

Estimating the Changing Rate of Anaerobic Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons in the Presence of Petroleum Hydrocarbons

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ABSTRACT

Recent laboratory and field results demonstrate that different chlorinated aliphatic hydrocarbons (CAHs) ultimately can be transformed into innocuous chemical compounds in many aquifer systems. Transformation can be the result of either cometabolic reactions or reduction oxidation (redox) reactions. In the latter, chlorinated compounds such as tetrachloroethene (PCE), trichloroethene (TCE), and dichloroethene (DCE) can be used in anaerobic, reducing aquifers as alternate electron acceptors during the oxidation of organic matter such as the petroleum hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX). When used as electron acceptors, these CAH compounds are sequentially dechlorinated into less chlorinated compounds such as vinyl chloride (VC) or ethene. While the rate of petroleum hydrocarbon degradation is generally reasonably approximated as a first-order process, it is not clear that the degradation of electron acceptors such as CAH compounds are best estimated in a similar manner. Because the rate of reductive dechlorination of CAHs in the presence of petroleum hydrocarbons is a function of both the concentration of the petroleum hydrocarbons and the concentration of the electron acceptors themselves, a second-order kinetic model may provide a better approximation of the rate of BTEX/CAH degradation over time and distance.

Several methodologies may be used to estimate the rate of reductive dechlorination of CAH compounds when they are being used to oxidize BTEX compounds. Both first-order and second-order approximations of CAH degradation rates can be useful in predicting CAH/BTEX plume behavior, although the second-order approximation will be especially useful in determining whether the system will first exhaust the available supply of electron donors (i.e., starve) or electron acceptors (i.e., strangle).

INTRODUCTION

Numerous laboratory and field studies have shown that microorganisms indigenous to the subsurface environment can degrade a variety of fuel hydrocarbons and CAHs (e.g., Chapelle, 1993; Young and Cerniglia, 1995). During biodegradation, microorganisms transform available nutrients into forms useful for energy and cell reproduction by facilitating the transfer of electrons from donors to acceptors. This results in oxidation of the electron donor and reduction of the electron acceptor. Electron donors include natural organic material and fuel hydrocarbons such as the BTEX compounds. When fuel hydrocarbons are utilized as the primary electron donor for microbial metabolism, these compounds are typically completely degraded or detoxified (Bouwer, 1992). Electron acceptors are elements or compounds that occur in relatively oxidized states. Important inorganic electron acceptors commonly found in groundwater include dissolved oxygen (DO), nitrate, manganese, ferric iron, sulfate, and carbon

dioxide. The reduction of these inorganic electron acceptors during fuel hydrocarbon oxidation causes measurable changes in groundwater chemistry. The reduction in concentration of inorganic electron acceptors along groundwater flowpaths can be used qualitatively to document biodegradation (Wiedemeier *et al.*, 1995) and quantitatively to estimate degradation rates (McAllister and Chiang, 1994; Wilson *et al.*, 1994; Chapelle *et al.*, 1996).

In addition to these common inorganic electron acceptors, recent laboratory and field data suggest that CAH compounds may serve as alternate (organic) electron acceptors when sufficient organic substrate is available in the system (e.g., Gossett and Zinder, 1996). The presence of elevated concentrations of organic substrate in the aquifer (e.g., from a fuel spill) results in a surplus of electron donors, effectively increasing the reducing potential of the groundwater. If an appropriate succession of biological mediators is available to facilitate redox reactions between surplus electron donors and electron acceptors, the more common inorganic electron acceptors such as DO, nitrate, and ferric iron will be reduced (depleted). Once the oxidizing potential of the system has been sufficiently reduced to allow sulfate reduction, the microorganisms may facilitate equally thermodynamically favorable redox reactions between the remaining surplus electron donors and alternate (organic) electron acceptors such as the CAH compounds. During these reactions, the fuel hydrocarbons (electron donors) will be completely oxidized to water and carbon dioxide, and the CAH compounds (electron acceptors) will be sequentially dehalogenated to less chlorinated compounds such as ethene.

Consequently, the effectiveness of natural chemical attenuation processes at minimizing downgradient migration and eventually eliminating contaminant mass depends on the rates of microbial degradation processes (National Research Council, 1993; Salanitro, 1993; Wiedemeier *et al.*, 1995, Chapelle *et al.*, 1996). The use of substrates such as organic electron donors and electron acceptors by microorganisms for microbial growth generally follows enzyme saturation (Monod and variations on Monod) kinetics, which is derived from the Michaelis-Menten enzyme kinetics equation:

$$v = \left(\frac{v_{\max}SX}{K_s + S} \right) \quad (1)$$

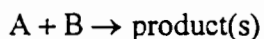
where v is the rate of substrate uptake (moles/time), v_{\max} is the maximum rate of substrate uptake (moles/time-gram cells), K_s is the concentration of substrate at which $v = 0.5 v_{\max}$ (moles/L), S is the concentration of substrate (moles/L), and X is the mass of cells (grams). When the uptake of a substrate is limited by enzyme availability (e.g., at low substrate concentrations, $S \ll K_s$), and when the microbial mass is neither increasing or decreasing with time (i.e., growth = loss), the Michaelis-Menten equation can be approximated by first-order kinetics:

$$v \approx kS \quad (2)$$

where k is a rate constant (time^{-1}). The first-order reaction rate dependence has implications on degradation rates at low concentrations: the reaction rates become progressively slower with decreasing substrate concentration.

First-order kinetics are believed to reasonably approximate microbial degradation of BTEX in aquifers because the system is generally assumed to be limited by one substrate, the organic electron donor. This generally is a reasonable assumption when only inorganic electron acceptors, which can be infinitely supplied from upgradient groundwater or infiltrating precipitation migrating into surplus electron donor mass, are being used in coupled redox reactions. The first-order assumption also simplifies fate and transport modeling of a complex phenomenon. Once the effects of nondestructive attenuation processes such as advection, dispersion, and sorption on microbially reactive compounds in groundwater are quantified, the apparent mass loss of BTEX along groundwater flowpaths at several sites have been shown to be reasonably approximated by a first-order degradation rate constant (McAllister and Chiang, 1994; Buscheck and Alcantar, 1995; Wiedemeier *et al.*, 1995 and 1996a; Chapelle *et al.*, 1996).

