a small percentage of DCE isomers in manufactured dichloroethene (the primary being 1,1-DCE) (Bouwer, 1994). *Trans*-1,2-DCE also is a byproduct of TCE dechlorination, but generally constitutes less than 10 percent of the total DCE.

We considered three source scenarios for this study: (1) pure TCE, (2) pure PCE such as may leak from a underground storage tank, and (3) a mixture of PCE, TCE, DCE and VC that may result

from a landfill or industrial facility. The assumed source concentrations for case (3) were taken from a field investigation of a PCE-contaminated industrial plant in Texas where concentrations of PCE, TCE, and DCE next to the source were 10 micromoles per liter (μM), 4 μM , and 4 μM respectively (Beeman et al., 1994). To these we added 2 μM VC to show how the proportion of VC might change under both the absence and presence of dechlorination.

We also assumed that equilibrium exists between the liquid DNAPL and dissolved DNAPL at the source area; source concentrations do not significantly change by degradation, advection, sorption, or volatilization, and that the liquid DNAPL continuously provides dissolved mass to groundwater. We plotted data points on the ternary diagrams as circles having radii as the natural logarithm of the sum of the chlorinated ethene mass concentrations. By doing this, we are able to also show how total chlorinated ethene mass concentrations change as well as changes in their relative molar proportions.

Mathematical Simulations

We used the well documented and widely cited one-dimensional advective-dispersive with degradation transport model, CHAIN, by Van Genuchten (1985) to simulate the fate and transport of the chlorinated ethenes in groundwater. This analytical model incorporates up to four sequential first-order decay reactions as “chain” members. We designated the plume fronts calculated by the model by iso-concentration contours below which practical quantitation is infeasible using standard analytical methods, about 1 microgram per liter ($\mu\text{g/L}$).

We assumed for the modeling experiments that the porous medium was a saturated, isotropic, and homogeneous sand aquifer with a uniform hydraulic gradient of 0.005 and seepage velocity of 0.2 m/d and that the organic matter content was 1 percent of the total matrix mass for sorption simulations. These properties are typical of glacial outwash or beach sand deposits. We fully recognize that most contaminated hydrogeologic settings are not of this kind and are usually heterogeneous and anisotropic. However, our intent is to test whether ternary diagrams are useful tools to identify why concentrations of chlorinated ethenes measured in routine monitoring may change along flow paths and with time, rather than to develop a quantitative predictive tool using these diagrams. Therefore, we feel our simplification of “reality” to one-dimensional transport and homogeneous and isotropic conditions is appropriate.

The partial differential equations describing one-dimensional advective-dispersive with degradation transport under steady-state flow and linear equilibrium transport can be written:

$$R_f^i (\delta C^i / \delta t) = D_h (\delta^2 C^i / \delta x^2) - v (\delta C^i / \delta x) + \mu^{i-1} R_f^{i-1} C^{i-1} - k^i R_f^i C^i \quad (1)$$

where:

C^i = the concentration of solute i ,

v = the average linear groundwater velocity,

$D_h (= av)$ = the coefficient of horizontal hydrodynamic dispersion,

α = the aquifer dispersivity,

R_f^i = the retardation factor of solute i ,

k^i = the total first-order decay rate of solute i , and

μ^i = the growth rate of solute i due to reductive dechlorination of the parent product ($i-1$).

$i = 1,2,3,4$ refers to sequential chlorinated ethenes; PCE, TCE, DC, and VC

The partial differential equation was solved for a semi-infinite system E ($0 \leq x < \infty$) using first-type (or concentration-type) boundary conditions (van Genuchten, 1985):

$$\begin{aligned} \text{for } t \geq 0 \text{ and } x = \infty, & \quad C^i = 0; \\ \text{for } x \geq 0 \text{ and } t \leq 0, & \quad C^i = 0; \text{ and} \\ \text{for } x = 0 \text{ and } t > 0, & \quad C^i = C_o^i \end{aligned}$$

where:

t = elapsed time of release [T],
 C^i = concentration of solute i ($i=1,2,3,4$) [M/L³];
 C_o^i = source concentration of solute i [M/L³]; and
 x = distance downgradient from the source [L].

