Biodegradation Rates for Fuel Hydrocarbons and Chlorinated Solvents in Groundwater

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Abstract: Numerous studies presented in the general literature have shown that the key mechanism affecting the rate and extent of migration of a contaminant plume is biodegradation since it removes contaminant mass and reduces average plume concentrations. This paper attempts to address the importance of biodegradation for fuel and chlorinated solvent plumes and to present a comprehensive review of rates of biodegradation obtained from field and laboratory studies. Data from approximately 280 studies are statistically analyzed to determine ranges of biodegradation rates for various contaminants under different redox conditions. A review of 133 studies for fuel hydrocarbons has yielded first-order biodegradation coefficients up to 0.445 day^{-1} under aerobic conditions and up to 0.522 day^{-1} under anaerobic conditions in 90% of the cases. A median rate constant for benzene of 0.3% day^{-1} was estimated from all studies, while those for toluene, ethylbenzene, and xylenes were estimated to be 4, 0.3, and 0.4% day^{-1}, respectively. On the other hand, data from 138 studies with chlorinated solvents show that the less chlorinated compounds biodegrade in the 90% of the cases with rate constants lower than 1.35 day^{-1} under aerobic conditions and that highly chlorinated compounds biodegrade with decay coefficients up to 1.28 day^{-1} in 90% of the anoxic experiments. Median decay coefficients derived from all studies were 4.9, 0.07, 0.42, 0.86, 1.02, 0.44, and 4.7 day^{-1} for carbon tetrachloride, dichloroethane (DCA), *cis*-1,2-dichloroethene (*cis*-1,2-DCE), tetrachloroethene (PCE), trichloroethane (TCA), trichloroethene (TCE), and vinyl chloride, respectively. The rate constants presented in this study can be used in screening and modeling studies and to guide the assessment of natural attenuation as a viable remedial technology at contaminated sites. represent a compilation of available literature data.

Introduction

Natural attenuation can be defined as the sum of processes that without human intervention causes a contaminant plume to experience a decline in both its concentration and size over time. Natural attenuation encompasses the processes of advection, dispersion, sorption, biotic, and abiotic reactions. Petroleum hydrocarbons and chlorinated solvents, contaminants commonly found dissolved in groundwater, have been shown in recent studies to attenuate by a variety of these processes. A significant number of studies have identified biodegradation as the key attenuation process for fuel hydrocarbons and chlorinated solvents. These studies argue (appropriately) that biodegradation compared with the other attenuation mechanisms causes a net loss of contaminant mass within the plume and lowers average plume concentrations over time. The remaining attenuation processes of advection, dispersion, sorption, and volatilization either do not remove contaminant mass from the aquifer or they transfer the contaminants to other phases in the environment.

This research focuses on assessing the relative importance of biodegradation as a natural attenuation mechanism by estimating biodegradation rates for fuels and chlorinated solvents based on reported values in the general literature. The objective of the study was to determine appropriate ranges for biological decay rates in groundwater systems as well as the most preferred patterns of biodegradation for these compounds.

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Over 280 published articles were reviewed and the resulting data were assembled into a database and analyzed for statistical trends and indicator variables.

A number of questions or hypotheses relating to biodegradation of fuels and chlorinated solvents were explored using the biodegradation database:

- To what extent are biodegradation rates compound specific and site specific?
- How well do laboratory rates for a given compound compare with field-derived values?
- How do aerobic rates compare to anaerobic rates for biodegradation?
- How do the degradation rates compare for different electron acceptor regimes?
- What are the most favorable redox conditions for the biodegradation of these compounds?

Biodegradation of Fuels and Chlorinated Solvents

Biodegradation refers to a series of biochemical reactions mediated by microorganisms that act to break down organic compounds into other substances. A compound can undergo biodegradation as an electron donor, as an electron acceptor, or via cometabolism. In the two first cases, the compound serves as a source of carbon and energy, promoting bacterial growth. In contrast, when a compound biodegrades through cometabolism, the subsurface bacteria do not derive any benefits from that degradation and the compound is biodegraded by an enzyme produced during the degradation of the primary substrate. Biodegradation can occur in the presence or absence of dissolved oxygen or under aerobic and anaerobic conditions, respectively.

For biodegradation to occur, certain requirements have to be met. These requirements include the presence of microorganisms capable of degrading the specific compound, the presence of organic carbon as an energy source, a carbon source (the organic compound in this case), the presence of electron acceptors, adequate amount of nutrients (nitrogen, phosphorus, calcium, magnesium, and iron), and appropriate environmental conditions such as ambient temperature, absence of toxic materials, and a pH close to 7 (Lim, 1998). Biological growth can occur within a wide range of temperatures, but for most organisms the optimum range is 10 to 35°C (Wilson et al., 1996). In general, temperatures below the optimum range have a more significant impact on growth rate than temperatures above this range; growth rates double with every 10°C increase until the optimum range is reached (Metcalf and Eddy Inc., 1991).

Biodegradation of Fuel Hydrocarbons

Benzene, toluene, ethylbenzene, and xylene (BTEX) compounds are readily biodegradable as primary substrates, although cometabolism of *p*-xylene (Chang et al., 1993), benzene-dependent cometabolism of toluene, and toluene-dependent cometabolism of *o*-xylene (Alvarez and Vogel, 1991; Alvarez and Vogel, 1995) have also been suggested. The chemical reaction governing hydrocarbon biodegradation can be written as:

$$\text{hydrocarbon} + \text{electron acceptors} + \text{nutrients}$$
$$\xrightarrow{\text{microorganisms}} CO_2 + H_2O + \text{byproducts} + \text{energy}$$

During the reaction, the hydrocarbon is oxidized (gives electrons) and the electron acceptor is reduced (receives electrons). The primary electron acceptors that support fuel hydrocarbon biodegradation include O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, and CO_2.

A large number of microcosm studies have demonstrated that BTEX compounds are readily biodegradable in aerobic environments (Alvarez and Vogel, 1991; Barker et al., 1987; Durant et al., 1995; Hutchins and Wilson, 1991; Kuhn et al., 1985; Lee et al., 1994; Zhang and Bouwer, 1997). Additionally, some field studies present strong evidence of intrinsic bioremediation due (at least in part) to aerobic respiration (Barker et al., 1987; Chiang et al., 1989; Wiedemeier et al., 1995). Chapelle (1993) found that aerobic respiration is the most preferred reaction in an environment with dissolved oxygen and microorganisms capable of aerobic respiration. The literature studies reviewed in this research differed on the relative order and rate of biodegradation between the different constituents. Toluene, for instance, has been found to be more readily biodegradable under aerobic conditions than benzene (Karlson and Frankenberger, 1989; Thomas et al., 1990; Wilson et al., 1990). On the contrary, Alvarez and Vogel (1991) concluded that under aerobic conditions, benzene degrades with higher rates than toluene.

BTEX compounds have been also found to biodegrade under anaerobic conditions via denitrification (Acton and Barker, 1992; Barbaro et al., 1992; Hutchins, 1991; Hutchins et al., 1991; Kuhn et al., 1988; Wiedemeier et al., 1995; Zeyer et al., 1986), sulfate-reduction (Acton and Barker, 1992; Edwards et al., 1991; Edwards et al., 1992; Thierrin et al., 1995), iron-reduction (Lovley and Lonergan, 1990), manganese-reduction (Yaniga et al., 1985), and methanogenesis (Acton and Barker, 1992; Barker and Mayfield, 1988; Kazumi et al., 1997). Benzene, however, has been shown to be recalcitrant in laboratory experiments under denitrifying conditions (Alvarez and Vogel, 1995).

Biodegradation of Chlorinated Solvents

Initially thought of as being nonbiodegradable, chlorinated solvents have been recently shown to biodegrade under various redox conditions. Although not completely understood, knowledge about their different biodegradation pathways is increasing (see, for example, Bradley and Chapelle, 1996; Bradley and Chapelle, 1997; Cox et al., 1994; Dolan and McCarty, 1994; Ellis et al., 1996; Huismann et al., 1995; Imbrigiotta et al., 1996; Klecka et al., 1996; Kuhn et al., 1985; Lee et al., 1995; Ligé et al., 1995; Odom et al., 1995; Strand et al., 1990; Vogel et al., 1987; Vogel and McCarty, 1985; Weaver et al., 1996; Wiedemeier et al., 1996a).

Chlorinated solvents can biodegrade through three different pathways: as electron donors, as electron acceptors, or through cometabolism. The most important mechanism for biodegradation of highly chlorinated solvents is their use as electron acceptors. This process, referred to as reductive dechlorination, requires an electron donor. Typical electron donors include BTEX compounds and landfill leachate. In general, the more highly chlorinated solvents can be reductively dechlorinated. In this case, chlorine atoms are sequentially removed and replaced by hydrogen atoms. This sequence might be interrupted if the environment becomes highly oxidized (high concentration of electron acceptors) or if there is a depletion of electron donors. Examples of this sequence of reactions include:

PCE* ➡ TCE ➡ DCE ➡ VC ➡ ethene ➡ ethane

1,1,1-TCA ➡ 1,1-DCA ➡ chloroethane

The use of chlorinated solvents as electron donors is probable only for the less oxidized compounds (i.e., vinyl chloride, DCE, and DCA) under aerobic and anaerobic environments (Bradley and Chapelle, 1996; Davis and Carpenter, 1990; Wilson et al., 1982). Electron acceptors that can be used by microorganisms to oxidize chlorinated solvents include nitrate, ferric iron oxyhydroxide, sulfate, and carbon dioxide (Wiedemeier et al., 1996b).

Finally, chlorinated solvents can be indirectly biodegraded via cometabolism. Some of the primary substrates that support cometabolism of chlorinated solvents are methane, ethene, propane, toluene, and phenol. This type of process is possible under natural conditions; however, it is not the predominant process in many chlorinated solvent plumes (Wiedemeier et al, 1999). Mainly because the chlorinated solvents can compete with the primary substrate to obtain an enzyme necessary for their degradation (competitive inhibition), and also because some of the intermediate products can be toxic to the microorganism (product toxicity) (McCarty, 1997).

Kinetic Expressions Used to Estimate Biodegradation Rates

The biodegradation studies reviewed in this research have generally used one of three kinetic expressions for estimating a degradation rate. The kinetics used include Monod kinetics, and zero- and first-order expressions.

Monod and Michaelis-Menten Kinetics

Monod kinetics (Monod, 1949) describe the growth of microorganisms on a limiting substrate. They are represented mathematically by:

$$\mu = \mu_{\max} \frac{S}{S + K_s} - k_d \tag{1}$$

Where μ is the growth rate [T^{-1}], $\mu_{\max}$ is the maximum growth rate [T^{-1}], S is the growth-limiting substrate concentration [ML^{-3}], K_s is the half-saturation constant or the substrate concentration that allows the bacterial population to grow at half of the maximum growth rate [ML^{-3}], and k_d is the microbial decay rate [T^{-1}].

The change in substrate concentration using Monod kinetics is given by:

$$\frac{dS}{dt} = -\frac{\mu_{\max}}{Y} B\left(\frac{S}{S + K_s}\right) \tag{2}$$

Where Y is a yield coefficient that represents the mass of biomass produced per substrate utilized [MM^{-1}], and B is the biomass concentration [ML^{-3}].

Enzymatic reactions can be described by the same type of equation. The model usually used to describe enzyme kinetics is the Michaelis-Menten rate law.

$$v = V \frac{S}{S + K_m} \tag{3}$$

Where v is the velocity or rate at a specific concentration [$ML^{-3}T^{-1}$], V is the maximum rate of reaction

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* Tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), vinyl chloride (VC), 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethane (1,1-DCA).

$[ML^{-3}T^{-1}]$, S is the substrate concentration $[ML^{-3}]$, and K_m is the substrate concentration that gives half maximal reaction velocity $[ML^{-3}]$.

Zero-Order Kinetics

When the substrate concentration is much greater than the half saturation concentration ($S>>K_s$), equation (2) may be re-written as:

$$\frac{dS}{dt} = -\frac{\mu_{max}}{Y}B \tag{4}$$

or

$$\frac{dS}{dt} = -v_m = k_0 \tag{5}$$

Where v_m is the substrate utilization rate $[ML^{-3}T^{-1}]$, also known as the zero-order biodegradation rate. The value of k_o can be determined, for example, from laboratory microcosm studies by calculating the slope of the best-fit line from a plot of concentration vs. time data.