Use of the first-order approximation also may be appropriate to estimate rates of dechlorination of CAH compounds if it is assumed that the utilization of the primary substrate (electron donor or BTEX) is not dependent on the presence of CAH compounds (electron acceptor). This may be a reasonable assumption if sufficient electron donor mass is available (i.e., significant BTEX concentrations) or if the microbial population capable of facilitating redox reactions between BTEX and CAH is small and exhibiting low growth rates relative to other microbial populations. However, the use of first-order kinetics may not be appropriate when more than one substrate is limiting microbial degradation rates or when microbial mass is increasing or decreasing (i.e., ΔX). Because the oxidation of BTEX depends on the reduction of inorganic electron acceptors or CAH compounds, these types of redox reactions can be defined as bimolecular reactions



where the rate of change of [B], assumed to be the electron donor, is

$$\frac{-d[B]}{dt} = k[B][A] \quad (3)$$

where k is a second-order rate constant (mass/time), and the disappearance (or degradation) of B is first-order in both [B] and [A], the electron acceptor(s). This means that the rate of degradation of B (BTEX) depends both on the concentration of B (BTEX) and the concentration of A (electron acceptors). Conversely, the same is true of [A]: the degradation of the electron acceptors is first-order in both [B] and [A]. Intuitively, this makes sense in terms of how these types of degradation reactions occur: if insufficient electron acceptor mass is available to oxidize the fuel hydrocarbon mass, the reaction will stall (i.e., the system will strangle); if insufficient electron donor mass is available, degradation will cease (i.e., the system will starve). The former is important in terms of predicting the maximum downgradient migration and persistence of a dissolved BTEX plume. The latter may be extremely important for mixed BTEX/CAH plumes to determine whether "natural" reductive dechlorination processes can minimize CAH migration and achieve complete dechlorination before complete oxidation (degradation) of BTEX occurs.

The remaining sections of this paper presents several methodologies for estimating both first-order CAH dechlorination rates and second-order BTEX/CAH degradation rates. Site data from several groundwater plumes, collected as part of a nationwide project sponsored by the Air Force Center for Environmental Excellence, are used to illustrate these different methods. A comparative analysis of the predicted degradation rates and their implications on the remedial decision-making process also is presented.

FIRST-ORDER DECAY ESTIMATION METHODS

The change in a solute's concentration in groundwater over time often can be estimated using the linear form of the first-order kinetic model:

$$C = C_0 e^{-kt} \quad (4)$$

where C = concentration at time t [$\mu\text{g/L}$], C_0 = source concentration [$\mu\text{g/L}$], k = overall attenuation rate (first-order rate constant) [day^{-1}]

Using this relationship, a total first-order attenuation rate can be estimated for a site by producing a log-linear plot of total contaminant concentration versus travel time for a series of points along the flowpath of a contaminant plume. If the data plot along a straight line, the relationship is first-order, and an exponential regression analysis can be performed, with the slope of the resulting equation equivalent to the total attenuation rate. This overall attenuation rate groups all processes acting to reduce contaminant concentrations and includes advection, dispersion, dilution from recharge, sorption, volatilization, and biodegradation. This approach is

very sensitive to hydrogeologic variability, as well as to the proximity of the sampled points to the dominant flow path of the plume, both laterally and vertically. This can contribute to the generation of less than desirable correlation coefficients (R^2) and bring the first-order assumption into question.

Total chlorinated ethene attenuation rates have been estimated for three sites: a former fire training area at Plattsburgh Air Force Base (AFB) (FT-002), a former fire training area at Cape Canaveral Air Station (AS) (FT-17), and a former bomber assembly plant at Offutt AFB (Bldg. 301). A brief summary of historical site information is provided in Table 1; site characterization data are summarized in Table 2. Total estimated chlorinated ethene attenuation rates for the three sites (Table 3) ranged from 0.00021 to 0.00051 day⁻¹, with the magnitude of the rates closely tied to the average retarded contaminant velocity. As an example, a log-linear plot of data collected from Plattsburgh AFB in 1995 is provided in Figure 1.

ESTIMATING FIRST-ORDER BIODEGRADATION FOR A STEADY-STATE PLUME

In order to ensure that some portion of observed decreases in contaminant concentrations can be attributed to biodegradation, measured contaminant concentrations must be corrected for the effects of dispersion, dilution, and sorption. Buscheck and Alcantar (1995) derive a relationship that allows calculation of first-order biodegradation rate constants for steady-state plumes. This method involves coupling the regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) to an analytical solution for one-dimensional, steady-state, contaminant transport that includes advection, dispersion, sorption, and biodegradation.

The relationship developed by Buscheck and Alcantar (1995) was applied to the data from all three sites, although each of these plumes is suspected to be expanding. As expected, the rates attributed to biodegradation are less than the total attenuation rates, with estimated rates ranging from one-half to three-quarters of the total attenuation rate. Data and results are presented in Tables 2 and 3, respectively. Figure 2 provides, as an example, the log-linear plot used in the calculation of the 1995 Plattsburgh AFB biodegradation rate. Because this technique uses the same concentration data as the total attenuation technique, it is equally sensitive to sampling locations and hydrogeologic variability.

For an expanding plume, this first-order approximation can be viewed as an upper bound on the biodegradation rate. Use of this method results in an overestimation of the rate of biodegradation because a typical expanding plume exhibits decreasing source area concentrations, increasing downgradient (and crossgradient) concentrations, or both. Over time, these changes result in a decreasing slope on a log-linear plot, and consequently a decreasing biodegradation rate.

ESTIMATING FIRST-ORDER REDUCTIVE DECHLORINATION: THE CARBON CORE AS A TRACER

A convenient way to isolate the rate of biodegradation from other attenuation processes is to use as tracers compounds or elements associated with the contaminant plume that are relatively unaffected or predictably affected by biological processes occurring within the aquifer. When present, the trimethylbenzene isomers associated with fuels can serve as useful tracers under certain geochemical conditions (Wiedemeier *et al.*, 1995 and 1996a). Likewise, chloride, a degradation product of chlorinated solvent biodegradation has the potential to serve as a useful tracer (Wiedemeier *et al.*, 1996b). This section describes a tracer method that can be used with reductively dehalogenated solvent plumes, and involves tracking the "carbon" core of the chlorinated compounds in relation to the remaining chlorine mass.

Measured tracer and contaminant concentrations from a minimum of two points along a flow path can be used to estimate the amount of contaminant remaining at each point if biodegradation had been the only attenuation process operating to reduce contaminant concentrations. To

accomplish this, it is assumed that the fraction of contaminant remaining as a result of all attenuation processes is equivalent to the fraction of contaminant remaining as a result of non-destructive attenuation mechanisms only, multiplied by the fraction of contaminant remaining as a result of biodegradation. The fraction of contaminant remaining as a result of all attenuation processes can be computed from the measured contaminant concentrations at two points along a flow path. The fraction of contaminant remaining as a result of non-destructive attenuation mechanisms only can be estimated from the tracer concentrations at the same two points, because an ideal tracer is affected by non-destructive attenuation mechanisms to the same degree as the contaminant of interest and is not affected by biologic processes. The following equation uses these assumptions to solve for the estimated downgradient contaminant concentration if biodegradation had been the only attenuation process operating between two points (i and $i-1$) along the flow path:

$$C_{i,corr} = C_{i-1,corr} \left(\frac{C_i}{C_{i-1}} \right) \left(\frac{T_{i-1}}{T_i} \right) \quad (5)$$

where $C_{i,corr}$ = corrected contaminant concentration at point i ; $C_{i-1,corr}$ = corrected contaminant concentration at point $i-1$ (Note that if point $i-1$ is the first or most upgradient point, $C_{i-1,corr}$ is equivalent to the observed contaminant concentration.); C_i = observed contaminant concentration at point i ; C_{i-1} = observed contaminant concentration at point $i-1$; T_i = observed tracer concentration at point i ; and T_{i-1} = observed tracer concentration at point $i-1$.

