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INTRINSIC BIOATTENUATION FOR SUBSURFACE RESTORATION

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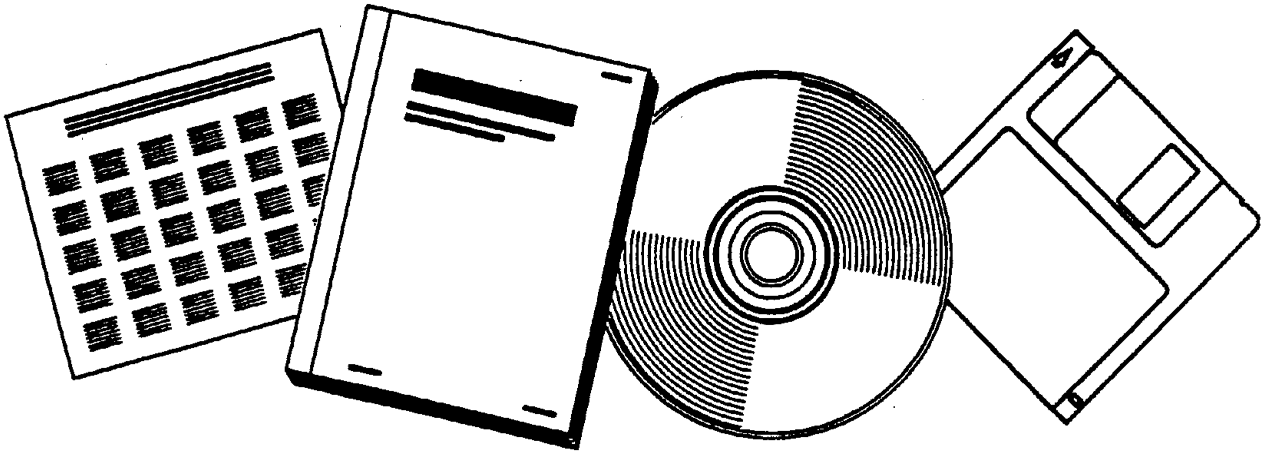

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Intrinsic Bioattenuation for Subsurface Restoration

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ABSTRACT

Intrinsic bioattenuation has recently evolved as a viable remediation alternative at a number of sites where the risk of exposure to contaminants is within acceptable standards. Important mechanisms controlling the instrinsic bioattenuation include advection, dispersion, sorption, dissolution from a residual source, and abiotic and biological transformations. Since intrinsic bioattenuation is a plume management strategy, it requires characterizing and monitoring these processes. Intrinsic bioattenuation involves an assessment of risks to public health and the environment, and consequently requires prediction of the fate and transport of contaminants at the candidate sites. This paper reviews the processes controlling intrinsic bioremediation and summarizes case histories where intrinsic bioattenuation has been observed at sites contaminated with petroleum hydrocarbons and chlorinated solvents. The key steps in evaluating natural attenuation as a remedial alternative are summarized.

INTRODUCTION

In the absence of human intervention, many contaminant plumes will develop until they reach a quasi-steady-state condition. At steady-state, the contaminant plume is no longer growing in extent and may shrink somewhat over time. Major processes controlling the size of the steady-state plume include (1) release of dissolved contaminants from the source area, (2) downgradient transport of the contaminants and mixing with uncontaminated groundwater, (3) volatilization, and (4) abiotic and biologically mediated transformations of the contaminants of concern.

Intrinsic bioattenuation is a plume management strategy where the natural assimilation processes are monitored and used to limit adverse impacts of groundwater contamination. This strategy also requires an assessment of risks to public health and other environmental receptors. A successful implementation of intrinsic bioattenuation at a field site requires adequate site hydrogeological, chemical, and biological characterization; detailed data analysis to determine whether contaminants are being attenuated and/or removed from the aquifer; modeling of the fate and transport of the dissolved groundwater plume; and, finally, long-term monitoring to confirm and ensure protection of human health and the environment.

PROCESSES CONTROLLING THE STEADY-STATE CONTAMINANT DISTRIBUTION

Physical

The primary physical processes affecting the distribution of contaminants in groundwater include advection, dispersion, sorption, volatilization, and dissolution from residual contaminants located in the source area. Advection is the process by which contaminants are transported with the flow of groundwater. Dispersion accounts for mechanical and molecular mixing processes. Both advection and dispersion reduce contaminant concentrations but do not cause a net loss of mass of contaminants in the aquifer. Higher advection and dispersion cause more spreading and more dilution of a dissolved contaminant plume.

Sorption describes the partitioning of contaminants between the aqueous phase and the solid aquifer matrix. Sorptive processes also tend to reduce the dissolved contaminant concentrations and limit the migration of the aqueous-phase plume, but they do not result in a loss of contaminant mass from the aquifer. Under steady-state conditions, sorption will not affect the final contaminant distribution; however, sorption will delay the development of a steady-state plume.

Volatilization refers to the partitioning of a contaminant between the aqueous phase in the saturated zone and the vapor phase in the unsaturated zone. While volatilization actually removes mass from the aquifer, it is not thought to be a significant attenuation mechanism except in situations where the groundwater table is less than 15 ft deep and the unsaturated zone consists of relatively transmissive soils. Chiang et al. (1989) estimated that volatilization resulted in a mass loss of benzene of less than 5% at a gas plant facility in Michigan.

Dissolution from residual contaminants located in the source area is by far the most significant physical process that controls the extent of a contaminant plume. In the case of petroleum hydrocarbons, contaminants may dissolve from a lens of mobile hydrocarbons floating on the water table or from residual hydrocarbons trapped in the soil matrix above and/or below the water table. Seasonal fluctuations in the water table can cause additional "smearing" and dissolution from residual source areas. Until sources are depleted, a contaminant plume will expand until it reaches a quasi-steady-state.

Abiotic and Biologically Mediated Transformations

Aerobic and anaerobic biodegradation processes are believed to account for both contaminant concentration reduction and loss of pollutant mass from the aquifer. Abiotic transformations, such as hydrolysis and dehydrohalogenation, also attenuate concentrations and contaminant mass in an aquifer; but are only significant for specific chemicals such as chlorinated solvents.

Aerobic biodegradation relies on dissolved oxygen as the electron acceptor used by the microorganisms. Petroleum hydrocarbons are generally very amenable to aerobic biodegradation in aquifers with dissolved oxygen concentrations exceeding 1 to 2 mg/L. Many shallow water table aquifers will contain background dissolved oxygen concentrations between 1 to 12 mg/L depending on the temperature of the groundwater. While aerobic biodegradation takes place at relatively higher rates than anaerobic processes, it is often limited by the available supply of oxygen to a contaminant plume. Once the background dissolved oxygen is consumed in the center of the plume, aerobic biodegradation is limited to the edges of the contaminant plume where the dissolved contaminants come into contact with oxygen-rich groundwaters.

Anaerobic processes refer to a variety of biodegradation mechanisms that use NO_3^-, SO_4^{2-}, Fe^{+3}, and CO_2 as terminal electron acceptors. Anaerobic biodegradation dominates the interior of a contaminant plume. Both petroleum hydrocarbons and chlorinated solvents are believed to biodegrade to varying degrees under anaerobic conditions. However, the rates of biodegradation are often slower than under aerobic conditions.

Hydrocarbon Biodegradation. Most organic compounds found in crude, refined oil and fuels are known to degrade under aerobic conditions. The aerobic biodegradation of benzene, toluene, ethylbenzene, xylene, napthalene, methylnapthalenes, dibenzofuran, and fluorene has been confirmed by a large number of laboratory and field studies. Aerobic processes are relatively fast and limited by the rate at which oxygen is supplied to a contaminant plume. Because of this phenomenon, Rifai et al. (1988) modeled aerobic biodegradation as an instantaneous reaction between oxygen and the hydrocarbons.

Current research efforts have also shown that monoaromatic compounds degrade under anaerobic conditions. This biodegradation occurs with NO_3^- (Evans et al. 1991), Fe^{3+} (Lovley and Lonergan 1990), SO_4^{2-} (Edwards et al. 1991), and carbon dioxide (Grbic-Galic and Vogel 1987; Wilson et al. 1986) as electron acceptors.

Benzene has been found to be recalcitrant to anaerobic biodegradation in laboratory studies using nitrate and sulfate as electron acceptors (Kuhn et al. 1989; Edwards et al. 1991). However, some laboratory and field studies demonstrated the degradation of all monoaromatic hydrocarbons under denitrifying, sulfate reducing and methanogenic conditions (Major et al. 1988; Cozzarelli et al. 1990; Vogel and Grbic-Galic 1986; Barker and Wilson 1992; Wilson et al. 1994a). The aromatic compounds may be oxidized first to phenols or organic acids, then transformed to volatile fatty acids before complete mineralization. Anaerobic biodegradation of aromatic hydrocarbons is therefore associated with the production of fatty acids, methane, carbon dioxide, solubilization of iron, and reduction of nitrate and sulfate.