First-Order Kinetics

If the substrate concentration is much smaller than the half-saturation concentration ($S<<K_s$), the expression ($S/S+K_s$) approximates (S/K_s) and Eq. (2) may be expressed as:

$$\frac{dS}{dt} = -\frac{\mu_{max}}{Y}B\left(\frac{S}{K_s}\right) = \frac{v_m}{K_s}\cdot S \tag{6}$$

The expression (v_m/K_s) represents the first-order biodegradation rate constant (λ) $[T^{-1}]$. Consequently, equation (6) is written as:

$$\frac{dS}{dt} = -\lambda S \tag{7}$$

Equation 7 shows that the transformation rate depends on substrate concentration. It is important to mention that even though this assumption is valid only when substrate concentration is much lower than the half-saturation constant, first-order biodegradation models have been widely used for the broad ranges of contaminant concentrations. Additionally, the majority of analytical and numerical models incorporate a first-order expression to estimate biodegradation independent of contaminant concentration.

The first-order biodegradation rate constant (λ) can be estimated, for example, from laboratory microcosm data by evaluating the slope of the best-fit line on a plot of concentration vs. time using a semi-logarithmic scale for concentrations. Rate constants are commonly reported as a compound-specific half-life, derived using:

$$t_{1/2} = \frac{\ln 2}{\lambda} \tag{8}$$

It should be mentioned that zero- and first-order models assume a steady-state biomass density or little or no increase in microbial cell numbers (Schmidt et al., 1985).

Determination of Decay Coefficients in This Study

Several assumptions were made in this study to analyze field and laboratory data reported in the literature. These include:

- Whenever reported, rates were input into the database using the reported reaction order.
- If no reference of reaction order was given, a first-order model was used to estimate the biodegradation coefficient when sufficient data were presented:

  $$\lambda = \frac{1}{t}\ln\left(\frac{S_0}{S}\right) \tag{9}$$

  Where, *t* is the incubation time (retention time in column studies), S_0 is the initial substrate concentration, and S is the final concentration for laboratory studies. For field studies, t is the travel time between two adjacent points, S_0 is the contaminant concentration at the upgradient point, and S is the contaminant concentration at the downgradient point. The data were corrected in both cases for abiotic processes.
- When a compound was completely degraded, the first-order biodegradation rate was calculated assuming a final concentration equal to the detection limit. In this case, the rate was reported as equal to or greater than the obtained value.
- Field studies reporting aerobic decay rates were considered as combined aerobic/anaerobic rates, as it is more than likely that the reported decay rate is an overall estimate that combines both aerobic and anaerobic processes. This assumption was necessary because the majority of the field aerobic biodegradation studies did not account for anaerobic processes in reporting degradation rates.

It is important to point out that most investigators attempt to account for the effect of abiotic processes (primarily advection and dispersion) when deriving a biological kinetic rate coefficient from their data. This is most commonly done through the monitoring of nondegrading tracer compounds and through the calibration of field data to groundwater fate and transport models. With respect to biological decay rates derived using groundwater fate and transport models, it should be noted that the biodecay rate is specific to the model being used and also the certainty in the fitted biodecay rate is limited by the certainty in all of the other relevant input parameters (McNab and Dooher, 1998). In many of the more common groundwater fate and transport models, small changes in biodecay rate and groundwater velocity can translate into significant changes in predicted chemical concentration distributions.

Rate Constants for BTEX Biodegradation

A total of 133 studies (field and laboratory) were used to estimate BTEX biodegradation constants. Eighteen (18) of these studies reported Monod kinetics, 21 reported zero-order rates, and 94 studies reported first-order kinetics. Among all the BTEX studies, 40 experiments were conducted under aerobic conditions, 18 under mixed aerobic/anaerobic environments, and 75 under anaerobic conditions. Forty-two (42) out of 94 studies reporting first-order decay coefficients were laboratory experiments, while 52 were field/in situ studies. Within the 21 studies reporting zero-order rates, 14 correspond to laboratory experiments, and 7 to field studies. All the studies reporting Monod kinetics correspond to laboratory experiments, and only two of them were developed under anaerobic conditions.

Michaelis-Menten Rate Estimates

Table 1 summarizes the data from the 18 laboratory studies that reported Michaelis-Menten kinetics. As can be seen in Table 1, the values for the half-saturation constant (K_s) for toluene, benzene, and xylenes varied between 0.034 to 20.27 mg/L, 0.31 to 20.31 mg/L, and 0.75 to 15.92 mg/L, respectively. In addition, the maximum specific degradation rate (μ_m/Y) varied from 0.004 to 58.5 mg/mg-day for toluene, between 0.78 and 25.07 mg/mg-day for benzene, and from 3.03 to 51.4 mg/mg-day for xylene. These data indicate that the specific conditions in the experiment greatly affect the resulting rates. Alexander and Scow (1989) considered that some of the factors that may cause this wide variation include the nature of the studied culture (i.e., pure or mixed), competition among different cultures for the substrate, media in which the experiment was run (aqueous solution or soil-water mixture), temperature, size of the microbial population, and availability of electron acceptors and nutrients, among others.

Zero-Order Rate Estimates

Data from 21 studies reported zero-order biodegradation rates for BTEX (Table 2). It can be seen from Table 2 that zero-order rates for BTEX ranged from 0 to 239 mg/L-day with a mean of 6.4, 12.6, 0.12, 0.19, 0.19, and 2.1 mg/L-day for benzene, toluene, ethylbenzene, *m*-xylene, *o*-xylene, and *p*-xylene, respectively. The zero-order decay data in Table 2 indicate that toluene is the most readily biodegradable compound under aerobic environments with a median rate of 5 mg/L-day and *o*-xylene is the least biodegradable compound with a median zero-order rate of 0.03 mg/L-day. Under anaerobic conditions the compounds that showed the highest and the lowest median rates of biodegradation are *p*-xylene (0.56 mg/L-day) and benzene (0 mg/L-day), respectively.

First-Order Rate Constant Estimates

Reported first-order decay coefficients are summarized in Table 3 and Figures 1, 2, and 3. Table 3 presents the mean, standard deviation, and 90th percentile as well as the range of reported values, whereas Figures 1 through 3 present median values, 25th, and 75th percentiles. As can be seen in Table 3, the range minimum-90th percentile for overall first-order rate constants for BTEX is 0 to 0.438 day^{-1} with mean values equal to 0.06, 0.25, 0.12, 0.06, 0.02, and 0.04 day^{-1} for benzene, toluene, ethylbenzene, *m*-xylene, *o*-xylene, and *p*-xylene, respectively. These constants were obtained at temperatures that varied between 6 and 36°C. The data in Table 3 indicate that the range minimum-90th for aerobic and anaerobic decay coefficients was the same (0 to 0.445 day^{-1}), while for field rates from aerobic/anaerobic studies it was 0 to 0.914 day^{-1}. Benzene had the highest mean value under aerobic conditions (0.34 day^{-1}), while toluene exhibited the highest mean anaerobic coefficient (0.23 day^{-1}). Considering overall rates, ethylbenzene exhibited the lowest median value (0.003 day^{-1}), while toluene had the highest (0.04 day^{-1}, see Figure 1).

Laboratory Versus Field Rate Constants. A comparison between laboratory and field results indicates that biodegradation constants obtained from laboratory studies are generally higher than field constants (see Figures 2 and 3). This result was expected because laboratory studies maintain favorable ambient conditions for biodegradation. For instance, the temperature range for laboratory studies was 10 to 36°C, which is higher than the range of groundwater temperatures reported in the field studies (6 to 22°C); knowing that higher temperatures favor microbial activity, it was

Table 1. Michaelis-Menten parameters for BTEX compounds

Compound	Type of Study	Redox Environment	Culture	μ_{max} (d^{-1})	Doubling Time (d)	Half-Saturation, K_S (mg/L)	Yield, Y (mg/mg)	Max. Specific Degradation Rate, μ_{max}/Y (mg/mg-d)	Initial Conc., S_o (mg/L)	Reference
Benzene	Microcosm	Aerobic				12.20		8.30	<100	Alvarez et al., 1991
	Laboratory	Aerobic	*Pseudomonas strain* B1	8.05		3.17	1.04	7.74	10.00	Chang et al., 1993
	Microcosm	Aerobic		8.30		12.20	0.50	16.60		Chen et al., 1992
	Microcosm	Aerobic		3.84		20.31			10-110	Goldsmith and Balderson, 1988
	Respirometry	Aerobic		1.83		10.80	0.39	4.70		Grady et al., 1989
	Flow-through column	Aerobic		0.89-5.26		5.47				Kelly et al., 1996
	Microcosm	Aerobic		1.18		0.31	1.50	0.78	6.20	Kelly et al., 1996
	Microcosm	Aerobic	*Pseudomonas strain* PPO1	10.56		3.36	0.65	16.25		Oh et al., 1994
	Microcosm	Aerobic	Consortium	16.32		12.22	0.71	22.99		Oh et al., 1994
	Microcosm	Aerobic	Aerobic mixed	12.96		6.00	0.60	7.78		Park and Cowan, 1997
	Laboratory, sludge from wastewater treatment plant	Aerobic		6.77		6.57	0.27	25.07	20-100	Tabak et al., 1991
Toluene	Microcosm	Aerobic		0.65-6.0		<0.1	0.5-1.5	1.3-4.0	24-27	Allen-King et al., 1994
	Microcosm	Aerobic				17.40		9.90	<100	Alvarez et al., 1991
	Microcosm	Aerobic	*Pseudomonas sp.* T2 (marine strain). Uninduced cells	0.00		0.33	0.01	0.00	1-30	Button, 1985
	Microcosm	Aerobic	*Pseudomonas sp.* T2 (marine strain). Induced cells	3.08		0.43	0.28	11.00	1-30	Button, 1985
	Laboratory	Aerobic	*Pseudomonas strain* B2	13.03		1.22	1.96	6.65	10.00	Chang et al., 1993
	Laboratory	Aerobic	*Pseudomonas strain* X1	10.84		1.88	0.99	10.95	10.00	Chang et al., 1993
	Microcosm	Aerobic		9.90		17.40	0.50	19.80		Chen et al., 1992
	Microcosm	Sulfate-reducing			22.00		0.10		8-12	Edwards et al., 1992
	Microcosm	Aerobic		6.24		20.27				Goldsmith and Balderson, 1988
	Microcosm	Nitrate-reducing		4.80		0.15	0.29	16.80		Jorgensen et al., 1991
	Flow-through column	Aerobic		2.09-12.48		1.57				Kelly et al., 1996
	Microcosm	Aerobic		1.10		0.28	1.70	0.65	9.20	Kelly et al., 1996
	Column	Aerobic		0.21		0.65	0.43	0.49	3.00	MacQuarrie et al., 1990
	Microcosm	Aerobic	*Pseudomonas strain* PPO2	37.44		15.07	0.64	58.50		Oh et al., 1994
	Microcosm	Aerobic	Consortium	36.00		11.03	0.71	50.70		Oh et al., 1994
	Microcosm	Aerobic	Aerobic mixed	18.96		10.00	0.60	11.38		Park and Cowan, 1997
	Microcosm	Aerobic	*Pseudomonas sp.* T2 (marine strain). Uninduced cells	0.00		0.03	0.10	0.01		Robertson and Button, 1987
	Microcosm	Aerobic	*Pseudomonas sp.* T2 (marine strain). Induced cells	0.03		0.04	0.10	0.33		Robertson and Button, 1987
	Microcosm	Aerobic				0.04mg/g		0.00	1.96	Swindoll et al., 1988
	Laboratory, sludge from wastewater treatment plant	Aerobic		12.55		7.75	0.36	34.87	20-100	Tabak et al., 1991
	Chemostat	Aerobic	*Pseudomonas putida*	4.22			1.42	2.97		Vecht et al., 1988
Ethylbenzene	Laboratory, sludge from wastewater treatment plant	Aerobic		5.18		10.07	0.34	15.25	20-100	Tabak et al., 1991
m-Xylene	Microcosm	Sulfate-reducing			20.00		0.14		8-12	Edwards et al., 1992
	Laboratory, sludge from wastewater treatment plant	Aerobic		2.95		0.75	0.26	11.35	20-100	Tabak et al., 1991
o-Xylene	Microcosm	Aerobic		2.03	0.00		0.67	3.03	0.02	Corseuil and Weber, 1994
p-Xylene	Microcosm	Aerobic		3.12		15.93				Goldsmith and Balderson, 1988
	Laboratory, sludge from wastewater treatment plant	Aerobic		3.36		2.47	0.36	9.33	20-100	Tabak et al., 1991
Xylenes	Laboratory	Aerobic	*Pseudomonas strain X2*	12.85		4.55	0.25	51.40	10.00	Chang et al., 1993
	Flow-through column	Aerobic		1.49-9		0.85				Kelly et al., 1996
	Microcosm	Aerobic		9.19		13.27	1.30	7.07	6.40	Kelly et al., 1996
	Microcosm	Aerobic		6.67		5.52	1.30	5.13	6.40	Kelly et al., 1996

anticipated to obtain faster rates in laboratory experiments. However, when comparing median values, the differences between field and laboratory studies were extremely small (less than one order of magnitude). There were two notable exceptions in this case: toluene and ethylbenzene. For these compounds, the ranges of anaerobic rate coefficients from field studies had very high maximum values, which come from one in situ column study reported by Patterson et al. (1993).