This equation can be used to estimate the theoretical contaminant concentration resulting from biodegradation alone for every point along a flow path on the basis of the measured contaminant concentration at the point of plume origin and the contaminant/tracer ratios between consecutive points along the flow path. This series of points can then be used to estimate a first-order rate of biodegradation as described for estimating total attenuation rates.

During reductive dechlorination, the source chlorinated solvent undergoes successive transformations involving the replacement of a chlorine atom by a hydrogen atom; however, the carbon core of both the parent and daughter compounds remains unchanged (i.e., no carbon bonds are broken). The carbon core is subject to the same non-destructive attenuation mechanisms that act on the larger chlorinated molecule, but it is unaffected by biologically mediated reductive dechlorination. For this reason, tracking the carbon core of dissolved chlorinated solvents can serve as a theoretically perfect "tracer" for biodegradation via reductive dechlorination.

In order to use the carbon core of the chlorinated parent and daughter compounds as a "tracer" for reductive dechlorination, "equivalents" for the dissolved mass of carbon and chlorine must be calculated for each point along a flow path. The "equivalents" are calculated by first converting contaminant concentrations into molar concentrations. For chlorinated ethenes, the carbon equivalent is calculated by multiplying the number of carbon atoms per molecule of chlorinated ethene (2) by the sum of the molar concentrations for PCE, TCE, DCE, VC, and ethene:

$$Ceq_i = 2 (M_{PCE,i} + M_{TCE,i} + M_{DCE,i} + M_{VC,i} + M_{Ethene,i}) \quad (6)$$

where Ceq_i = carbon equivalent at point i ; $M_{PCE,i}$ = molar concentration of PCE at point i ; $M_{TCE,i}$ = molar concentration of TCE at point i ; $M_{DCE,i}$ = molar concentration of DCE at point i ; $M_{VC,i}$ = molar concentration of VC at point i ; and $M_{Ethene,i}$ = molar concentration of ethene at point i .

The chlorine "equivalent" is defined as the sum of the products of molar concentration and chlorine atoms per molecule for each parent and daughter compound. For the chlorinated ethenes, the numbers of chlorine atoms per molecule are 4 for PCE, 3 for TCE, 2 for DCE, 1 for VC, and 0 for ethene:

$$C_{\text{leq}_i} = (M_{\text{PCE}_i} * 4) + (M_{\text{TCE}_i} * 3) + (M_{\text{DCE}_i} * 2) + M_{\text{VC}_i} \quad (7)$$

where C_{leq_i} = chlorine equivalent at point i.

Using equation 5, and substituting C_{eq} for tracer concentrations and C_{leq} for observed contaminant concentrations, yields the theoretical total CAH concentrations at downgradient locations if reductive dechlorination had been the only natural attenuation process operating along the flow path. The same process can be used to determine the theoretical chlorine equivalents. Chlorine equivalents, carbon equivalents, the corrected total CAH concentrations, and the corrected chlorine equivalents for the Cape Canaveral AS, Plattsburgh AFB, and Offutt AFB sites are presented in Table 4. The corrected CAH concentrations are useful for comparison to other techniques; the corrected chlorine equivalents simplify visualization of the reductive dechlorination rate. Either the corrected total CAH concentrations or corrected chlorine equivalents can be used to calculate identical first-order rates for dechlorination (Table 3). An example log-linear plot is provided in Figure 3 for the 1995 Plattsburgh AFB calculation.

The results serve to illustrate two important aspects of this technique. First, the calculated first-order rate is for reductive dechlorination only. The Bldg. 301 plume at Offutt AFB is characterized by predominantly aerobic conditions and low daughter product concentrations throughout large portions of the plume; therefore, reductive dechlorination is expected only in isolated portions of the plume. This technique estimates a low reductive dechlorination rate with a low R^2 because limited reductive dechlorination appears to be occurring both at the head and the tail of the plume; however, little to no reductive dechlorination occurs through the central portion of the plume. Anaerobic, reducing conditions with large daughter product concentrations prevail at the fire training areas at Cape Canaveral AS and Plattsburgh AFB. Consequently, both have reductive dechlorination rates estimated with a high degree of correlation.

Secondly, the rate estimate does not adequately assess the total biodegradation rate if biodegradation mechanisms other than reductive dechlorination are operant. Alternate biodegradation avenues are available for lower molecular weight solvents such as VC as groundwater conditions become less reducing. For instance, at the Plattsburgh AFB FT-002 site, groundwater geochemistry becomes less reducing between 2,000 and 2,500 feet downgradient from the source area; therefore, a reductive dechlorination rate cannot be calculated beyond this point. The combination of slowing reductive dechlorination rates and the destruction of VC (and perhaps other parent and daughter products) by alternate biodegradation processes renders the technique inappropriate.

SECOND-ORDER DEGRADATION RATE ESTIMATES

Although a first-order rate assumption may provide a reasonable approximation of how BTEX and CAH compounds are degrading in groundwater systems, this approach may neglect the importance of the electron donor-electron acceptor redox couples or the variable rate of biomass growth expected throughout the plume. As discussed previously, a first-order kinetic model may not provide the best approximation of how CAH compounds are dechlorinated (biodegraded) in the presence of another limited substrate, the electron donor (BTEX). Because highly-chlorinated CAH compounds are rarely used as primary substrates for microbial metabolism (e.g., McCarty and Semprini, 1994), the dechlorination of these compounds is dependent upon the microbial utilization of a primary substrate such as BTEX. Therefore, the degradation kinetics of this dual-dependency reaction may be more appropriately approximated by a bimolecular reaction rate expression (see equation 3). The linear form of this second-order equation is:

$$\frac{1}{[A]_0 + [B]_0} \ln \left[\frac{[A]_0[B]}{[B]_0[A]} \right] = kt \quad (8)$$

where $[B]_0$ = initial concentration of electron donor ($\mu\text{g/L}$); $[B]$ = measured concentration of electron donor ($\mu\text{g/L}$); $[A]_0$ = initial stoichiometry-normalized concentration of electron acceptor ($\mu\text{g/L}$); $[A]$ = measured stoichiometry-normalized concentration of electron acceptors ($\mu\text{g/L}$), and k = second-order degradation rate constant ($\text{L}/\mu\text{g}\text{-day}$). Table 5 presents the stoichiometry-normalized concentrations of these electron acceptors measured at the Plattsburgh AFB FT-002 site, which were used to estimate second-order rate constants. The reason that stoichiometry-normalized electron acceptor concentrations were used to develop second-order reaction rate constants was to develop a weighted estimate of oxidizing potential.