Adaptation of an aromatic plume to nitrate as a terminal electron acceptor seems to occur readily once oxygen is depleted. Natural biodegradation through nitrate respiration should be similar to oxidative biodegradation. Depending on its concentration, sulfate can also be an important electron acceptor. Acton and Barker (1992) demonstrated the sulfate reduction of toluene and m-xylene in a forced gradient injection experiment at an active landfill in Ontario, Canada. Benzene, o-xylene, ethylbenzene, and 1, 2, 4- trimethylbenzene were not degraded at the site.

CAH Transformation. Chlorinated solvents, consisting primarily of chlorinated aliphatic hydrocarbons (CAHs), can be transformed by chemical and biological processes to form a variety of other CAHs (McCarty, 1994). Reduction of tetrachloroethene (PCE) and trichloroethene (TCE) to ethene has occurred at many sites, although transformations are often not complete. Freedman and Gossett (1989) provided evidence for the conversion of PCE and TCE to ethene and de Bruin et al. (1992) reported complete reduction to ethane. McCarty (1994) lists the possible transformations for a number of the predominant chlorinated solvents in groundwater (Table 1). McCarty (1994) indicates that methanogenesis is the most favorable mechanism for complete reduction of PCE and TCE to ethene.

A number of researchers have confirmed the biological transformation of CAHs at field sites. Major et al. (1991) reported evidence for bioattenuation of PCE to ethene and ethane at a chemical transfer facility in North Toronto. Fiorenza et al. (1994) presented data on the chemical and biological transformation of trichlorethane (TCA) to 1, 1-DCA and that of PCE and TCE to cis-DCE, vinyl chloride (VC), and ethene at a manufacturing plant in Ontario. Beck (1994) reported the degradation of 1, 1, 1-trichloroethane (TCA), PCE, and TCE to ethene and methane at the Dover AFB in Delaware. McCarty and Wilson (1992), Haston et al. (1994), Kitanidis et al. (1993), McCarty et al. (1991), and Wilson et al. (1994b) confirmed the intrinsic biodegradation of chlorinated solvents at the St. Joseph, Michigan, Superfund site.

In addition to biological transformations, chemical transformations of some CAHs can occur in groundwater through elimination or hydrolysis. TCA is one of the main chlorinated solvents that can be transformed chemically in groundwater under all conditions likely to be found and within a reasonable time frame (McCarty 1994). The rate of chemical transformations is usually expressed using a first-order reaction. TCA chemical transformation, for example, leads to the formation of 1,1-DCE and acetic acid with a reported average half-life of less than 1 year at a temperature of 20°C.

CASE STUDY — INTRINSIC BIOREMEDIATION OF A UST RELEASE

The underground storage tank release in Rocky Point, North Carolina, provides a representative example of a dissolved benzene, toluene, ethyl benzene, and xylene (BTEX) plume undergoing intrinsic biodegradation using oxygen, nitrate, iron, and sulfate as terminal electron acceptors (Borden et al. 1995). The water table aquifer consists of mostly fine-grained, dark gray or greenish gray, micaceous, glauconitic, slightly silty, and compact quartz sand. The sand appears to be very homogeneous throughout the site with only a few exceptions. This sand is overlain by lower permeability clays and clayey sands that form a surface confining layer throughout the site. The average groundwater velocity is approximately 30 m/yr. The organic carbon content of the sand is relatively low (0.1%), and consequently sorption is not a major attenuation mechanism for the moderately soluble BTEX fraction.

Spatial Distribution of BTEX and Indicator Parameters

Background groundwater contains moderate levels of dissolved oxygen (2 to 3 mg/L), nitrate (1 to 6 mg/L as N), and sulfate (20 to 30 mg/L). Background dissolved iron is low (< 0.5 mg/L) and the groundwater is acidic (pH < 5) with low buffering capacity (alkalinity ~ 6 mg/L as $CaCO_3$) and low levels of dissolved CO_2 (15 to 30 mg/L as C). At the upgradient edge of the BTEX plume, residual hydrocarbon is trapped below the water table in the sand aquifer. As uncontaminated groundwater enters this region, soluble hydrocarbons partition out of the nonaqueous-phase (NAPL) and into the aqueous phase. Figure 1 shows the observed variation in BTEX components, electron acceptors, and indicator parameters in a profile along the dissolved hydrocarbon plume centerline. Several distinct zones can be identified where different oxidation-reduction processes dominate.

At the upgradient edge of the BTEX plume, a portion of the soluble hydrocarbons released from the residual NAPL are immediately degraded using oxygen and nitrate carried into this zone by the flowing groundwater. Dissolved iron increases to 29 mg/L due to reduction of insoluble iron oxides associated with the sediment. In this region, the dominant electron acceptor is nitrate followed by iron and oxygen. Dissolved CO_2 increases from 16 to 60 mg/L as carbon (C) due to oxidation of organic matter. The pH also rises from ~ 4.7 to 5.8 due to consumption of H^+ during iron reduction.

During transport downgradient from the source, toluene and o-xylene decline rapidly followed by m, p-xylene and benzene. Ethylbenzene does not decline notably with distance. This pattern is apparently due to preferential biodegradation of the o-xylene isomer (and toluene) by subsurface microorganisms. Sulfate decreases from 34 to 0.7 mg/L, total sulfur decreases from 37 to 5 mg/L as SO_4, and dissolved iron increases from 29 to 65 mg/L. The large decline in sulfate and increase in dissolved iron indicate that both sulfate and iron reduction are occurring. The smaller decline in total sulfur suggests that sulfate is being reduced but is not being removed as ferrous sulfide (FeS) precipitates. Ion chromatographic analysis of the groundwater indicates that thiosulfate is a major component of the nonsulfate sulfur. Oxygen and nitrate are not significant electron acceptors in this portion of the plume since they were already consumed during transport through the source area.

The dissolved hydrocarbon plume becomes slightly narrower with distance downgradient. The limited spreading of the plume is apparently due to the combined effects of anaerobic biodegradation in the plume center and aerobic biodegradation at the sides of the plume. The background dissolved oxygen concentration varies from 2 to 3 mg/L, whereas in the center of the plume dissolved oxygen is below the field detection limit (0.3 mg/L). As the plume spreads in width due to dispersion, oxygen in the uncontaminated groundwater mixes with BTEX, enhancing biodegradation at the plume sides. The zone of highest BTEX concentration also moves vertically downward with increasing distance downgradient. The vertical drop along the length of the plume is due to surficial groundwater recharge that both adds a layer of clean, uncontaminated water on top of the plume and enhances biodegradation by introducing oxygen and other electron acceptors with the recharge water.

Rates of Intrinsic Bioremediation

Field implementation of intrinsic bioremediation requires an accurate estimation of in situ biodegradation rates. Three different approaches were applied at the Rocky Point site to estimate intrinsic bioremediation rates: (1) comparing of peak contaminant concentrations in monitoring wells versus travel time from the source (Borden et al. 1994); (2) monitoring laboratory microcosms under ambient (anaerobic) aquifer conditions (Hunt et al. 1995); and (3) monitoring of in-situ test chambers to determine compound loss over time (Hunt et al. 1995). The in situ test chambers were installed approximately midway down the plume in the iron-reducing zone at the same location used to collect the sediment for the laboratory microcosms. Results from each of these approaches are compared in Table 2.

In the laboratory microcosms, a distinct order of biodegradation was observed. Toluene and o-xylene appeared to be the most biodegradable followed by m-, p-xylene and benzene, with ethylbenzene being the least biodegradable. This same order of disappearance is also seen in the field data. Unfortunately, the rates of biodegradation estimated from the field data are vastly different from the laboratory data. In the laboratory microcosms, the benzene, toluene, and xylene isomers were degraded from between 2,000 and 3,000 µg/L each to below detection limit in 400 days. Ethylbenzene was only slightly degraded over this period. If similar biodegradation rates were observed in the field, the benzene, toluene, and xylene plumes would completely biodegrade over 100 to 200 ft. Yet significant concentrations of these dissolved hydrocarbons persist over 1,300 ft downgradient from the source. The cause of this discrepancy is not well understood.

Figures 2a and 2b show the vertical distribution of benzene, ethylbenzene, m-, p-xylene, and two trimethylbenzene isomers (mesitylene and pseudocumene) in a multilevel sampler located 800 ft downgradient from the source near the location of the in situ test columns. The concentrations of toluene and o-xylene were too low to be shown on these figures. In both figures, the vertical distribution of the more recalcitrant compounds (benzene, ethylbenzene, and mesitylene) is relatively consistent. In contrast, there are large changes in the concentration of the more biodegradable compounds (m-, p-xylene and pseudocumene). This suggests that the rate of biodegradation may be significantly different between adjoining layers.

The observed differences in field and laboratory biodegradation rates could be due to changes in the activity of different layers against the pollutants. In the field, if one layer is not active against the pollutants, the vertically averaged concentration measured with long-screened wells would remain high and the apparent biodegradation rate would be low. In contrast, within in situ test columns and laboratory microcosms, groundwater is forced into contact with sediment of differing activities. This would result in a higher apparent biodegradation rate.