Table 2. Summary of zero-order decay rates for BTEX compounds (mg/L-day)

		Aerobic			Aerobic/Anaerobic	Anaerobic		
	All Studies	In Situ & Laboratory	In Situ Studies[a]	Laboratory Studies	Field Studies	Field & Laboratory	Field/In Situ[a] Studies	Laboratory Studies
BENZENE								
Number of rates[b]	26	11	1	10	1	14	5	9
Minimum	0.000	0.003		0.003		0.000	0.000	0.000
25th percentile	0.000	0.024		0.149		0.000	0.000	0.000
Median	0.002	0.520		3.760		0.000	0.000	0.000
75th percentile	0.383	30.500		33.250		0.001	0.000	0.001
90th percentile	30.500	45.000		45.700		0.002	0.000	0.002
Maximum	52.000	52.000		52.000		0.004	0.001	0.004
Mean	6.389	15.099		16.607		0.001	0.000	0.001
Standard deviation	15.018	20.474		20.928		0.001	0.000	0.001
Geometric mean[c]	0.000	0.790	0.000	1.170	0.000	0.000	0.000	0.000
TOLUENE								
Number of rates[b]	28	9		9	2	18	5	13
Minimum	0.000	0.004		0.004		0.000	0.007	0.000
25th percentile	0.042	0.400		0.400		0.059	0.007	0.090
Median	0.285	5.000		5.000		0.154	0.090	0.230
75th percentile	0.480	20.000		20.000		0.375	0.108	0.380
90th percentile	20.900	28.000		28.000		0.484	0.367	0.454
Maximum	239.000	48.000		48.000		239.000	0.540	239.000
Mean	12.581	12.203		12.203		13.467	0.150	18.589
Standard deviation	45.590	16.152		16.152		56.286	0.223	66.225
Geometric mean[c]	0.147	1.309		1.309	19.040	0.055	0.047	0.058
ETHYLBENZENE								
Number of rates[b]	11	2		2		9	5	4
Minimum	0.000					0.000	0.003	
25th percentile	0.004					0.003	0.005	
Median	0.067					0.050	0.050	
75th percentile	0.240					0.130	0.067	
90th percentile	0.300					0.230	0.213	
Maximum	0.310					0.310	0.310	
Mean	0.122	0.285		0.285		0.086	0.087	0.085
Standard deviation	0.127	0.021		0.021		0.110	0.128	0.103
Geometric mean[c]	0.002	0.285		0.285		0.001	0.028	0.000
***m*-XYLENE**								
Number of rates[b]	11	3		3	1	7	5	2
Minimum	0.005					0.005	0.005	
25th percentile	0.027					0.053	0.006	
Median	0.108					0.108	0.100	
75th percentile	0.240					0.165	0.108	
90th percentile	0.300					0.494	0.613	
Maximum	0.950					0.950	0.950	
Mean	0.195	0.206		0.206		0.214	0.234	0.165
Standard deviation	0.272	0.154		0.154		0.331	0.403	0.035
Geometric mean[c]	0.077	0.134		0.134		0.070	0.050	0.163
***o*-XYLENE**								
Number of rates[b]	18	5		5	1	12	5	7
Minimum	0.000	0.002		0.002		0.000	0.000	0.038
25th percentile	0.007	0.002		0.002		0.007	0.002	0.106
Median	0.065	0.030		0.030		0.106	0.007	0.130
75th percentile	0.323	0.300		0.300		0.525	0.007	0.530
90th percentile	0.564	0.318		0.318		0.612	0.375	0.632
Maximum	0.770	0.330		0.330		0.770	0.620	0.770
Mean	0.196	0.133		0.133		0.237	0.127	0.316
Standard deviation	0.253	0.167		0.167		0.287	0.275	0.288
Geometric mean[c]	0.017	0.024		0.024		0.015	0.000	0.198
***p*-XYLENE**								
Number of rates[b]	11	5		5	1	5		5
Minimum	0.000	0.000		0.000		0.056		0.056
25th percentile	0.043	0.000		0.000		0.240		0.240
Median	0.560	2.000		2.000		0.560		0.560
75th percentile	1.790	6.000		6.000		0.630		0.630
90th percentile	6.000	9.600		9.600		1.200		1.200
Maximum	12.000	12.000		12.000		1.580		1.580
Mean	2.100	4.000		4.000		0.613		0.613
Standard deviation	3.725	5.099		5.099		0.589		0.589
Geometric mean[c]	0.011	0.000		0.000		0.376		0.376

[a] In situ studies include in situ microcosms and in situ columns

[b] All the zero-order rates provided were calculated by the authors of the respective studies

[c] To calculate the geometric mean, values equal to zero were included as 10^{-10}.

Aerobic Versus Anaerobic Rate Constants. Figures 2 and 3 illustrate the BTEX degradation data for aerobic and anaerobic conditions, respectively. The data in Figure 2 indicate that benzene has the highest median aerobic value (0.20 day^{-1}), while *o*-xylene showed the lowest (0.035 day^{-1}). The data in Figure 2 also illustrate that in general the BTEX compounds had very similar minimum-75th percentile ranges for aerobic degradation rates. This is not the case for anaerobic conditions (see Figure 3). Toluene exhibited a median of 0.03 day^{-1}, which is the highest anaerobic value among the BTEX compounds. The data in Figures 2 and 3 also show that, with the exception of ethylbenzene (for lack of data), aerobic biodegradation of BTEX

Table 3. Summary of first-order decay rates for BTEX compounds (day^{-1})

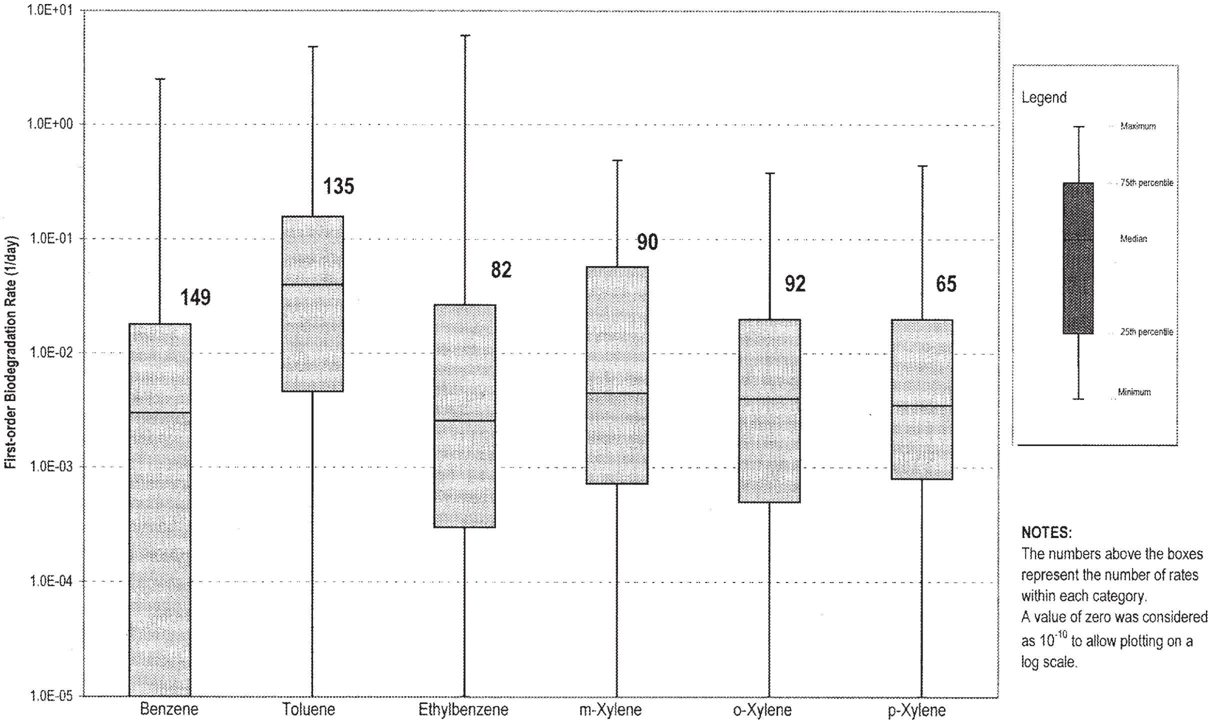
		Aerobic			Aerobic/Anaerobic	Anaerobic		
	All Studies	Field & Laboratory	In Situ Studies[a]	Laboratory Studies	Field Studies	Field & Laboratory	Field/In Situ[a] Studies	Laboratory Studies
BENZENE								
Number of rates	150	26	3	23	20	104	45	59
Number of reported rates	80	14	3	11	15	51	32	19
Number of calculated rates[b]	70	12	0	12	5	53	13	40
Mean	0.065	0.335	0.333	0.335	0.010	0.008	0.003	0.012
Standard deviation	0.275	0.599		0.637	0.020	0.016	0.006	0.020
90th percentile	0.141	0.445		0.389	0.013	0.024	0.009	0.045
Geometric mean[c]	0.000	0.025	0.311	0.018	0.001	0.000	0.000	0.000
Range reported rates	0-2.5	0-2.5	0.2-0.5	0-2.5	0-0.087	0-0.089	0-0.023	0-0.089
TOLUENE								
Number of rates	135	16	3	13	13	106	43	63
Number of reported rates	65	12	3	9	8	45	27	18
Number of calculated rates[b]	70	4	0	4	5	61	16	45
Mean	0.250	0.262	0.233	0.268	0.382	0.232	0.237	0.228
Standard deviation	0.705	0.384		0.424	1.328	0.640	0.733	0.573
90th percentile	0.438	0.390		0.372	0.091	0.445	0.266	0.522
Geometric mean[c]	0.009	0.142	0.200	0.132	0.002	0.007	0.013	0.005
Range reported rates	0-4.8	0.016-1.63	0.1-0.4	0.016-1.63	0-4.8	0-4.32	0-4.32	0-3.28
ETHYLBENZENE								
Number of rates	82				13	69	33	36
Number of reported rates	41				9	32	21	11
Number of calculated rates[b]	41				4	37	12	25
Mean	0.126				0.010	0.148	0.218	0.083
Standard deviation	0.676				0.021	0.735	1.057	0.140
90th percentile	0.208				0.020	0.229	0.034	0.283
Geometric mean[c]	0.000				0.001	0.000	0.000	0.000
Range reported rates	0-6.048				0-0.078	0-6.048	0-6.048	0-0.48
***m*-XYLENE**								
Number of rates	90	4		4	13	73	30	43
Number of reported rates	38	0		0	8	30	18	12
Number of calculated rates[b]	52	4		4	5	43	12	31
Mean	0.058	0.163		0.163	0.004	0.062	0.031	0.084
Standard deviation	0.107				0.007	0.107	0.061	0.125
90th percentile	0.210				0.006	0.210	0.066	0.252
Geometric mean[c]	0.001	0.066		0.066	0.001	0.001	0.001	0.000
Range reported rates	0-0.49	0.008-0.43		0.008-0.43	0-0.025	0-0.49	0-0.32	0-0.49
***o*-XYLENE**								
Number of rates	92	10	3	7	12	70	27	43
Number of reported rates	45	6	3	3	7	32	21	11
Number of calculated rates[b]	47	4	0	4	5	38	6	32
Mean	0.021	0.086	0.060	0.097	0.005	0.015	0.019	0.012
Standard deviation	0.051	0.116		0.139	0.008	0.031	0.044	0.018
90th percentile	0.040	0.205		0.263	0.019	0.037	0.042	0.035
Geometric mean[c]	0.000	0.046	0.054	0.043	0.001	0.000	0.000	0.000
Range reported rates	0-0.38	0.008-0.38	0.04-0.1	0.008-0.38	0-0.023	0-0.214	0-0.214	0-0.075
***p*-XYLENE**								
Number of rates	65	3		3	15	47	25	22
Number of reported rates	42	0	0	0	10	32	21	11
Number of calculated rates[b]	23	3	0	3	5	15	4	11
Mean	0.038	0.207		0.207	0.007	0.037	0.013	0.064
Standard deviation	0.094				0.009	0.090	0.020	0.126
90th percentile	0.075				0.018	0.072	0.035	0.204
Geometric mean[c]	0.000	0.086	0.000	0.086	0.002	0.000	0.001	0.000
Range reported rates	0-0.44	0.008-0.43		0.008-0.43	0.0001-0.031	0-0.44	0-0.081	0-0.44