If the objective of the second-order approximation is to estimate the rate of CAH degradation in the presence of petroleum hydrocarbons, no significant concentration correction for the effects of nondestructive attenuation processes (i.e., advective-dispersive transport and sorption) is necessary. These nondestructive attenuation processes will have the same general concentration-reducing effects on anthropogenic organic electron acceptors (CAH) and anthropogenic organic electron donors (BTEX). Both of these types of compounds will be advectively transported and dispersed from the source area, and are subject to sorption. Although the sorptive characteristics of the BTEX compounds are slightly greater than that of the CAH compounds, the organic carbon content of the saturated soils at some sites (e.g., Plattsburgh) may be low enough to minimize significant retardation. In contrast, if the objective of the second-order approximation was to estimate the rate of degradation of anthropogenic electron donors (BTEX) in the presence of only natural electron acceptors (i.e., the common inorganic electron acceptors), the concentration-reducing effects of nondestructive attenuation processes on the BTEX compounds would have to be considered. To simplify this example, this paper investigates only the second-order relationship between CAHs and BTEX at Plattsburgh, where limited contaminant sorption is expected.

Figures 4 and 5 present the second-order reaction rate constants derived for BTEX-CAH redox reactions for the Plattsburgh AFB FT-002 site (1993 and 1995 sampling events). The second-order reaction rate constant is equal to the slope of the best fit line as a function of the second-order linear expression and contaminant transport time (days). Although the coefficients of correlation (R^2) indicate that the data are reasonably approximated by the second-order relationship, the correlation is not as strong as suggested by the first-order methods. The lack of absolute correlation may be a function of limiting the reaction dependency to only anthropogenic chemicals, rather than accounting for the effects of inorganic electron acceptors known to be involved in redox reactions at the site. Additionally, the lower correlation may be a reflection of the slight difference between the effects of nondestructive attenuation processes on the electron donors and electron acceptors.

These estimated second-order rate constants can then be used to estimate the changing degradation rates for redox reactions involving CAH compounds in the presence of BTEX as a function of distance from the source and/or time as follows:

$$\text{degradation rate } (\mu\text{g/L-day}) = k[B][A] \quad (9)$$

Table 5 also presents the calculated degradation rates at different points along the groundwater flowpath and for different sampling events. As these estimates indicate, the rate of degradation is fairly high when sufficient concentrations of both electron donors and electron acceptors are present. This result is consistent with the measured chloride concentrations, that suggest dechlorination is occurring at and immediately downgradient from the core of the BTEX/CAH plume (Table 5). However, as the concentrations of each diminish, the rate of degradation decreases. Notably, the estimated degradation rate at the Plattsburgh FT-002 site during the 1995 sampling event was lower than that estimated from the 1993 sampling data. These results suggest the rate of degradation is changing both as a function of distance along the plume flowpath and as a function of time.

These results may be significant in terms of anticipating whether CAH plumes can be "naturally" dechlorinated to less chlorinated compounds such as ethene. When the concentration of the electron donor has been sufficiently oxidized and/or when the electron acceptor "out migrates" the electron donor, the rates of degradation will decrease and possibly even cease. For example, at the Plattsburgh FT-002 site this means that as the CAH mass migrates beyond the available electron donor mass (see Table 5), the rate of degradation becomes significantly less than that predicted to be occurring in the core of the plume. Unfortunately, these results mean that the remaining CAH mass may not be subject to further degradation via reductive dechlorination processes. Degradation may still occur, however, if the remaining CAH mass is amenable to oxidation reactions (e.g., vinyl chloride).

DISCUSSION

A comparative analysis of the results of these methodologies is warranted. For the Plattsburgh AFB FT-002 site, the biodegradation rates estimated using a first-order assumption are similar to the average rate estimated using the second-order approximation (see Tables 3 and 5). The average CAH reductive dechlorination rate estimated using the first-order approximation based on the 1993 sampling event is 0.00011 day^{-1} (which corresponds to a half-life of about 17 years). The average BTEX-CAH biodegradation rate estimated using the second-order approach is about 0.00014 day^{-1} (which corresponds to a half-life of 13.5 years). Although these methods yield apparently comparable average biodegradation rates, the second-order approximation clearly shows how the rate of biodegradation of BTEX-CAH can vary within a plume, both as a function of location and time. Specifically, the second-order biodegradation rate estimated for the plume core at the Plattsburgh AFB FT-002 site from the 1993 sampling data is almost twice the estimated average biodegradation rate. This results in a half-life of about 8 years within the plume core. As the electron donors and electron acceptors migrate away from the source area, the biodegradation rate decreases due to the rate-limiting availability of both compounds. For example, by the time the measured BTEX decreases by two orders of magnitude from the source area concentration (i.e., at well MW-02-042), the biodegradation rate has decreased by more than two orders of magnitude. This effectively increases the half-life of remaining mass in the part of the plume to about 900 years! Of course, other destructive attenuation mechanisms such as oxidation processes (rather than reductive processes) may play a large role in attenuation at this point.

Similar relationships are illustrated by comparing the 1993 data sets and the 1995 data sets. The first-order biodegradation rate based on 1995 sampling results is about half the biodegradation rate estimated from 1993 sampling results. The difference in the second-order biodegradation rates between these two sampling events is even more marked. In the source area, the rate of biodegradation estimated in 1995 was only about 37 percent of the rate estimated in 1993. This reduction in biodegradation rate may be attributable to the availability of the electron donor. In 1993, the proportion of electron donor mass to organic electron acceptors decreased by about 38 percent between 1993 and 1995. This suggests that the reduction in electron donor mass may become rate-limiting over time, even in the source area.

These biodegradation rate estimate methodologies provide valuable information that should be factored into the remedial decision-making process. The first-order biodegradation estimates provide a good indicator of observed dechlorination at a single point in time as averaged across a plume flowpath. However, the second-order degradation estimates show that biodegradation rates are variable, which can have a profound effect on the anticipated effectiveness of natural chemical attenuation processes and the need to implement additional engineered actions or exposure controls.