Conceptually, these boundary conditions describe a groundwater system initially free of chlorinated ethenes, which are then introduced at time 0 as a continuous source. The analytical solution of the partial differential equation for a solute i , independent of the growth terms, is (van Genuchten, 1985):

$$C^i = C_o^i / 2 \{ \exp[((v - w)x) / (2D_h)] \operatorname{erfc} [(R_f^i x - wt) / (2(D_h R_f^i t)^{0.5})] + \exp[((v + w)x) / (2D_h)] \operatorname{erfc} [(R_f^i x + wt) / (2(D_h R_f^i t)^{0.5})] \} \quad (2)$$

where:

$$w = (v^2 + 4 D_h R_f^i k^i)^{0.5} \quad (3)$$

The first-order decay term (k) includes the mass removal processes of volatilization, hydrolysis, aerobic biodegradation and anaerobic biodegradation, the latter of which has been shown to follow first-order kinetics (e.g. Corapcioglu and Hossain, 1991).

As one chlorinated ethene is transformed into another by dehalogenation, the growth of the “daughter” product is added in the analytical solution of the full equation in the CHAIN model to calculate all members of the biodegradation sequence. The solution to the complete version of Equation (1) is long and complex, and for brevity is not included in this discussion. It can be found in van Genuchten (1985). We used the dechlorination rate constants in Ellis (1996) and Ellis et al. (1996) for our simulations. Of course, on a site specific basis, dechlorination rate constants may differ from those we used, but as a first approximation the relative order of magnitudes of the rates should remain about the same.

The retardation factor (R_f^i) used in Equation (1) relates the average linear groundwater velocity to that of the solute front, and equals V_{gw} / V_{solute}^i . The retardation factor used in the fate and transport model was determined from (Domenico and Schwartz, 1990):

$$R_f^i = 1 + [(1-n)/n] \rho_b K_d^i \quad (4)$$

where:

n = aquifer effective porosity;

ρ_b = aquifer sediment grain density;

K_d^i = aqueous-solid distribution coefficient; and

R_f^i = retardation factor for solute i

A chlorinated ethene's distribution coefficient (K_d^i) is related to the aquifer matrix by:

$$K_d^i = K_{oc}^i f_{oc} \tag{5}$$

where:

K_{oc}^i = organic carbon partition coefficient, and

f_{oc} = fraction of organic carbon in the aquifer sediment.

This relationship implies that the degree of sorption is linearly related to the amount of organic carbon in the sediment. K_{oc} is in turn related to the octanol-water partition coefficient (K_{ow}) according to the following relationship (Olsen and Davis, 1990):

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006. \tag{6}$$

We chose to use Equation (6) to determine the K_d 's used in the retardation numerical experiments because of its accuracy with respect to chlorinated ethenes (Olsen and Davis, 1990). We used the K_{ow} values provided in Howard (1991) for our simulations.

Development of dissolved plumes was simulated to distances of up to about 1,200 meters downgradient from the source area for up to 5 years. The effects of dispersion over distance and time were simulated using a dispersivity value of 10 meters over a flow path of 1,200 meters. Although we recognize that there is significant debate over what are appropriate values for dispersivity, we chose this dispersivity value from similar theoretical modeling efforts described by Pickens and Lennox (1976) for reactive contaminants in a steady groundwater flow system.