[a] In situ studies include in situ microcosms and in situ columns

[b] When enough information was provided by the authors of a study, the authors of this paper calculated the rate coefficient assuming first-order kinetics

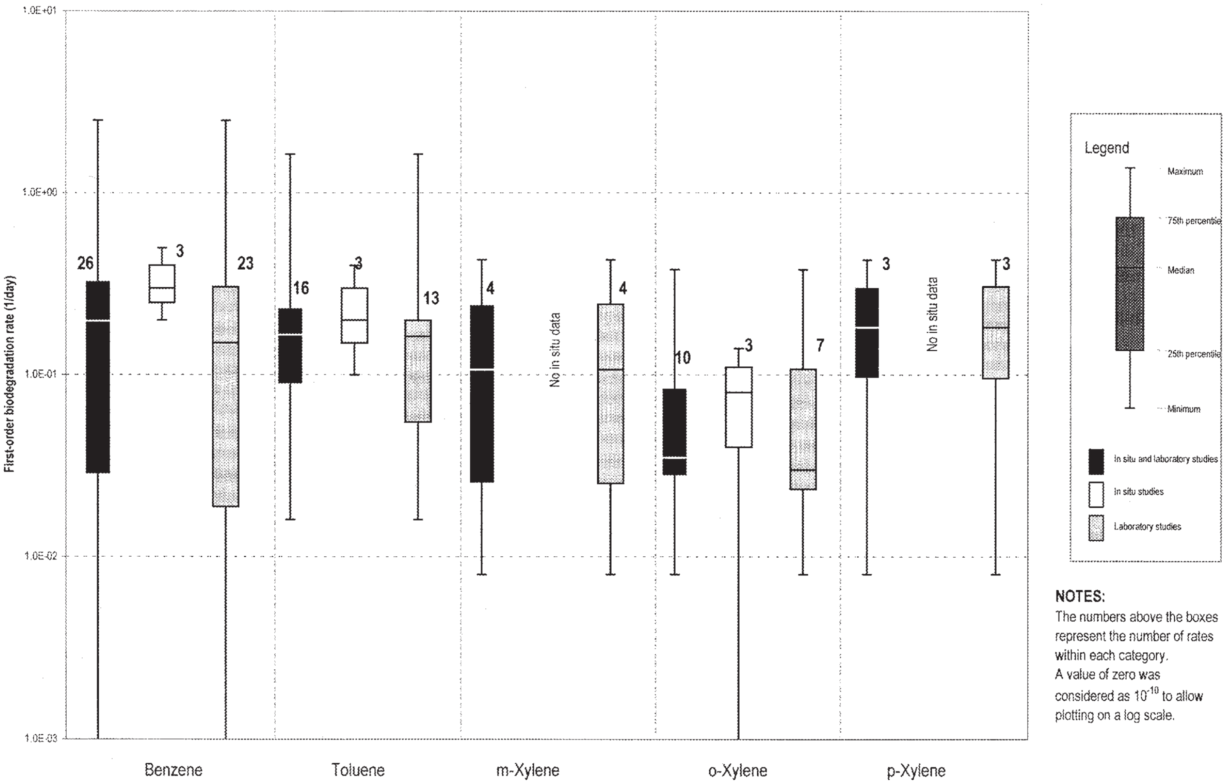
[c] To calculate the geometric mean, values equal to zero were included as 10^{-10}.

compounds generally occurs at faster rates than anaerobic biodegradation. This is based on comparing aerobic and anaerobic median rate constants from all reported studies. Benzene data showed the biggest difference (three orders of magnitude) between aerobic and anaerobic coefficients. The data in Figure 3 indicate that the range of reported anaerobic constants for benzene is very wide. However, 42% of the studies (mostly laboratory experiments) reported recalcitrance under anaerobic conditions. Field studies, ironically, showed little difference between the sizes of benzene plumes and other TEX plumes at these sites. Possible explanations for this difference between laboratory and field phenomena include insufficient time in laboratory experiments for adaptation to occur and experimenting with benzene by itself instead of in a mixture, as is commonly found in the environment.



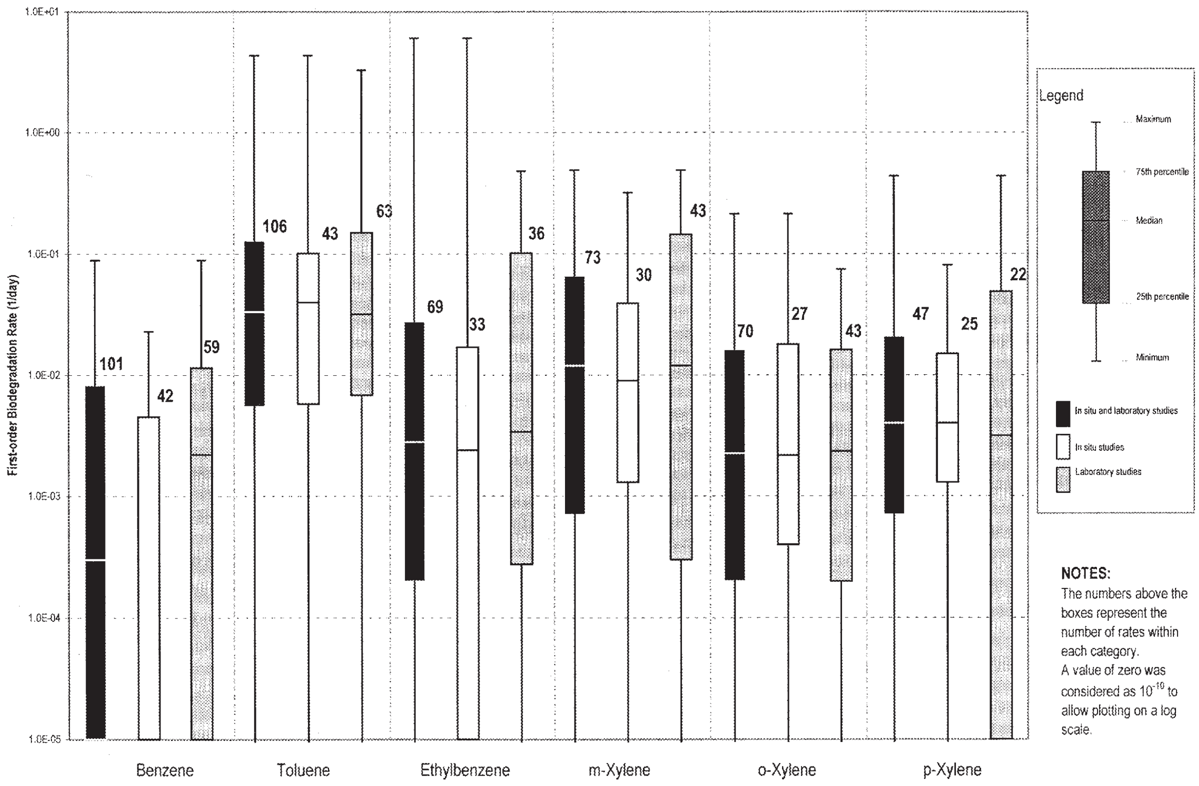
NOTES:
The numbers above the boxes represent the number of rates within each category.
A value of zero was considered as 10^{-10} to allow plotting on a log scale.

Figure 1. Overall rates of BTEX biodegradation.



NOTES:
The numbers above the boxes represent the number of rates within each category.
A value of zero was considered as 10^{-10} to allow plotting on a log scale.

Figure 2. Aerobic rates for BTEX compounds.



NOTES:
The numbers above the boxes represent the number of rates within each category.
A value of zero was considered as 10^{-10} to allow plotting on a log scale.

Figure 3. Anaerobic rates for BTEX compounds.

Rate Constants for Various Electron Acceptors

In order to determine the most favorable patterns for biodegradation of fuel hydrocarbons, minimum-90th percentile range and median values of rate coefficients under different electron-accepting processes were evaluated for each compound. Results of the analysis can be seen in Table 4. For instance, benzene exhibited decay coefficients via aerobic respiration, iron reduction, and sulfate reduction within the minimum-90th percentile ranges 0 to 0.445 day^{-1}, 0 to 0.024 day^{-1}, and 0 to 0.023 day^{-1}, respectively. Toluene biodegradation was reported under all terminal electron-accepting processes (TEAPs) with median rate constants equal to 0.17 day^{-1} for aerobic respiration, 0.09 day^{-1} for nitrate reduction, 0.01 day^{-1} for iron reduction, 0.02 day^{-1} for methanogenesis, and 0.04 day^{-1} for sulfate reduction. Median values for anaerobic biodegradation of ethylbenzene varied between 0.0006 day^{-1} for sulfate reduction and 0.016 day^{-1} for nitrate reduction. Aerobic respiration was the preferred pattern for the xylene isomers with median values varying from 0.035 day^{-1} to 0.183 day^{-1}.

In all cases, aerobic respiration showed the highest decay constants. However, the TEAP for which the compounds showed the highest decay rates under anaerobic processes varied from one compound to another. For example, anaerobic biodegradation of benzene was observed under iron- and sulfate-reducing environments (median coefficients equal to 0.005 day^{-1} and 0.003 day^{-1}, respectively). The possibility of biodegradation via either nitrate reduction or methanogenesis was not clearly established (median values equal to zero). For toluene, nitrate appeared to be the most preferred electron acceptor under anaerobic conditions with a median value of 0.09 day^{-1}, whereas iron reduction showed the lowest rate coefficient (0.01 day^{-1}). The highest anaerobic median rate coefficients for ethylbenzene and xylenes were obtained under nitrate-reducing (0.016 day^{-1}) and sulfate-reducing (0.056 day^{-1}) conditions, respectively.