REFERENCES

- Bouwer, E.J., 1992, Bioremediation of Subsurface Contaminants, In: Mitchell, R., ed.: Environmental Microbiology. Wiley-Liss, New York, New York.
- Buscheck, T.E., and Alcantar, C.M., 1995, Regression techniques and analytical solutions to demonstrate intrinsic bioremediation. Proceedings, 1995 Battelle International Conference on In-Situ and On Site Bioreclamation, April 24-27, 1995, San Diego, CA.
- Chapelle, F.H., 1993, Ground-water Microbiology and Geochemistry. John Wiley and Sons, Inc., New York, NY.
- Chapelle, F.H., Bradley, P.M., Lovley, D.R., and Vroblesky, D.A., 1996, Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods. Ground Water, v. 34, n., 4, pp. 691-698.
- Gossett, J.M. and Zinder, S.H., 1996, Microbiological aspects relevant to natural attenuation of chlorinated ethenes: In proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water, Dallas, TX, September 1996, EPA/540/R-96/509.
- McAllister, P.M., and Chiang, C.Y., 1994, A practical approach to evaluating natural attenuation of contaminants in ground water. Ground Water Monitoring Review, v. 14, pp. 161-173.
- McCarty, P.L., and Semprini, L., 1994, Ground-Water Treatment for Chlorinated Solvents, In: Handbook of Bioremediation. Lewis Publishers, Boca Raton, FL. 1994.
- National Research Council, 1993, In situ bioremediation: when does it work? National Academy Press, Washington, D.C., 207pp.
- Salanitro, J.P., 1993, The role of bioattenuation in the management of aromatic hydrocarbon plumes in aquifers. Ground Water Monitoring, v. 13, pp. 150-161.
- Wiedemeier, T.H., Wilson, J.T., Kampbell, D.H., Miller, R.N., and Hansen, J.E., 1995, Technical protocol for implementing intrinsic remediation with long-term monitoring for natural chemical attenuation for fuel contamination dissolved in groundwater. Prepared for the Air Force Environmental Center for Environmental Excellence, Brooks Air Force Base, Texas.
- Wiedemeier, T.H., Swanson, M.A., Wilson, J.T., Kampbell, D.H., Miller, R.N., and Hansen, J.E., 1996a, Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in ground water: Ground Water Monitoring and Remediation, v. 16, no. 3, p. 186-194.
- Wiedemeier, T.H., Swanson, M.A., Moutoux, D.E., Gordon, E.K., Hansen, J.E., Haas, P., Wilson J.T., Kampbell, D.H., and Chapelle, F.H., 1996b, DRAFT Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater. Prepared for the Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas. In preparation.
- Wilson, J.T., Weaver, J.W., and Kampbell, D.H., 1994, Intrinsic bioremediation of JP-4 jet fuel. Proceedings, Symposium on Intrinsic Bioremediation of Ground Water, August 30-September 1, 1994, Denver, CO, pp. 60-72.
- Young, L.Y. and Cerniglia, C.E., eds., 1995, Microbiological Transformation and Degradation of Toxic Organic Chemicals: Wiley-Liss, New York.

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**TABLE 1
SUMMARY OF SITE INFORMATION**

Sampling Location	Historical Use	Contamination Type and Concentration	Age of Release	Length of Plume	Hydrogeologic Parameters
<i>Cape Canaveral</i>	Fire training and drum storage area operating between 1965 and 1985.	Comingled waste fuels and solvents	Chronic release from 1965 to 1985.	Approximately 1,200 feet to surface water discharge point	Groundwater Velocity: 0.27 ft/day Contaminant Velocity: 0.16 ft/day Dispersivity: 130 feet
<i>Plattsburgh</i>	Fire training area operating between 1950's and 1989.	Comingled waste fuels and solvents	Chronic release from the 1950's to 1989.	More than 3,100 feet	Groundwater Velocity: 0.39 ft/day Contaminant Velocity: 0.30 ft/day Dispersivity: 300 feet
<i>Offutt</i>	Bomber assembly from 1944 to 1945; guided missile assembly from 1959 to 1965.	Solvents used in degreasing operations	Unknown	Approximately 3,000 feet	Groundwater Velocity: 0.35 ft/day Contaminant Velocity: 0.29 ft/day Dispersivity: 250 feet

**TABLE 2
SUMMARY OF SITE CHARACTERIZATION DATA**

Sampling Location	Distance from Source (feet)	Predicted CAH Travel Time (days)	PCE (µg/L)	TCE (µg/L)	Total 1,2-DCE (µg/L)	VC (µg/L)	Ethene & Ethane (µg/L)	Total PCE, TCE, DCE, & VC (µg/L)
<i>Cape Canaveral</i>								
CCFTA2-9S	0	0	56	15,800	98,889	3,080	30	117,825
MP-3	775	4,880	BDL	220	3,502	3,080	243	6,802
CPT-4	885	5,572	BDL	16.5	781.9	797	BDL	1,595
MP-6	1,145	7,209	BDL	24.3	1,216	2,520	120	3,760
CCFTA2-14	1,270	7,996	BDL	42	996	6,520	228	7,558
MP-4S	1,320	8,311	BDL	19	575	5,024	153	5,618
<i>Plattsburgh</i>								
MW-02-014 (1993)	0	0	BDL	1,030	9,050	4.5	3.2	10,085
84-M (1993)	460	1,523	BDL	BDL	1,320	1,050	28.4	2,370
MW-02-019 (1993)	730	2,417	BDL	1.9	3,540	384	39	3,926
MW-02-042 (1993)	2,600	8,607	BDL	98.5	1,570	2.2	3.5	1,671
MW-02-043 (1993)	3,750	12,414	BDL	373	10.6	BDL	BDL	384
Point A (1995)	0	0	BDL	25,280	51,412	BDL	BDL	76,692
Point B (1995)	970	3,211	BDL	2	14,968	897	35	15,867
Point C (1995)	1,240	4,105	BDL	3	10,035	1,430	182	11,468
Point E (1995)	2,560	8,474	BDL	24	2,218	8	BDL	2,250
Point F (1995)	3,103	10,272	BDL	1	226	5	BDL	232
Point A (1996)	0	0	BDL	580	12,626	BDL	BDL	13,206
Point B (1996)	970	3,211	BDL	1	9,376	1,520	13	10,897
Point C (1996)	1,240	4,105	BDL	1	10,326	1,050	170	11,377
Point D (1996)	2,050	6,786	BDL	BDL	1,423	524	4	1,947
Point E (1996)	2,560	8,474	BDL	17	1,051	12	BDL	1,080
Point F (1996)	3,103	10,272	BDL	BDL	177	4	BDL	181
<i>Offutt</i>								
MW7I	0	0	BDL	17,500	1,235	BDL	BDL	18,735
MW18	420	1,461	BDL	3,610	4	BDL	BDL	3,614
MW14	510	1,774	BDL	2,940	11.5	BDL	BDL	2,952
MW8I	980	3,409	BDL	201	BDL	BDL	BDL	201
MW9S	1,460	5,078	BDL	372	23	1	BDL	396
TW1	2,020	7,026	BDL	438	58	BDL	BDL	496
MW11	2,520	8,765	BDL	15.2	77.3	BDL	BDL	92.5