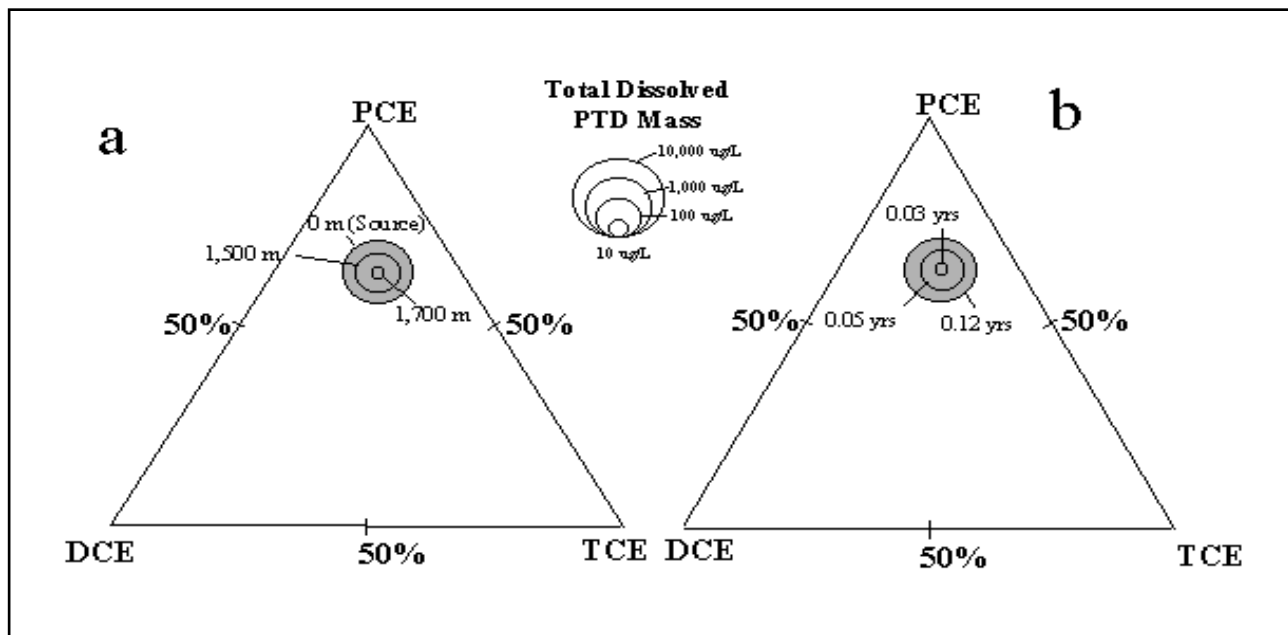


Figure 1. PTD ternary plots showing the effects of advection and dispersion with: a) distance after 5 years from the release; and b) at 30 meters with time from a simulated continuous mixed PTD source. Note how the proportions of tetrachloroethene, trichloroethene and dichloroethene all plot the same locations as that of the source, with total PTD concentrations making a series of concentric rings around it.

RESULTS

The effect of advection and dispersion only on dissolved DNAPL plumes is to produce plots of concentrations along a flow path or with time defined by a series of rings around the location of the source (Figure 1). With distance from the source, total concentrations of chlorinated ethenes decrease and with time, total concentrations increase at a given location along a flow path.

Hydrophobic sorption with advection and dispersion causes the proportions of dissolved DNAPL on ternary diagrams to move along a clearly defined trajectory (Figure 2). VC is the least sorptive and therefore moves the farthest along a groundwater flow path, followed by increasing proportions of the less mobile solutes, DCE, TCE, and PCE, respectively. The modeled PTD/Distance path for

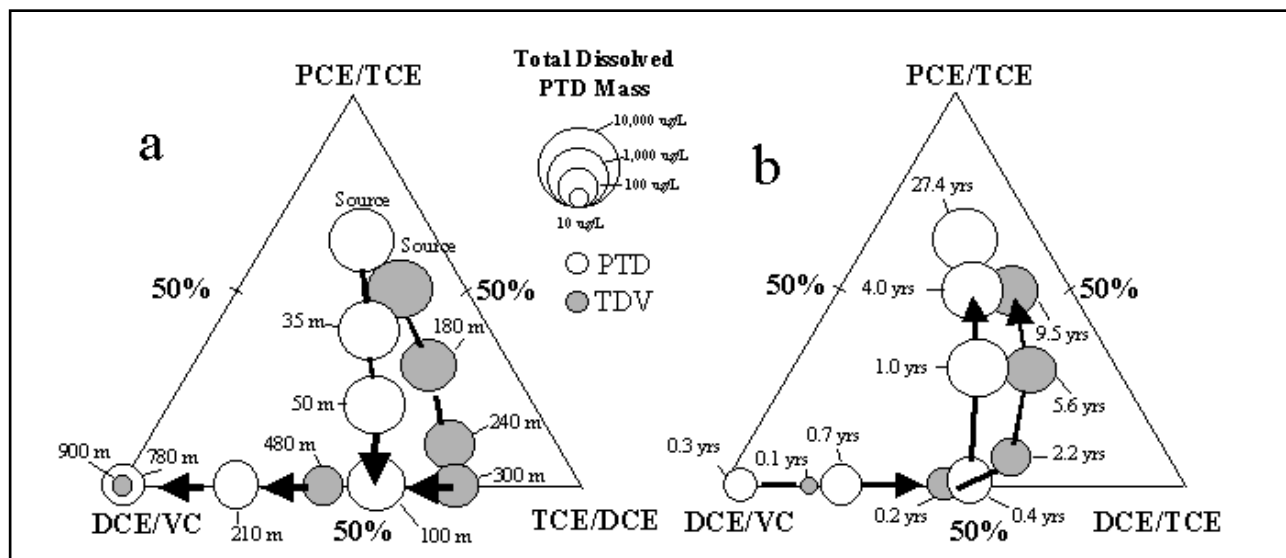


Figure 2. PTD/TDV ternary plots showing the effects of advection, dispersion and hydrophobic sorption with a) distance after 5 years from the release; and b) at 30 meters with time from a continuous mixed PTD source. Note how with distance the trajectory the data make from the source trends sharply towards the least chlorinated limb of the ternary diagram. With time, data move along the least chlorinated limb and then abruptly towards the source location.

hydrophobic sorption of the mixed DNAPL source originates at the source area and then moves to the middle of the TCE-DCE limb (Figure 2a). The TDV/Distance path also originates near the source area, but in this case, moves in a straight line to DCE-VC limb (Figure 2a) as a result of increased VC production. Total concentrations of dissolved DNAPL decreased with distance, indicating that dissolved DNAPL mass is being removed from the groundwater by sorption as well as being diluted by hydrodynamic dispersion.

A TDV/Time path for a location about 30 meters from the source area documents the initial arrival of VC and then moves towards the DCE apex (Figure 2b). Eventually, TCE appears and the path orients toward the source area of the diagram with increasing concentrations of total dissolved DNAPL with time. In similar fashion, concentrations on a PTD/ Time path first originate at the DCE apex, then move along the TCE-DCE leg of the diagram (Figure 2b), eventually reaching the source area location.

Dechlorination paths on ternary diagrams showed, as anticipated, increased proportions of byproducts with distance and over time as solute mass was transformed. Five years after the modeled release of a pure PCE source (10µM, 1,658 µg/L), dechlorination defined a curved

trajectory along a flow path, with the proportions of dissolved DNAPL initially moving towards the DCE apex but with rapid decrease in concentrations of total dissolved DNAPL (Figure 3a). Similarly, for pure TCE and mixed DNAPL sources, the distance paths move first towards the DCE apex and then to the VC apex, and for brevity are not included in this discussion.

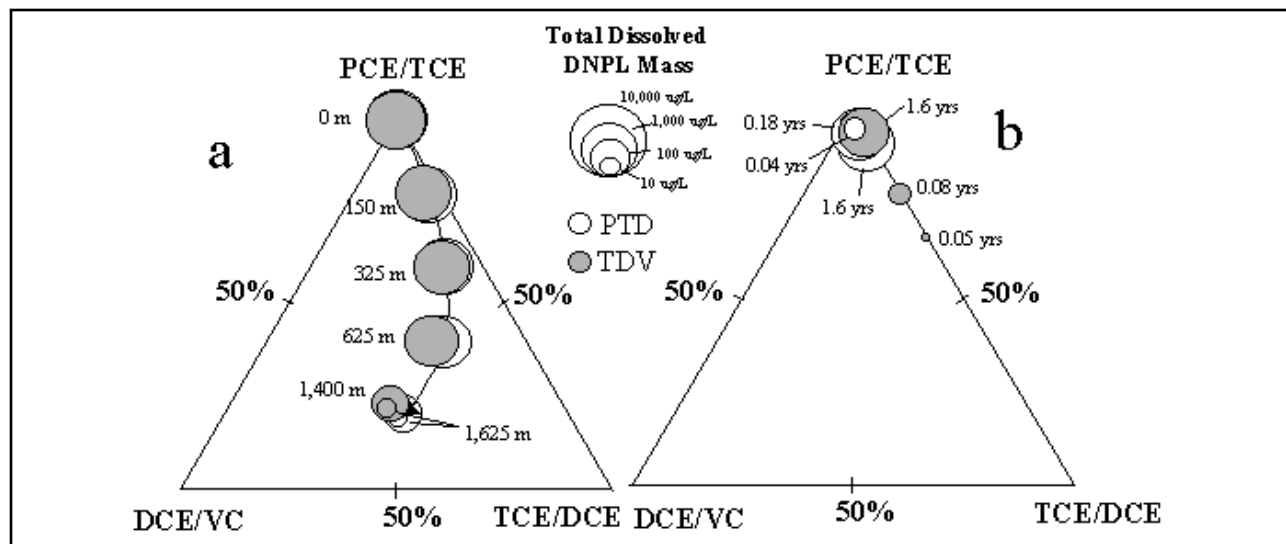


Figure 3. PTD/TDV ternary plots showing the effects of advection dispersion and dechlorination with: a) distance after 5 years from the release; and b) at 30 meters with time from a continuous pure PCE and pure TCE source. Note how with distance the trajectory the data make from the source trends in an arcuate curve towards the least chlorinated apex of the ternary diagram. The distance of the monitoring location along the flow path of 30 meters was too close to the source to clearly document the effects of dechlorination as a ternary diagram under the simulation conditions.

On TDV and PTD/Time paths for a location 30 meters from the source, there was little change in the position of the dissolved chlorinated ethenes on the ternary diagram, probably because advection of the dissolved solute mass to the location was too fast to see the biodegradation changes in the simulation experiments (Figure 3b). Simulations of combined processes affecting dissolved DNAPL concentrations along a downgradient groundwater flow path from a source produced Time and Distance paths on ternary diagrams that, logically, were a blend of those produced by sorption and dehalogenation alone and will not be discussed in detail.

CASE STUDIES

Dissolved DNAPL concentrations from three field cases were plotted on ternary diagrams to test the practical applicability of using the generalized trends on ternary diagrams determined from our simulations to characterize the processes controlling dissolved DNAPL fate and transport from routine regulatory monitoring data.

The first case study is a landfill site in central New York. TCE, cis-1,2-DCE, and VC were detected in a downgradient well used to monitor groundwater quality leaving the landfill which was built over an unconsolidated aquifer of glacial origin. The presence of dechlorination transformation products suggested that dechlorination was occurring in the dissolved DNAPL plume. Yet, undetectable concentrations of methane and sulfide, coupled with dissolved oxygen concentrations greater than 1 milligram per liter (mg/L), indicated that much of the groundwater in monitoring wells was oxygenated and that anoxic dehalogenation should not occur. Indeed, a TDV/Time path prepared for samples collected from a monitoring well located about 50 meters downgradient from the

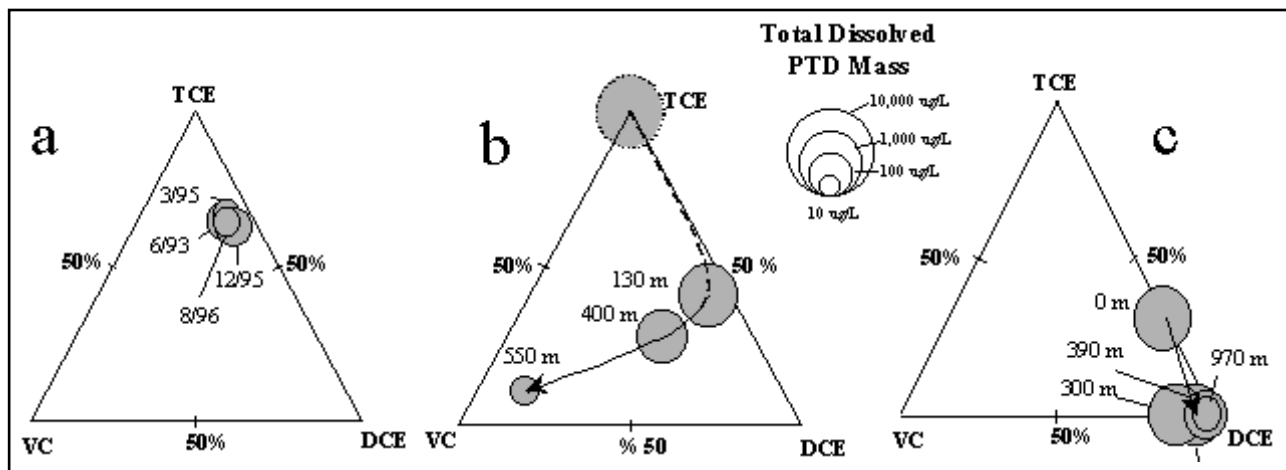


Figure 4. TDV-distance ternary diagram showing: a) mostly advection along a flow path and minimal sorption or biodegradation of TDV at a central New York landfill. Note how the data all cluster at one location; b) clear dehalogenation from a pure TCE source along a flow path at an industrial facility in Michigan; and c) probably sorption of TDV at the Plattsburgh Air Force Base (NY) downgradient of the source area where anoxia caused biodegradation of a pure TCE source.

source showed proportions of dissolved DNAPL as illustrated on Figure 4a. Note on Figure 4a how the data plot at about the same location on the diagram. At this site, natural biodegradation probably only occurs at the source area and intrinsic biodegradation is ineffective over the major part of the plume area proper.

The second case study is an auto parts manufacturer located in St. Joseph, Michigan (Weaver et al., 1996a, Weaver et al., 1996b). TCE in groundwater in an unconfined glacial sand aquifer downgradient of the site made this site part of the USEPA Superfund list. Reductive dechlorination of the TCE plume was believed to occur along flow paths because dissolved DNAPL plumes coincided with plumes defined by low concentrations of dissolved oxygen and sulfate and a high concentration of dissolved methane, all of which suggest anoxia. Indeed, in this case, dissolved DNAPL data collected along flow paths from the source area define a curved dechlorination path with increasing VC proportions with distance, consistent with the theoretical trends described in the simulations for dispersion with dechlorination (Figure 4b).

The third site was a solvent contamination investigation of a former fire training area at Plattsburgh Air Force Base in New York (Wiedemeier et al., 1996). Activities at the site resulted in the contamination of an unconfined sand aquifer by a mixture of fuel hydrocarbons and chlorinated solvents (TCE, cis-1,2-DCE, and VC). The dissolved DNAPL plume immediately surrounding the source area and extending approximately 500 meters downgradient is characterized by reduced iron, sulfur and nitrogen species, and the absence of oxygen, all of which suggest anaerobic conditions. From 500 meters to about 1,000 meters from the source, groundwater becomes aerobic and VC can be oxidized to CO_2 .

Groundwater samples were plotted on a TDV/Distance diagram (Figure 4c). The Distance path originated along the TCE-DCE side of the diagram, oriented toward the DCE apex. The overall shape of the path appeared to follow a straight line similar to sorption trajectories. Once again, it is likely that most of the dechlorination of TCE at the site occurred at or proximate to the source. Further dechlorination did not appreciably occur in the major part of the plume area, which appears to lose dissolved DNAPL mass more by sorption.

DISCUSSION AND CONCLUSIONS

The results of our study show that ternary diagrams can be very useful tools to examine the fate and transport mechanisms for dissolved DNAPL contamination from routine monitoring at contaminated aquifers. Although we have not done the simulation experiments, the fate and transport of the chlorinated ethane series (tetrachloroethane, trichloroethane, dichloroethane, and methylene chloride) might be expected to follow generically the same sort of trends on ternary diagrams as do the chlorinated ethenes we did simulate. Whether dissolved DNAPL/distance and/or time plots on ternary diagrams define straight or curved lines can help determine the extent to which dehalogenation and/or sorption of dissolved DNAPL occurs as groundwater moves downgradient, or whether hydrodynamic dispersion is the only mechanism that modifies dissolved DNAPL concentrations.

The results of our simulation study, designed to test the utility of ternary diagrams as a diagnostic tool, should apply to other hydrogeologic scenarios so long as plotted analyses fall on clear downgradient flow paths. Although contaminated aquifers may have different aquifer properties, native geochemistries, and DNAPL source compositions, we see little reason why, at least qualitatively, the trajectories of the dissolved DNAPL/distance and dissolved DNAPL/time plots on ternary diagrams should differ from what we have determined, unless biological mediation substantively changes the relative kinetics of dehalogenation from what has been seen in both experiments and field studies.

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