The degradation order is variable according to site-specific conditions. In fact, comparison of some

Table 4. Summary of BTEX first-order decay rates sorted by electron-acceptor (day^{-1})

		Redox Process					
	All Studies	Aerobic Respiration	Nitrate Reduction	Iron Reduction	Sulfate Reduction	Methanogenesis	Mixed
BENZENE							
Number of rates	149	26	41	20	16	15	25
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000
25th percentile	0.000	0.028	0.000	0.000	0.000	0.000	0.001
Median	0.003	0.198	0.000	0.005	0.003	0.000	0.004
75th percentile	0.018	0.330	0.006	0.011	0.006	0.006	0.010
90th percentile	0.142	0.445	0.030	0.024	0.023	0.033	0.019
Maximum	2.500	2.500	0.089	0.034	0.049	0.077	0.087
Mean	0.065	0.335	0.008	0.009	0.008	0.010	0.009
Standard deviation	0.276	0.599	0.019	0.011	0.013	0.022	0.018
TOLUENE							
Number of rates	135	16	49	13	14	24	17
Minimum	0.000	0.016	0.000	0.000	0.000	0.000	0.000
25th percentile	0.005	0.089	0.015	0.002	0.010	0.008	0.001
Median	0.040	0.167	0.090	0.010	0.035	0.021	0.004
75th percentile	0.158	0.235	0.434	0.012	0.080	0.045	0.045
90th percentile	0.438	0.390	1.466	0.034	0.181	0.090	0.084
Maximum	4.800	1.630	4.320	0.045	0.210	0.186	4.800
Mean	0.250	0.262	0.459	0.012	0.062	0.037	0.302
Standard deviation	0.705	0.384	0.891	0.014	0.072	0.046	1.160
ETHYLBENZENE							
Number of rates	82		37	7	8	12	17
Minimum	0.000		0.000	0.000	0.000	0.000	0.000
25th percentile	0.000		0.001	0.000	0.000	0.000	0.001
Median	0.003		0.016	0.002	0.001	0.001	0.002
75th percentile	0.027		0.188	0.002	0.004	0.013	0.006
90th percentile	0.208		0.428	0.009	0.006	0.028	0.025
Maximum	6.048		6.048	0.017	0.007	0.054	0.078
Mean	0.126		0.270	0.003	0.002	0.010	0.010
Standard deviation	0.676		0.994	0.006	0.003	0.017	0.019
***m*-XYLENE**							
Number of rates	90	4	41	8	7	12	16
Minimum	0.000	0.008	0.000	0.001	0.004	0.000	0.000
25th percentile	0.001	0.025	0.000	0.001	0.017	0.000	0.000
Median	0.005	0.107	0.017	0.002	0.056	0.001	0.002
75th percentile	0.058	0.245	0.160	0.016	0.076	0.026	0.004
90th percentile	0.210	0.356	0.260	0.025	0.180	0.057	0.010
Maximum	0.490	0.430	0.490	0.037	0.320	0.104	0.025
Mean	0.058	0.163	0.089	0.010	0.081	0.019	0.004
Standard deviation	0.107	0.194	0.127	0.013	0.110	0.033	0.007
***o*-XYLENE**							
Number of rates	92	10	38	8	6	12	16
Minimum	0.000	0.008	0.000	0.000	0.000	0.000	0.000
25th percentile	0.001	0.028	0.000	0.001	0.002	0.000	0.001
Median	0.004	0.035	0.005	0.002	0.011	0.001	0.003
75th percentile	0.020	0.085	0.020	0.002	0.046	0.007	0.008
90th percentile	0.040	0.205	0.030	0.006	0.070	0.069	0.022
Maximum	0.380	0.380	0.068	0.016	0.084	0.214	0.057
Mean	0.021	0.086	0.012	0.003	0.027	0.026	0.009
Standard deviation	0.051	0.116	0.015	0.005	0.035	0.063	0.015
***p*-XYLENE**							
Number of rates	65	3	21	8	4	10	18
Minimum	0.000	0.008	0.000	0.001	0.002	0.000	0.000
25th percentile	0.001		0.000	0.001	0.004	0.001	0.001
Median	0.004		0.008	0.002	0.009	0.003	0.002
75th percentile	0.020		0.054	0.016	0.016	0.019	0.008
90th percentile	0.075		0.207	0.025	0.020	0.060	0.018
Maximum	0.440	0.430	0.440	0.037	0.022	0.081	0.031
Mean	0.038	0.207	0.068	0.010	0.011	0.018	0.006
Standard deviation	0.094	0.212	0.128	0.013	0.009	0.028	0.009

studies with more than one BTEX compound leads to different sequences. For instance, B. Wilson et al. (1994) reported field rates of BTEX biodegradation at Traverse City under methanogenic conditions with the following order: toluene>*o*-xylene>*m*,*p*-xylene> benzene, while a study performed at Eglin AFB with

CO_2 as the main electron acceptor reported rates with the sequence: *o*-xylene>toluene>ethylbenzene>*m,p*-xylene>benzene (J. Wilson et al., 1994). Experiments performed at Arvida Research Site (Borden et al., 1994) reported the sequence toluene>*o*-xylene>*m,p*-xylene>benzene when iron reduction is the main terminal electron-accepting process. In contrast, Wilson et al. (1996) reported rates from a field study at Tibbetts Road, where Fe(III) was the main electron acceptor, with the following order of biodegradability: toluene>*m*-xylene>*o,p*-xylene>ethylbenzene> benzene.

Rate Constants for Chlorinated Solvent Biodegradation

As with fuels, data from 138 studies (field and laboratory) were evaluated to estimate biodegradation coefficients for chlorinated compounds. Thirteen (13) of these studies reported Michaelis-Menten kinetics, 28 reported zero-order rates, and 97 studies reported first-order constants. Among all the studies for chlorinated compounds, 56 experiments were conducted under aerobic conditions, 5 under mixed aerobic/anaerobic environments, and 77 under anaerobic conditions. Fifty-seven (57) of the studies reporting first-order rates were laboratory experiments, while 40 were field/in situ studies. Among the studies reporting zero-order rates, 12 correspond to laboratory experiments and 16 to field studies. All the data reporting Michaelis-Menten kinetics came from laboratory studies.

Michaelis-Menten Rates

Data from 13 studies reporting Monod kinetics are presented in Table 5. Half-saturation constants varied from 0.6 mg/L to 29.5 mg/L for TCE and from 0.17 mg/L to 28 mg/L for DCE. Additionally, reported maximum specific degradation rates were within the ranges 0.038 to 478.59 $mg_{compound}/mg_{protein}$-day for TCE, and 0 to 11,115 $mg_{compound}/mg_{protein}$-day for DCE. As observed with data for BTEX, the particular conditions of the experiment cause the measured parameters to vary widely.

Zero-Order Rates

A summary of more than 40 studies reporting zero-order rates is included in Table 6. The reported zero-order rates ranged from 0 to 19.8 mg/L-day with mean values for anaerobic rates of 0.04, 2.14, 1.80, 1.74, and 0.11 mg/L-day for carbon tetrachloride, DCE, PCE, TCE, and vinyl chloride, respectively. TCE appeared to be reductively dechlorinated at the fastest rate coefficient, with a median equal to 0.76 mg/L-day. In contrast, vinyl chloride exhibited the slowest rate coefficient of reductive dechlorination with a median value of 0.01 mg/L-day.

First-Order Rate Constants

Table 7 contains a summary of first order decay coefficients from both field and laboratory studies. As can be seen in Table 7, first-order rate constants for chlorinated solvents varied from 0 to 1.03 day^{-1} in 90% of the cases, with mean values equal to 0.11, 0.02, 0.14, 0.05, 0.26, 0.17, and 0.23 day^{-1} for carbon tetrachloride, DCA, DCE, PCE, TCA, TCE, and vinyl chloride, respectively. The range minimum-90th percentile for aerobic rates was 0 to 1.35 day^{-1}, while for anaerobic rates it was 0 to 1.11 day^{-1}. Field rates from aerobic/anaerobic studies ranged from 0 to 1.96 day^{-1}. The compound that showed the highest mean value under aerobic conditions was vinyl chloride (1.73 day^{-1}), while TCA exhibited the highest mean anaerobic rate coefficient (0.35 day^{-1}).

Overall, first-order rate coefficients of chlorinated solvent biodegradation were plotted in Figure 4. The data in Figure 4 show that carbon tetrachloride exhibited decay coefficients between 0.004 and 0.49 day^{-1}; DCA presented coefficients from 0 day^{-1} to 0.131 day^{-1}; rate constants for DCE varied up to 1.96 day^{-1}; PCE, TCA, and TCE exhibited rate coefficients within the ranges 0 to 0.41 day^{-1}, 0 to 2.33 day^{-1}, and 0 to 313 day^{-1}, respectively; and vinyl chloride showed decay constants varying from 0 to 1.96 day^{-1}. The highest and lowest median rate constants were exhibited by TCA (0.26 day^{-1}) and DCA (0.02 day^{-1}), respectively. These decay coefficients were obtained in studies conducted at temperatures between 4 and 30°C.

Figures 5 and 6 depict the different ranges of decay coefficients for chlorinated compounds under aerobic and anaerobic conditions, respectively. The data in Figure 5 show that the ranges minimum-75th percentile for aerobic biodegradation of chlorinated solvents are 0.014 to 0.123 day^{-1}, 0 to 0.714 day^{-1}, 0 to 0.037 day^{-1}, 0 to 0.04 day^{-1}, 0.024 to 0.88 day^{-1}, and 0.055 to 1.62 day^{-1} for DCA, DCE, PCE, TCA, TCE, and vinyl chloride, respectively. Vinyl chloride had the highest median value (1.04 day^{-1}), while TCA showed the lowest median value (0.013 day^{-1}). In addition, anaerobic rate constants, as depicted in Figure 6, had ranges minimum-75th percentile between 0.004 to 0.16 day^{-1} for carbon tetrachloride, 0 to 0.003 day^{-1} for DCA, 0 to 0.006 day^{-1} for DCE, 0 to 0.11 day^{-1} for PCE, 0 to 0.67 day^{-1} for TCA, 0 to 0.008 day^{-1} for TCE, and 0 to 0.27 day^{-1} for vinyl chloride.

Table 5. Michaelis-Menten Parameters for Chlorinated Solvents

Compound	Type of Study	Redox Environment	Culture	μ_{max} (day^{-1})	Half-Saturation, K_s (mg/L)	Yield, Y (mg/mg)	Max. Specific Degradation Rate, μ_{max}/Y (mg/mg-day)	Initial Conc., S_o (mg/L)	Reference
1,1,1-TCA	Continuous reactor	Aerobic	*Methylosinus trichosporium* OB3b		28.46		4.60	>93.10	Oldenhuis et al., 1991
1,1-DCE	Growth reactor	Aerobic-cometabolism (methane)	Mixed methanotrophic culture	1.37	0.43		0-11115	0.01	Anderson and McCarty, 1996
	Continuous reactor	Aerobic	*Methylosinus trichosporium* OB3b		0.48		0.84	1.94-2.91	Oldenhuis et al., 1991
1,2-DCA	Continuous reactor	Aerobic	*Methylosinus trichosporium* OB3b		7.62		9.26	4.95-6.93	Oldenhuis et al., 1991
cis-1,2-DCE	Growth reactor	Aerobic-cometabolism (phenol)	Filamentous phenol-oxidizers				0.27-1.50		Bielefeldt et al., 1994
	Continuous reactor	Aerobic	*Methylosinus trichosporium* OB3b		2.91		25.40	12.60-25.20	Oldenhuis et al., 1991
	Methanogenic fluidized bed reactor	Anaerobic			28.00				Ballapragada et al., 1997
trans-1,2-DCE	Continuous reactor	Aerobic	*Methylosinus trichosporium* OB3b		14.34		46.19	8.72-14.74	Oldenhuis et al., 1991
	Growth reactor	Aerobic-cometabolism (methane)	Mixed methanotrophic culture	0.68	0.17		0.00-0.44	4.70	Anderson and McCarty, 1996
PCE	Methanogenic fluidized bed reactor	Anaerobic			12.00				Ballapragada et al., 1997
	Biofilm reactor						0.00	0.99	Fathepure and Tiedje, 1994
	Fed-batch reactor	Anaerobic	Methanogenic consortium	0.47					Gao et al., 1995
TCE	Growth reactor	Aerobic			0.37		0.53	14.70	Alvarez-Cohen and McCarty, 1991
	Growth reactor	Aerobic-cometabolism (formate)			8.20		7.60	10.10	Alvarez-Cohen and McCarty, 1991
	Growth reactor	Aerobic-cometabolism (methane)	Mixed methanotrophic culture	1.07	0.13		0.00-1.13	1.00	Anderson and McCarty, 1996
	Methanogenic fluidized bed reactor	Anaerobic			19.00				Ballapragada et al., 1997
	Growth reactor	Aerobic-cometabolism (phenol)	Filamentous phenol-oxidizers				0.10-0.25		Bielefeldt et al., 1994
	Microcosm	Aerobic-cometabolism (toluene)		0.77-1.65		0.52	1.50	0.66	Jenal-Wanner and McCarty, 1997
	Microcosm	Aerobic-cometabolism (phenol)		0.88-1.43		0.40	3.00	0.66	Jenal-Wanner and McCarty, 1997
	Growth reactor	Aerobic-cometabolism (propane)	Propane-oxidizing culture		0.60		0.04	3.00	Keenan et al., 1994
	Batch	Aerobic	Methylomonas methanica 68-1		29.48	0.10	438.59		Koh et al., 1994
	Batch	Aerobic	*Methylosinus trichosporium* OB3b		16.51	0.08	187.70		Koh et al., 1994
	Continuous reactor	Aerobic	*Methylosinus trichosporium* OB3b		19.00		54.71	9.17-13.10	Oldenhuis et al., 1991
	Continuous reactor	Aerobic-cometabolism (methane)	Mixed methanotrophic culture			0.01			Strand et al., 1994
Vinyl chloride	Methanogenic fluidized bed reactor	Anaerobic			23.00				Ballapragada et al., 1997
	Small-Column Microcosm	Aerobic-cometabolism (methane)				1.00-3.50		1.00-17.00	Dolan and McCarty, 1995

Laboratory vs. Field Rate Constants

A comparison between field and laboratory biodegradation constants for anaerobic studies shows that constants obtained from laboratory studies are generally higher that those obtained from field studies (Figure 6). All the studied compounds showed higher median value of rate constants in laboratory studies than in field studies with PCE exhibiting the greatest laboratory/field median coefficient ratio (125). The other compounds showed differences up to one order of magnitude. The ranges of the reported rate constants were also greater for laboratory studies than for field studies.

Table 6. Summary zero-order decay rates for reductive dechlorination obtained from laboratory studies (mg/L-day)

	Carbon Tetrachloride	*cis*-1,2-DCE	DCE (all other isomers)	PCE	TCE	Vinyl Chloride
Number of rates[a]	8	18	8	29	7	9
Minimum	0.022	0.013	0.009	0.013	0.314	0.002
25th percentile	0.024	0.183	0.023	0.288	0.511	0.006
Median	0.029	0.511	0.250	0.577	0.760	0.011
75th percentile	0.042	1.318	1.385	1.040	1.297	0.075
90th percentile	0.049	3.348	2.021	2.801	3.798	0.379
Maximum	0.054	16.958	3.470	19.800	7.490	0.495
Mean	0.034	1.854	0.850	1.863	1.740	0.107
Standard deviation	0.012	3.939	1.213	4.162	2.567	0.184
Geometric mean[b]	0.000	15.513	1.471	17.323	6.590	0.034

[a] All the zero-order rates provided were calculated by the authors of the respective studies

[b] To calculate the geometric mean, values equal to zero were included as 10^{-10}.

Aerobic Vs. Anaerobic Rate Constants. As would be expected, highly chlorinated compounds (i.e., PCE and TCA) showed faster rate constants under anaerobic conditions (i.e., reductive dechlorination). PCE, however, exhibited higher median and 75th values under aerobic than under anaerobic conditions (see Figures 5 and 6). In contrast, DCE, DCA, and vinyl chloride, less chlorinated compounds, showed differences between median values from aerobic and anaerobic data of 4-, 34-, and 147-fold, respectively.

First-Order Rate Constants among Different Redox Conditions. Table 8 contains coefficients of chlorinated solvent biodegradation under different redox conditions. Data show that reductive dechlorination does not occur if there is nitrate in the environment. Most of the studies reported reductive dechlorination under sulfate-reducing and methanogenic conditions, which suggests that those are the most favorable redox conditions for the biodegradation of the highly chlorinated solvents.

Patterns of Biodegradation of Fuels and Chlorinated Solvents

Patterns of BTEX Biodegradation

The biodegradability of BTEX under different TEAPs was determined based on the number of studies reporting recalcitrance of a compound under a specific redox condition. Such analysis was performed by ranking the frequency of biodegradation of a compound under determined TEAP into five categories. A summary of the results is presented in Table 9. As can be seen in Table 9, benzene has very high potential for aerobic biodegradation because only 8% of the studies reported recalcitrance. Benzene also exhibited potential for biodegradation via iron reduction, although the reaction is slower than aerobic respiration (median half-life of 140 days vs. median half-life of 4 days under aerobic respiration). Toluene seems to be a readily biodegradable compound under aerobic and anaerobic conditions with the maximum percentage of recalcitrance (13%) occurring under fermentative conditions (methanogenesis). No data were found for the aerobic biodegradation of ethylbenzene. Nevertheless, ethylbenzene exhibited a high potential for biodegradation via denitrification and moderate potential via iron reduction with 19 and 29% of the studies reporting recalcitrance, respectively. The xylene isomers had variable patterns of biodegradation. For instance, sulfate reduction has the highest potential for biodegradation of *m*-xylene, as none of the studies reported recalcitrance and the median half-life was only 12 days. Iron reduction presented a very high possibility for the biodegradation of *m*-xylene as well with 0% recalcitrance, but with a longer half-life than sulfate reduction (283 days). The processes that had the highest potential for biodegradation of *o*-xylene and *p*-xylene were aerobic respiration and methanogenesis, respectively, with no studies reporting recalcitrance.

Patterns of Chlorinated Solvent Biodegradation

The biodegradability under different electron acceptors for each one of the chlorinated solvents was analyzed in the same way performed for BTEX. As summarized in Table 10, DCA presented very high potential for biodegradation via aerobic cometabolism and re-

Table 7. Summary first-order decay rates for chlorinated solvents (day^{-1})

		Aerobic Oxidation			Aerobic Cometabolism				Aerobic/Anaerobic	Reductive Dechlorination			Anaerobic Oxidation		
	All Studies	In Situ & Laboratory	In Situ Studies[a]	Laboratory	Field & Laboratory	In Situ Studies[a]	Laboratory	Overall Aerobic	Field Studies	Field & Laboratory	Field/In Situ[a] Studies	Laboratory	Field & Laboratory	Field/In Situ[a] Studies	Laboratory
CARBON TETRACHLORIDE															
Number of rates	13	1	1		1	1		2		11	7	4			
Number of reported rates	0	0	0		0	0		0		0	0	0			
Number of calculated rates[b]	13	1	1		1	1		2		11	7	4			
Mean	0.108							0.019		0.124	0.141	0.093			
Standard deviation	0.134									0.140	0.174				
90th percentile	0.216									0.230	0.334				
Geometric mean[c]	0.054									0.065	0.060	0.075			
Range reported rates	0.0037-0.49							0.016-0.022		0.004-0.490	0.004-0.490	0.023-0.160			
DCA (all isomers)															
Number of rates	25	2		2	5		5	7		18	16	2			
Number of reported rates	16	2		2	0		0	2		14	14	0			
Number of calculated rates[b]	9	0		0	5		5	5		4	2	2			
Mean	0.017				0.067		0.067	0.048		0.005	0.002	0.036			
Standard deviation	0.036				0.056		0.056	0.056		0.012	0.003				
90th percentile	0.046				0.128		0.128	0.126		0.016	0.004				
Geometric mean[c]	0.001	0.000		0.000	0.046		0.046	0.000		0.001	0.001	0.035			
Range reported rates	0-0.131				0.014-0.131		0.014-0.131	0-0.131		0-0.044	0-0.011	0.028-0.044			
***cis*-1,2-DCE**															
Number of rates	34				5	3	2		4	25	17	8			
Number of reported rates	24				2	2	0		4	18	13	5			
Number of calculated rates[b]	10				3	1	2		0	7	4	3			
Mean	0.004				0.476	0.885	0.187		0.000	0.004	0.002	0.014			
Standard deviation	0.395				0.787	0.843	0.250		0.003	0.048	0.031	0.069			
90th percentile	0.257				1.680	1.820	0.399		0.006	0.069	0.013	0.117			
Geometric mean[c]	0.004				0.476	0.885	0.187		0.000	0.004	0.002	0.014			
Range reported rates	0-1.960				0.081-1.960	0.281-1.96	0.081-0.434		0-0.008	0-0.200	0-0.130	0.001-0.200			
DCE (all other isomers)															
Number of rates	27				8	4	4			19	16	3			
Number of reported rates	14				2	0	2			12	12	0			
Number of calculated rates[b]	13				6	4	2			7	4	3			
Mean	0.149				0.458	0.720	0.196			0.019	0.003	0.101			
Standard deviation	0.302				0.416	0.316	0.347			0.061	0.001	0.147			
90th percentile	0.666				0.845	1.012	0.521			0.012	0.005	0.220			
Geometric mean[c]	0.003				0.002	0.670	0.000			0.004	0.003	0.039			
Range reported rates	0-1.150				0-1.150	0.390-1.150	0-0.714			0.001-0.270	0.001-0.006	0.010-0.270			
PCE															
Number of rates	50	10	3	7	3		3	13	1	36	13	23			
Number of reported rates	31	5	3	2	1	0	1	6	1	23	9	14			
Number of calculated rates[b]	19	5	0	5	2	0	2	7	0	13	4	9			
Mean	0.051	0.001	0.000	0.001	0.025		0.025	0.006		0.068	0.010	0.101			
Standard deviation	0.084	0.001		0.002				0.015		0.093	0.022	0.101			
90th percentile	0.153	0.003		0.003				0.017		0.185	0.022	0.212			
Geometric mean[c]	0.000	0.000		0.000	0.000	0.000	0.000	0.000		0.002	0.000	0.024			
Range reported rates	0-0.410	0-0.004	0.000	0-0.004	0-0.054		0-0.054	0-0.054		0-0.410	0-0.080	0-0.410			
TCA															
Number of rates	47	11	2	9	5		5	16		31	10	21			
Number of reported rates	27	7	2	5	1	0	1	8		19	3	16			
Number of calculated rates[b]	20	4	0	4	4	0	4	8		12	7	5			
Mean	0.261	0.002		0.003	0.247		0.247	0.079		0.355	0.029	0.511			
Standard deviation	0.502	0.007		0.007	0.522		0.522	0.294		0.562	0.039	0.629			
90th percentile	1.026	0.009		0.005	0.723		0.723	0.030		1.110	0.058	1.280			
Geometric meanc	0.000	0.000		0.000	0.001		0.001	0.000		0.003	0.000	0.007			
Range reported rates	0-2.330	0-0.022		0-0.022	0-1.180		0-1.180	0-1.180		0-2.330	0-0.125	0-2.330			

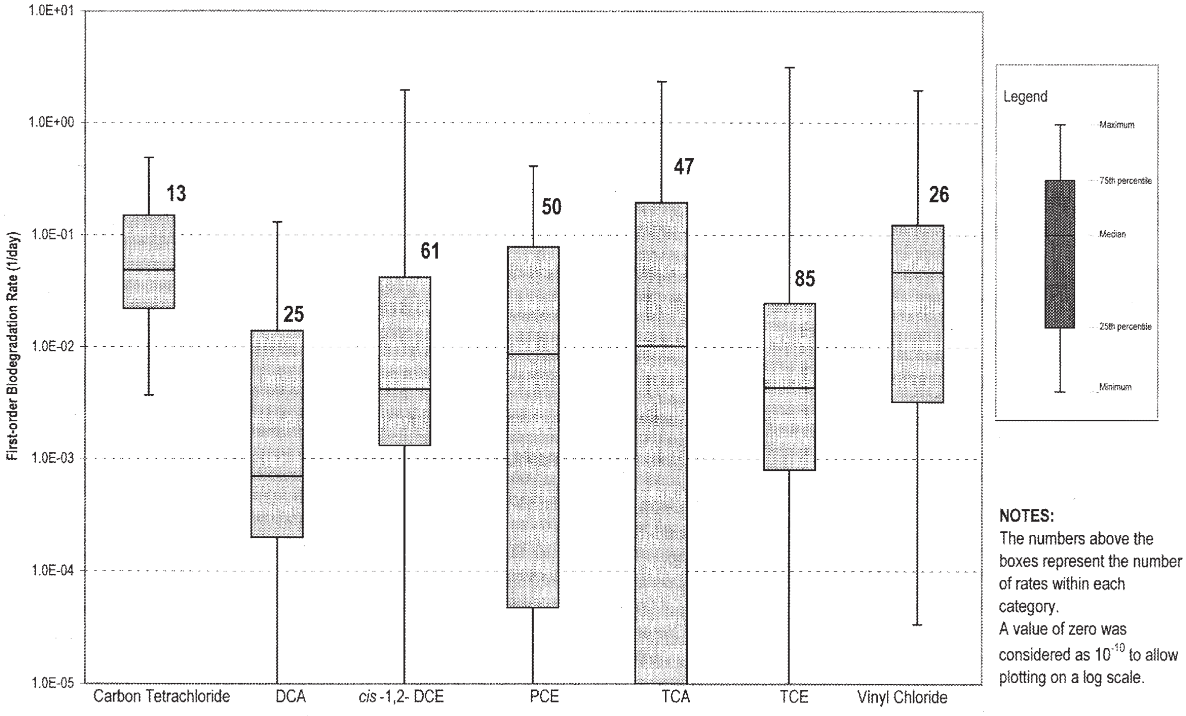
Table 7. Summary first-order decay rates for chlorinated solvents (day^{-1}) (continued)

		Aerobic Oxidation			Aerobic Cometabolism				Aerobic/Anaerobic	Reductive Dechlorination			Anaerobic Oxidation		
	All Studies	In Situ & Laboratory	In Situ Studies[a]	Laboratory	Field & Laboratory	In Situ Studies[a]	Laboratory	Overall Aerobic	Field Studies	Field & Laboratory	Field/In Situ[a] Studies	Laboratory	Field & Laboratory	Field/In Situ[a] Studies	Laboratory
TCE															
Number of rates	86	12	2	10	17	3	14	29	1	56	32	24			
Number of reported rates	52	6	2	0	7	2	5	13	1	38	26	12			
Number of calculated rates[b]	34	6	0	10	10	1	9	16	0	18	6	12			
Mean	0.173	0.005		0.006	0.586	0.948	0.509	0.346		0.086	0.003	0.196			
Standard deviation	0.475	0.010		0.011	0.566		0.524	0.517		0.434	0.005	0.654			
90th percentile	0.636	0.025		0.026	1.418		1.265	1.354		0.022	0.006	0.337			
Geometric mean[c]	0.001	0.000		0.000	0.309	0.582	0.269	0.001		0.001	0.000	0.012			
Range reported rates	0-3.130	0-0.028		0-0.028	0.024-1.650	0.105-1.41	0.024-1.650	0-1.650		0-3.130	0-0.023	0-3.130			
VINYL CHLORIDE															
Number of rates	26	4		4	4	2	2	8	3	8	4	4	7	1	6
Number of reported rates	8	0		0	0	0	0	0	2	5	4	1	1	1	0
Number of calculated rates[b]	18	4		4	4	2	2	8	1	3	0	3	6	0	6
Mean	0.229	0.087		0.087	1.023	1.730	0.316	0.555	0.004	0.153	0.003	0.303	0.042		0.049
Standard deviation	0.476							0.756		0.228			0.048		0.048
90th percentile	0.946							0.107		0.499			0.104		0.107
Geometric mean[c]	0.023	0.080	0.000	0.080	0.552	1.715	0.178	0.211	0.002	0.007	0.001	0.036	0.018		0.028
Range reported rates	0-1.960	0.043-0.125		0.043-0.125	0.055-1.960	1.500-1.960	0.055-0.576	0.043-0.120	0.001-0.009	0-0.520	0-0.007	0-0.520	0.001-0.120		0.008-0.120

[a] In situ studies include in situ microcosms and in situ columns

[b] When enough information was provided by the authors of a study, the authors of this paper calculated the rate coefficient assuming first-order kinetics

[c] To calculate the geometric mean, values equal to zero were included as 10^{-10}.



NOTES:
The numbers above the boxes represent the number of rates within each category.
A value of zero was considered as 10^{-10} to allow plotting on a log scale.

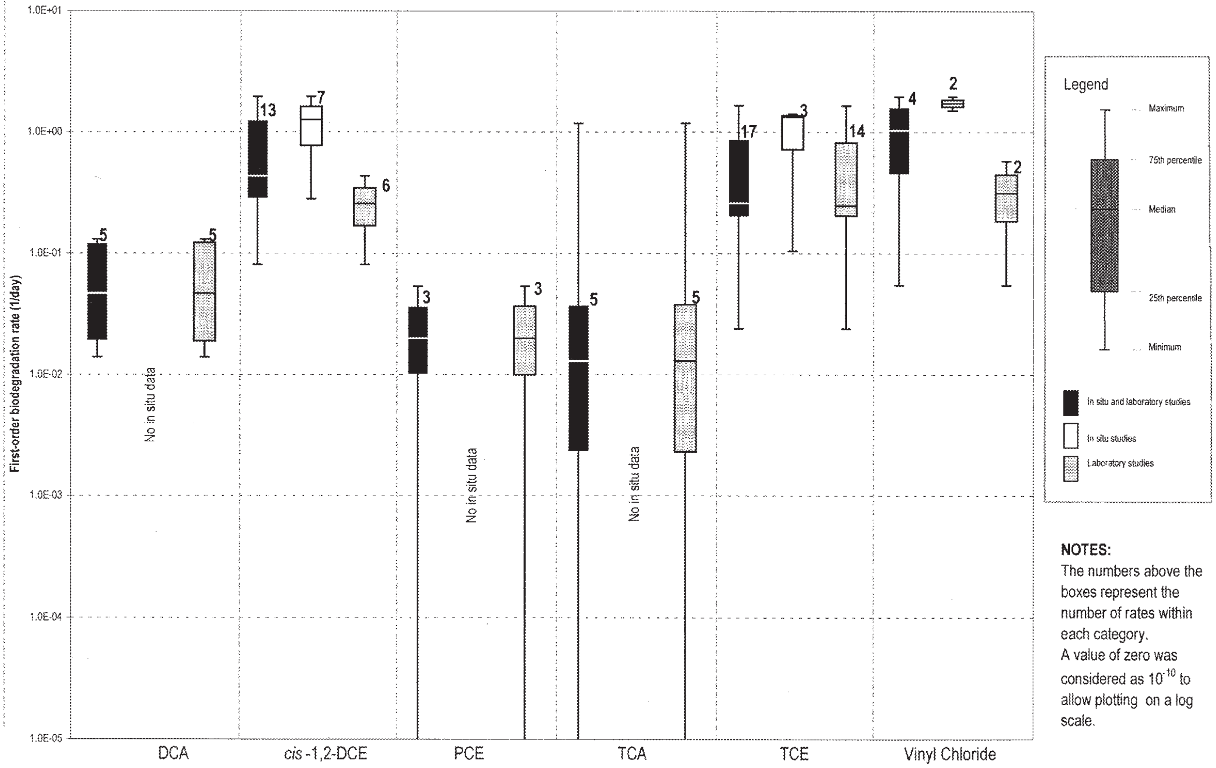
Figure 4. Overall rates of chlorinated solvent biodegradation

ductive dechlorination with none of the studies reporting recalcitrance. Median half-lives for this compound were 1260 days and 15 days for reductive dechlorination and cometabolism, respectively. DCE exhibited a high potential for aerobic cometabolism with 11% of the studies showing recalcitrance and a very short median half-life (1 day). None of the 44 studies on reductive dechlorination of DCE reported recalcitrance, which leads to the conclusion that DCE may undergo this process, although with a relatively slow rate (median half-life equal to 234 days). The process that exhibited the highest potential for biodegradation of PCE and TCA was reductive dechlorination with 86 and 84% of the analyzed studies showing biotransformation, respectively. Median half-lives for reductive dechlorination of PCE and TCA were 34 and 24 days, respectively. With respect to TCE, none of the 17 studies reporting aerobic cometabolism (most of them laboratory studies) showed recalcitrance and the median half-life was very short (3 days). Reductive dechlorination also appeared to be a very good alternative for biotransformation of TCE with only 9% of 56 studies reporting recalcitrance and median half-life equal to 201 days. Finally, vinyl chloride exhibited a very high potential for biodegradation under aerobic conditions with no studies showing recalcitrance and median half-lives of 8 days and 0.462 days for oxidation and cometabolism, respectively.

Summary and Conclusions

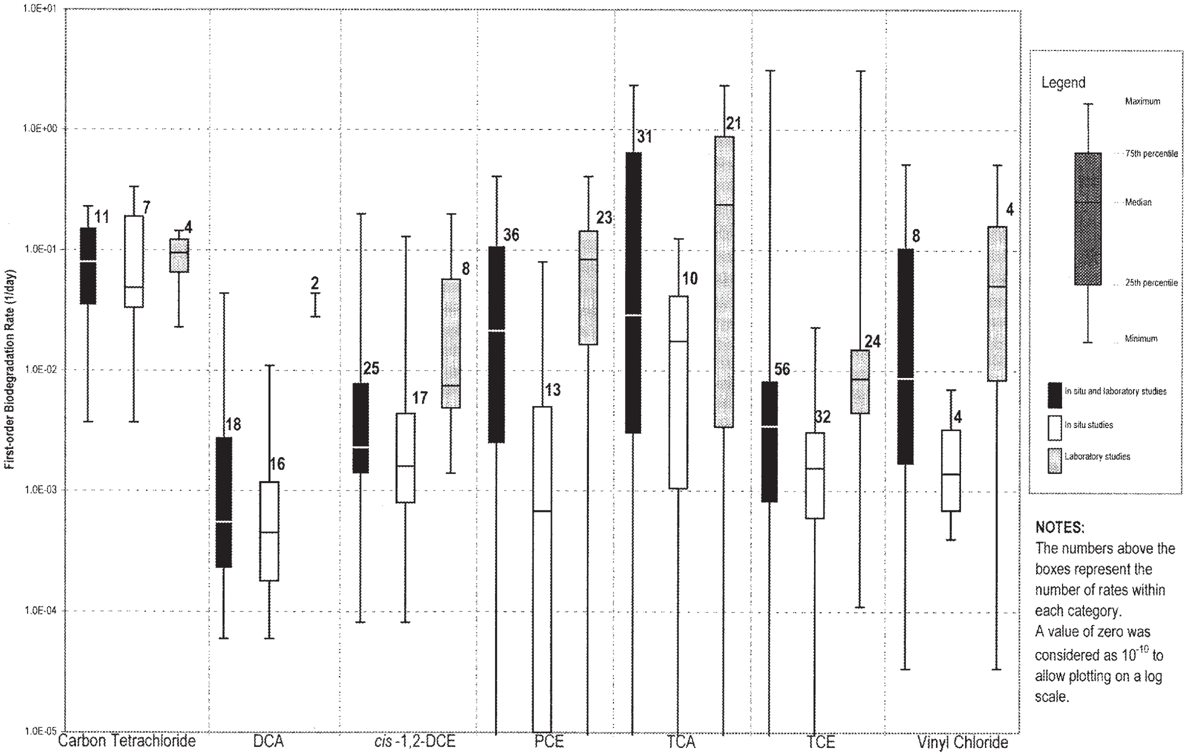
The present study compiled an extensive database of reported decay rates for BTEX and chlorinated solvent compounds. The resulting database can be used to draw conclusions regarding the biodegradation of fuel and chlorinated compounds at the laboratory and field scales:

- Both BTEX compounds and chlorinated solvents have been demonstrated in field and laboratory studies to biodegrade under a variety of electron acceptor conditions. The rate at which each one of these compounds biodegrades is highly dependent on both the compound itself and site-specific conditions.
- Ranges of decay coefficients derived from laboratory studies were always higher than those from field studies. This was expected because ambient conditions that favor biodegradation can be easily controlled at the laboratory-scale.



NOTES:
The numbers above the boxes represent the number of rates within each category.
A value of zero was considered as 10^{-10} to allow plotting on a log scale.

Figure 5. Rates of aerobic cometabolism of chlorinated solvents.



NOTES:
The numbers above the boxes represent the number of rates within each category.
A value of zero was considered as 10^{-10} to allow plotting on a log scale.

Figure 6. Anaerobic rates for chlorinated solvent.