TABLE 3
ESTIMATED FIRST-ORDER ATTENUATION RATES

Sampling Location	Total Attenuation (day ⁻¹)	Steady-State Plume Biodegradation (day ⁻¹)	R ² for Total Attenuation and Steady-State Plume Biodegradation	Reductive Dehalogenation (day ⁻¹)	R ² for Reductive Dehalogenation
<i>Cape Canaveral</i>					
January 1996	0.00036	0.00026	0.59	0.000085	0.97
<i>Plattsburgh</i>					
December 1993	0.00021	0.00017	0.84	0.000112	1.0
August 1995	0.00052	0.00025	0.95	0.000063	0.98
May 1996	0.00042	0.00025	0.86	0.000033	0.99
<i>Offutt</i>					
June 1996	0.00051	0.00029	0.75	0.000029	0.53

TABLE 4
FIRST-ORDER REDUCTIVE DEHALOGENATION RATE CALCULATION

Sampling Location	Carbon Equivalents (μM/L)	Chlorine Equivalents (μM/L)	Corrected CAH (μg/L)
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<i>Cape Canaveral</i>			
CCFTA2-9S	2,382	2,452	117,799
MP-3	191	127	75,647
CPT-4	42	29	79,956
MP-6	115	66	65,849
CCFTA2-14	246	126	58,526
MP-4S	184	93	57,704
<i>Offutt</i>			
MW71	292	425	18,735
MW18	55	83	19,287
MW14	45	67	19,263
MW81	3	5	19,296
MW9S	6	9	18,735
TW1	8	11	18,318
MW11	2	2	13,679

Sampling Location	Carbon Equivalents (μM/L)	Chlorine Equivalents (μM/L)	Corrected CAH (μg/L)
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<i>Plattsburgh</i>			
MW-02-014 (199	1,446	1,638	10,088
84-M (1993)	340	323	8,462
MW-02-019 (199	266	230	7,703
MW-02-042 (199	46	46	8,913
MW-02-043 (199	5	5	8,769
Point A (1995)	1,446	1,638	76,692
Point B (1995)	340	323	64,332
Point C (1995)	266	230	58,560
Point E (1995)	46	46	67,762
Point F (1995)	5	5	66,670
Point A (1996)	269	274	13,206
Point B (1996)	243	218	11,644
Point C (1996)	259	230	11,541
Point D (1996)	46	38	10,566
Point E (1996)	22	22	12,957
Point F (1996)	4	4	12,773

TABLE 5
DERIVATION OF SECOND-ORDER RATE CONSTANTS
AND DEGRADATION RATES

Plattsburgh FT-002 Sampling Location	Measured BTEX (µg/L)	Measured Total CAHs (µg/L)	Measured Chloride (µg/L)	Stoichiometric- Normalized Total CAHs (µg/L)	Estimated Second-Order Rate (µg/L-day)	Estimated Second-Order Rate (day ⁻¹)
MW-02-014 (1993)	6,010	10,080	63,500	7,974	2.27	0.00023
84-M (1993)	2,751	1,320	94,300	1,073	0.14	0.00010
MW-02-019 (1993)	2,399	3,542	42,400	2,879	0.32	0.000090
MW-02-042 (1993)	57	1,669	11,300	1,335	0.0036	0.0000021
MW-02-043 (1993)	0	384	930	191	0.0000058	0.00000015
AVERAGE of first three points					0.5460	0.00014
Point A (1995)	16,790	76,692	63,000	56,936	6.32	0.000082
Point B (1995)	3,060	14,970	48,000	12,170	0.22	0.000015
Point C (1995)	3,543	10,038	46,000	8,160	0.17	0.000017
Point D (1995)	89	1,423	14,000	1,157	0.00062	0.00000044
Point E (1995)	40	2,242	20,000	1,817	0.00044	0.00000020
Point F (1995)	2	227	3,000	185	0.0000022	0.000000010
AVERAGE of first four points					1.1205	0.000029