CASE STUDY — INTRINSIC BIOREMEDIATION OF TCE IN GROUND WATER

The groundwater at the St. Joseph, Michigan, site is contaminated with chlorinated aliphatic hydrocarbons at concentrations ranging from 10 to 100 mg/L. The contaminants are divided into eastern and western plumes as the suspected sources were situated over a groundwater divide. Both plumes contain TCE, cis- and trans- 1, 2-dichloroethene (c-DCE and t-DCE), 1, 1, -dichloroethene (1, 1 -DCE), and VC. Significant levels of ethene and methane were measured at the site (Kitanidis et al. 1993 and McCarty and Wilson 1992), confirming the natural attenuation of TCE.

McCarty and Wilson (1992) delineated contours of the chemical oxygen demand (COD, a surrogate for the capacity of a donor to supply electrons) and correlated them with contours of chlorinated aliphatic compounds (see Figure 3). The authors found a correlation between COD decrease and transformations of TCE to VC. Also shown in Figure 3 are the locations of three transects where data were collected for the detailed bioattenuation characterization. Table 3 summarizes the electrons released by TCE reduction to different products, along with the equivalent amount of COD decrease. Essentially, the reduction of 1 mole or 131 g of TCE to ethene releases six electrons, and an equivalent decrease of 48 g of COD is needed.

Table 4 summarizes the CAHs, ethene, and methane found at some of the monitoring locations. The average concentration of methane at depths of 25 m or more was 6 mg/L. This concentration of methane corresponds to an equivalent COD decrease of 24 mg/L. However, Wilson and McCarty (1992) measured COD decrease, as high as 200 mg/L. They attribute this inconsistency to either dilution effects between the lagoon and the detailed characterization location or to the presence of other electron acceptors such as nitrate and sulfate.

Apparent Degradation Constants

Wilson et al. (1994b) studied the western plume at the site to estimate the contaminant mass flux and to estimate apparent degradation constants. Data collected in 1991 from three transects near the source of the western plume and data collected in 1992 from two additional transects were used in the analysis (see Figure 4 for locations of the transects). The mass estimates combined with the flow velocities were used to estimate the mass flux at each transect. As would be expected, the mass fluxes decline toward the downgradient edge of the plume.

The mass per unit thickness of TCE at transects 2, 4, and 5 was used to estimate first-order degradation constants. Table 5 lists the computed apparent loss coefficients for three different estimates of the hydraulic conductivity at the site. The rate for TCE degradation ranges from 0.0048 to 0.011 wk^{-1} between the upgradient transects 2 and 4. This rate increases up to 0.023 wk^{-1} between transects 4 and Lake Michigan.

DEMONSTRATING INTRINSIC BIOREMEDIATION IN THE FIELD

Initial Monitoring to Determine if Intrinsic Bioremediation is Feasible

Extensive field monitoring is initially conducted to determine if intrinsic bioremediation is feasible as a remedial alternative at a site. Rifai (1990) and Borden (1990) proposed preliminary sampling protocols for soils, groundwater, and soil gas (see Table 6). These protocols were intended for underground storage tank sites and mostly focused on defining the electron acceptor distribution in the groundwater and on quantifying the by-products of biodegradation in groundwater, and soil gas. Since then, the Air Force Center for Environmental Excellence (AFCEE) has developed a detailed protocol for site characterization in support of the natural attenuation alternative at Air Force facilities (Wiedemeier et al. 1994).

At a minimum, site characterization in an intrinsic bioattenuation protocol should provide data on the location and extent of contaminant sources, the extent and distribution of dissolved contaminants, groundwater geochemical data (i.e., concentrations of electron acceptors and by-products of biodegradation mechanisms), geologic characterization data, and hydrogeologic parameters such as hydraulic conductivity, gradients, and potential migration pathways.

The site characterization data are analyzed to quantify the extent of intrinsic bioattenuation. Overall, three indicators of natural attenuation can be developed from this information:

1. Compound disappearance: one of the most convincing arguments for natural attenuation involves demonstrating the disappearance of a dissolved organic chemical at the site relative to the persistence of another "conservative" or "recalcitrant" organic (internal standard). In some cases, it is sufficient to demonstrate that the extent of migration of the organic of concern is less than that of the "conservative" tracer, and thus its transport downgradient is being limited by natural attenuation. In cases where compound disappearance cannot be related to an internal standard, it may be possible to demonstrate mass loss as a function of time for the organic of interest. Another alternative involves analyzing the peak concentrations of the organic at the different monitoring wells downgradient from the source. This analysis should demonstrate the overall decline of these concentrations as a function of time and distance.

2. Loss of electron donors: measuring dissolved oxygen concentrations and those of other electron acceptors can provide a key indicator of natural attenuation. Reduced oxygen, nitrate, and sulfate concentrations within the plume relative to their background concentrations are considered to be strong evidence of intrinsic bioattenuation. Many field studies, for instance, have correlated depressed oxygen concentrations within the center of a plume with high concentrations of the dissolved contaminant.

3. Degradation products: the accumulation of dissolved iron and the production of carbon dioxide, hydrogen sulfide, and methane are additional indicators of biological attenuation at intrinsic bioremediation sites.

One of the interesting questions that is currently being investigated by researchers is whether it may be possible to complete a mass balance on the supply of electron donors and electron acceptors at a given field site. This question is complicated, because of sampling and field data collection limitations. Other complicating factors involve the temporal nature of the distributions of the electron acceptors and donors.

Risk Assessment

The successful application of the natural attenuation alternative involves an exposure and risk assessment analysis that considers the location of receptors at a site in relation to the extent of the contaminant plume. While a detailed discussion of risk assessment is beyond the scope of this paper, it is important to note that intrinsic bioremediation will only be viable as a remedial alternative if it can be demonstrated that little risk to human health and the environment will be incurred as a consequence of this management strategy. To demonstrate the viability of intrinsic bioremediation, it maybe necessary to conduct fate and transport predictions of the future conditions at contaminated sites.

Prediction of Plume Migration — Modeling Approaches

Two key questions need to be answered when determining the viability of natural attenuation as a remediation alternative: (1) How far will the dissolved plume migrate before it is attenuated to below a predetermined cleanup standard? and (2) How long will it take for the attenuation process to "cleanup" the plume? Both questions can be readily answered using analytical and numerical models of fate and transport. Analytical models are simpler to use, but they are limited in their capabilities to simplified hydrogeologic scenarios. Numerical models are more complicated, but can be used to simulate heterogeneous systems and more complex hydrogeologic and contaminant scenarios.

Numerous fate and transport models have been developed over the years. The majority of these models simulate advection, dispersion, and sorption and some form of source representation. A smaller number of these models, however, can actually simulate complex biological and chemical transformation processes. In the analytical modeling arena-, the most common method for simulating biodegradation is through the use of a first-order decay coefficient. The contaminant of concern is assumed to biodegrade exponentially, and the modeler specifies the first-order decay constant for a given site and a given contaminant. This leaves the modeler with the dilemma of selecting a first-order decay constant.

While many laboratory and field studies have developed first-order decay constants for a variety of contaminants under a number of hydrogeologic scenarios, these constants are not readily transferable to other sites. Another problem noted by Rifai (1994) is that the first-order decay model does not account for electron acceptor limitations and thus can overestimate the effect of biodegradation on a given system. Connor et al. (1994) proposed using an instantaneous reaction expression similar to that used in BIOPLUME II (Rifai et al. 1988) as an alternative to the first-order decay model. Additionally, Rifai and Hopkins (1994) have developed, through modeling with BIOPLUME II, "electron-acceptor" limited decay coefficients for scenarios with contaminant sources removed and continuous contaminant sources (Tables 7a and 7b) to provide more "applicable" decay constants.

Finally, and for sites where a long history of monitoring exists, it may be possible to estimate a first-order decay constant based on the observed mass loss in the aquifer. The dissolved concentrations for different sampling events are used to generate an estimate of the dissolved mass in the aquifer as a function of time. The resulting data allow the modeler to estimate a first-order decay constant. It should be mentioned, however, that this procedure is highly dependent on the density of the sampling network and would not be very accurate for sites with a limited number of monitoring wells.

Numerical models, as mentioned earlier; can provide more simulation capabilities than analytical models. The BIOPLUME II model (Rifai et al. 1988) allows the user to simulate a heterogeneous aquifer system with a variable flow field. The BIOPLUME II model is one of the few two-dimensional models in two dimensions that can simulate the transport of an electron acceptor (oxygen in this case) and its reactions with the aquifer contaminants. The model currently simulates the instantaneous reaction between oxygen and aromatic hydrocarbons. Rifai et al. (1995) are extending the BIOPLUME II model to allow the simulation of multiple electron acceptors within a contaminant plume. A number of other numerical biodegradation models exist in addition to BIOPLUME II (Table 8). The majority of these models, however, are either one-dimensional or of a proprietary nature.

One of the difficulties encountered in using numerical models is determining what data are required and how to incorporate the field data into the modeling process. Most fate and transport models require an estimate of the aquifer thickness, matrix conductivity, porosity, and sorptive characteristics. Additionally, most models require some description of the hydraulic and hydrologic stresses on the system in the form of boundary conditions or recharge and discharge specification.