Table 8. Summary of Chlorinated Solvent First-order Decay Rates Sorted by Redox Conditions (day^{-1})

				Reductive Dechlorination					Anaerobic Oxidation
	All Studies	Aerobic Oxidation	Cometabolism	Nitrate Reducing	Iron Reducing	Sulfate Reducing	Methanogenesis	Mixed	Iron Reducing
CARBON TETRACHLORIDE									
Number of rates	13	1	1	6	2		2		
Minimum	0.004			0.021					
25th percentile	0.022			0.047					
Median	0.049			0.065					
75th percentile	0.150			0.103					
90th percentile	0.216			0.135					
Maximum	0.490			0.160					
Mean	0.108			0.078	0.117		0.320		
Standard deviation	0.134			0.051					
DCA (all isomers)									
Number of rates	25	2	5			13	3		
Minimum	0.000		0.014			0.000			
25th percentile	0.000		0.019			0.000			
Median	0.001		0.047			0.000			
75th percentile	0.014		0.123			0.001			
90th percentile	0.046		0.128			0.002			
Maximum	0.131		0.131			0.028			
Mean	0.017	0.000	0.067			0.003	0.006		
Standard deviation	0.036		0.056			0.008			
DCE (all isomers)									
Number of rates	61		13		8	3	8	2	
Minimum	0.000		0.000		0.000		0.002		
25th percentile	0.002		0.081		0.001		0.007		
Median	0.004		0.434		0.002		0.016		
75th percentile	0.050		0.714		0.003		0.058		
90th percentile	0.434		1.238		0.004		0.117		
Maximum	1.960		1.960		0.005		0.200		
Mean	0.141		0.591		0.002	0.045	0.047	0.001	
Standard deviation	0.354		0.581		0.002		0.068		
PCE									
Number of rates	50	10	3	3	2	1	22	1	
Minimum	0.000	0.000					0.000		
25th percentile	0.000	0.000					0.013		
Median	0.009	0.000					0.080		
75th percentile	0.079	0.002					0.147		
90th percentile	0.153	0.003					0.214		
Maximum	0.410	0.004					0.410		
Mean	0.051	0.001	0.025	0.000	0.004		0.100		
Standard deviation	0.084	0.001					0.104		
TCA									
Number of rates	47	11	5	4	1	2	17	1	
Minimum	0.000	0.000	0.000	0.000			0.003		
25th percentile	0.000	0.000	0.002	0.000			0.025		
Median	0.010	0.000	0.013	0.000			0.125		
75th percentile	0.195	0.000	0.038	0.000			0.880		
90th percentile	1.026	0.001	0.723	0.000			1.178		
Maximum	2.330	0.022	1.180	0.000			2.330		
Mean	0.261	0.002	0.247	0.000		0.010	0.498		
Standard deviation	0.502	0.007	0.522				0.652		
TCE									
Number of rates	85	11	17	1	11	7	10	2	
Minimum	0.000	0.000	0.024		0.000	0.002	0.000		
25th percentile	0.001	0.000	0.200		0.001	0.005	0.001		
Median	0.005	0.000	0.260		0.002	0.008	0.004		
75th percentile	0.025	0.003	0.880		0.004	0.018	0.008		
90th percentile	0.636	0.025	1.418		0.010	0.023	0.022		
Maximum	3.130	0.028	1.650		0.011	0.023	0.109		
Mean	0.175	0.005	0.586		0.003	0.011	0.015	0.001	
Standard deviation	0.477	0.010	0.566		0.004	0.009	0.033		
VINYL CHLORIDE									
Number of rates	27	4	5		2		3		7
Minimum	0.000	0.043	0.055						0.001
25th percentile	0.005	0.064	0.576						0.008
Median	0.051	0.091	1.500						0.012
75th percentile	0.163	0.114	1.960						0.073
90th percentile	0.946	0.121	5.596						0.104
Maximum	8.020	0.125	8.020						0.120
Mean	0.518	0.087	2.422		0.260		0.230		0.042
Standard deviation	1.570	0.037	3.218						0.048

Table 9. Biodegradability of BTEX compounds

		Redox Process					
	All Studies	Aerobic Respiration	Nitrate Reduction	Iron Reduction	Methanogenesis	Sulfate Reduction	Mixed
BENZENE							
Number of rates	149	26	41	20	15	16	25
Number of rates (recalcitrant)	47	2	23	4	8	6	3
Half-life (days)[a]	231	4	NC	140	NC	267	198
% Rates recalcitrant	32%	8%	56%	20%	53%	38%	12%
Potential for biodegradation[b]	**Sometimes**	**Almost always**	**Very Barely**	**Frequently**	**Barely**	**Sometimes**	**Frequently**
TOLUENE							
Number of rates	135	16	49	13	24	14	17
Number of rates (recalcitrant)	9	0	3	1	3	0	2
Half-life (days)[a]	17	4	8	70	34	20	173
% Rates recalcitrant	7%	0%	6%	8%	13%	0%	12%
Potential for biodegradation	**Almost always**	**Almost always**	**Almost always**	**Almost always**	**Almost always**	**Almost always**	**Almost always**
ETHYLBENZENE							
Number of rates	82		37	7	12	8	17
Number of rates (recalcitrant)	18		7	2	3	4	2
Half-life (days)[a]	270		44	462	660	1260	289
% Rates recalcitrant	22%		19%	29%	25%	50%	12%
Potential for biodegradation	**Frequently**	**NA**	**Frequently**	**Sometimes**	**Frequently**	**Sometimes**	**Frequently**
***m*-XYLENE**							
Number of rates	90	4	41	8	12	7	16
Number of rates (recalcitrant)	13	0	9	0	2	0	2
Half-life (days)[a]	154	6	41	283	693	12	308
% Rates recalcitrant	14%	0%	22%	0%	17%	0%	13%
Potential for biodegradation	**Frequently**	**NA**	**Frequently**	**Almost always**	**Frequently**	**Almost always**	**Frequently**
***o*-XYLENE**							
Number of rates	92	10	38	8	12	6	16
Number of rates (recalcitrant)	16	0	8	2	2	2	2
Half-life (days)[a]	173	20	154	384	660	66	262
% Rates recalcitrant	17%	0%	21%	25%	17%	33%	13%
Potential for biodegradation	**Frequently**	**Almost always**	**Frequently**	**Frequently**	**Frequently**	**Sometimes**	**Frequently**
***p*-XYLENE**							
Number of rates	65	3	21	8	10	4	18
Number of rates (recalcitrant)	10	0	8	0	1	0	1
Half-life (days)[a]	196	4	87	378	277	73	295
% Rates recalcitrant	15%	0%	38%	0%	10%	0%	6%
Potential for biodegradation	**Frequently**	**NA**	**Sometimes**	**Almost always**	**Frequently**	**NA**	**Almost always**

[a] Median value from the reported studies.

[b] Quantitative estimation based on % occurrence of recalcitrance.

NA Insufficient information

NC Not calculable (l=0)

Scale	
% Recalcitrance	**Biodegradability**
< 10%	Almost always
10%-25%	Frequently
25%-50%	Sometimes
50%-75%	Barely
>75%	Almost never

- The minimum-90th percentile range of reported first-order biodegradation coefficients for BTEX compounds were 0 to 0.445 day^{-1} and 0 to 0.522 day^{-1} under aerobic and anaerobic conditions, respectively.
- The median reported decay coefficients for benzene, toluene, and xylene under aerobic conditions were very similar with an average median value of 0.16 per day. Under anaerobic conditions, however, median rate constants differed by orders of magnitude, with the smallest being that for benzene (0.03% per day) and the highest for toluene (3.3% per day).
- For all the fuel hydrocarbons, aerobic respiration showed the highest biodegradation coefficients. However, under anaerobic conditions the compounds exhibited different preferred electron acceptors. Benzene, for instance, showed the highest median value under iron reduction (0.5% per day). For toluene, nitrate appeared to be the most preferred electron acceptor yielding a median rate of 0.09 day^{-1}. The highest anaerobic median rate constants for ethylbenzene and xylenes were obtained under nitrate-reducing (0.0158 day^{-1}) and sulfate-reducing (0.056 day^{-1}) conditions, respectively.
- Concerning the relative order of biodegradability of BTEX compounds under different electron-accepting processes, it can be concluded that when fuel hydrocarbons are being transformed via aerobic respiration, benzene is the compound that biodegrades fastest followed by *p*-xylene, toluene, *m*-xylene, and *o*-xylene (from the standpoint of

Table 10. Biodegradability of chlorinated solvents

		Process			
	All Studies	Aerobic Oxidation	Cometabolism	Reductive Dechlorination	Anaerobic Oxidation
CARBON TETRACHLORIDE					
Number of rates	13	1	1	11	
Number of rates (recalcitrant)	0	0	0	0	
Half-life (days)[a]	14	NC	NC	9	
% Rates recalcitrant	0%	0%	0%	0%	
Potential for biodegradation[b]	**Almost always**	**NA**	**NA**	**Almost always**	
DCA (all isomers)					
Number of rates	25	2	5	18	
Number of rates (recalcitrant)	2	2	0	0	
Half-life (days)[a]	990	NC	15	1260	
% Rates recalcitrant	8%	100%	0%	0%	
Potential for biodegradation	**Almost always**	**NA**	**Almost always**	**Almost always**	
DCE (all isomers)					
Number of rates	61		13	44	
Number of rates (recalcitrant)	3		2	0	
Half-life (days)[a]	173		2	234	
% Rates recalcitrant	5%		15%	0%	
Potential for biodegradation	**Almost always**		**Frequently**	**Almost always**	
PCE					
Number of rates	50	10	3	36	
Number of rates (recalcitrant)	14	6	1	5	
Half-life (days)[a]	80	NC	35	32	
% Rates recalcitrant	28%	60%	33%	14%	
Potential for biodegradation	**Sometimes**	**Barely**	**NA**	**Frequently**	
TCA					
Number of rates	47	11	5	31	
Number of rates (recalcitrant)	14	8	1	5	
Half-life (days)[a]	68	NC	53	24	
% Rates recalcitrant	30%	73%	20%	16%	
Potential for biodegradation	**Sometimes**	**Barely**	**Frequently**	**Frequently**	
TCE					
Number of rates	85	11	17	56	
Number of rates (recalcitrant)	12	6	0	5	
Half-life (days)[a]	151	NC	3	201	
% Rates recalcitrant	14%	55%	0%	9%	
Potential for biodegradation	**Frequently**	**Barely**	**Almost always**	**Almost always**	
VINYL CHLORIDE					
Number of rates	27	4	5	15	7
Number of rates (recalcitrant)	0	0	0	0	0
Half-life (days)[a]	14	8	0.462	80	58
% Rates recalcitrant	0%	0%	0%	0%	0%
Potential for biodegradation[b]	**Almost always**	**Almost always**	**Almost always**	**Almost always**	**Almost always**

[a] Median value from the reported studies

[b] Quantitative estimation based on % occurrence of recalcitrance

NA Insufficient information

NC Not calculable (1–0)

Scale

% Recalcitrance	**Biodegradability**
< 10%	Almost always
10%-25%	Frequently
25%-50%	Sometimes
50%-75%	Barely
>75%	Almost never

median values). Among all anaerobic processes, toluene is the compound that biodegrades first, with the exception of sulfate reduction under which *m*-xylene has the greatest median decay coefficient.

- Overall, toluene exhibited very high potential for biodegradation with only 7% of 135 studies reporting recalcitrance, while benzene showed a low potential for anaerobic biodegradation with 38% of 117 studies reporting recalcitrance and a high potential under aerobic conditions with 8% of 26 studies reporting recalcitrance.
- The minimum-90th percentile ranges of first-order decay coefficients reported in literature for chlorinated solvents were 0 to 1.42 day^{-1} and 0 to 1.28 day^{-1} under aerobic and anaerobic conditions, respectively.
- The higher-chlorinated solvents biodegrade anaerobically with an average median rate constant of 0.033 day^{-1}, while the less-chlorinated solvents

biodegrade aerobically with an average median coefficient of 0.16 day^{-1}.

- Among the less-chlorinated solvents, the most readily biodegradable compound under both aerobic oxidation and cometabolism was vinyl chloride. On the other hand, TCA was the higher-chlorinated compound that exhibited the highest median decay constant for reductive dechlorination.
- The median reported degradation rate coefficients for chlorinated compounds varied up to two orders of magnitude, and they were lowest for DCA (0.07% per day) and highest for vinyl chloride (5.1% per day).
- Carbon tetrachloride, DCA, DCE, and vinyl chloride had very high potential of biodegradation with 0, 8, 5, and 0% of studies reporting recalcitrance, respectively. TCE showed a high potential of biodegradation with 14% of 85 studies reporting recalcitrance, whereas PCE and TCA evidenced moderate potential of biodegradation with 28 and 30% of recalcitrance, respectively.

The database presented in this paper illustrates the published biodegradation rate data in the general literature as of 1998 for BTEX and chlorinated hydrocarbons. This compilation provides reported ranges of zero-order, first-order and Michaelis-Menten kinetic coefficients for a total of 14 compounds. The data compilation also provides some insight into the patterns of biodegradation observed at the field- and laboratory-scales. The most straightforward use of the database is a comparative tool when one is interested in assessing how the derived biodecay rate from a site compares with values already reported in the literature. Others might use the information in this database, along with attenuation models (e.g., Bioscreen [Newell et al., 1996], Biochlor [Aziz et al., 1999], BIOPLUME III [Rifai et al., 1997], etc.), to estimate the range of behaviors expected at a specific site, prior to groundwater monitoring network design and data collection. It is not recommended that the results in this database be used with predictive models as an alternative to site-specific groundwater monitoring.

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