FIGURE 1
PLATTSBURGH TOTAL ATTENUATION RATE FROM 1995
DATA

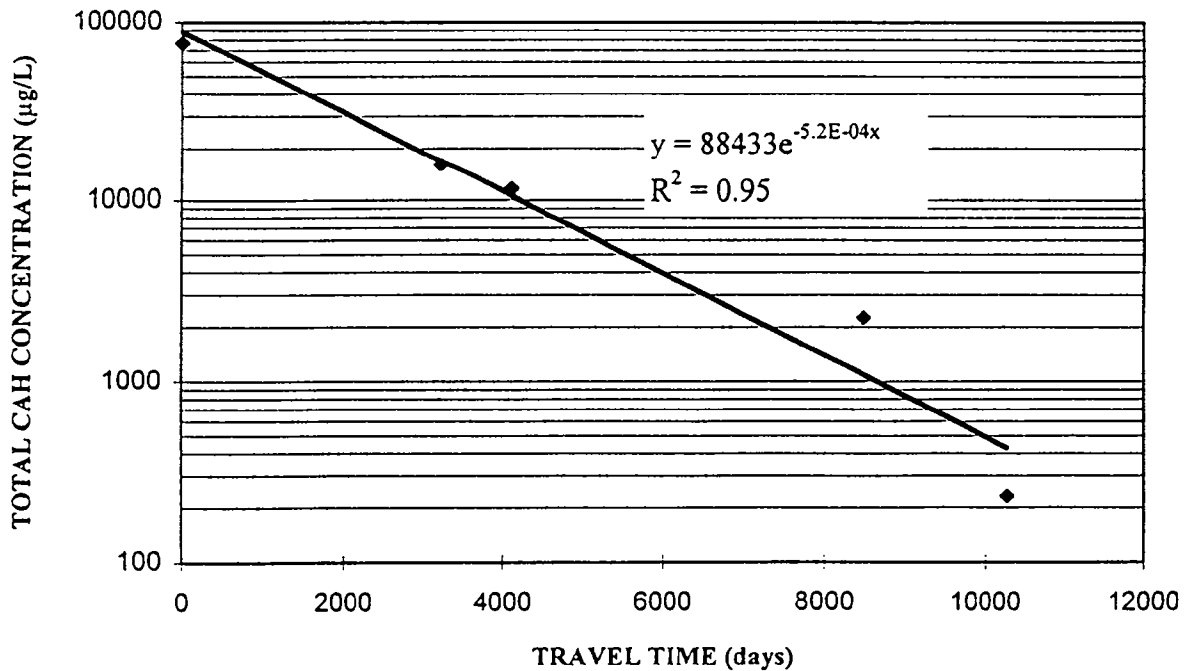


FIGURE 2
PLATTSBURGH BIODEGRADATION RATE ASSUMING STEADY-STATE CONDITIONS FROM 1995 DATA

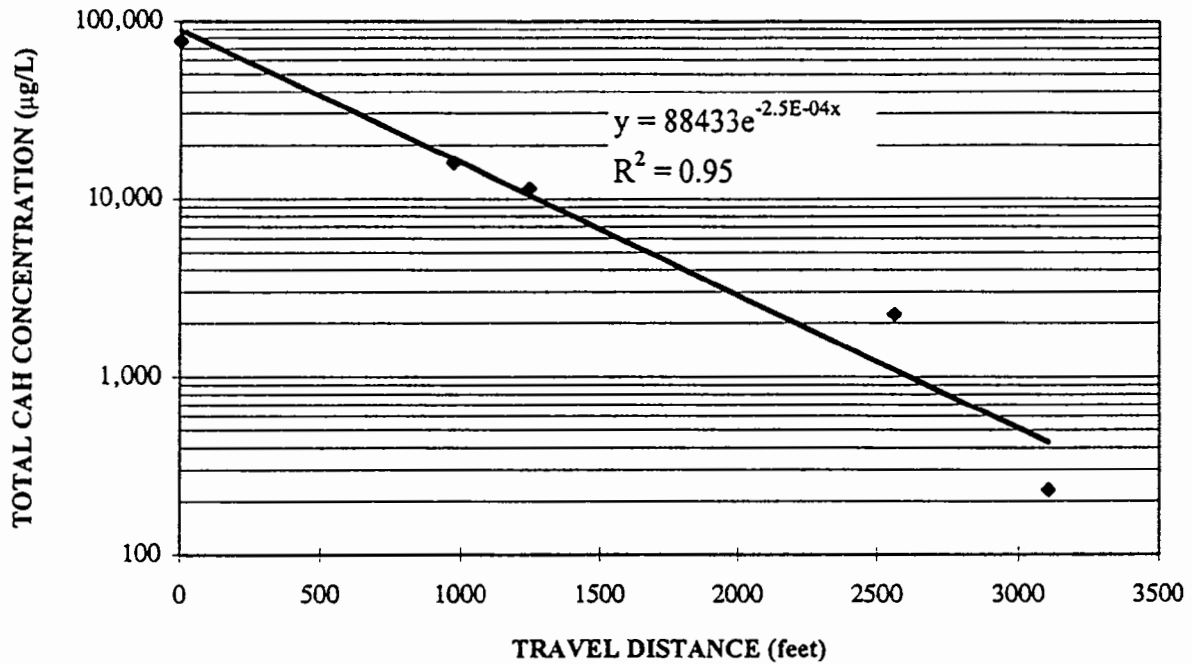


FIGURE 3
PLATTSBURGH REDUCTIVE DECHLORINATION RATE FROM 1995 DATA

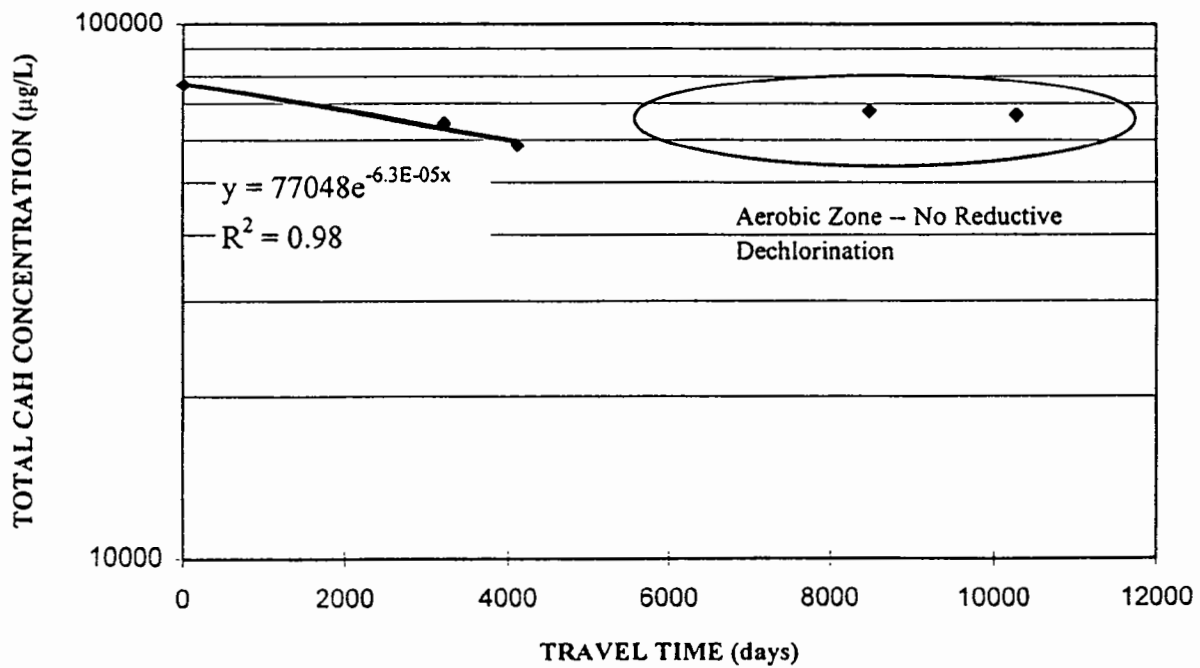


FIGURE 4
MEASURED BTEX vs. STOICHIOMETRIC CAH (1993)