One of the most complicated parameters to estimate for numerical models is the source representation because, in most cases, the history of contamination at the site is not known with any degree of certainty. Finally, biodegradation models require input on the electron acceptor availability within the aquifer.

The process of simulating natural attenuation at a site using a numerical model requires: (1) calibrating the model to the hydraulics at the site so that the model can emulate the direction of flow and observed groundwater velocities in the field; and (2) calibrating the model to simulate existing contamination conditions. Once those two steps have been completed, the numerical model can be used to determine the distribution of contaminants at the site as a function of time.

One of the problems faced in modeling intrinsic bioattenuation of organic chemicals at sites is the fact that the observed data usually incorporate the effects of advection, dispersion, sorption and biodegradation. Therefore, it may be difficult to estimate the advective and dispersive components independently from these data. A possible solution is to use a "conservative tracer" or an "internal standard" in the calibration of the numerical model that does not sorb or biodegrade. For example, when simulating gasoline spills, it may be possible to use MTBE concentrations in the calibration process if the data exist Methyl terbutyl ether (MTBE) does not sorb or biodegrade and thus would reflect the advective and dispersive characteristics of the aquifer). The biodegradation and sorption of the aromatic hydrocarbons within the gasoline plume can be readily estimated by comparing the BTEX plume to the MTBE plume. Wiedemeier et al. (1995) have also suggested the use of tetramethylbenzene as a more recalcitrant internal standard at fuel spill sites.

SUMMARY OF INTRINSIC BIOREMEDIATION FIELD SITES

Over the past decade, a large number of sites undergoing intrinsic bioremediation have been studied in detail. Some of the major characteristics of selected sites are provided in Table 9. Upgradient background concentrations of oxygen, nitrate, and sulfate provide an indication of the concentrations potentially available for biodegradation. Elevated concentrations of Fe^{+2} and CH_4 in the plume reflect the importance of iron reduction and methanogenic fermentation. At many sites, significant concentrations of iron, nitrate and sulfate are available to support hydrocarbon biodegradation. Although methane fermentation has been documented at several sites, it appears to be less important than iron and sulfate reduction.

Biodegradation results from field and laboratory studies are reported in Table 10. Laboratory results are reported only if the laboratory study was designed to simulate field conditions. Effective decay rates have been estimated in the field using several approaches. The most reliable approach is to calculate a mass balance for a known mass of contaminant injected into an aquifer using a dense network of monitoring points. This approach is feasible only when a pulse of contaminant is injected. For continuous sources at steady-state, the degradation rates may be calculated from the change in total mass flux across several lines of monitoring wells. Both the mass balance and mass flux approaches are expensive to implement because of the high number of monitoring points required. At most field sites, the only feasible approach is to estimate the degradation rate from a plot of peak contaminant concentration versus travel time from the source. This general approach has been modified by normalizing the contaminant concentrations to an 'internal standard' that is poorly biodegradable, has similar sorption and volatilization properties as the contaminant, and is present in the waste source. Ideally, the internal standard approach should correct for changes in concentration due to dilution.

There is a wide range in reported biodegradation rates. Reported first order degradation rates for benzene range from non detectable to approximately 1% per day, with an average of approximately 0.2% per day. Degradation rates for other hydrocarbons were typically somewhat higher, but in the same general range. Higher biodegradation rates occur most frequently at sites containing higher concentrations of sulfate in the background water and higher concentrations of dissolved iron in the plume. Where high concentrations of methane are observed, biodegradation rates are often lower.

SUMMARY

Past research has shown that intrinsic bioremediation can control the migration of dissolved hydrocarbon plumes. Field biodegradation rates are often lower than would be expected based on laboratory results, but are often sufficient to contain the contaminant plumes within reasonable transport distances. Fewer data are available on chlorinated hydrocarbon plumes, but ongoing studies suggest that intrinsic bioremediation may also be technically feasible at these sites. At many sites intrinsic bioremediation alone may be the best alternative available for risk management.

Intrinsic bioremediation will be the preferred alternative when the costs of conventional remediation are high, the problem compounds are easily biodegradable, aquifer conditions are appropriate, there are no nearby groundwater receptors, and/or there is a well-defined surface water discharge. Intrinsic bioremediation alone may not be the best alternative when the costs of conventional remediation are moderate to low and/or there is a large source of poorly degradable compounds. Norris et al. (1994) argue that, at some sites, it may be more cost effective to implement some low-level activities (e.g., limited air sparging or venting) than to rely on intrinsic bioremediation as the only management technique. If these limited remediation activities can shorten the monitoring period by several years, they may more than pay for themselves in reduced long-term monitoring costs.

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Sand
Decay Rates (per day)

	Dissolved Oxygen			
Gradient	12mg/L	9mg/L	6mg/L	3mg/L
0.01	3.8E-04	2.5E-04	1.8E-04	1.0E-04
0.001	1.0E-06	1.0E-06	7.5E-07	7.5E-07

Silt
Decay Rates (per day)

	Dissolved Oxygen			
Gradient	12mg/L	9mg/L	6mg/L	3mg/L
0.01	1.0E-05	1.0E-05	7.5E-06	5.0E-06

Clay
Decay Rates (per day)

	Dissolved Oxygen			
Gradient	12mg/L	9mg/L	6mg/L	3mg/L
0.01	1.0E-05	1.0E-05	1.0E-06	1.0E-06

Note:
The decay rates listed in this table were obtained through Bioplume II model simulations.
A continuous source scenario assuming 100 mg/L was injected at a rate of 10 gal/day in the sand hydrogeologic environment.
A lower injection rate, 1 gal/day, was used in the silt and clay hydrogeologic environment to minimize mounding in the model.
Centerline concentrations at different receptor well locations modeled for oxygen-limited degradation were matched to concentrations using first-order decay.

Sand
Decay Rates (per day)

	Dissolved Oxygen			
Gradient	**12mg/L**	**9mg/L**	**6mg/L**	**3mg/L**
0.01	-3.2E-01	-2.1E-01	-1.3E-01	-6.8E-02
0.001	-3.3E-02	-2.4E-02	-1.7E-02	-1.0E-02
0.0001	-8.7E-03	-6.3E-03	-4.1E-03	-2.5E-03

Silt
Decay Rates (per day)

	Dissolved Oxygen			
Gradient	12mg/L	9mg/L	6mg/L	3mg/L
0.01	-5.8E-03	-4.1E-03	-3.0E-03	-1.6E-03
0.001	-2.8E-04	-2.4E-04	-2.1E-04	-1.8E-04
0.0001	-2.5E-05	-2.4E-04	-2.1E-05	-2.3E-05

Clay
Decay Rates (per day)

	Dissolved Oxygen			
Gradient	12mg/L	9mg/L	6mg/L	3mg/L
0.01	-4.0E-04	-3.4E-04	-3.0E-04	-2.6E-04
0.001	-2.1E-04	-3.5E-05	-3.0E-05	-2.7E-05
0.0001	-4.3E-06	-3.7E-06	-3.2E-06	-2.9E-06

Note:
The decay rates listed in this table were obtained through Bioplume II model simulations.
A removed source scenario assuming a plume 45 ft wide and 50 ft long with an initial concentration of 10 mg/L was simulated. Log of present mass dissolved at 1 month to 5 to 10 years was plotted over time. The decay rate is the slope of the plotted line.

Name	Description	Author(s)
-	1-D, aerobic, microcolony, Monod	Molz et al. (1986)
BIOPLUME	1-D, aerobic, Monod	Borden et al. (1986)
-	1-D, analytical first order	Domenico (1987)
BIO1D	1-D, aerobic & anaerobic, Monod	Srinivasan and Mercer (1988)
-	1-D, cometabolic, Monod	Semprini and McCarty (1991)
-	1-D, aerobic anaerobic, nutrient limitations, microcolony, Monod	
-	1-D, aerobic, cometabolic, multiple substrates, fermentative, Monod	Celia et al. (1989)
BIOPLUME II	2-D, aerobic, instantaneous	Rifai et al. (1988)
-	2-D, Monod	MacQuarrie et al. (1990)
BIOPLUS	2-D, aerobic, Monod	Wheeler et al. (1987)
ULTRA	2-D, first order	Tucker et al. (1986)
-	2-D, denitrification	Kinzelbach et al. (1991)
-	2-D, Monod, Biofilm	Odencrantz et al. (1990)

(From Bedient et al., Ground Water Contamination: Transport and Remediation. Prentice Hall. NJ. 1994)

			Background			Plume	
Site	Aquifer Type	pH	O_2 (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	Fe^{+2} (mg/L)	CH_4 (mg/L)
Borden, Ontario (Barker et al. 1987)	glaciolacustrine, medium to fine sand						
Borden, Ontario (Barbaro et al. 1992)	glaciolacustrine, medium to fine sand	7.4	<0.07	<0.05	220		
Rocky Point, NC (Borden et al. 1995)	marine, fine sand	4.7	2.5	6	30	102	0.4
Kalkaska, MI (Chiang et al. 1989)	medium-course sand, gravel interbeds	5.5-7.0	9	0.8	1-6		
Columbus, MS (MacIntyre et al. 1993)	fluvial, heterogeneous sands and clays		2.6-3.8				
Sleeping Bear, MI (Wilson et al. 1994a)	glacial outwash, course sand/gravel	6.4	2.4	15	20	17-28	24-30
Eglin AFB, FL (Wilson et al. 1994a)	sands and silty peats	5.6-6.7				8.	17
Hill AFB-1, UT (Wiedemeier et al. 1994)	thin channel sands in deltaic deposits	~7	6	8	100	50	2
Patrick AFB, FL (Wiedemeier et al. 1994)	fine to course marine sand with shell fragments	~7	3.7	0.3	86	1.9	14.6
Fairfax, VA (Buscheck et al. 1993)		5	2.5-4			43	
Sampson Co., NC (Borden personal communication 1995)	clayey and silty sands	4-5	8	17	6	0.4	<0.01
Traverse City (Wilson et al. 1990)	glaciolacustrine, medium sand with gravel	7	9	3	10	12	17
Broward Co., FL (Caldwell et al. 1992)		7.2	2-3	0.3	<5	1.8	
Pensacola, FL (Godsy et al. 1992; Bekins et al. 1993)	poorly sorted fine to course deltaic sands	6.9	0.04	2	6	33	13
Bermidji, MN (Baedecker et al. 1993)	glacial outwash, course sand with silt layers	7.6	7.7	0.001	2	16	12
Galloway, NJ (Cozzarelli and Baedecker 1992)	fine to course sand, perched water table on clay lense	4.7	6	9	24	37	.007
Perth, Australia (Thierrin et al. 1993)	medium to fine aeolian sand	5.8	0.4	0.1	20-100	1.4	
Manufacturing Plant (Davis et al. 1994)	glacial silty sand over bedrock	6.9	1.5	<0.005			
Cliffs-Dow (Klecka et al. 1990)	course sand and gravels	6.1	1.2	1.7	48		
Hill AFB-2, UT (Dupont et al. 1994)			4	6.9			

Site	Contaminant	V (m/d)	Field Results	Laboratory Results
Borden, Ontario (Barker et al. 1987)	BTX stock solution injected into uncontaminated aquifer	0.09	Zero-order decay rates from mass balance method: benz. = 30 mg d^{-1}; tol. = 37 mg d^{-1}; *m*-xyl. = 47 mg d^{-1}; *p*-xyl. = 55 mg d^{-1}; *o*-xyl. = 33 mg d^{-1}.	Zero-order decay rates (per 1,800 L) from aerobic microcosms; benz. = 58 d^{-1}; tol. = 61 mg d^{-1}; *m*-xyl. = 50 mg d^{-1}; *p*-xyl. = 65 mg d^{-1}; *o*-xyl. = 54 mg d^{-1}.
Borden, Ontario (Barbaro et al. 1992)	stock solution contacted with gasoline then injected into leachate plume	0.09	% loss over 4 m travel.	
Rocky Point, NC (Borden et al. 1995)	residual gasoline from UST	0.08	Rates from conc. vs. travel time: benz. = 0.0002 d^{-1}; tol. = 0.0021 d^{-1}; e-benz. = 0.0015 d^{-1}; *mp*-xyl. = 0.0013 d^{-1}; *o*-xyl. = 0.0021 d^{-1}.	Rates from Fe/SO_4 reducing microcosms; benz. = 0.024 d^{-1}; tol. = 0.045 d^{-1}; e-benz. = 0.002 d^{-1}; *mp*-xyl. = 0.02 d^{-1}; *o*-xyl. = 0.056 d^{-1}.
Kalkaska, MI (Chiang et al. 1989)	natural gas condensate-BTEX	0.2	Rates from mass balance: benz. = 0.0095 d^{-1}.	Rates from aerobic microcosms: BTX = 0.01 to 0.1 d^{-1}.
Columbus, MS (MacIntyre et al. 1993)	stock solution of benzene, *p*-xylene, naphthalene, *o*-dichlorobenzene		Tritium used as non-reactive tracer. Mineralization proven using ^{14}C - *p*-xyl. Rates from mass balance: benz. = 0.0070 d^{-1}; *p*-xyl. = 0.0107 d^{-1}; naphthalene = 0.0064 d^{-1}; *o*-DCB = 0.0046 d^{-1}.	
Sleeping Bear, MI (Wilson et al. 1994; Schafer, 1994)	residual gasoline from UST release - BTEX	0-0.4	Rates from conc. vs. travel time using 2,3-dimethylpentane as an internal standard: benz. = N.S.; tol. = 0.02 - 0.07 d^{-1}; e-benz.. = 0.03 - 0.011 d^{-1}; *m*-xyl. = 0.004 - 0.014 d^{-1}; *p*-xyl. = 0.002 - 0.010 d^{-1}; *o*-xyl. = 0.004 - 0.011 d^{-1}.	Rates from methanogenic microcosms: benz. = N.S.; tol. = 0.007 - 0.04 d^{-1}; e-benz. = N.S.; *mp*-xyl. = N.S.; *o*-xyl. = N.S. 12 to 16 mg/L CH_4 produced in lab microcosms.
Indian River, FL (Kemblowski et al 1987)	gasoline from UST - BTEX	0.06	Conc. vs. travel time: benz. = 0.0085 d^{-1}.	1st-order rates from aerobic microcosms: benz. = 0.02 to 0.2 d^{-1}.

Site	Contaminant	V (m/d)	Field Results	Laboratory Results
Morgan Hill, CA (Kemblowski et al 1987)	gasoline - BTEX	0.05	Rates from conc. vs. travel time: benz. = 0.0035 d^{-1}.	
Eglin AFB, FL (Wilson et al. 1994)	JP-4 from POL depot	1.3	Rates from conc. vs. travel time using 1,2,4-trimethylbenzene as internal standard: benz. = B.D.; tol. = 0.05 to 0.013 d^{-1}; e-benz. = 0.03 to 0.05 d^{-1}; *m*-xyl. = 0.02 to 0.1 d^{-1}; *p*-xyl. = 0.02 to 0.08 d^{-1}; *o*-xyl. = 0.21 d^{-1}.	
Hill AFB, UT (Wiedemeier et al. 1994)	JP-4 from POL depot	0.5	Rates from conc. vs. travel time using total trimethylbenzene as internal standard: benz. = 0.03 to 0.09 d^{-1}; e-benz. = 0.01 to 0.08 d^{-1}; *p*-xyl. = 0.01 to 0.03 d^{-1}; *m*-xyl. = 0 to 0.03 d^{-1}; *o*-xyl. = 0 to 0.02 d^{-1}. Toluene rate not calculable.	
Patrick AFB, FL (Wiedemeier et al. 1994)	700 gallons unleaded gasoline from UST	0.13	Rates from conc. vs. travel time using total methane as internal standard; benz. = 0 to 0.004 d^{-1}; tol. = 0.0006 to 0.004 d^{-1}; e-benz. = 0.0001 to 0.004 d^{-1}; *p*-xyl. = 0.001 to 0.003 d^{-1}; *m*-xyl. = 0.001 to 0.004 d^{-1}; *o*-xyl. = 0.004 to 0.02 d^{-1}.	
Fairfax, VA (Buscheck et al. 1993)		0.015	Rates from conc. vs. travel time: benz. = 0.00055 d^{-1}; tol. = 0.00045 d^{-1}; e-benz. = 0.00045 d^{-1}; *mpo*-xyl. = 0.00040 d^{-1}.	
San Francisco, CA (Buscheck et al. 1993)		0.03	Rates from conc. vs. travel time: benz. = 0.0028 d^{-1}; tol. = 0.0022 d^{-1}; e-benz. = 0.0033 d^{-1}; *mpo*-xyl. = 0.0023 d^{-1}.	

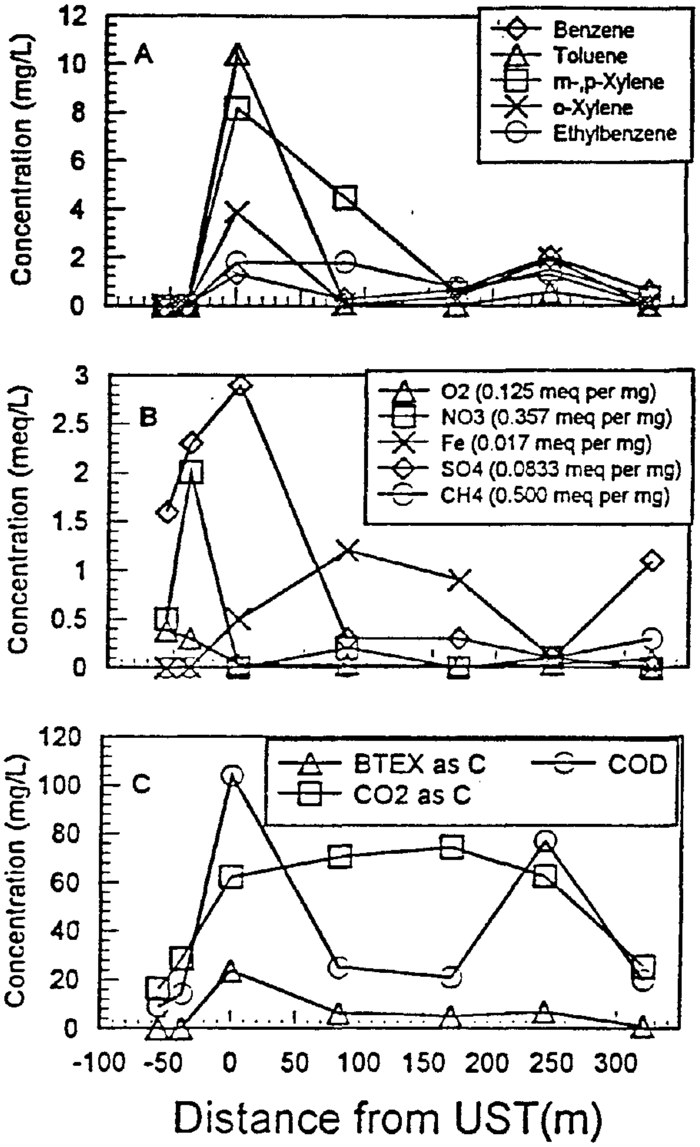
Site	Contaminant	V (m/d)	Field Results	Laboratory Results
Alameda County, CA (Buscheck et al. 1993)	gasoline - BTEX	.01	Rates from conc. vs. travel time: benz. = 0.0020 d^{-1}; tol. = 0.0017 d^{-1}; e-benz. = 0.0020 d^{-1}; *mpo*-xyl. = 0.0017 d^{-1}.	
Elko County, NV (Buscheck et al. 1993)	gasoline - BTEX	0.04	Rates from conc. vs. travel time: benz. = 0.001 d^{-1}.	
Sampson Co., NC (Borden personal communication 1995)	gasoline from UST - BTEX/MTBE	0.04	High nitrate concentrations in groundwater may enhance biodegradation 1st-order rates from mass flux: MTBE = 0.0006 d^{-1}; benz. = 0.0006 d^{-1}; tol. = 0.0021 d^{-1}; e-benz. = 0.0023 d^{-1}; *mp*-xyl. = 0.0016 d^{-1}; *o*-xyl. = 0.0009 d^{-1}.	Toluene and ethylbenzene rapidly degraded in denitrifying microcosms after a 56-day lag period.
Traverse City (Wilson et al. 1990)	aviation gasoline from UST - BTEX	1.5	Rates from conc. vs. travel time: benz. = 0.001 d^{-1}; tol. = 0.2 d^{-1}; *mpo*-xyl. = 0.004 d^{-1}.	Anaerobic microcosm rates: benz. = 0.07 d^{-1}; tol. = 0.04 d^{-1}; *mp*-xyl. = 0.06 d^{-1}; *o*-xyl. = 0.07 d^{-1}. Methane produced in microcosms.
Broward Co., FL (Caldwell et al. 1992)	gasoline from UST - BTEX and MTBE	0.1	Anaerobic decay rate from matching BIOPLUME for total BTEX = 0.00012 d^{-1}. Aerobic decay will increase net biodegradation.	
Pensacola, FL (Bekins et al. 1993)	creosote - phenols	0.3 to 1.2	Selected phenols were completely degraded over a 100-day travel time through methanogenic aquifer.	Selected phenols were completely degraded over 100 to 200 days in methanogenic microcosms.
Bemidji, MN (Baedecker et al. 1993)	crude oil - BTEX	0.25	tol. and *o*-xyl. depleted over 20 m (200 d travel time); benz. and e-benz. depleted over 100 m. Downgradient migration was limited by mixing with uncontaminated water.	98% benz. loss in 125 d and 99% tol. loss in 45 d in anaerobic microcosms.

Site	Contaminant	V (m/d)	Field Results	Laboratory Results
Perth, Australia (Thierrin et al. 1993)	gasoline from UST - BTEX	0.4	Rates from conc. vs. travel time: benz. = N.S.; tol. = 0.006 d^{-1}; e-benz. = 0.003 d^{-1}; *mp*-xyl. = 0.004 d^{-1}; *o*-xyl. = 0.006 d^{-1}; naphthalene = 0.004 d^{-1}. Field (plume scale) rates closely match rates from tracer test using deuterated compounds.	Anaerobic columns with 14 mg/L SO$_4$ benz. = N.S. tol. = 2.3 d^{-1} e-benz. = N.S. *o*-xyl. = N.S.
Manufacturing Plant (Davis et a. 1994)	benzene only	0.16	BIO1D match to field data showed benzene decay rate > 0.01 d^{-1}.	Over 90% benzene loss over 77 days in methanogenic and sulfate-reducing microcosms.
Cliffs-Dow (Klecka et al. 1990)	charcoal wastes, phenols, naphthalene	0.2 to 0.46	All organics degraded within 100 m of source.	All organics degraded in aerobic microcosms within 30 to 60 d.

Hill AFB-2, UT (Dupont et al. 1994)	18,000 gallon UST	0.14	Rates from mass balance: 1st order for TPH = 0.005 d^{-1}.
			Zero order for:
			benz. = 0.02 kg/d;
			e-benz. = 0.06 kg/d;
			p-xyl. = 0.06 kg/d.	

Gas Plant (Piontek et al. 1994)	NAPL released from natural gas plant - BTEX		105 reduction in BTEX over 100 m.	
Picatinny Arsenal, NJ (Martin and Imbrigiotta 1994)	TCE, 1,1,1-trichloroethane and metals from plating wastewater	0.3 to 1.0	Spatial distribution of TCE, DCE, and VC indicate reductive dechlorination.	Anaerobic Microcosms: TCE = 0.0001 to 0.003 d^{-1}.
St. Joseph, MI (Wilson et al. 1994)	TCE from lagoons/dry wells	0.1	Rates from mass flux: TCE = 0.001 - 0.003 d^{-1}.	
Finger Lakes, NY (Major et al. 1994)	TCE, acetone, methanol		Spatial distribution of TCE, DCE, VC, and ethene were indicative of reductive dechlorination.	

benz. = benzene, tol. = toluene, e-benz. = ethylbenzene, xyl. = xylenes.
N.S. = not significant.


A
Concentration (mg/L)
0
2
4
6
8
10
12
Benzene
Toluene
m-,p-Xylene
o-Xylene
Ethylbenzene
B
Concentration (meq/L)
0
0.5
1
1.5
2
2.5
3
O2 (0.125 meq per mg)
NO3 (0.357 meq per mg)
Fe (0.017 meq per mg)
SO4 (0.0833 meq per mg)
CH4 (0.500 meq per mg)
C
Concentration (mg/L)
0
20
40
60
80
100
120
BTEX as C
CO2 as C
COD
-100
-50
0
50
100
150
200
250
300
Distance from UST(m)

Transform product	Mol. Wt.	Half Reaction	Equiv. COD decrease g COD/g product[a]
Methane	16	$CO_2+8H^{+}+8e^{-}\rightarrow CH_4+2H_2O$	4
DCE	97	$CHCl=CCl_2+H^{+}2e^{-}\rightarrow CHCl=CHCl+Cl^{-}$	0.16
VC	62.5	$CHCl=CCl_2+2H^{+}+4e^{-}\rightarrow CH_2=CHCl+2Cl^{-}$	0.51
Ethene	28	$CHCl=CCl_2+3H^{+}+6e^{-}\rightarrow CH_2=CH_2+3Cl^{-}$	1.71

(a) From ($O_2+4H^{-}+4e^{-}\rightarrow 2H_2O$), the half-reaction for oxygen, one electron equivalent of COD equals one-fourth mole of molecular oxygen or 8 grams, thus equiv. COD Decrease = (8n/Mol. Wt), where n is the number of electrons in the half-reaction.

Sample[a]		TCE	1.1DCE	cDCE	tDCE	VC	Ethene	CH_4	Total
1-2-70	mg/L	4.03	0.09	4.14	0.81	3.19	6.62	4.61	
	Equiv. COD Decrease, mg/L	0.00	0.01	0.66	0.13	0.41	11.32	18.44	30.97
	% of Equiv. COD	0.0	0.0	2.1	0.4	1.3	36.6	59.5	
1-3-75	mg/L	12.80	0.27	16.90	0.67	56.40	2.25	6.62	
	Equiv. COD Decrease, mg/L	0.00	0.04	2.70	0.11	28.80	3.84	26.00	61.5
	% of Equiv. COD	0.0	0.1	4.4	0.2	46.8	6.2	42.2	
22-1-75	mg/L	0.44	0.09	13.40	0.21	1.46	3.15	7.43	
	Equiv. COD Decrease, mg/L	0.00	0.01	2.14	0.03	0.74	5.39	29.72	38.03
	% of Equiv. COD	0.0	0.0	5.6	0.1	1.9	14.2	78.1	
2-6-65	mg/L	0.51		4.70	0.03	2.66	4.27	11.72	
	Equiv. COD Decrease, mg/L	0.00	0.00	0.75	0.00	1.36	5.98	46.88	54.97
	% of Equiv. COD	0.0	0.0	1.4	0.0	2.5	10.9	85.3	
3-2-80	mg/L	2.53	0.01	0.90	0.03	0.27	4.87	11.59	
	Equiv. COD Decrease, mg/L	0.00	0.00	0.14	0.00	0.14	8.32	46.36	54.96
	% of Equiv. COD	0.0	0.0	0.3	0.0	0.3	15.1	84.4	

(a) First value is transect number, second value is borehole number, and third value is depth of sample below ground surface in feet.

Apparent Loss Coefficients at St. Joseph, MI
Transect 2 to 4

	Low Conductivity Estimate (1/wk)	Avg. Conductivity Estimate (1/wk)	High Conductivity Estimate (1/wk)
TCE	0.0048	0.0074	0.011
cDCE	0.0064	0.0097	0.013
tDCE	0.0076	0.012	0.0016
1,1-DCE	0.0066	0.010	0.0135
VC	0.0023	0.0035	0.0047

Apparent Loss Coefficients at St. Joseph, MI
Transect 4 to 5

	Low Conductivity Estimate (1/wk)	Avg. Conductivity Estimate (1/wk)	High Conductivity Estimate (1/wk)
TCE	0.016	0.025	0.033
cDCE	0.010	0.016	0.021
tDCE	0.010	0.016	0.021
1,1-DCE	0.012	0.018	0.024
VC	0.011	0.017	0.023

Apparent Coefficients at St. Joseph, MI
Transect 5 to Lake

	Low Conductivity Estimate (1/wk)	Avg. Conductivity Estimate (1/wk)	High Conductivity Estimate (1/wk)
TCE	0.011	0.018	0.023
cDCE	0.038	0.059	0.079
tDCE	0.0092	0.014	0.019
1,1-DCE	-	-	-
VC	0.053	0.081	0.11

KEYWORD LIST

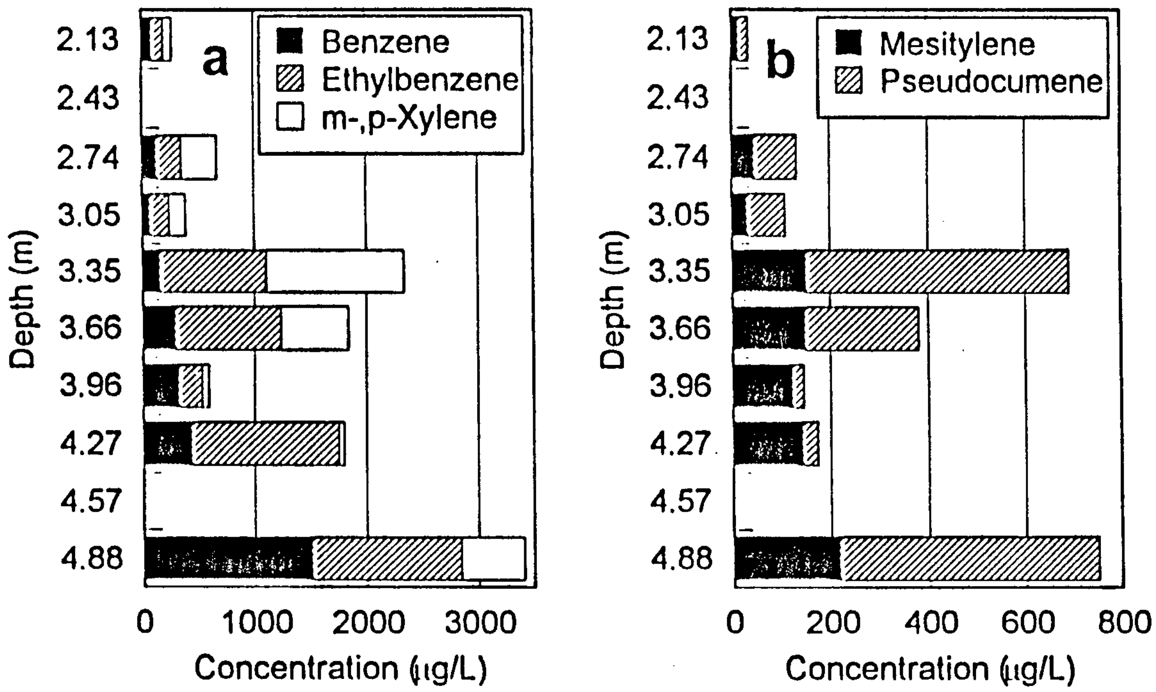
indicator parameters
intrinsic bioattenuation
risk assessment
numerical models
hydrocarbon degradation

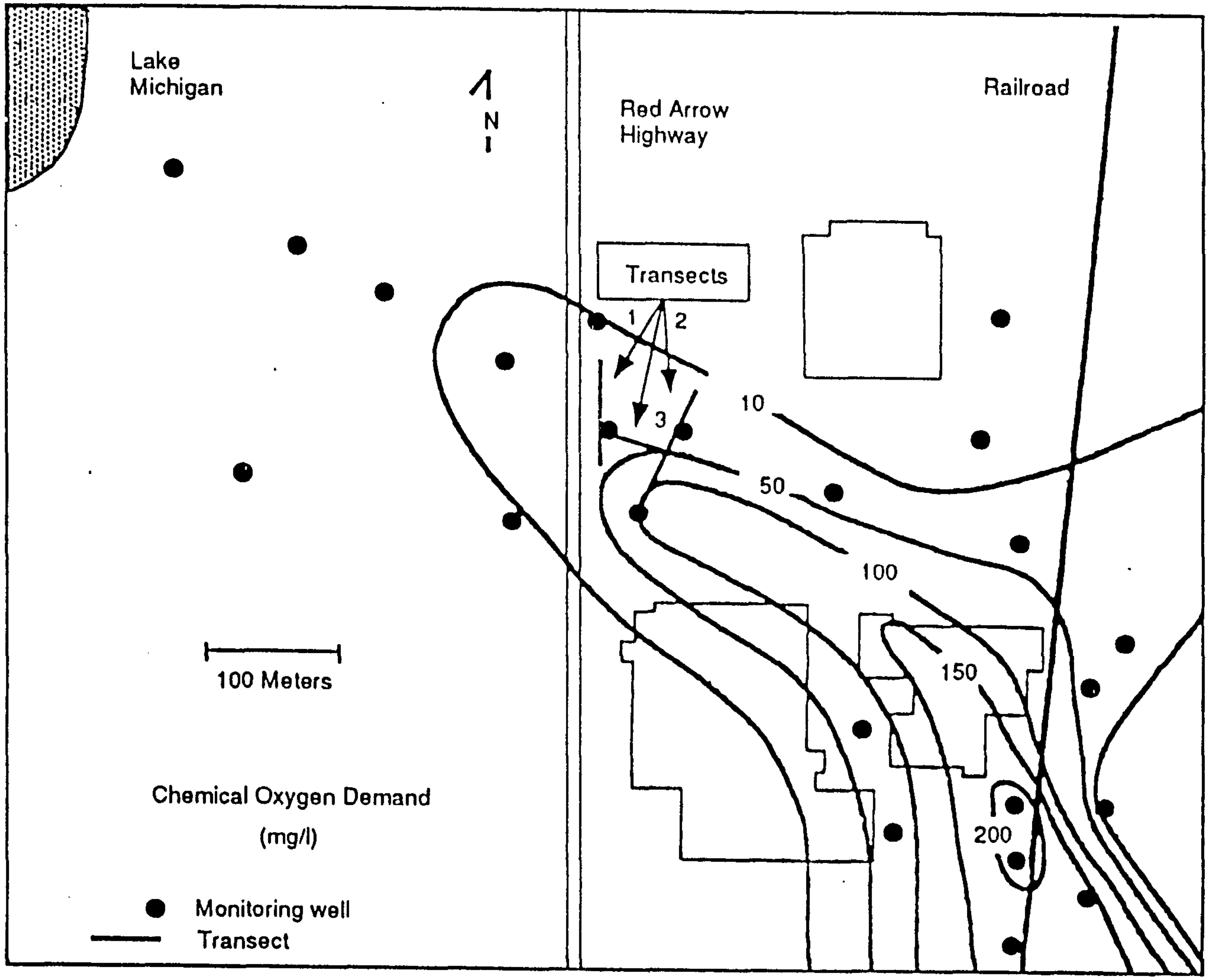
	Redox Environment			
Chlorinated Solvent	**All**	**Denitrification**	**Sulfate Reduction**	**Methanogenesis**
Carbon tetrachloride		CT→CF	CT→CO_2+Cl	
1,1,1-Trichloroethane	TCA→1,1-DCE +CH_3COOH		TCA→1,1-DCA	TCA→CO_2+Cl
Tetrachloroethylene			PCE→1,2-DCE	PCE→ethene
Trichloroethylene			TCE→1,2-DCE	TCE→ethene

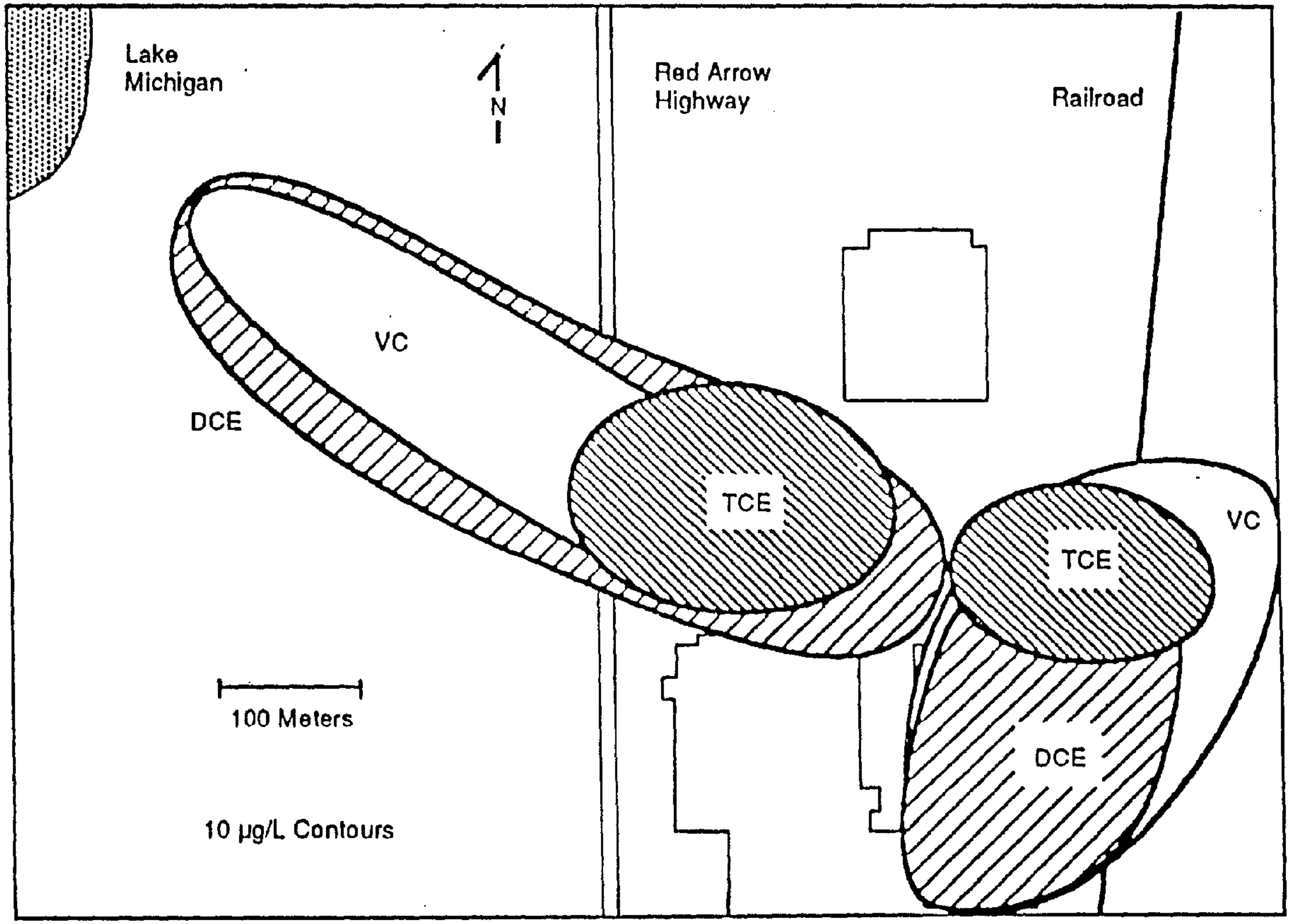
Compound	**Field Rate (d^{-1})**	**Laboratory Rate (d^{-1})**	**In Situ Rate (d^{-1})**
Benzene	0.0002	0.024	0.004
Toluene	0.0021	0.045	0.012
Ethylbenzene	0.0015	0.002	N.S.(a)
o-Xylene	0.0021	0.056	N.S.
m-,*p*-Xylene	0.0013	0.02(b)	0.014

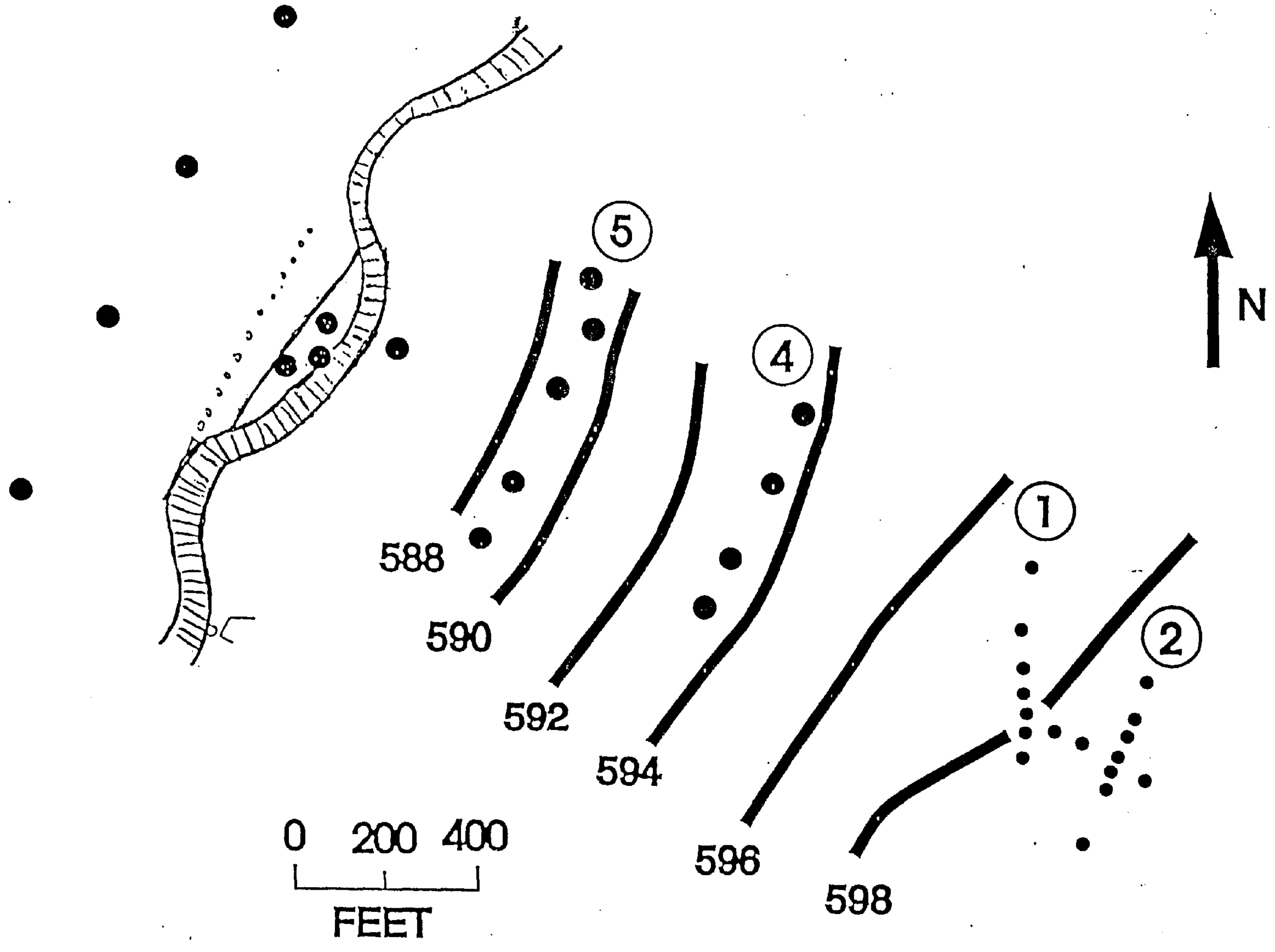
(a) Not significant at 95% level.

(b) Only *m*-xylene in laboratory microcosms.


a
Benzene
Ethylbenzene
m-,p-Xylene
Depth (m)
2.13
2.43
2.74
3.05
3.35
3.66
3.96
4.27
4.57
4.88
0
1000
2000
3000
Concentration (µg/L)
b
Mesitylene
Pseudocumene
Depth (m)
2.13
2.43
2.74
3.05
3.35
3.66
3.96
4.27
4.57
4.88
0
200
400
600
800
Concentration (µg/L)


Lake
Michigan
N
Red Arrow
Highway
Railroad
Transects
1
2
3
10
50
100
150
200
100 Meters
Chemical Oxygen Demand
(mg/l)
Monitoring well
Transect


Lake
Michigan
N
Red Arrow
Highway
Railroad
VC
DCE
TCE
TCE
VC
DCE
100 Meters
10 µg/L Contours


N
⑤
④
①
②
588
590
592
594
596
598
0
200
400
FEET

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