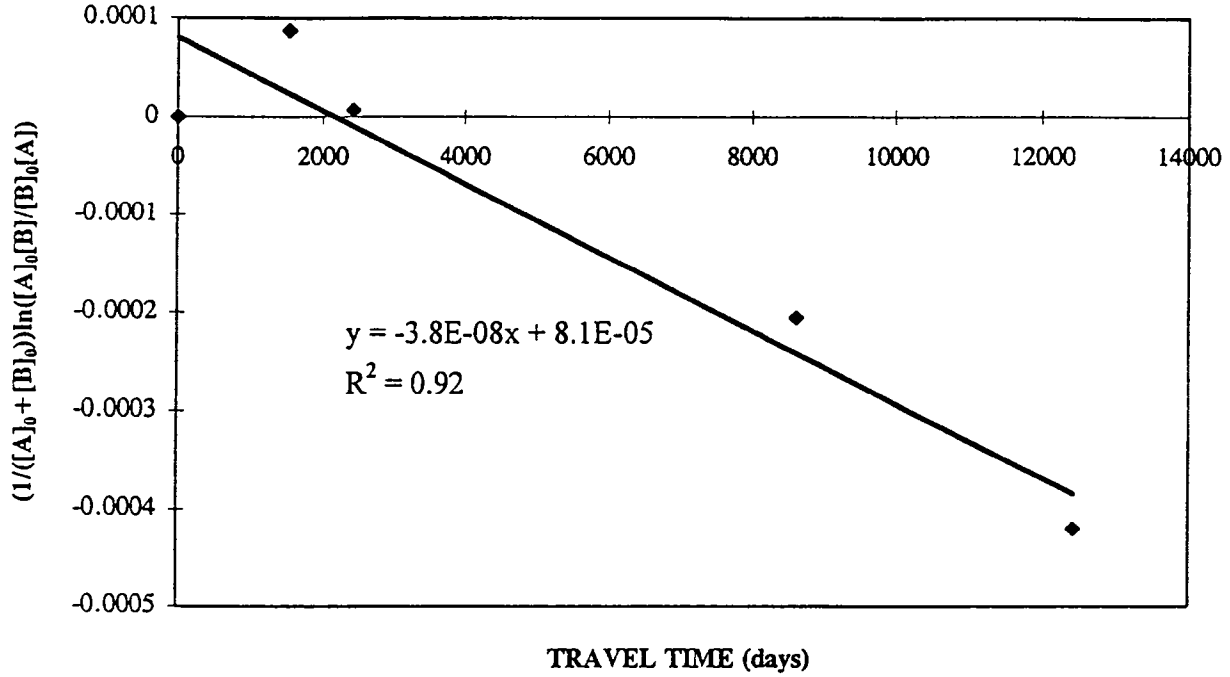
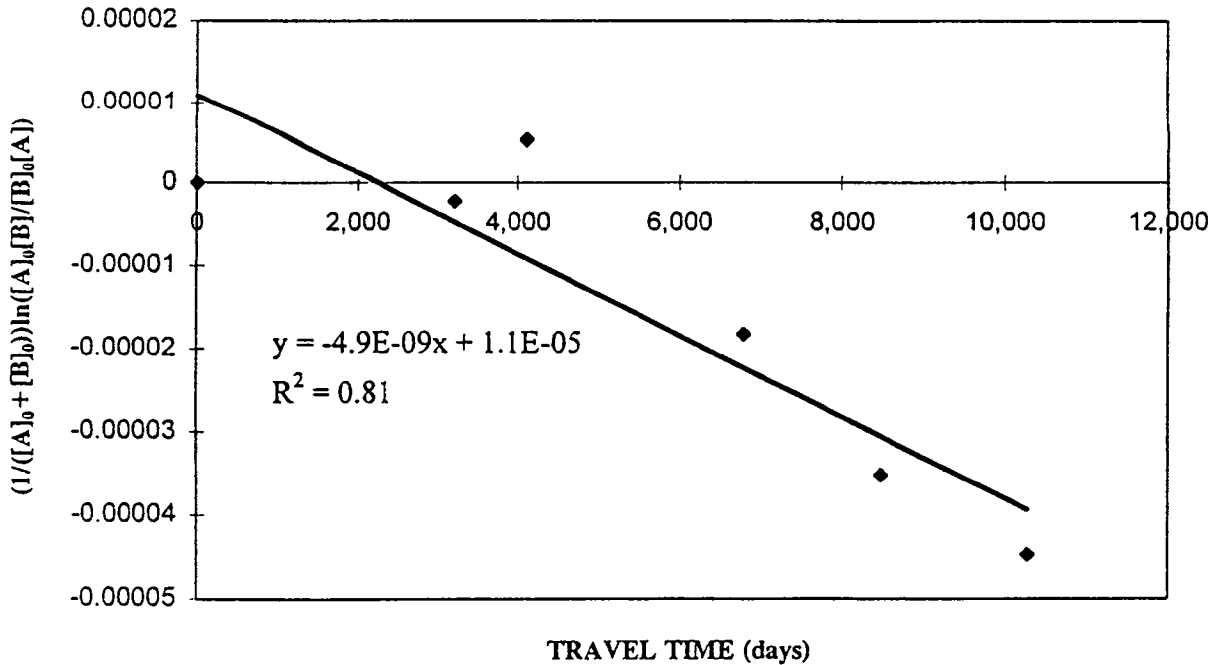


FIGURE 5
MEASURED BTEX vs. STOICHIOMETRIC CAH (1995)



TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/A-96/123		2.	3. RE
4. TITLE AND SUBTITLE Estimating the Changing Rate of Anaerobic Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons in the Presence of Petroleum Hydrocarbons		5. REI	
7. AUTHOR(S) Dave E. Moutoux, Leigh Alvarado Benson, Matthew A. Swanson, & Todd Wiedemeier (1) John T. Wilson (2) Jerry E. Hansen (3) John Lenhart (4)		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS (1) Parsons Engineering Science, Inc. (2) US EPA, National Risk Management Research Lab (3) Air Force Center for Environmental Excellence (4) Division Environmental Science & Engineering,		10. PROGRAM ELEMENT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS U. S. EPA, NRMRL, SPRD P.O. Box 1198 Ada, Oklahoma 74820		11. CONTRACT/GRANT NO. In-House RPK2 Colorado School of Mines	
		13. TYPE OF REPORT AND PERIOD COVERED BOOK CHAPTER	
		14. SPONSORING AGENCY CODE EPA/600/15	

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Recent laboratory and field results demonstrate that different chlorinated aliphatic hydrocarbons (CAHs) ultimately can be transformed into innocuous chemical compounds in many aquifer systems. Transformation can be the result of either cometabolic reactions or reduction oxidation (redox) reactions. In the latter, chlorinated compounds such as tetrachloroethene (PCE), trichloroethene (TCE), and dichloroethene (DCE) can be used in anaerobic, reducing aquifers as alternate electron acceptors during the oxidation of organic matter such as the petroleum hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX). When used as electron acceptors, these CAH compounds are sequentially dechlorinated into less chlorinated compounds such as vinyl chloride (VC) or ethene. While the rate of petroleum hydrocarbon degradation is generally reasonably approximated as a first-order process, it is not clear that the degradation of electron acceptors such as CAH compounds are best estimated in a similar manner. Because the rate of reductive dechlorination of CAHs in the presence of petroleum hydrocarbons is a function of both the concentration of the petroleum hydrocarbons and the concentration of the electron acceptors themselves, a second-order kinetic model may provide a better approximation of the rate of BTEX/CAH degradation over time and distance.

Several methodologies may be used to estimate the rate of reductive dechlorination of CAH compounds when they are being used to oxidize BTEX compounds. Both first-order and second-order approximations of CAH degradation rates can be useful in predicting CAH/BTEX plume behavior, although the second-order approximation will be especially useful in determining whether the system will first exhaust the available supply of electron donors (i.e., starve) or electron acceptors (i.e., strangle).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field Group

18. DISTRIBUTION STATEMENT Release To Public	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 15
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE