FINAL REPORT

Anaerobic Biodegradation of Organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies

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TABLE OF CONTENTS

LIST OF TABLES

1. INTRODUCTION

In 1988, the U.S. Environmental Protection Agency (EPA) promulgated a protocol for determining anaerobic biodegradation of compounds in groundwater [Toxic Substances Control Act (TSCA) final test rule of June 15, 1988; 53 Fed. Reg. 22300, 40 CFR section 795.54, "Anaerobic microbiological transformation rate data for chemicals in the subsurface environment"]. EPA has indicated that this standard protocol is the only acceptable methodology for the development of data to characterize environmental biodegradation rates of organic chemicals in groundwater. The data developed from this protocol are intended to provide an assessment of the general persistence in groundwater of the compound of interest. Such data are then acceptable for use in EPA's regulatory models (*e.g.*, EPA Composite Model for leachate migration with Transformation Products (EPACMTP)) that are used to evaluate exposure from chemical transport in groundwater. This protocol is extremely expensive to conduct since it requires aquifer samples from at least six sites with varying groundwater temperature and geochemistry and the biodegradation rate data are developed during a 64 week study period. The samples must be evaluated through use of specific field and laboratory procedures that are designed to maintain anaerobic conditions that are representative of field conditions.

In recent proposed rulemakings, including the Hazardous Waste Identification Rule (HWIR) Exit proposal (Fed. Reg. 60: 66344-66469), and past modeling efforts for other regulations (*e.g.*, the Toxicity Characteristic rule), the Agency has chosen to set biodegradation rate constants to zero for every constituent. However, biodegradation is the most important degradation process affecting the subsurface mass transport of most organic compounds. The Agency has stated that the use of zero rate constants is due to the uncertainty regarding the inherent anaerobic biodegradability and/or lack of sufficient data characterizing the rate constants for those compounds known to be biodegradable under anaerobic conditions (55 Fed. Reg. 11823-4). For most compounds, biodegradation will occur under both aerobic and anaerobic conditions. However, in promulgating the TSCA protocol, EPA has stated that it will only consider anaerobic data because 1) laboratory aerobic rates overestimate field aerobic rates; 2) many aquifers have only low concentrations of dissolved oxygen, or are anaerobic; and 3) anaerobic conditions will dominate in a contaminant plume because of rapid utilization of oxygen during the biodegradation process, and the slow rates at which oxygen can be replenished in groundwater.

The focus of this project has been to demonstrate that for a number of organic chemicals, there is sufficient laboratory and field data from a variety of studies to provide adequate characterization of the biodegradability of the chemicals under diverse groundwater environments. In the following, Syracuse Research Corporation (SRC) has reviewed the available anaerobic groundwater biodegradation literature for many common organic chemicals and identified biodegradation rate constants from these studies. SRC has then proposed an appropriate biodegradation rate constant range for each chemical which could be used in the EPACMTP model.

2. TECHNICAL APPROACH

2.1. Literature Search

Initially two lists were received from the API consortium, a primary list with 44 compounds and an alternative list with 33 compounds; from these two lists, SRC was asked to select 45 compounds which had available anaerobic biodegradation data. This was accomplished using the BIOLOG file of the Environmental Fate Data Base (EFDB) (Howard et al. 1986). A rapid search of BIOLOG was used to eliminate compounds in the first two lists that were not indexed under anaerobic studies. Secondly, compounds that were indexed in BIOLOG under "anaerobic" and "sewage" only (not groundwater studies) were removed, as were mixtures of compounds, such as PCB's, as biodegradation would need to be assessed for each individual compound in the mixture. As several compounds were then needed to complete the final list, the entire BIOLOG database was scanned and compounds with available groundwater biodegradation data were compiled into a list which was presented to the API consortium. The remainder of the compounds were agreed upon and a final list of 44 compounds was obtained (Table 1).

The literature compilation began with an electronic search of two files in SRC's EFDB, DATALOG and BIOLOG, as sources of extensive biodegradation information. Currently, there are nearly 288,000 catalogued records for 15,575 compounds in DATALOG and 56,000 records for 7491 compounds in BIOLOG. BIOLOG search terms were used to identify anaerobic studies that used a mixed population of microbes from soil, sediment, or water. DATALOG was searched for useful field, ecosystem, monitoring, and biodegradation studies. Relevant papers were retrieved and summarized in the database. In addition to the literature searches, the reference section of every retrieved paper was scanned in order to identify additional relevant articles. To be included in this database, the study was required: 1) to use aquifer material, groundwater, or leachate (preferably from an anaerobic site, if stated) and 2) to be incubated under anaerobic conditions. Studies where the aquifer material was seeded with microorganisms from other sources, *e.g.* sewage, pond sediment, and enrichment culture experiments were not included.

The database was constructed in PARADOX with fields for information about the site including location and type of site (*e.g.* spill site, industrial location, pristine site, landfill), the sampling protocol and method of analysis, the type of study (*e.g.* field, laboratory microcosm, *in situ* microcosm), whether the compound was present alone or found in the presence of others, pH, temperature, dissolved oxygen concentrations, redox conditions, initial and final concentrations of the compound, a published or calculated rate constant, length of the study, lag period, control results, general comments (to accommodate other important information) and an abbreviated reference from which the information was retrieved.

A stand-alone version of the biodegradation database was developed using the run-time version of Microsoft Access. This database application guides the user through the chemical selection process and results in the display of a summary study table. The complete set of data collected for this project can then be displayed for each record.

Table 1. Final List of Compounds

CAS Number	Chemical Name
000056-23-5	Carbon Tetrachloride
000064-19-7	Acetic Acid
000067-56-1	Methanol
000067-64-1	Acetone
000067-66-3	Chloroform
000071-43-2	Benzene
000071-55-6	1,1,1-Trichloroethane
000075-01-4	Vinyl Chloride
000075-09-2	Dichloromethane
000075-69-4	Trichlorofluoromethane
000075-71-8	Dichlorodifluoromethane
000076-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane
000078-93-3	Methyl Ethyl Ketone
000079-00-5	1,1,2-Trichloroethane
000079-01-6	Trichloroethylene
000079-34-5	1,1,2,2-Tetrachloroethane
000083-32-9	Acenaphthene
000085-01-8	Phenanthrene
000086-73-7	Fluorene
000087-86-5	Pentachlorophenol
000088-06-2	2,4,6-Trichlorophenol
000090-12-0	1-Methylnaphthalene
000091-20-3	Naphthalene
000092-52-4	1,1'-Biphenyl
000095-47-6	o-Xylene
000095-48-7	o-Cresol
000098-82-8	Cumene
000098-95-3	Nitrobenzene
000100-41-4	Ethylbenzene
000100-42-5	Styrene
000103-82-2	Phenylacetic Acid
000106-42-3	p-Xylene
000106-44-5	p-Cresol
000107-06-2	1,2-Dichloroethane
000108-10-1	Methyl Isobutyl Ketone
000108-38-3	m-Xylene
000108-39-4	m-Cresol
000108-67-8	1,3,5-Trimethylbenzene
000108-88-3	Toluene
000108-95-2	Phenol
000110-86-1	Pyridine
000120-83-2	2,4-Dichlorophenol
000123-91-1	Dioxane
000127-18-4	Tetrachloroethylene

2.2. Definition and Use of Biodegradation Rate Constants

Over time, a compound will biodegrade at a particular rate and the biodegradation kinetics will be dependent on the environmental conditions and the availability and concentration of the substrate. The Monod equation was developed to describe the growth of a population of microbes in the presence of a carbon source. At low concentrations of substrate, the microbial population is small. With increasing substrate concentrations the microbial population grows until a maximum growth rate is reached. This is mathematically described by:

$$\mu = \frac{\mu_{max} S}{K_s + S} \quad \textbf{(1)}$$

where μ=growth rate of the microbe, S=substrate concentration, μ_{max}=maximum growth rate of the microbe, and K_s=a constant defined as the value of S at which $\mu=0.5\mu_{max}$. The Monod equation is best used when the microbial population is growing in size in relation to the substrate concentration (Alexander 1994).

Both first and zero-order rate constants are calculated when little to no increase in microbial cell numbers is seen (Schmidt et al. 1985). This will occur where the cell density is high compared to the substrate concentration. In this case, biodegradation kinetics are better represented by the classic Michaelis-Menton equation for enzyme kinetics as it is assumed that the reaction rate of the individual cells and not the microbial population is increasing in relation to increasing substrate concentrations:

$$v = \frac{V_{max} S}{K_m + S} \quad \textbf{(2)}$$

where v=reaction rate (μ in the Monod equation), V_{max}=maximum reaction rate (μ_{max} in the Monod equation), and K_m is the Michaelis constant (K_s in the Monod equation) (Alexander 1994).

2.2.1. Zero-Order Rate Constants

A zero-order rate constant is calculated when the substrate concentration is much greater than K_m so that as the substrate is biodegraded, the rate of biodegradation is not affected, *i.e.* loss is independent of substrate concentration. The rate of a zero-order reaction is linear (a constant amount of the substrate is lost per unit of time) and is represented by the differential:

$$\frac{dS}{dt} = k_0 \quad \textbf{(3)}$$

and the integral:

$$k_0 = \frac{S_0 - S}{t} \quad \textbf{(4)}$$

where S_0=initial substrate concentration, S=substrate concentration at time=t, and k_0=the zero-order rate constant (expressed as concentration/time, *e.g*. µg/L/day). In the biodegradation database, zero-order rate constants are reported only where the author has determined this value; in general, most authors reported first-order rate constants. If a rate constant was not reported and a value could be determined from the presented experimental data, SRC assumed first-order rate kinetics. A more accurate but time consuming approach would have been to plot the substrate concentration versus time. A straight line would signify zero-order kinetics and an exponential curve (or a straight line on a log linear paper) would indicate first-order kinetics. Priority was given to the determination of a first-order rate constant as the EPACMTP model, used to determine the fate of these compounds in an aquifer environment, requires the input of a first-order rate constant. This may not be strictly correct in all situations, such as when the substrate is present at high concentrations (above K_s), when substrate concentrations are toxic to the microbial population, when another substrate(s) is limiting the biodegradation rate or when the microbial population is significantly increasing or decreasing in size (Chapelle FH et al. 1996). First-order rate constants are, however, commonly used to describe kinetics in natural systems often because of the lack of sufficient data points and the ease with which these values can be calculated.

2.2.2. First-Order Rate Constants

First-order rate constants are used as a convenient approximation of the kinetics of degradation of test substrates where there is no growth of the microbial population and a low concentration of the test substrate is present. Under these circumstances, the substrate concentration is lower than K_m and, over time, both the concentration of substrate and rate of degradation drop in proportion with each other. Thus, unlike zero-order kinetics, the rate of biodegradation in a first-order reaction is dependent on the substrate concentration and is represented by the differential:

$$\frac{dS}{dt} = k_1 S \quad \textbf{(5)}$$

and the integral:

$$k_1 = \frac{\ln \frac{S_0}{S}}{t} \quad \textbf{(6)}$$

where S_0=initial substrate concentration, S=substrate concentration at time=t, and k_1=the first-order rate constant. During first-order rate reactions, the loss of substrate is exponential and follows a logarithmic curve. Buscheck et al. (1993) states that first-order rate constants are generally appropriate for soluble plumes where a contaminant concentration of less than 1000 Og/L is present.

The rate constant is used to correlate the rate of the reaction with time. In a first-order reaction, a constant percent of the substrate is lost with time and the rate is described by either percent per time or the half-life. The half-life is easily visualized and is more commonly used. In contrast, a zero-order rate constant by definition equals the rate and is given in units of concentration/time. This is because the rate is linear and loss is constant with time.

The objective of this project was to obtain first-order rate constants for the biodegradation of selected organic compounds under anaerobic groundwater environments. The EPACMTP model requires a first-order rate constant as input data. When first-order rates (half-lives, %/day) were reported in a study, they were converted to first-order rate constants. Several papers summarized in the database reported zero-order rate constants; converting these to first-order rate constants required 1) evidence that the reaction was concentration dependent and 2) data showing substrate loss versus time. This information was often not available. Zero-order rate constants were generally not converted during this project with a few exceptions [for example, papers by Hutchins and Wilson (1991) and Wilson WG et al. (1986)]. In these papers, figures were presented showing substrate loss with time; in the database, the published zero-order rate constant is reported in the database field "rate constant" and a calculated first-order rate constant is reported in the database "comments" field. The conversion of a zero-order rate constant to a first-order rate constant would result in a bias toward a faster predicted rate. Loss of substrate in the early portion of an experiment with a first-order rate is very rapid (exponential loss) followed by a long period of time with very little loss. In a zero-order rate, loss of substrate is proportional to time.

In one major exception, the zero-order rate constants reported for the ketones were used to estimate first-order rate constant for input into the EPA model. This is the only case where zero-order rate constants were actually used to determine a recommended biodegradation rate constant; this was done because 1) the best available data were zero-order and 2) both acetone and methyl ethyl ketone were known to readily biodegrade. But in determining a recommended range of rate constants, it was noted that this conversion generally results in a half-life that is considerably less than expected and that this does not provide a conservative value.

Biodegradation rate constants less than $1x10^{-4}$/day (a half-life of about 19 years) were not reported in the literature. This may be because the variation between experimental and control results in this case may be so small that no difference can be statistically determined and a rate value can not be established. Wiedemeier et al. (1996B) states that optimally run laboratory microcosm studies, run over an 18 month period, can resolve biotic and abiotic losses with a rate detection limit of 0.001-0.0005/day.

2.3. Calculation of First-Order Rate Constants

Rate constants were collected from eight types of groundwater study: batch reactor, batch reactor with a groundwater inoculum, column studies, field studies, groundwater grab sample, groundwater inoculum, *in situ* microcosm and laboratory microcosm studies; most summarized studies were either field or laboratory microcosm studies. The information obtained from these studies ranged from published first-order rate constants to simply an indication or contraindication of biodegradation. In some cases, insufficient data were available to assess whether biodegradation had occurred; for these studies the rate constant field was left blank. When published first-order rate constants were not available but sufficient information was presented to calculate a value, the rate constant was calculated by SRC. To ensure that loss of a contaminant was due to biodegradation and not just to abiotic or transport processes, an appropriate control was necessary to correct the data set. This can be a problem in laboratory studies which are incubated for a long period of time. Mercuric chloride is known to adsorb to the clay component of the aquifer sediment reducing its efficacy whereas sodium azide only inhibits bacteria containing cytochromes (often not effective for strict anaerobes) (Wiedemeier et al. 1996B). In addition, autoclaving may not be totally suitable, probably due to incomplete sterilization (Dobbins et al. 1992).

2.3.1. Laboratory Studies

A control was used in laboratory studies to correct for non-biodegradation processes such as sorption to sediment or the glass jar, headspace volatilization, etc. Data from laboratory studies (batch reactor, batch reactor with a groundwater inoculum, column, groundwater grab sample, groundwater inoculum, and laboratory microcosm studies) were obtained from graphs or tables giving concentrations of the compound of interest at specific timepoints. Often lag periods were seen which is usually attributed to the need for acclimation (Alexander 1994). The initial microbial species present, their relative numbers, metabolic state and ability to acclimate once exposed to a chemical are likely to vary considerably depending upon environmental parameters such as temperature, conductivity, pH, oxygen concentration, redox potential, concentration, the presence/absence of electron acceptors and donors, and effects, both synergistic and antagonistic, of associated microflora (Howard & Banerjee 1984).

Lag periods were established either from the discussion in the paper or from looking at the data and an appropriate inital and final concentration was chosen. The value used for the initial concentration was the concentration present following the lag period; therefore, all rate calculations calculated for this project are independent of the associated lag period. Where a value of "0 Og/L" was reached as a final timepoint, an earlier time was chosen for the kinetics calculation; the use of zero as a denominator in the first-order rate equation would result in an "infinite" value. If the concentration reached zero by the first timepoint, then calculation of an accurate rate constant was not possible; however, a "greater than" value could be estimated. If the concentration reached a value other than zero but leveled off at that point for the remainder of the experiment, the final concentration and time were chosen at the point where the concentration leveled off. In column studies, the time field in the database contains the retention time for the column, which is the value (O t) used to calculate the rate constant; column experiments were usually run for long periods of time, often over 100 days, which would allow for the development of an acclimated microbial population.

The initial and final concentrations of the control within the chosen time period were obtained and the experimental data corrected for the loss shown by the control using the following equation:

$$C_{f,corr} = C_f \frac{Z_i}{Z_f} \quad \textbf{(7)}$$

where: $C_{f,corr}$=corrected final concentration of the contaminant (corrected for non-biodegradation loss
C_f=final contaminant concentration, uncorrected
Z_i=initial control concentration
Z_f=final control concentration.

A first-order rate constant was then calculated for laboratory data using the corrected final contaminant concentration as follows:

$$k_1 = \frac{\ln \frac{C_i}{C_{f,corr}}}{\Delta t} \quad \textbf{(8)}$$

where: C_i=initial contaminant concentration
$C_{f,corr}$=corrected final concentration of the contaminant (corrected for non-biodegradation loss)
Ot=time interval
k_1=first-order rate constant

2.3.2. Field and *in situ* Microcosm Studies

In situ microcosms were designed to isolate a portion of the aquifer in order to make measurements directly in the field. This device is essentially a pipe divided into a test chamber and an equipment chamber, with two screens that permit water to be pumped both into and out of the interior of the pipe. More detailed information can be found in Gillham et al. (1990). Groundwater is pumped to the surface, spiked with the compounds of interest plus other nutrients and/or electron acceptors if wanted and then reinjected. Because the test zone is isolated from the main aquifer, advective and dispersive processes are not important to the study results. Often this method is used to give very specific results for a particular redox regime within an aquifer, particularly in a leachate plume where redox conditions can rapidly change (Nielsen et al. 1995A). The data obtained from this type of study was similar to

that for a laboratory microcosm where loss of substrate is monitored with time; rate constants were calculated using the same method as for the laboratory studies.

Data from field studies were generally reported for 1) plume studies where monitoring wells were placed along the centerline of a contaminant plume or for 2) continuous injection experiments where monitoring wells were placed in fences along the flow path fairly close to the injection point (often 2 and 5 meters away). Loss of a contaminant does not necessarily indicate that the compound has undergone biodegradation. Significant loss in concentration along a flow path is often reported for compounds simply due to non-biological processes such as advection, dispersion, sorption, and dilution. However, degradation is the only mechanism which leads to an actual loss of the contaminant.

The effect of dispersion and sorption during an injection experiment is to both flatten and spread the curve of time versus substrate concentration. In these experiments, the substrate concentration may "initially increase as if only dispersion were acting; however, with time, and as the microbial population adapts, this concentration may decrease to a lower, steady-state concentration based on the kinetics of biodegradation for that compound" (Roberts et al. 1980). In some cases, such as for toluene (Barbaro et al. 1993), the contaminant may be readily biodegraded, particularly by an adapted population, and no breakthrough of the compound is seen.

The most convenient way to correct for such non-biodegradation processes in both plume and injection studies is to use compounds present in the contaminant plume or injection mixture that are 1) biologically recalcitrant and 2) have similar properties, such as Henry's Law constant and soil sorption coefficient, as the contaminant of interest (Wiedemeier et al. 1996B). Compounds such as dimethylpentane (Wilson JT et al. 1994B), the trimethylbenzene isomers (Wiedemeier et al. 1995A, 1996A), and tetramethylbenzene (Cozzarelli et al. 1990) have been used as conservative tracers to correct for non-biodegradation loss. Difficulties with this approach can occur, particularly when the compound used as the tracer is also biodegraded to some extent. This is seen with the trimethylbenzenes which are recalcitrant under anaerobic conditions but readily degrade in an aerobic environment. If some biodegradation of the tracer does occur, the estimated rate constant however, will be less than the actual value, *i.e.* it will be a conservative value. Some studies use either chloride or bromide ion as a tracer and this can be appropriate in many circumstances. When the contaminant plume contains chlorinated compounds, reductive dechlorination may result in increased chlorine concentrations along the flow path; in this case it would be necessary to conduct a mass balance of the chlorinated compounds and chlorine along the flow path to determine the proper correction factor for loss of the compound of interest.

The method of obtaining a normalized data set from field data was taken from Wiedemeier et al. (1996B). "Measured tracer and contaminant concentrations from a minimum of two points along a flow path can be used to estimate the amount of contaminant remaining at each point if biodegradation had been the only attenuation process using the following equation:

$$C_{i,corr} = C_{i-1,corr} \frac{C_i}{C_{i-1}} \frac{T_{i-1}}{T_i} \quad \textbf{(9)}$$

where: $C_{i,corr}$=corrected contaminant concentration at point i (downgradient site)
$C_{i-1,corr}$=corrected contaminant concentration at point i-1 (upgradient site; if this is the most upgradient point then this value is equivalent to the observed contaminant concentration)
C_i=observed contaminant concentration at point i
C_{i-1}=observed contaminant concentraiton at point i-1
T_i=observed tracer concentration at point i
T_{i-1}=observed tracer concentration at point i-1

If one is estimating the biodegradation rate between only two points (A and B), then this equation simplifies to:

$$C_{B,corr} = C_B \frac{T_A}{T_B} \quad \textbf{(10)}$$

where: $C_{B,corr}$=corrected contaminant concentration at downgradient point B
C_B=observed contaminant concentration at downgradient point B
T_A=observed tracer concentration at upgradient point A
T_B=observed tracer concentration at downgradient point B."

Once a normalized/corrected data set is obtained then calculation of the first-order rate constant from field data can be completed using the first-order rate equation:

$$k_1 = \frac{\ln \frac{C_A}{C_{B,corr}}}{\Delta t} \quad \textbf{(11)}$$

where: C_A=observed contaminant concentration at upgradient point A
Ot=time interval
k_1=first-order rate constant.

In a field study, the time (Ot) required for groundwater to move from one well to the next along a flow path can be estimated by dividing the distance between the wells by the flow velocity. When a flow

velocity was not available but the hydraulic conductivity (K), hydraulic gradient (i) and effective porosity (O) were, an estimated seepage velocity (*V*) was calculated using the following equation (Wiedemeier et al. 1996B):

$$V = \frac{(K)(i)}{\phi} \qquad \textbf{(12)}$$

Some papers reported a retarded flow velocity for the contaminant, particularly when the conservative tracer was chloride or bromide ion. This occurs when the contaminant has a greater affinity to the aquifer matrix than the conservative tracer (a greater soil sorption or Koc value). For the purposes of this database, unless the authors reported a retarded flow velocity for a particular compound, we assumed that the aquifer contained low concentrations of organic carbon and that sorption was not important. According to Wiedemeier et al. (1996B) this assumption should be valid for f_{oc} values less than 0.001 (f_{oc} is the fraction of solid organic carbon in the aquifer sediment).

Wiedemeier et al. (1996) compared two methods for the approximation of biodegradation rate constants of BTEX under field conditions. The first approach was summarized above and requires the use of a conservative tracer and the calculation of a normalized data set. The second method makes the assumption that the contaminant plume has reached dynamic steady-state equilibrium so that contaminants within the plume are both attenuated and produced (from the source area) at the same rate. Buscheck and Alcantar (1995) use a one-dimensional analytical solution to determine the first-order kinetics of biodegradation under steady-state conditions.

$$\lambda = \frac{v_c}{4\alpha_x}\left(\left[1 + 2\alpha_x \frac{k}{v_x}\right]^2 - 1\right) \qquad \textbf{(13)}$$

where: O=first-order biological decay rate
O=retarded contaminant velocity in the x-direction
O_x=dispersivity
k/O_x=slope of line formed by making a log-linear plot of contaminant concentration versus distance downgradient along the flow path.

In the study by Wiedemeier et al. (1996), both methods gave comparable rate constants for the BTEX compounds. SRC did not calculate rate constants using the Buscheck and Alcantar method.

A mass balance approach was used by some researchers to determine the rate of biodegradation of specific contaminants in groundwater during a field study. Mass flux of the studied contaminant through a line/cluster of wells (a transect) is used instead of monitoring loss of the contaminant at specific points down the middle of a plume, as is typical for a plume centerline study. The mass flux method is thought

to remove the “effects of vertical and transverse dispersion and nonideal well placement” (Borden et al. 1997). In addition, the use of a conservative tracer is not necessary. However, this method requires that the mass flux of the studied compound is stabilized in the groundwater system before a rate constant can be determined. Wiedemeier et al. (1996B), suggests that the calculations involved are approximate and that often many of the required parameters necessary for the modeling are not available.

3. RESULTS

In this section, each compound is reviewed with an individual summary table listing all summarized studies and if sufficient data were available, a second table with information from just the field and *in situ* microcosm studies. Included in each review, whenever possible, is a recommended range of first-order rate constants or a specific first-order rate constant that could be used for input into the EPACMTP model.

3.1. BTEX Compounds

Eight types of groundwater study were recognized in this search: batch reactor, batch reactor with a groundwater inoculum, column studies, field studies, groundwater grab sample, groundwater inoculum, *in situ* microcosm and laboratory microcosm studies. As stated earlier, most summarized experiments were either field or laboratory microcosm studies and the information obtained from these studies ranged from published first-order rate constants to simply an indication or contraindication of biodegradation. Compounds such as the BTEX mixture (Benzene, Toluene, Ethylbenzene, o-, m-, and p-Xylene) had information on biodegradation from many different site locations and incubation conditions. For these compounds, sufficient rate constant data were present in the literature so that comparisons of 1) field versus laboratory study values, and 2) values under various redox conditions could be made.

A comparison of both range (dispersion) and mean (central tendency) values was made between 1) laboratory and 2) field/*in situ* microcosm studies, to determine whether significant differences existed for the collected biodegradation rates (Table 2). Laboratory microcosm studies are believed to give very good evidence of biodegradation at a specific site. They are the only way to obtain an "absolute mass balance" on a contaminant and in some cases, microcosm rate constant values should be used over field-determined values (in special site-specific cases where groundwater flow direction is shown to vary often with time) (Wilson BH et al. 1996). In addition, the formation and measurement of metabolites can definitively show the biodegradation of the contaminant of interest. However, results from a laboratory microcosm can be greatly influenced by many factors such as the source, collection, and condition of the aquifer material and groundwater (*e.g.* what is a representative source of material for that site?), the ratio of sediment to groundwater used in the microcosm, the type of sampling (repetitive or sacrificed), incubation conditions (*e.g.* substrate concentration, temperature), and the length of the study period (and its effect particularly on the initial microbial population during a long study period) (Wiedemeier et al. 1996B). The mixing of a natural sample during its collection or the construction of a microcosm may result in a "disturbance artifact" which can be seen as either an increase (Davis and Olsen 1990) or a decrease (Weiner and Lovley, in press) in the microbial activity of the sample. The influence of transport processes also cannot be accounted for in a microcosm experiment. Alternatively, field studies provide environmentally relevant data for a specific site, essentially showing whether the compound of interest can or cannot be biodegraded at that location. Rate constants from field studies are felt to have the greatest weight for modeling purposes (Wiedemeier et al. 1996B) thus for the BTEX compounds, values have been recommended solely from field-scale (field and *in situ* microcosm) studies.

When mean first-order rate constant values from field/*in situ* microcosm versus laboratory studies were compared for the BTEX compounds the differences were surprisingly small (Table 2). In all cases, except for o-xylene, the mean value for laboratory studies was higher. The same mean rate constant was measured for o-xylene for both types of study. It is generally recognized that laboratory microcosm studies will often measure higher rates of biodegradation than field type studies (Wiedemeier et al. 1996B). Mean laboratory rate values for toluene, ethylbenzene, o-xylene and m-xylene were adjusted to reduce the influence of a handful of studies which reported rate constants much higher than the remainder of the summarized studies for that compound. Patterson et al. (1993) presents data for a column study with rates for the BTEX compounds that are 10 to 100 times greater than any other published study. Several studies by Hutchins report very high rate constants but only when the contaminant is present by itself; the addition of other carbon compounds to the microcosm always results in a lower rate constant value (Hutchins 1991A; Hutchins et al. 1991; Hutchins 1993; Hutchins 1997). Removing these high values resulted in the mean laboratory rate constants reported in Table 2. In general, with the exception of ethylbenzene and p-xylene, the data set for the BTEX compounds appeared to give a one to two-fold higher rate constant under laboratory conditions than in an actual aquifer environment.

Range and mean values were determined for all summarized studies for each BTEX compound under different terminal electron-accepting processes and these values were compared (Table 2). It is believed that site-specific differences in biodegradation rates are due to the presence of microbial communities defined by the dominant electron acceptor present at that location and time (Wiedemeier et al. 1995A; Dobbins et al. 1992). Microbial electron-accepting processes include oxygen reduction (aerobic respiration), nitrate reduction, Mn(IV) reduction, Fe(III) reduction, sulfate reduction, and methanogenesis; each process is believed to be facilitated by a different set of microbes, *e.g.* methanogens and sulfate reducers. Following a spill of BTEX and the resulting contamination of a shallow aquifer underlying the spill zone, a large amount of organic carbon will be present and therefore, the plume area will not be electron-donor limited. Microbial metabolism is then limited by the electron acceptors available. Dissolved oxygen is usually the preferred electron acceptor for the degradation of organic compounds by microbes as it often provides the greatest energy yield (Wiedemeier et al. 1995A). Often, aerobic conditions are initially found in aquifer systems. However, many spills result in a plume of contamination where dissolved oxygen is rapidly depleted due to aerobic respiration; once the dissolved oxygen concentration has dropped sufficiently (to 0.5-1 mg/L), anaerobic bacteria are able to function (Lovley 1997). Nitrate is often found in aquifers impacted by anthropogenic sources and is the next most preferred electron acceptor. Once nitrate is depleted, manganese(IV), iron(III), and sulfate are often sequentially used; these are generally naturally abundant in many aquifers. CO_2 becomes the terminal acceptor in the most reducing environments, producing methane during the process of methanogenesis (Smith 1997). It should be emphasized that within an aquifer, even along a single flow path in an aquifer, the terminal electron-accepting process can vary with time and location resulting in several different redox conditions for a single field study.

Redox analysis of the BTEX data was completed. Sites/studies with multiple redox classifications were not included in the analysis. Many studies (up to one quarter) were excluded because several redox conditions were present; these were mainly field studies, because redox conditions often changed along a flow path. In addition, the size of the data sets for each terminal electron accepting process was different and multiple studies by the same laboratory or at the same site may have had a weighting effect on the data set. Nitrate-reducing conditions did not necessarily provide the highest rate constants for the BTEX compounds. Often sulfate-reducing environments had similar, if not greater, mean first-order rate constant values, such as for benzene, o-xylene and p-xylene (Table 2). If high rate constant values for m-xylene under nitrate-reducing conditions are removed (Patterson et al. 1993), its mean value also becomes much closer to those measured under sulfate-reducing conditions (0.070 vs 0.091/day, respectively). The rate constant values reported for sulfate-reducing environments were generally measured for aquifer material from four to five sites whereas numerous sites and types of studies are reported for nitrate-reducing environments. Thus the similarity of rate constants from the two redox regimes may reflect the limited number of sampling sites for the sulfate-reducing conditions. A limited number of sampling sites may also explain why iron-reducing conditions were shown to be the least favorable for the biodegradation of the BTEX compounds; here, rate constants were lower than those reported for methanogenic environments. Only two sites were classified solely as iron-reducing, Tibbetts Road, NH and Rocky Point, NC, and a comparison with other non-iron-reducing sites shows these two locations to have relatively low rates of biodegradation for all the BTEX compounds.

Therefore it was felt that because of the above concerns, recommended rate constants could not be determined for specific redox conditions for the BTEX compounds. However, this comparison did highlight one very important aspect which is frequently alluded to in the literature; biodegradation rates tend to be site-specific. Thus, some sites have greater measured biodegradation potential than others, *e.g.* the Tibbetts Road site has lower measured biodegradation rates than the Seal Beach or Hill AFB sites for all BTEX compounds. A large study using sediment samples collected from three different aquifers in the United States showed that biodegradation rates varied both within and among aquifer locations with variation measured at up to two orders of magnitude for one compound at a single site (Dobbins et al. 1992). Because of this site specificity and because sufficient information was available, a range of first-order biodegradation rate constant values were given for each BTEX compound. The lower value in this range represents the lowest reported and "reasonable" rate constant and the upper value was the mean value for all field/*in situ* microcosm studies.

Table 2. Summary Table of First-Order Anaerobic Biodegradation Rate Constants for the BTEX Compounds

Study Type	Benzene	Toluene	Ethylbenzene	o-Xylene	m-Xylene	p-Xylene
Range, all studies	0-0.071[ab]	0-5.18	0-6.5	0-0.68	0-1.7	0-0.24
Mean, all studies	0.0046 n=113	0.37 n=150	0.13 n=94	0.030 n=93	0.068 n=86	0.031 n=55
Mean, laboratory studies	0.0059 n=66	0.12 n=64	0.059 n=44	0.024 n=49	0.062 n=41	0.043 n=26
Range, field/*in situ* studies	0-0.038	0-0.30	0-0.15	0-0.21	0-0.32	0-0.057
Mean, field/*in situ* studies	0.0036 n=41	0.059 n=46	0.015 n=37	0.025[c] n=33	0.039[c] n=34	0.014[c] n=26
Range, NO3-reducing studies	0-0.045	0-5.18	0-6.5	0-0.68	0-1.7	0-0.24
Mean, NO3-reducing studies	0.0023 n=38	0.63 n=42	0.28 n=34	0.040 n=38	0.12 n=35	0.047 n=18
Range, Fe-reducing studies	0-0.024	0-0.087	0-0.0032	0-0.056	0-0.02	0-0.02
Mean, Fe-reducing studies	0.0035 n=11	0.021 n=10	0.0011 n=8	0.0078 n=8	0.0052 n=8	0.0050 n=8
Range, SO4-reducing studies	0-0.047	0.011-0.11	0-0.029	0-0.16	0.024-0.17	0.032-0.17
Mean, SO4-reducing studies	0.016 n=9	0.049 n=9	0.0098 n=7	0.065 n=5	0.091 n=4	0.079 n=3
Range, methanogenic studies	0-0.052	0-0.186	0-0.46	0-0.21	0-0.10	0-0.08
Mean, methanogenic studies	0.005 n=16	0.029 n=22	0.05 n=14	0.021 n=11	0.021 n=8	0.015 n=7

[a]First-order rate constants in units of $days^{-1}$

[b]Studies reporting "biodegrades" or zero-order rate constants were assigned a value equal to the mean of the positive rate constant values.

[c]When only the papers in common for the 3 xylenes were examined, the mean field/*in situ* microcosm rate constant values for the xylenes were as follows: o-xylene=0.021/day, m-xylene=0.016/day, and p-xylene=0.015/day (calculated for the field and *in situ* microcosm studies only).

3.1.1. Benzene

Benzene is regarded as recalcitrant under strictly anaerobic conditions (Colberg & Young 1995). Its symmetrical ring structure is believed to be resistant to cleavage as functional groups, which act to disrupt the electron symmetry of ring structures, are not present (Gibson & Subramanian 1984). Under aerobic conditions, benzene is readily biodegraded; bacteria are able to attack the ring using oxygen, forming catechol as a product (Colberg & Young 1995). However, in the last decade, anaerobic biodegradation of benzene in both laboratory and field studies of aquifers has been reported (Table 2). First-order rate constants located during the literature search for field and *in situ* microcosm studies alone (Table 4) ranged from 0 to 0.038/day with a mean value of 0.0036/day. However, the majority of the published studies show that benzene is not anaerobically biodegraded (Table 3).

The number of authors reporting the anaerobic biodegradation of this compound in field sites was surprising. Measured rate constants were obtained for benzene from Rocky Point, NC (Rifai 1995), Tibbetts Road, Barrington, NH (Wilson BH et al. 1996), Sleeping Bear Dunes National Lakeshore, MI (Wilson JT et al. 1994B), Traverse City, MI (Wilson BH et al. 1990), Hill AFB, UT (Wiedemeier et al. 1996; Dupont et al. 1994), Patrick AFB, FL (Wiedemeier et al. 1995), Sampson County, NC (Borden et al. 1997) and Bemidji, MN (Cozzarelli et al. 1990) sites. However, as benzene is rapidly degraded in the presence of oxygen, it is possible that these rate constants reflect aerobic biodegradation along the flow path. Dissolved oxygen concentrations are often greater along plume boundaries and aerobic microsites may be present within the aquifer matrix.

A closer look at the numerous anaerobic laboratory studies, where oxygen conditions can be strictly controlled, shows that biodegradation of benzene has also been reported under laboratory conditions using aquifer material from Rocky Point, NC (Barlaz et al. 1995), the Tibbetts Road site, Barrington, NH (Wilson BH et al. 1996), Sleeping Bear Dunes National Park (Kazumi et al. 1997), Traverse City, MI (Hutchins 1992; Wilson BH et al. 1990), CFB Borden, Ontario (Major et al. 1988), Seal Beach, CA (Kazumi et al. 1997; Edwards & Grbic-Galic 1992), Norman, OK (Wilson BH et al. 1986), and Bemidji, MN (Baedecker et al. 1993). In some cases, the authors added nutrients or electron acceptors to the laboratory microcosm in an attempt to encourage biodegradation. A recent laboratory study by Kazumi et al. (1997), using radiolabeled benzene as a sole carbon source, shows that benzene was biodegraded to $^{14}CO_2$ with measured rate constants of 0 to 0.0048/day by aquifer microorganisms under methanogenic and sulfate-reducing conditions. These experiments ran for 320-520 days, suggesting that biodegradation of benzene under anaerobic conditions might occur if the incubation period is sufficiently long. In the same study, labeled benzene, present as the sole carbon source, was not biodegraded in aquifer sediment collected from a landfill site after three years of incubation. Thus, while long incubation periods may be necessary to show biodegradation activity in aquifer sediment collected from some locations, some sites may simply not be able to measurably biodegrade benzene. Edwards and Grbic-Galic (1994), using radiolabeled benzene as a sole carbon source, report biodegradation to $^{14}CO_2$ in laboratory microcosm studies (lag times of 30-100 days). Two other laboratory studies using radiolabeled benzene as a sole carbon source reported no biodegradation of benzene after 36 (Chapelle et al. 1996) and 14 (Kemblowski et al. 1987) day incubation periods.

Chapelle et al. (1996) intentionally allowed his study to run for this period of time in order to preserve the microbial population as it might be found in the undisturbed aquifer; incubating a microcosm for hundreds of days often will select for different microbial consortia that might not be as active in the natural environment. Lovley (1997) suggests that laboratory studies showing degradation after long lag periods, as is often the case for the benzene studies, are not generally felt to be a good indicator of *in situ* biodegradability. Conversely, as stated above, Kazumi et al. (1997) reports that "long incubation times may be necessary to show that biodegradation is evident" in laboratory microcosm studies.

Anaerobic biodegradation of benzene in laboratory microcosms is most often reported when benzene is present as the sole carbon source. This suggests that biodegradation of benzene in BTEX contaminated sediments may be inhibited during the consumption of the other "favored" TEX compounds by the indigenous microbial population (Krumholz et al. 1996). It is hypothesized that once the other hydrocarbons in a contaminant plume have been removed that anaerobic benzene biodegradation may occur in the field. However, without substantiating field evidence it is difficult at this time to predict the behavior of benzene under these circumstances. Other authors have demonstrated that after the majority of the other contaminants are biodegraded, oxygen levels can increase in the groundwater leading to aerobic biodegradation of benzene at the plume periphery (Wiedemeier et al. (1995A).

While the field studies above are highlighted because anaerobic biodegradation of benzene was shown for these locations, the field/*in situ* microcosm data indicates that benzene was not biodegraded at many sites (Table 4). Evidence supporting the biodegradation of benzene was reported at seven different sites; no biodegradation of benzene was reported for nine other sites with two sites, Sleeping Bear Dunes National Park, MI and Patrick Air Force Base, FL, (these two sites were not included in the tally of positive/negative sites) showing both biodegradation and no biodegradation of benzene depending on the study and/or the flowpath segment studied. Studies reporting no biodegradation of benzene were examined in further detail. Many of the field/*in situ* studies reporting biodegradation are for 1) plume studies and 2) studies with fairly long reported residence times. Most of these studies have also been published within the last five years. This reflects a growing feeling that biodegradation of benzene may occur under anaerobic conditions in groundwater; however, this degradation may occur over much longer time periods than that for the remaining TEX compounds. The authors of the two plume studies which report no biodegradation of benzene qualify their results by suggesting in both cases that a short residence time at that particular site (Sleeping Bear Dunes, MI and Eglin AFB, FL) did not allow for benzene biodegradation (Wilson,JT et al. 1994B; Wilson,JT et al. 1994A).

In addition, many of the field studies reporting no anaerobic biodegradation are for injection experiments. Some of these studies were run for long periods of time; however, instead of measuring the loss of benzene along a flow path hundreds of meters long, as seen in some plume studies, loss is measured at two to up to seventeen meters (in the available studies) along the flow path from the injection point to piezometer fences or monitoring wells. This results in fairly short residence times although the actual study/injection period may be over a year in length (Barbaro et al. 1992). In some

of the longer studies, the microbial population is expected to become acclimated to benzene, possibly resulting in increased biodegradation rates; however, this was not shown by the published data. Two injection experiments used labeled benzene. Thierrin et al. (1995) reported that deuterated benzene was not anaerobically biodegraded over a 17 meter distance (91 days). Rugge et al. (1995), using ^{14}C radiolabel, was unable to show anaerobic biodegradation of benzene over a 6 month study period with monitoring at 2 meters.

Although the data suggest that short residence times in the field may not show anaerobic biodegradation of benzene whereas longer residence times might, based on this data set, it would be speculative to say that biodegradation would have occurred if only the compound had been in contact with the aquifer for a longer period of time. While this may be true for some sites, it is not possible at this time to make this statement for all the studies showing a negative result.

Degradation of benzene in "real-world" groundwater environments is, however, often reported; synoptic reviews of hundreds of gasoline release sites in two states show that over 90% of the benzene plumes studied decreased to less than 5 ppb at a distance of less than 260 feet from the source in California (Mace et al. 1997) and that 90% of the benzene plumes decreased to less than 10 ppb in less than 380 feet from the source in Texas (Rice et al. 1995). These sites are almost always shallow groundwater sites and the biodegradation seen is likely due to aerobic biodegradation of benzene at the plume periphery. Oxygen concentrations were available for only 41 of 271 sites in California with a median value of 3.8 mg/L dissolved oxygen. Oxygen concentrations were compiled but not discussed by the Texas report. The authors of these studies have also provided degradation rate distributions for these plume populations with the study in Texas reporting a median decline rate of 0.002/day. The California study reported a median of 0.0008/day, with 10 and 90% quartiles of 0.002 to 0.0004/day (negative trend analysis of changes in the log of average site benzene concentrations with time), and 0.0004/day, with 10 and 90% quartiles of 0.0003 to 0.0016/day (positive trend analysis of changes in the log of average site benzene concentrations with time) for 271 sites. Biodegradation of a contaminant plume is probably best seen as a combination of aerobic biodegradation at the periphery and anaerobic biodegradation within the plume (Wiedemeier et al. 1995A). While it is beyond the scope of this literature review, it should be emphasized that benzene readily biodegrades under aerobic conditions and this may play an important role in limiting the mass transport of dissolved benzene in many groundwater cases.

Conditions such as temperature and redox environment did not appear to be correlated to the anaerobic biodegradation of benzene in aquifer environments. Mean first-order rate constant values for nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic studies are 0.0023/day, 0.0035/day, 0.016/day, and 0.0050/day, respectively. These numbers are reported for studies where only a single redox condition was present. Many field studies reported multiple redox conditions along a single flow path and thus, are not included in this redox analysis. Field and *in situ* microcosm studies by Reinhard et al. (1996), Barbaro et al. (1992), Acton and Barker (1992), and Hilton et al. (1992) attempted to enhance biodegradation rates by the addition of nitrate with the injection mixture. Some

authors have shown that nitrate may not enhance the biodegradation of benzene (Lovley 1997) and thus these results may not accurately represent the potential for biodegradation at that aquifer site.

This review of anaerobic benzene biodegradation rates provides a relatively complex and conflicting picture of the process of anaerobic biodegradation in groundwater. It is therefore difficult to provide a recommended first order rate constant that could be used to characterize anaerobic benzene biodegradation in fate and transport models. Anaerobic benzene biodegradation appears to be more site specific than is true for the other monoaromatic hydrocarbons, as current data suggests that it may not occur at all at some sites. A range of values for anaerobic biodegradation of this compound is suggested with the lower limit equal to 0 (*e.g.* this compound is not biodegraded anaerobically), which was the lowest measured field value, to 0.0033/day (half-life of 210 days), which is the mean value for the entire field/*in situ* microcosm data set. The inclusion of an upper limit to this range is in recognition that recently published data suggest that anaerobic biodegradation of benzene can occur along a contaminant plume.

Table 3. All Summarized Studies for Benzene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	NO3	Batch reactor	410-1600 ug/L	41	NB		Reinhard,M et al. (1991)
Denmark	Meth	Batch reactor, groundwater inoculum	130 ug/L	150	NB		Lyngkilde,J et al. (1992)
Northern Michigan	NO3	Column	20000 ug/L	42			Anid,PJ et al. (1993)
Lower Glatt Valley, Switzerland	NO3	Column	26500 ug/L	6	NB		Kuhn,EP et al. (1988)
Seal Beach, CA	Meth	Column	0.079 umol/g	570	NB		Haag,F et al. (1991)
Seal Beach, CA	Meth	Column	0.079 umol/g	68	NB		Haag,F et al. (1991)
Swan Coastal Plain, Western Australia	NO3	Column	990 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1080 ug/L	13-14	NB		Patterson,BM et al. (1993)
Traverse City, MI	NO3	Column	~380 ug/L	100	Possible		Hutchins,SR et al. (1992)
George Air Force Base, CA	NO3/SO4	Field	1620 ug/L	153			Wilson,JT et al. (1995A)
Hanahan, SC	SO4	Field	60;350 ug/L	165			Chapelle,FH et al. (1996)
Tibbetts Road Site, Barrington, NH	Fe	Field	493 ug/L	876	0.00011/day		Wilson,BH et al. (1996)
Rocky Point, NC	Fe	Field			0.0002/day		Rifai,HS et al. (1995)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	230 ug/L	35	0.00043/day		Wilson,JT et al. (1994B)
Sampson County, NC	NO3	Field			0.0006-0.0014/day		Borden,RC et al. (1997)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	3120 ug/L		0.002-0.004/day		Barlaz,MA et al. (1993)
Tibbetts Road Site, Barrington, NH	Fe	Field	510 ug/L	2336	0.0022/day		Wilson,BH et al. (1996)
Noordwijk landfill, The Netherlands		Field	100 ug/L	3650	0.0063/day		Zoeteman,BCJ et al. (1981)
Traverse City, MI	Meth	Field		70	0.00714 /day		Wilson,BH et al. (1990)
Hill AFB, Utah	SO4	Field	5600 ug/L	228	0.0072-0.046/day		Wiedemeier,TH et al. (1995)
Patrick AFB, FL	Meth	Field	724 ug/L	1200	0.01/day	760	Wiedemeier,TH et al. (1995)
Bemidji, MN	Meth/Fe/Mn	Field			0.017/day		Cozzarelli,IM et al. (1990)
Hill AFB, Utah	SO4	Field	5600 ug/L	250	0.028/day		Wiedemeier,TH et al. (1996)
Hill AFB, Utah	SO4	Field	5600 ug/L	250	0.038/day		Wiedemeier,TH et al. (1996)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Hill AFB, Utah		Field		630	11.2 mg/day		Dupont,RR et al. (1994)
Tibbetts Road Site, Barrington, NH	Fe	Field	493 ug/L	3650	>0.0017/day		Wilson,BH et al. (1996)
	NO3	Field	241 ug/L	80	NB		Reinhard,M et al. (1996)
CFB Borden aquifer, Ontario, Canada	NO3	Field	4671 ug/L	56	NB		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	4384 ug/L	11	NB		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	4774 ug/L	11	NB		Barbaro,JR et al. (1992)
Eglin AFB, FL	Meth	Field	100 ug/L	35	NB		Wilson,JT et al. (1994A)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	~165 ug/L	21	NB		Rugge,K et al. (1995)
North Bay landfill, Ontario Canada	Meth	Field	66 ug/L		NB		Reinhard,M et al. (1984)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~175 ug/L	51	NB		Acton,DW & Barker,JF (1992)
Seal Beach, CA	SO4	Field	150-230 ug/L	60	NB		Beller,HR et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	230 ug/L	70-105	NB		Wilson,JT et al. (1994B)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	253 ug/L	35	NB		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	253 ug/L	70-105	NB		Wilson,JT et al. (1994B)
Swan Coastal Plain, Western Australia	SO4/Fe	Field	5200 ug/L	71	NB		Thierrin,J et al. (1995)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	3 ug/L	71	NB		Lyngkilde,J & Christensen,TH (1992)
Western New Mexico	NO3	Field	600 ug/L	7	NB		Hilton,J et al. (1992)
	SO4	Field	241 ug/L	60	Possible		Reinhard,M et al. (1996)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	20000 ug/L	85	0.0045/day		Morgan,P et al. (1993)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	20000 ug/L	85	0.0073/day		Morgan,P et al. (1993)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	200 ug/L	85	0.022/day	14	Morgan,P et al. (1993)
Florida		Groundwater grab sample		90	NB		Delfino,JJ et al. (1989)
Fredensborg, Denmark	NO3	Groundwater grab sample	900 ug/L	380	NB		Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	900 ug/L	60	NB		Flyvbjerg,J et al. (1993)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Uiterburen, The Netherlands	NO3	Groundwater grab sample	~590 ug/L	85	NB		Morgan,P et al. (1993)
West Valley, NY		Groundwater grab sample	Not quantified	60	Possible		Francis,AJ (1982)
Rocky Point, NC	Fe	In situ microcosm			0.004/day		Rifai,HS et al. (1995)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	130	0.0041/day	121	Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		251	0.0049/day	155	Hunt,MJ et al. (1995)
CFB Borden aquifer, Ontario, Canada	NO3/SO4	In situ microcosm	140 ug/L	125	NB		Acton,DW & Barker,JF (1992)
CFB Borden aquifer, Ontario, Canada	NO3/SO4	In situ microcosm	140 ug/L	125	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
Southwestern Ontario, Canada	NO3	In situ microcosm	390 ug/L	28	NB		Gillham,RW et al. (1990)
Vejen city landfill, Denmark		In situ microcosm	26 ug/L	90	NB		Lyngkilde,J et al. (1992)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L		NB		Nielsen,PH & Christensen,TH (1994)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	NO3	In situ microcosm	150 ug/L		NB		Nielsen,PH & Christensen,TH (1994)
Bemidji, MN	Meth/Fe/Mn	Lab microcosm	2726 ug/L	61	0.0015/day		Cozzarelli,IM et al. (1994)
Sleeping Bear Dunes Natl Lakeshore, MI	SO4	Lab microcosm	3609 ug/L	500	0.0022/day	400	Kazumi,J et al. (1997)
CFB Borden aquifer, Ontario, Canada		Lab microcosm	3000 ug/L	62	0.0029/day		Major,DW et al. (1988)
Hanahan, SC	SO4	Lab microcosm	600 ug/L	36	0.003/day		Chapelle,FH et al. (1996)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth	Lab microcosm	3609 ug/L	520	0.0039/day	420	Kazumi,J et al. (1997)
Seal Beach, CA	SO4	Lab microcosm	4114 ug/L	320	0.0048/day	120	Kazumi,J et al. (1997)
Tibbetts Road Site, Barrington, NH	Fe	Lab microcosm	329 ug/L	294	0.0065/day		Wilson,BH et al. (1996)
Norman, OK	Meth	Lab microcosm	613 ug/L	280	0.0074/day	140	Wilson,BH et al. (1986)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	NO3	Lab microcosm	3800 ug/L	13	0.0095/day		Hutchins,SR (1992)
Rocky Point, NC	SO4/Fe	Lab microcosm	2000 ug/L	403	0.0237/day	184	Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	Lab microcosm	3500 ug/L	403	0.0237/day	184	Hunt,MJ et al. (1995)
Rocky Point, NC	Fe	Lab microcosm	2000-3000 ug/L	400	0.024/day		Rifai,HS et al. (1995)
Bemidji,MN	Meth/Fe/Mn	Lab microcosm	781 ug/L	125	0.031/day		Baedecker,MJ et al. (1993)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	3000 ug/L	62	0.045/day		Major,DW et al. (1988)
Eastern seaboard, USA	SO4	Lab microcosm	~880 ug/kg	77	0.047/day	8	Davis,JW et al. (1994)
Eastern seaboard, USA	Meth	Lab microcosm	~880 ug/kg	77	0.052/day	21	Davis,JW et al. (1994)
Traverse City, MI	Meth/Fe	Lab microcosm	450 ug/L	28	0.071/day		Wilson,BH et al. (1990)
Seal Beach, CA	SO4	Lab microcosm	7030 ug/L	134	148 ug/L-day	30-60	Edwards,EA & Grbic-Galic,D (1992)
Seal Beach, CA	SO4	Lab microcosm	10935 ug/L	134	289 ug/L-day	30-60	Edwards,EA & Grbic-Galic,D (1992)
Seal Beach, CA	SO4	Lab microcosm	15622 ug/L	134	31 ug/L-day	70-100	Edwards,EA & Grbic-Galic,D (1992)
Seal Beach, CA	SO4	Lab microcosm	7030 ug/L	134	62 ug/L-day	30-60	Edwards,EA & Grbic-Galic,D (1992)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	SO4	Lab microcosm	3124 ug/L	134	78 ug/L-day	30-60	Edwards,EA & Grbic-Galic,D (1992)
CFB Borden aquifer, Ontario, Canada	SO4	Lab microcosm	4803 ug/L	420	NB		API (1994)
CFB Borden aquifer, Ontario, Canada		Lab microcosm	3000 ug/L	60	NB		Barker,JF et al. (1987)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	2825 ug/L	452	NB		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	2880 ug/L	452	NB		Barbaro,JR et al. (1992)
Eastern seaboard, USA	NO3	Lab microcosm	~840 ug/kg	68	NB		Davis,JW et al. (1994)
Ft. Bragg, NC	NO3	Lab microcosm	1600 ug/L	250	NB		Kao,CM & Borden,RC (1997)
Hanahan, SC	Fe	Lab microcosm	10 umol/kg sediment	160	NB		Lovley,DR et al. (1994)
Hanahan, SC	Fe	Lab microcosm	781 ug/L	95	NB		Lovley,DR et al. (1996)
Hanahan, SC	Meth	Lab microcosm	781 ug/L	105	NB		Lovley,DR et al. (1996)
Hanahan, SC	Meth	Lab microcosm	600 ug/L	36	NB		Chapelle,FH et al. (1996)
Indian River County, FL		Lab microcosm	50 ug/L	14	NB		Kemblowski,MW et al. (1987)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Indian River County, FL		Lab microcosm	500 ug/L	14	NB		Kemblowski,MW et al. (1987)
Indian River County, FL		Lab microcosm	5000 ug/L	14	NB		Kemblowski,MW et al. (1987)
Norman, OK	Meth/SO4	Lab microcosm	100000-300000 ug/L	1095	NB		Kazumi,J et al. (1997)
Norman, OK	Meth/SO4	Lab microcosm	108 ug/L	1095	NB		Kazumi,J et al. (1997)
North Bay landfill, Ontario Canada	Meth	Lab microcosm	128.3 ug/L	187	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	NO3	Lab microcosm	146.0 ug/L	187	NB		Acton,DW & Barker,JF (1992)
Rocky Point, NC	Meth	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Sampson County, NC	NO3	Lab microcosm	2000 ug/L	260	NB		Borden,RC et al. (1997)
Seal Beach, CA	NO3	Lab microcosm	2700 ug/L	39	NB		Ball,HA & Reinhard,M (1996)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	SO4	Lab microcosm	3500 ug/L	39	NB		Ball,HA & Reinhard,M (1996)
Seal Beach, CA	SO4	Lab microcosm	~5000 ug/L	270	NB		Edwards,EA et al. (1992)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth	Lab microcosm			NB		Barlaz,MA et al. (1993)
Sleeping Bear Dunes Natl Lakeshore, MI	NO3	Lab microcosm	1650 ug/L	120	NB		Kao,CM & Borden,RC (1997)
Sleeping Bear Dunes Natl Lakeshore, MI	NO3	Lab microcosm	3609 ug/L	530	NB		Kazumi,J et al. (1997)
Traverse City, MI		Lab microcosm	~3600 ug/L	100	NB		Hutchins,SR (1991)
Traverse City, MI	N2O	Lab microcosm	~3600 ug/L	100	NB		Hutchins,SR (1991)
Traverse City, MI	NO3	Lab microcosm	14000 ug/L	8	NB		Hutchins,SR (1993)
Traverse City, MI	NO3	Lab microcosm	~12500 ug/L	50	NB		Hutchins,SR (1993)
Traverse City, MI	NO3	Lab microcosm	~3600 ug/L	100	NB		Hutchins,SR (1991)
Traverse City, MI	NO3	Lab microcosm	4000 ug/L	100	NB		Hutchins,SR & Wilson,JT (1991)
Traverse City, MI	NO3	Lab microcosm	~5500 ug/L	356	NB		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	7000 ug/L	56	NB		Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	7500 ug/L	160	NB		Hutchins,SR et al. (1991)

Table 3. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	Fe	Lab microcosm	43 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/Fe/NO3	Lab microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	50 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	NO3	Lab microcosm	4 ug/L	450	NB		Albrechtsen,HJ et al. (1994)

Table 4. Field and *in situ* Microcosm Studies for Benzene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
George Air Force Base, CA	NO3/SO4	Field	1620 ug/L	153			Wilson,JT et al. (1995A)
Hanahan, SC	SO4	Field	60;350 ug/L	165			Chapelle,FH et al. (1996)
Tibbetts Road Site, Barrington, NH	Fe	Field	493 ug/L	876	0.00011/day		Wilson,BH et al. (1996)
Rocky Point, NC	Fe	Field			0.0002/day		Rifai,HS et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	230 ug/L	35	0.00043/day		Wilson,JT et al. (1994B)
Sampson County, NC	NO3	Field			0.0006-0.0014/day		Borden,RC et al. (1997)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	3120 ug/L		0.002-0.004/day		Barlaz,MA et al. (1993)
Tibbetts Road Site, Barrington, NH	Fe	Field	510 ug/L	2336	0.0022/day		Wilson,BH et al. (1996)
Rocky Point, NC	Fe	In situ microcosm			0.004/day		Rifai,HS et al. (1995)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	130	0.0041/day	121	Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		251	0.0049/day	155	Hunt,MJ et al. (1995)
Noordwijk landfill, The Netherlands		Field	100 ug/L	3650	0.0063/day		Zoeteman,BCJ et al. (1981)

Table 4. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	Meth	Field		70	0.00714 /day		Wilson,BH et al. (1990)
Hill AFB, Utah	SO4	Field	5600 ug/L	228	0.0072-0.046/day		Wiedemeier,TH et al. (1995)
Patrick AFB, FL	Meth	Field	724 ug/L	1200	0.01/day	760	Wiedemeier,TH et al. (1995)
Bemidji, MN	Meth/Fe/Mn	Field			0.017/day		Cozzarelli,IM et al. (1990)
Hill AFB, Utah	SO4	Field	5600 ug/L	250	0.028/day		Wiedemeier,TH et al. (1996)
Hill AFB, Utah	SO4	Field	5600 ug/L	250	0.038/day		Wiedemeier,TH et al. (1996)
Hill AFB, Utah		Field		630	11.2 mg/day		Dupont,RR et al. (1994)
Tibbetts Road Site, Barrington, NH	Fe	Field	493 ug/L	3650	>0.0017/day		Wilson,BH et al. (1996)
	NO3	Field	241 ug/L	80	NB		Reinhard,M et al. (1996)
CFB Borden aquifer, Ontario, Canada	NO3	Field	4671 ug/L	56	NB		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	4384 ug/L	11	NB		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	4774 ug/L	11	NB		Barbaro,JR et al. (1992)

Table 4. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
CFB Borden aquifer, Ontario, Canada	NO3/SO4	In situ microcosm	140 ug/L	125	NB		Acton,DW & Barker,JF (1992)
CFB Borden aquifer, Ontario, Canada	NO3/SO4	In situ microcosm	140 ug/L	125	NB		Acton,DW & Barker,JF (1992)
Eglin AFB, FL	Meth	Field	100 ug/L	35	NB		Wilson,JT et al. (1994A)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	~165 ug/L	21	NB		Rugge,K et al. (1995)
North Bay landfill, Ontario Canada	Meth	Field	66 ug/L		NB		Reinhard,M et al. (1984)
North Bay landfill, Ontario Canada	Meth/NO3	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~175 ug/L	51	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
Seal Beach, CA	SO4	Field	150-230 ug/L	60	NB		Beller,HR et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	230 ug/L	70-105	NB		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	253 ug/L	35	NB		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	253 ug/L	70-105	NB		Wilson,JT et al. (1994B)

Table 4. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Southwestern Ontario, Canada	NO3	In situ microcosm	390 ug/L	28	NB		Gillham,RW et al. (1990)
Swan Coastal Plain, Western Australia	SO4/Fe	Field	5200 ug/L	71	NB		Thierrin,J et al. (1995)
Vejen city landfill, Denmark		In situ microcosm	26 ug/L	90	NB		Lyngkilde,J et al. (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L		NB		Nielsen,PH & Christensen,TH (1994)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	3 ug/L	71	NB		Lyngkilde,J & Christensen,TH (1992)
Vejen city landfill, Denmark	NO3	In situ microcosm	150 ug/L		NB		Nielsen,PH & Christensen,TH (1994)
Western New Mexico	NO3	Field	600 ug/L	7	NB		Hilton,J et al. (1992)
	SO4	Field	241 ug/L	60	Possible		Reinhard,M et al. (1996)

3.1.2. Toluene

Unlike benzene, numerous studies, both field and laboratory, show that toluene biodegrades under anaerobic conditions in aquifer environments (Table 5). Toluene was biodegraded in nitrate-reducing, sulfate-reducing, methanogenic, and iron-reducing aquifer environments. Several anaerobic transformation pathways have been reported for this compound including 1) oxidation of the methyl group with the formation of benzoic acid, 2) carboxylation of the aromatic ring forming toluic acid, 3) hydroxylation of the methyl group forming benzyl alcohol, and 4) p-hydroxylation of the aromatic ring forming p-cresol (Colberg & Young 1995). First-order rate constants for field and *in situ* microcosm studies only (Table 6), ranged from 0 to 0.30/day with a mean value of 0.059/day; however, under iron-reducing conditions in the field toluene appeared to biodegrade more slowly (mean=0.0043/day, for a limited number of study sites).

A range of rate constants was believed to be most appropriate for this compound. In order to determine an appropriate lower limit, studies reporting no biodegradation were examined more closely to determine whether this was a reasonable value. Five of 41 field/*in situ* microcosm studies reported that toluene was not biodegraded, four of these were *in situ* microcosm studies (Acton & Barker 1992; Lyngkilde et al. 1992; Nielsen et al. 1992). The study by Acton and Barker reported no biodegradation of toluene for a nitrate-amended microcosm but biodegradation was reported for a sulfate-amended *in situ* microcosm with a rate constant of 0.19/day, indicating that toluene was biodegraded at the North Bay site. A second *in situ* microcosm reporting no biodegradation of toluene was amended with both sulfate and lactate; an unamended microcosm for the same site, the CFB Borden site, had a measured rate constant of 0.083/day for toluene. The continuous field injection experiment by Rugge et al. (1995) reported no biodegradation of toluene by a 2 m piezometer fence over an injection period of 8 months; methanogenic, sulfate-reducing and iron-reducing conditions were encountered along the flow path. Other compounds such as benzene, trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane were also not biodegraded, although one might expect that the chlorinated aliphatic compounds would biodegrade in this environment. The *in situ* microcosm studies by Nielsen et al. (1992) reported no biodegradation for benzene, toluene, o-xylene, naphthalene, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene; only carbon tetrachloride was degraded under these anaerobic conditions. Other studies conducted at the same location, the Vejen city landfill, Denmark, reported biodegradation of toluene. A field study by Lyngkilde & Christensen (1992) reported a rate constant of 0.043/day and an *in situ* microcosm study by Nielsen et al. (1995B) reports the possibility of toluene biodegradation (1 of 10 *in situ* microcosms reported toluene biodegradation). After review of the papers reporting no biodegradation of toluene there does not appear to be substantive evidence that toluene is not biodegraded at any of the studied sites. Therefore, a lower limit of biodegradation was set at the lowest reported field study rate constant.

The rate of anaerobic biodegradation of toluene in aquifer environments appears to be related to the redox environment. Mean first-order rate constant values for nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic studies are 0.63/day, 0.021/day, 0.049/day, and 0.029/day, respectively. These numbers are reported for all summarized studies where only a single redox condition was

present. Many field studies reported multiple redox conditions along a single flow path and thus, were not included in this redox analysis. Toluene is most rapidly biodegraded under nitrate-reducing conditions. If the calculation of mean values for nitrate-reducing conditions does not include the results by Patterson et al. (1993) which were for a column study, and Hutchins et al. (1991), Hutchins (1991A), and Hutchins (1997), where toluene was the only added compound, this value drops to 0.21/day.

A range of recommended values seems most appropriate for this compound with the lower limit equal to 0.00099/day (half-life of 700 days), which was the lowest measured field value, to 0.059/day (half-life of 12 days), which is the mean value for the entire field/*in situ* microcosm data set. This is expected to give a fairly conservative range of values for the first-order rate constant of toluene.

Table 5. All Summarized Studies for Toluene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	NO3	Batch reactor	1000 ug/L	13			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	1100 ug/L	15			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	1200 ug/L	41			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	380 ug/L	30			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	400 ug/L	19			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	800 ug/L	27			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	90 ug/L				Reinhard,M et al. (1991)
Denmark	Meth	Batch reactor, groundwater inoculum	~140 ug/L	150	NB		Lyngkilde,J et al. (1992)
Northern Michigan	NO3	Column	20000 ug/L	42			Anid,PJ et al. (1993)
Seal Beach, CA	SO4?	Column	0.062 umol/g	570	0.5 nmol/g/d	4	Haag,F et al. (1991)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	1.73-4.32/day	31-57	Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	1.73-5.18/day	31	Patterson,BM et al. (1993)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	<4 days	1.73-5.18/day		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	<4 days	2.16-3.89/day		Patterson,BM et al. (1993)
Lower Glatt Valley, Switzerland	NO3	Column	35000 ug/L	6	>0.61/day		Kuhn,EP et al. (1988)
Seal Beach, CA	Meth	Column	0.062 umol/g	68	NB		Haag,F et al. (1991)
Bemidji, MN	Meth/Fe/Mn	Field					Cozzarelli,IM et al. (1990)
George Air Force Base, CA	NO3/SO4	Field	1500 ug/L	153			Wilson,JT et al. (1995A)
Sampson County, NC	NO3	Field			0.0005-0.0063/day		Borden,RC et al. (1997)
Tibbetts Road Site, Barrington, NH	Fe	Field	3850 ug/L	876	0.00099/day		Wilson,BH et al. (1996)
Rocky Point, NC	Fe	Field			0.0021/day		Rifai,HS et al. (1995)
Patrick AFB, FL	Meth	Field	737 ug/L	1200	0.003/day		Wiedemeier,TH et al. (1995)
Swan Coastal Plain, Western Australia	SO4/Fe	Field	4620 ug/L	71	0.0052-0.012/day		Thierrin,J et al. (1995)
Hanahan, SC	SO4	Field	350 ug/L	165	0.0075-0.03/day		Chapelle,FH et al. (1996)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Noordwijk landfill, The Netherlands		Field	300 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)
Western New Mexico	NO3	Field	7600 ug/L	7	0.02/day		Hilton,J et al. (1992)
Hill AFB, Utah	SO4	Field	5870 ug/L	250	0.023/day		Wiedemeier,TH et al. (1996)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	5300 ug/L	70-105	0.023/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	8200 ug/L	70-105	0.026/day		Wilson,JT et al. (1994B)
Hill AFB, Utah	SO4	Field	5870 ug/L	250	0.031/day		Wiedemeier,TH et al. (1996)
CFB Borden aquifer, Ontario, Canada	NO3	Field	2369 ug/L	56	0.038/day	100	Barbaro,JR et al. (1992)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	39 ug/L	71	0.043/day		Lyngkilde,J & Christensen,TH (1992)
Hill AFB, Utah	SO4	Field	5870 ug/L	102	0.045/day		Wiedemeier,TH et al. (1995)
Eglin AFB, FL	Meth	Field	5150 ug/L	35	0.05, 0.013/day		Wilson,JT et al. (1994A)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.053-0.067/day		Barlaz,MA et al. (1993)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	5300 ug/L	35	0.053/day		Wilson,JT et al. (1994B)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
	SO4	Field	200-300 ug/L	45	0.066/day		Reinhard,M et al. (1996)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~175 ug/L	51	0.066/day		Acton,DW & Barker,JF (1992)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	8200 ug/L	35	0.067/day		Wilson,JT et al. (1994B)
Seal Beach, CA	SO4	Field	184-276 ug/L	60	0.091/day		Beller,HR et al. (1995)
North Bay landfill, Ontario Canada	Meth/SO4	Field	73.3 ug/L	17	0.16/day		Acton,DW & Barker,JF (1992)
Traverse City, MI	Meth	Field		70	0.186/day		Wilson,BH et al. (1990)
	NO3	Field	210-290 ug/L	16	0.19/day		Reinhard,M et al. (1996)
CFB Borden aquifer, Ontario, Canada	NO3	Field	2296 ug/L	11	0.28/day		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	2587 ug/L	11	0.30/day	50	Barbaro,JR et al. (1992)
Hill AFB, Utah		Field		630	14.2 mg/day		Dupont,RR et al. (1994)
Traverse City, MI	NO3	Field	500 ug/L		90-540 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Tibbetts Road Site, Barrington, NH	Fe	Field	3850 ug/L	3650	>0.0023/day		Wilson,BH et al. (1996)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Tibbetts Road Site, Barrington, NH	Fe	Field	10000 ug/L	2336	>0.0039/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field	92.15 ug/L	320-640	Biodegrades		Cozzarelli,IM et al. (1994)
North Bay landfill, Ontario Canada	Meth	Field	83 ug/L		Biodegrades		Reinhard,M et al. (1984)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
West Valley, NY		Groundwater grab sample	13300 ug/L	60	0.0031/day		Francis,AJ (1982)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	1400 ug/L	85	0.011/day		Morgan,P et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	150 ug/L	38	0.036/day	15	Flyvbjerg,J et al. (1993)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	~1500 ug/L	28	0.062/day		Morgan,P et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	150 ug/L	48	0.073/day	25	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	150 ug/L	9	0.54/day	5	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	150 ug/L		Biodegrades	60	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	150 ug/L		Biodegrades	20	Flyvbjerg,J et al. (1993)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
North Bay landfill, Ontario Canada	Meth	In situ microcosm	80 ug/L	80	0.0064/day		Acton,DW & Barker,JF (1992)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	62	0.0115/day	13	Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm	2000 ug/L	75	0.0115/day	13	Hunt,MJ et al. (1995)
Rocky Point, NC	Fe	In situ microcosm			0.012/day		Rifai,HS et al. (1995)
CFB Borden aquifer, Ontario, Canada	NO3/SO4	In situ microcosm	120 ug/L	37	0.083/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	125 ug/L	18	0.10/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	20	0.19/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	125 ug/L	16	0.21/day		Acton,DW & Barker,JF (1992)
CFB Borden aquifer, Ontario, Canada	NO3/SO4	In situ microcosm	120 ug/L	125	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
Vejen city landfill, Denmark		In situ microcosm	32 ug/L	90	NB		Lyngkilde,J et al. (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	150-180	Possible		Nielsen,PH et al. (1995B)
Traverse City, MI	NO3	Lab microcosm	22700 ug/L	7			Hutchins,SR et al. (1991)
Ft. Bragg, NC	NO3	Lab microcosm	1600 ug/L	250	0.00029/day		Kao,CM & Borden,RC (1997)
CFB Borden aquifer, Ontario, Canada		Lab microcosm	3000 ug/L	62	0.0045/day		Major,DW et al. (1988)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth	Lab microcosm			0.0098/day		Barlaz,MA et al. (1993)
Hanahan, SC	SO4	Lab microcosm	90 ug/L	42	0.01/day		Chapelle,FH et al. (1996)
Tibbetts Road Site, Barrington, NH	Fe	Lab microcosm	399 ug/L	294	0.010/day		Wilson,BH et al. (1996)
Seal Beach, CA	SO4	Lab microcosm	7372 ug/L	105	0.011/day		Beller,HR et al. (1991)
Traverse City, MI		Lab microcosm	8017 ug/L	130	0.011/day		Sewell,GW & Gibson,SA (1991)
Piedmont province, North Carolina	Meth	Lab microcosm	161 ug/L	220	0.012/day		Johnston,JJ et al. (1996)
Traverse City, MI		Lab microcosm	~3350 ug/L	100	0.016/day	15	Hutchins,SR (1991)
Norman, OK	Meth	Lab microcosm	547 ug/L	280	0.018/day		Wilson,BH et al. (1986)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	Meth	Lab microcosm	9676 ug/L	22	0.020/day		Beller,HR et al. (1991)
Seal Beach, CA	SO4	Lab microcosm	7372 ug/L	49	0.026/day	5	Beller,HR et al. (1991)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	1603 ug/L	85	0.027/day		Barbaro,JR et al. (1992)
Traverse City, MI	NO3	Lab microcosm	5150 ug/L	160	0.029/day	49	Hutchins,SR et al. (1991)
Piedmont province, North Carolina	Meth	Lab microcosm	~2700 ug/L	208	0.032/day	99	Johnston,JJ et al. (1996)
Piedmont province, North Carolina	Meth	Lab microcosm	~650 ug/L	308	0.036/day	208	Johnston,JJ et al. (1996)
Traverse City, MI	Meth	Lab microcosm	9676 ug/L	60	0.036/day		Beller,HR et al. (1991)
Seal Beach, CA	SO4	Lab microcosm	~5000 ug/L	52	0.038/day		Edwards,EA et al. (1992)
Traverse City, MI	NO3	Lab microcosm	~6000 ug/L	55	0.040/day	15	Hutchins,SR (1991A)
Traverse City, MI	Meth/Fe	Lab microcosm	420 ug/L	28	0.043/day		Wilson,BH et al. (1990)
Traverse City, MI	NO3	Lab microcosm	5900 ug/L	160	0.043/day	49	Hutchins,SR et al. (1991)
Rocky Point, NC	SO4/Fe	Lab microcosm	2000 ug/L	140	0.0446/day	22	Barlaz,MA et al. (1995)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
SE coastal plain, NC	SO4/Fe	Lab microcosm		120	0.0446/day	22	Hunt,MJ et al. (1995)
Rocky Point, NC	Fe	Lab microcosm	2000-3000 ug/L	400	0.045/day		Rifai,HS et al. (1995)
Hanahan, SC	Fe	Lab microcosm	10 umol/kg sediment	14	0.05/day		Lovley,DR et al. (1994)
Traverse City, MI	NO3	Lab microcosm	~6000 ug/L	55	0.057/day	28	Hutchins,SR (1991A)
Piedmont province, North Carolina	Meth	Lab microcosm	189 ug/L	390	0.06/day	302	Johnston,JJ et al. (1996)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	3000 ug/L	62	0.061/day		Major,DW et al. (1988)
Piedmont province, North Carolina	Meth	Lab microcosm	~1000 ug/L	55	0.063/day		Johnston,JJ et al. (1996)
Sampson County, NC	NO3	Lab microcosm	2000 ug/L	90	0.085/day	50	Borden,RC et al. (1997)
Bemidji, MN	Fe	Lab microcosm	55284 ug/L	45	0.087/day		Lovley,DR et al. (1989)
Bemidji, MN	Meth/Fe/Mn	Lab microcosm	599 ug/L	45	0.093/day		Cozzarelli,IM et al. (1994)
Traverse City, MI	NO3	Lab microcosm	~2650 ug/L	14	0.096/day		Hutchins,SR (1991A)
Bemidji,MN	Meth/Fe/Mn	Lab microcosm	590 ug/L	45	0.10/day		Baedecker,MJ et al. (1993)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	SO4	Lab microcosm	2700 ug/L	18	0.11/day		Ball,HA & Reinhard,M (1996)
Traverse City, MI	NO3	Lab microcosm	~6000 ug/L	55	0.15/day	15	Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~2950 ug/L	22	0.23/day		Hutchins,SR (1991)
Traverse City, MI	NO3	Lab microcosm	5290 ug/L	35	0.24/day		Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	~2400 ug/L	7	0.25/day		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	5350 ug/L	35	0.25/day		Hutchins,SR et al. (1991)
Sleeping Bear Dunes Natl Lakeshore, MI	NO3	Lab microcosm	1600 ug/L	30	0.26/day	10	Kao,CM & Borden,RC (1997)
Traverse City, MI	NO3	Lab microcosm	3000 ug/L	13	0.43/day		Hutchins,SR (1992)
Traverse City, MI	NO3	Lab microcosm	5200 ug/L	2	0.47/day		Hutchins,SR (1993)
Traverse City, MI	NO3	Lab microcosm	12500 ug/L	2	0.54/day		Hutchins,SR (1993)
Traverse City, MI	NO3	Lab microcosm	27 ug/L	5	0.67 ug/L/day		Hutchins,SR (1997)
Seal Beach, CA	NO3	Lab microcosm	2700 ug/L	11	0.82/day		Ball,HA & Reinhard,M (1996)
Park City, KS	NO3	Lab microcosm	22 ug/L	0.6	0.98/day		Hutchins,SR (1997)
Seal Beach, CA	NO3	Lab microcosm	2700 ug/L	4	1.00/day		Ball,HA & Reinhard,M (1996)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	NO3	Lab microcosm	1900-2700 ug/L	5.1	1015-1442 ug/L/day	3.3	Hutchins,SR (1997)
Traverse City, MI	NO3	Lab microcosm	1900-2700 ug/L	5.1	1028-1461 ug/L/day	3.3	Hutchins,SR (1997)
Park City, KS	NO3	Lab microcosm	93 ug/L	1.1	149 ug/L/day		Hutchins,SR (1997)
Park City, KS	NO3	Lab microcosm	2470 ug/L	1.6	1640 ug/L/day		Hutchins,SR (1997)
Traverse City, MI	NO3	Lab microcosm	281 ug/L	3	181 ug/L/day		Hutchins,SR (1997)
Traverse City, MI	NO3	Lab microcosm	23600 ug/L	5	18600 ug/L/day	3	Hutchins,SR (1997)
Traverse City, MI	NO3	Lab microcosm	~22000 ug/L	3	2.57/day		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	3100 ug/L	20	200 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Traverse City, MI	NO3	Lab microcosm	2650 ug/L	4.5	2210 ug/L/day	3	Hutchins,SR (1997)
Traverse City, MI	NO3	Lab microcosm	25000 ug/L	5	3.36/day	2	Hutchins,SR et al. (1991)
Park City, KS	NO3	Lab microcosm	489 ug/L	1.1	561 ug/L/day		Hutchins,SR (1997)
Vejen city landfill, Denmark	Fe	Lab microcosm	180 ug/L	450	Biodegrades		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	160 ug/L	450	Biodegrades		Albrechtsen,HJ et al. (1994)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	NO3	Lab microcosm	16 ug/L	450	Biodegrades		Albrechtsen,HJ et al. (1994)
CFB Borden aquifer, Ontario, Canada	SO4	Lab microcosm	2585 ug/L	420	NB		API (1994)
CFB Borden aquifer, Ontario, Canada		Lab microcosm	3000 ug/L	60	NB		Barker,JF et al. (1987)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	1569 ug/L	452	NB		Barbaro,JR et al. (1992)
Hanahan, SC	Meth	Lab microcosm	10 umol/kg sediment	9	NB		Lovley,DR et al. (1994)
Hanahan, SC	Fe	Lab microcosm	90 ug/L	42	NB		Chapelle,FH et al. (1996)
Hanahan, SC	Meth	Lab microcosm	90 ug/L	42	NB		Chapelle,FH et al. (1996)
Hanahan, SC	NO3	Lab microcosm	90 ug/L	42	NB		Chapelle,FH et al. (1996)
North Bay landfill, Ontario Canada	Meth	Lab microcosm	124.0 ug/L	187	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	Lab microcosm	142.2 ug/L	187	NB		Acton,DW & Barker,JF (1992)
Piedmont province, North Carolina	Meth	Lab microcosm	~1500 ug/L	395	NB		Johnston,JJ et al. (1996)
Rocky Point, NC	Meth	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)

Table 5. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Traverse City, MI	NO3	Lab microcosm	~21000 ug/L	55	NB		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	25000 ug/L	10	NB		Hutchins,SR et al. (1991)
Vejen city landfill, Denmark	Meth/Fe/NO3	Lab microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)

Table 6. Field and *in situ* Microcosm Studies for Toluene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
George Air Force Base, CA	NO3/SO4	Field	1500 ug/L	153			Wilson,JT et al. (1995A)
Sampson County, NC	NO3	Field			0.0005-0.0063/day		Borden,RC et al. (1997)
Tibbetts Road Site, Barrington, NH	Fe	Field	3850 ug/L	876	0.00099/day		Wilson,BH et al. (1996)
Rocky Point, NC	Fe	Field			0.0021/day		Rifai,HS et al. (1995)
Patrick AFB, FL	Meth	Field	737 ug/L	1200	0.003/day		Wiedemeier,TH et al. (1995)
Swan Coastal Plain, Western Australia	SO4/Fe	Field	4620 ug/L	71	0.0052-0.012/day		Thierrin,J et al. (1995)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	80 ug/L	80	0.0064/day		Acton,DW & Barker,JF (1992)
Hanahan, SC	SO4	Field	350 ug/L	165	0.0075-0.03/day		Chapelle,FH et al. (1996)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	62	0.0115/day	13	Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm	2000 ug/L	75	0.0115/day	13	Hunt,MJ et al. (1995)
Rocky Point, NC	Fe	In situ microcosm			0.012/day		Rifai,HS et al. (1995)

Table 6. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Noordwijk landfill, The Netherlands		Field	300 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)
Western New Mexico	NO3	Field	7600 ug/L	7	0.02/day		Hilton,J et al. (1992)
Hill AFB, Utah	SO4	Field	5870 ug/L	250	0.023/day		Wiedemeier,TH et al. (1996)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	5300 ug/L	70-105	0.023/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	8200 ug/L	70-105	0.026/day		Wilson,JT et al. (1994B)
Hill AFB, Utah	SO4	Field	5870 ug/L	250	0.031/day		Wiedemeier,TH et al. (1996)
CFB Borden aquifer, Ontario, Canada	NO3	Field	2369 ug/L	56	0.038/day	100	Barbaro,JR et al. (1992)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	39 ug/L	71	0.043/day		Lyngkilde,J & Christensen,TH (1992)
Hill AFB, Utah	SO4	Field	5870 ug/L	102	0.045/day		Wiedemeier,TH et al. (1995)
Eglin AFB, FL	Meth	Field	5150 ug/L	35	0.05, 0.013/day		Wilson,JT et al. (1994A)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.053-0.067/day		Barlaz,MA et al. (1993)

Table 6. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	5300 ug/L	35	0.053/day		Wilson,JT et al. (1994B)
	SO4	Field	200-300 ug/L	45	0.066/day		Reinhard,M et al. (1996)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~175 ug/L	51	0.066/day		Acton,DW & Barker,JF (1992)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	8200 ug/L	35	0.067/day		Wilson,JT et al. (1994B)
CFB Borden aquifer, Ontario, Canada	NO3/SO4	In situ microcosm	120 ug/L	37	0.083/day		Acton,DW & Barker,JF (1992)
Seal Beach, CA	SO4	Field	184-276 ug/L	60	0.091/day		Beller,HR et al. (1995)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	125 ug/L	18	0.10/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	Field	73.3 ug/L	17	0.16/day		Acton,DW & Barker,JF (1992)
Traverse City, MI	Meth	Field		70	0.186/day		Wilson,BH et al. (1990)
	NO3	Field	210-290 ug/L	16	0.19/day		Reinhard,M et al. (1996)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	20	0.19/day		Acton,DW & Barker,JF (1992)

Table 6. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	125 ug/L	16	0.21/day		Acton,DW & Barker,JF (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	2296 ug/L	11	0.28/day		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	2587 ug/L	11	0.30/day	50	Barbaro,JR et al. (1992)
Hill AFB, Utah		Field		630	14.2 mg/day		Dupont,RR et al. (1994)
Traverse City, MI	NO3	Field	500 ug/L		90-540 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Tibbetts Road Site, Barrington, NH	Fe	Field	3850 ug/L	3650	>0.0023/day		Wilson,BH et al. (1996)
Tibbetts Road Site, Barrington, NH	Fe	Field	10000 ug/L	2336	>0.0039/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field	92.15 ug/L	320-640	Biodegrades		Cozzarelli,IM et al. (1994)
Bemidji, MN	Meth/Fe/Mn	Field			Biodegrades		Cozzarelli,IM et al. (1990)
North Bay landfill, Ontario Canada	Meth	Field	83 ug/L		Biodegrades		Reinhard,M et al. (1984)
CFB Borden aquifer, Ontario, Canada	NO3/SO4	In situ microcosm	120 ug/L	125	NB		Acton,DW & Barker,JF (1992)

Table 6. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
North Bay landfill, Ontario Canada	Meth/NO3	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
Vejen city landfill, Denmark		In situ microcosm	32 ug/L	90	NB		Lyngkilde,J et al. (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	150-180	Possible		Nielsen,PH et al. (1995B)

3.1.3. Ethylbenzene

Ethylbenzene was biodegraded in nitrate-reducing, sulfate-reducing, methanogenic, and iron-reducing aquifer environments (Table 7). In general, ethylbenzene is not as rapidly biodegraded as toluene but appears to be biodegraded at a similar rate as the xylene isomers. As with the other BTEX compounds, preference is given to field and *in situ* microcosm studies (Table 8) and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies alone ranged from 0 to 0.15/day with a mean value of 0.015/day.

In order to determine an appropriate lower limit for the recommended range, studies reporting no biodegradation were examined more closely to determine whether this was a reasonable value. Seven of thirty-four field/*in situ* microcosm studies reported a result of no biodegradation, three of these were *in situ* microcosm studies. Barbaro et al. (1992) reported the partial biodegradation of ethylbenzene in a field study with the presence of added nitrate (by the 1 m piezometer fence); these conditions resulted in a first-order rate constant of 0.026/day. At the same site but without added nitrate, ethylbenzene was not biodegraded by the 5 m fence which corresponded to a time of 56 days. Therefore, this site is capable of biodegrading ethylbenzene, but the rate may be much slower without the addition of nitrate. The continuous field injection experiment by Rugge et al. (1995) reported no biodegradation of ethylbenzene by the 2 m fence over an injection period of 8 months; methanogenic, sulfate-reducing and iron-reducing conditions were present. Other compounds such as benzene, toluene, trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane were also not biodegraded although one might expect that both toluene and the chlorinated aliphatic compounds would be in this environment. Two different authors reported no biodegradation of ethylbenzene at the North Bay landfill in Ontario during field studies (Reinhard et al. 1984; Acton & Barker 1992). However, results from 5 *in situ* microcosm experiments by Acton and Barker (1992) at the same site, led to the calculation of first-order anaerobic biodegradation rate constants ranging from 0 to 0.067/day (average=0.020/day). At the Rocky Point, NC site, a rate constant of 0.0015/day was obtained from field results (Rifai et al. 1995); however, *in situ* microcosm studies by Hunt et al. (1995) and Barlaz et al. (1995) reported no biodegradation of ethylbenzene over a period of more than 200 days. Laboratory microcosm studies by Hunt et al. (1995) reported biodegradation of ethylbenzene using Rocky Point sediment, but at rates 20-fold less than that of benzene. After a review of the papers reporting no biodegradation of ethylbenzene, there does not appear to be substantive evidence that this compound is not biodegraded at any of the studied sites. Therefore, a lower limit of biodegradation was set at the lowest reported field study rate constant.

Like toluene, the rate of anaerobic biodegradation of ethylbenzene in aquifer environments appears to be related to the redox environment. Mean first-order rate constant values for nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic studies are 0.28/day, 0.0011/day, 0.0098/day, and 0.05/day, respectively. These numbers are reported for all summarized studies where only a single redox condition was present. Many field studies reported multiple redox conditions along a single flow path and thus, were not included in this redox analysis. Ethylbenzene is most readily biodegraded under

denitrifying conditions; this value is also similar to the mean for all methanogenic studies. If the calculation of mean values for nitrate-reducing conditions does not include the results by Patterson et al. (1993) which were for a column study, the mean for this redox condition drops to 0.069/day.

A range of recommended values seems most appropriate for this compound with the lower limit equal to 0.00060/day (half-life of 1155 days), which was the lowest measured field value, to 0.015/day (half-life of 46 days), which is the mean value for the entire field/*in situ* microcosm data set. This is expected to give a fairly conservative range of values for the first-order rate constant of ethylbenzene.

Table 7. All Summarized Studies for Ethylbenzene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	NO3	Batch reactor	11 ug/L	15	Biodegrades		Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	17 ug/L		Biodegrades		Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	23 ug/L	19	Biodegrades		Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	40 ug/L	13	Biodegrades		Reinhard,M et al. (1991)
Lower Glatt Valley, Switzerland	NO3	Column	23360 ug/L	6	0.043/day		Kuhn,EP et al. (1988)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	0.86-6.5/day	130	Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	0.86-6.5/day	~90	Patterson,BM et al. (1993)
Seal Beach, CA	Meth	Column	0.054 umol/g	570	NB		Haag,F et al. (1991)
Seal Beach, CA	Meth	Column	0.054 umol/g	68	NB		Haag,F et al. (1991)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
George Air Force Base, CA	NO3/SO4	Field	210 ug/L	153			Wilson,JT et al. (1995A)
Tibbetts Road Site, Barrington, NH	Fe	Field	760 ug/L	876	0.00060/day		Wilson,BH et al. (1996)

Table 7. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Sampson County, NC	NO3	Field			0.0008-0.0058/day		Borden,RC et al. (1997)
Rocky Point, NC	Fe	Field			0.0015/day		Rifai,HS et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1500 ug/L	70-105	0.0024/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.003-0.010/day		Barlaz,MA et al. (1993)
Patrick AFB, FL	Meth	Field	823 ug/L	1200	0.0031/day		Wiedemeier,TH et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1700 ug/L	35	0.0031/day		Wilson,JT et al. (1994B)
Tibbetts Road Site, Barrington, NH	Fe	Field	1300 ug/L	2336	0.0032/day		Wilson,BH et al. (1996)
Seal Beach, CA	SO4	Field	212-319 ug/L	60	0.0066/day	17	Beller,HR et al. (1995)
Hill AFB, Utah	SO4	Field	955 ug/L	250	0.009/day		Wiedemeier,TH et al. (1996)
Western New Mexico	NO3	Field	475 ug/L	7	0.0092/day		Hilton,J et al. (1992)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1500 ug/L	35	0.0099/day		Wilson,JT et al. (1994B)
Hill AFB, Utah	SO4	Field	955 ug/L	250	0.010/day		Wiedemeier,TH et al. (1996)

Table 7. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1700 ug/L	70-105	0.011/day		Wilson,JT et al. (1994B)
	SO4	Field	200-300 ug/L	60	0.014/day		Reinhard,M et al. (1996)
Noordwijk landfill, The Netherlands		Field	300 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	96 ug/L	71	0.024/day		Lyngkilde,J & Christensen,TH (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	374 ug/L	11	0.026/day		Barbaro,JR et al. (1992)
Hill AFB, Utah	SO4	Field	955 ug/L	228	0.029/day	102	Wiedemeier,TH et al. (1995)
Eglin AFB, FL	Meth	Field	1700 ug/L	35	0.03, 0.05/day		Wilson,JT et al. (1994A)
	NO3	Field	210-290 ug/L	16	0.15/day		Reinhard,M et al. (1996)
Traverse City, MI	NO3	Field			50-310 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Tibbetts Road Site, Barrington, NH	Fe	Field	760 ug/L	3650	>0.0018/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field			Biodegrades		Cozzarelli,IM et al. (1990)

Table 7. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
CFB Borden aquifer, Ontario, Canada	NO3	Field	282 ug/L	56	NB		Barbaro,JR et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
North Bay landfill, Ontario Canada	Meth	Field	780 ug/L		NB		Reinhard,M et al. (1984)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~165 ug/L	51	NB		Acton,DW & Barker,JF (1992)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	155 ug/L	85	0.0047/day	30	Morgan,P et al. (1993)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	165 ug/L	85	0.055/day	30	Morgan,P et al. (1993)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	55 ug/L	80	0.0011/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	105	0.0053/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	120 ug/L	25	0.028/day	4	Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	80 ug/L	25	0.067/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
Rocky Point, NC	Fe	In situ microcosm			NB		Rifai,HS et al. (1995)

Table 7. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	217	NB		Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		251	NB		Hunt,MJ et al. (1995)
Ft. Bragg, NC	NO3	Lab microcosm	1600 ug/L	250	0.00060/day		Kao,CM & Borden,RC (1997)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	210 ug/L	452	0.001/day	84	Barbaro,JR et al. (1992)
Rocky Point, NC	SO4/Fe	Lab microcosm	2000 ug/L	403	0.0019/day		Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	Lab microcosm		403	0.0019/day		Hunt,MJ et al. (1995)
Rocky Point, NC	Fe	Lab microcosm	2000-3000 ug/L	400	0.002/day		Rifai,HS et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth	Lab microcosm			0.0029/day		Barlaz,MA et al. (1993)
Bemidji, MN	Meth/Fe/Mn	Lab microcosm	3472 ug/L	64	0.0055/day		Cozzarelli,IM et al. (1994)
Norman, OK	Meth	Lab microcosm	269 ug/L	280	0.0076/day	140	Wilson,BH et al. (1986)
Traverse City, MI	NO3	Lab microcosm	3340 ug/L	57	0.020/day	28	Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	22700 ug/L	14	0.045/day		Hutchins,SR et al. (1991)

Table 7. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	NO3	Lab microcosm	~4250 ug/L	84	0.055/day	28	Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~4250 ug/L	84	0.055/day	28	Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~4250 ug/L	84	0.055/day	28	Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~1850 ug/L	22	0.083/day		Hutchins,SR (1991)
Traverse City, MI	NO3	Lab microcosm	~22500 ug/L	28	0.084/day	13	Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	3240 ug/L	49	0.087/day	28	Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	~1500 ug/L	30	0.11/day	7	Hutchins,SR (1991A)
Traverse City, MI	Meth	Lab microcosm	9874 ug/L	25	0.12/day		Beller,HR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	~1550 ug/L	30	0.14/day	12	Hutchins,SR (1991A)
Seal Beach, CA	NO3	Lab microcosm	1000 ug/L	18	0.15/day		Ball,HA & Reinhard,M (1996)
Sleeping Bear Dunes Natl Lakeshore, MI	NO3	Lab microcosm	1400 ug/L	30	0.20/day	16	Kao,CM & Borden,RC (1997)
Seal Beach, CA	NO3	Lab microcosm	1000 ug/L	11	0.25/day		Ball,HA & Reinhard,M (1996)
Traverse City, MI	NO3	Lab microcosm	2100 ug/L	13	0.27/day		Hutchins,SR (1992)

Table 7. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	NO3	Lab microcosm	2100 ug/L	21	0.30/day		Hutchins,SR (1992)
Traverse City, MI	Meth	Lab microcosm	7432 ug/L	11	0.46/day		Beller,HR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	2050 ug/L	20	130 ug/L/day		Hutchins,SR & Wilson,JT (1991)
CFB Borden aquifer, Ontario, Canada	SO4	Lab microcosm	338 ug/L	420	NB		API (1994)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	205 ug/L	452	NB		Barbaro,JR et al. (1992)
North Bay landfill, Ontario Canada	Meth	Lab microcosm	112.0 ug/L	187	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	Lab microcosm	128.5 ug/L	187	NB		Acton,DW & Barker,JF (1992)
Rocky Point, NC	Meth	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Sampson County, NC	NO3	Lab microcosm	2000 ug/L	260	NB		Borden,RC et al. (1997)

Table 7. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	SO4	Lab microcosm	1000 ug/L	39	NB		Ball,HA & Reinhard,M (1996)
Seal Beach, CA	SO4	Lab microcosm	~5000 ug/L	270	NB		Edwards,EA et al. (1992)
Traverse City, MI		Lab microcosm	~2050 ug/L	100	NB		Hutchins,SR (1991)
Traverse City, MI	NO3	Lab microcosm	~19000 ug/L	55	NB		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	4530 ug/L	56	NB		Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	4200 ug/L	56	NB		Hutchins,SR et al. (1991)
Vejen city landfill, Denmark	Fe	Lab microcosm	430 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	380 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	NO3	Lab microcosm	43 ug/L	450	NB		Albrechtsen,HJ et al. (1994)

Table 8. Field and *in situ* Microcosm Studies for Ethylbenzene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
George Air Force Base, CA	NO3/SO4	Field	210 ug/L	153			Wilson,JT et al. (1995A)
Tibbetts Road Site, Barrington, NH	Fe	Field	760 ug/L	876	0.00060/day		Wilson,BH et al. (1996)
Sampson County, NC	NO3	Field			0.0008-0.0058/day		Borden,RC et al. (1997)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	55 ug/L	80	0.0011/day		Acton,DW & Barker,JF (1992)
Rocky Point, NC	Fe	Field			0.0015/day		Rifai,HS et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1500 ug/L	70-105	0.0024/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.003-0.010/day		Barlaz,MA et al. (1993)
Patrick AFB, FL	Meth	Field	823 ug/L	1200	0.0031/day		Wiedemeier,TH et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1700 ug/L	35	0.0031/day		Wilson,JT et al. (1994B)
Tibbetts Road Site, Barrington, NH	Fe	Field	1300 ug/L	2336	0.0032/day		Wilson,BH et al. (1996)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	105	0.0053/day		Acton,DW & Barker,JF (1992)
Seal Beach, CA	SO4	Field	212-319 ug/L	60	0.0066/day	17	Beller,HR et al. (1995)

Table 8. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Hill AFB, Utah	SO4	Field	955 ug/L	250	0.009/day		Wiedemeier,TH et al. (1996)
Western New Mexico	NO3	Field	475 ug/L	7	0.0092/day		Hilton,J et al. (1992)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1500 ug/L	35	0.0099/day		Wilson,JT et al. (1994B)
Hill AFB, Utah	SO4	Field	955 ug/L	250	0.010/day		Wiedemeier,TH et al. (1996)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1700 ug/L	70-105	0.011/day		Wilson,JT et al. (1994B)
	SO4	Field	200-300 ug/L	60	0.014/day		Reinhard,M et al. (1996)
Noordwijk landfill, The Netherlands		Field	300 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	96 ug/L	71	0.024/day		Lyngkilde,J & Christensen,TH (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Field	374 ug/L	11	0.026/day		Barbaro,JR et al. (1992)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	120 ug/L	25	0.028/day	4	Acton,DW & Barker,JF (1992)
Hill AFB, Utah	SO4	Field	955 ug/L	228	0.029/day	102	Wiedemeier,TH et al. (1995)
Eglin AFB, FL	Meth	Field	1700 ug/L	35	0.03, 0.05/day		Wilson,JT et al. (1994A)

Table 8. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	80 ug/L	25	0.067/day		Acton,DW & Barker,JF (1992)
	NO3	Field	210-290 ug/L	16	0.15/day		Reinhard,M et al. (1996)
Traverse City, MI	NO3	Field			50-310 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Tibbetts Road Site, Barrington, NH	Fe	Field	760 ug/L	3650	>0.0018/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field			Biodegrades		Cozzarelli,IM et al. (1990)
CFB Borden aquifer, Ontario, Canada	NO3	Field	282 ug/L	56	NB		Barbaro,JR et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
North Bay landfill, Ontario Canada	Meth	Field	780 ug/L		NB		Reinhard,M et al. (1984)
North Bay landfill, Ontario Canada	Meth/NO3	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~165 ug/L	51	NB		Acton,DW & Barker,JF (1992)
Rocky Point, NC	Fe	In situ microcosm			NB		Rifai,HS et al. (1995)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	217	NB		Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		251	NB		Hunt,MJ et al. (1995)

3.1.4. m-Xylene

m-Xylene was biodegraded in nitrate-reducing, sulfate-reducing, methanogenic, and iron-reducing aquifer environments (Table 9). In general it is not as readily biodegraded as toluene but appears to be biodegraded at a similar rate as ethylbenzene and the other xylene isomers. Again, preference is given to field and *in situ* microcosm studies and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies alone (Table 10) ranged from 0 to 0.32/day with a mean value of 0.039/day. This mean rate constant changes to 0.016/day and the range to 0 to 0.057/day when only field/*in situ* microcosm study papers in common with other xylenes are considered.

In order to determine an appropriate lower limit for the recommended range, studies reporting no biodegradation were examined more closely to determine whether this was a reasonable value. Two field and two *in situ* microcosm studies report that m-xylene was not biodegraded. Two *in situ* microcosms placed in the North Bay landfill site by Acton and Barker (1992) did not biodegrade m-xylene; *in situ* microcosms amended with sulfate rapidly biodegraded m-xylene while those amended with nitrate did not degrade this compound. A second *in situ* microcosm that did not biodegrade m-xylene was provided with added acetate; this was probably used as a preferential carbon source. Other BTEX compounds were also not biodegraded under these conditions. At the same location, these authors show anaerobic biodegradation of m-xylene during a field study indicating that m-xylene is capable of biodegradation at this site. A continuous field injection experiment by Rugge et al. (1995) reported no biodegradation of m-xylene by the 2 m piezometer fence over an injection period of 8 months; the flow path encountered methanogenic, sulfate-reducing and iron-reducing conditions. Other compounds such as benzene, toluene, trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane were also not biodegraded although one might expect that both toluene and the chlorinated aliphatic compounds would be biodegraded in this environment. Barbaro et al. (1992) reported the partial biodegradation of m-xylene in a field study with the presence of added nitrate (by the 1 m piezometer fence); these conditions resulted in a first-order rate constant of 0.026/day. At the same site but without the presence of added nitrate, m-xylene was not biodegraded by the 5 m fence which corresponded to a time of 56 days. Therefore, this site is capable of biodegrading m-xylene, but the rate may be much slower without the addition of nitrate. After a review of the papers reporting no biodegradation of m-xylene, there does not appear to be substantive evidence that this compound is not biodegraded at any of the studied sites. Therefore, a lower limit of biodegradation was set at the lowest reported field study rate constant.

Similar to other BTEX compounds, the rate of anaerobic biodegradation of m-xylene in aquifer environments may be related to the redox environment. Mean first-order rate constant values for nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic studies are 0.12/day, 0.0052/day, 0.091/day, and 0.021/day, respectively. These numbers are reported for all summarized studies where only a single redox condition was present. Many field studies reported multiple redox conditions along a single flow path and thus, were not included in this redox analysis. m-Xylene appears to be most readily biodegraded under nitrate-reducing conditions. If the calculation of mean values for nitrate-

reducing conditions does not include results by Hutchins (1993) for a study where only m-xylene was present, then the mean value under nitrate-reducing conditions drops to 0.070/day.

A range of recommended values seems most appropriate for this compound with the lower limit equal to 0.0012/day (half-life of 578 days), which was the lowest measured field value, to 0.016/day (half-life of 43 days), which is the mean value for the entire field/*in situ* microcosm data set in common with the other xylene isomers. This is expected to give a fairly conservative range of values for the first-order rate constant of m-xylene.

Table 9. All Summarized Studies for m-Xylene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	NO3	Batch reactor	120 ug/L				Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	230 ug/L	19			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	370 ug/L	13			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	440 ug/L	27			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	470 ug/L	15			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	470 ug/L	30			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	610 ug/L	41			Reinhard,M et al. (1991)
Lower Glatt Valley, Switzerland	NO3	Column	20170 ug/L	6	>0.49/day		Kuhn,EP et al. (1988)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)

Table 9. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
George Air Force Base, CA	NO3/SO4	Field	522 ug/L	153			Wilson,JT et al. (1995A)
Sampson County, NC	NO3	Field			0.0012-0.0035/day		Borden,RC et al. (1997)
Tibbetts Road Site, Barrington, NH	Fe	Field	360 ug/L	876	0.0012/day		Wilson,BH et al. (1996)
Rocky Point, NC	Fe	Field			0.0013/day		Rifai,HS et al. (1995)
Patrick AFB, FL	Meth	Field	2410 ug/L	1200	0.003/day		Wiedemeier,TH et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	3400 ug/L	70-105	0.0037/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2500 ug/L	35	0.0046/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.005-0.014/day		Barlaz,MA et al. (1993)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2500 ug/L	70-105	0.0083/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	3400 ug/L	35	0.014/day		Wilson,JT et al. (1994B)
Noordwijk landfill, The Netherlands		Field	300 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)
Eglin AFB, FL	Meth	Field	6750 ug/L	35	0.02, 0.1/day		Wilson,JT et al. (1994A)

Table 9. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Hill AFB, Utah	SO4	Field	5130 ug/L	228	0.024/day		Wiedemeier,TH et al. (1995)
CFB Borden aquifer, Ontario, Canada	NO3	Field	943 ug/L	11	0.026/day		Barbaro,JR et al. (1992)
	SO4	Field	200-300 ug/L	45	0.050/day		Reinhard,M et al. (1996)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	224 ug/L	71	0.057/day		Lyngkilde,J & Christensen,TH (1992)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~165 ug/L	51	0.087/day		Acton,DW & Barker,JF (1992)
Seal Beach, CA	SO4	Field	212-319 ug/L	60	0.12/day	17	Beller,HR et al. (1995)
	NO3	Field	210-290 ug/L	10	0.17/day		Reinhard,M et al. (1996)
Traverse City, MI	NO3	Field	600 ug/L		100-950 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Tibbetts Road Site, Barrington, NH	Fe	Field	360 ug/L	3650	>0.0016/day		Wilson,BH et al. (1996)
Tibbetts Road Site, Barrington, NH	Fe	Field	2500 ug/L	2336	>0.0033/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field	122 ug/L	320-640	Biodegrades		Cozzarelli,IM et al. (1994)

Table 9. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
North Bay landfill, Ontario Canada	Meth	Field	1100 ug/L		Biodegrades		Reinhard,M et al. (1984)
CFB Borden aquifer, Ontario, Canada	NO3	Field	693 ug/L	56	NB		Barbaro,JR et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	290 ug/L	85	0.0054/day		Morgan,P et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	80 ug/L	380	NB		Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	80 ug/L	60	NB		Flyvbjerg,J et al. (1993)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	275 ug/L	85	NB		Morgan,P et al. (1993)
Rocky Point, NC	Fe	In situ microcosm			0.014/day		Rifai,HS et al. (1995)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	130	0.0143/day	121	Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		251	0.0143/day	121	Hunt,MJ et al. (1995)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	75 ug/L	44	0.044/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	110 ug/L	48	0.056/day		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	12	0.32/day		Acton,DW & Barker,JF (1992)

Table 9. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
North Bay landfill, Ontario Canada	Meth	In situ microcosm	55 ug/L	80	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
Ft. Bragg, NC	NO3	Lab microcosm	1600 ug/L	250	0.00028/day		Kao,CM & Borden,RC (1997)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth	Lab microcosm			0.0006/day		Barlaz,MA et al. (1993)
CFB Borden aquifer, Ontario, Canada		Lab microcosm	3000 ug/L	62	0.0049/day		Major,DW et al. (1988)
Rocky Point, NC	Fe	Lab microcosm	2000-3000 ug/L	400	0.02/day		Rifai,HS et al. (1995)
Rocky Point, NC	SO4/Fe	Lab microcosm	2000 ug/L	297	0.0204/day		Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	Lab microcosm		184	0.0204/day		Hunt,MJ et al. (1995)
Traverse City, MI	NO3	Lab microcosm	~9000 ug/L	160	0.023/day	62	Hutchins,SR et al. (1991)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	3000 ug/L	62	0.031/day		Major,DW et al. (1988)
Sampson County, NC	NO3	Lab microcosm	2000 ug/L	260	0.033/day	150	Borden,RC et al. (1997)
Traverse City, MI	NO3	Lab microcosm	~3750 ug/L	55	0.04/day		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~3750 ug/L	55	0.04/day		Hutchins,SR (1991A)

Table 9. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	NO3	Lab microcosm	~3750 ug/L	55	0.054/day	14	Hutchins,SR (1991A)
Sleeping Bear Dunes Natl Lakeshore, MI	NO3	Lab microcosm	1400 ug/L	70	0.068/day	30	Kao,CM & Borden,RC (1997)
Traverse City, MI	NO3	Lab microcosm	~2050 ug/L	22	0.069/day		Hutchins,SR (1991)
Traverse City, MI	N2O	Lab microcosm	~2050 ug/L	35	0.085/day		Hutchins,SR (1991)
Traverse City, MI	NO3	Lab microcosm	15000 ug/L	28	0.085/day		Hutchins,SR (1991A)
Seal Beach, CA	NO3	Lab microcosm	2600 ug/L	25	0.10/day	11	Ball,HA & Reinhard,M (1996)
Seal Beach, CA	NO3	Lab microcosm	2600 ug/L	25	0.10/day	11	Ball,HA & Reinhard,M (1996)
Traverse City, MI	NO3	Lab microcosm	~1550 ug/L	60	0.11/day		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	6500 ug/L	56	0.14/day	28	Hutchins,SR et al. (1991)
Seal Beach, CA	SO4	Lab microcosm	2300 ug/L	39	0.17/day	17	Ball,HA & Reinhard,M (1996)
Traverse City, MI	NO3	Lab microcosm	~10250 ug/L	4	0.18/day		Hutchins,SR (1993)
Traverse City, MI	NO3	Lab microcosm	2100 ug/L	13	0.21/day		Hutchins,SR (1992)
Traverse City, MI	NO3	Lab microcosm	~1425 ug/L	30	0.22/day		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	6500 ug/L	42	0.24/day	28	Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	~5400 ug/L	4	1.7/day		Hutchins,SR (1993)

Table 9. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	NO3	Lab microcosm	2200 ug/L	20	140 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Vejen city landfill, Denmark	NO3	Lab microcosm	100 ug/L	450	Biodegrades		Albrechtsen,HJ et al. (1994)
CFB Borden aquifer, Ontario, Canada	SO4	Lab microcosm	800 ug/L	420	NB		API (1994)
CFB Borden aquifer, Ontario, Canada		Lab microcosm	3000 ug/L	60	NB		Barker,JF et al. (1987)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	519 ug/L	452	NB		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	533 ug/L	452	NB		Barbaro,JR et al. (1992)
North Bay landfill, Ontario Canada	Meth	Lab microcosm	119.3 ug/L	187	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	Lab microcosm	137.2 ug/L	187	NB		Acton,DW & Barker,JF (1992)
Rocky Point, NC	Meth	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)

Table 9. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI		Lab microcosm	~1850 ug/L	100	NB		Hutchins,SR (1991)
Traverse City, MI	NO3	Lab microcosm	~26000 ug/L	55	NB		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~9000 ug/L	160	NB		Hutchins,SR et al. (1991)
Vejen city landfill, Denmark	Fe	Lab microcosm	1100 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	920 ug/L	450	NB		Albrechtsen,HJ et al. (1994)

Table 10. Field and *in situ* Microcosm Studies for m-Xylene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
George Air Force Base, CA	NO3/SO4	Field	522 ug/L	153			Wilson,JT et al. (1995A)
Sampson County, NC	NO3	Field			0.0012-0.0035/day		Borden,RC et al. (1997)
Tibbetts Road Site, Barrington, NH	Fe	Field	360 ug/L	876	0.0012/day		Wilson,BH et al. (1996)
Rocky Point, NC	Fe	Field			0.0013/day		Rifai,HS et al. (1995)
Patrick AFB, FL	Meth	Field	2410 ug/L	1200	0.003/day		Wiedemeier,TH et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	3400 ug/L	70-105	0.0037/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2500 ug/L	35	0.0046/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.005-0.014/day		Barlaz,MA et al. (1993)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2500 ug/L	70-105	0.0083/day		Wilson,JT et al. (1994B)
Rocky Point, NC	Fe	In situ microcosm			0.014/day		Rifai,HS et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	3400 ug/L	35	0.014/day		Wilson,JT et al. (1994B)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	130	0.0143/day	121	Barlaz,MA et al. (1995)

Table 10. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
SE coastal plain, NC	SO4/Fe	In situ microcosm		251	0.0143/day	121	Hunt,MJ et al. (1995)
Noordwijk landfill, The Netherlands		Field	300 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)
Eglin AFB, FL	Meth	Field	6750 ug/L	35	0.02, 0.1/day		Wilson,JT et al. (1994A)
Hill AFB, Utah	SO4	Field	5130 ug/L	228	0.024/day		Wiedemeier,TH et al. (1995)
CFB Borden aquifer, Ontario, Canada	NO3	Field	943 ug/L	11	0.026/day		Barbaro,JR et al. (1992)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	75 ug/L	44	0.044/day		Acton,DW & Barker,JF (1992)
	SO4	Field	200-300 ug/L	45	0.050/day		Reinhard,M et al. (1996)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	110 ug/L	48	0.056/day		Acton,DW & Barker,JF (1992)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	224 ug/L	71	0.057/day		Lyngkilde,J & Christensen,TH (1992)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~165 ug/L	51	0.087/day		Acton,DW & Barker,JF (1992)
Seal Beach, CA	SO4	Field	212-319 ug/L	60	0.12/day	17	Beller,HR et al. (1995)

Table 10. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
	NO3	Field	210-290 ug/L	10	0.17/day		Reinhard,M et al. (1996)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	12	0.32/day		Acton,DW & Barker,JF (1992)
Traverse City, MI	NO3	Field	600 ug/L		100-950 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Tibbetts Road Site, Barrington, NH	Fe	Field	360 ug/L	3650	>0.0016/day		Wilson,BH et al. (1996)
Tibbetts Road Site, Barrington, NH	Fe	Field	2500 ug/L	2336	>0.0033/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field	122 ug/L	320-640	Biodegrades		Cozzarelli,IM et al. (1994)
North Bay landfill, Ontario Canada	Meth	Field	1100 ug/L		Biodegrades		Reinhard,M et al. (1984)
CFB Borden aquifer, Ontario, Canada	NO3	Field	693 ug/L	56	NB		Barbaro,JR et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
North Bay landfill, Ontario Canada	Meth	In situ microcosm	55 ug/L	80	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)

3.1.5. o-Xylene

o-Xylene was biodegraded in nitrate-reducing, sulfate-reducing, methanogenic, and iron-reducing aquifer environments (Table 11). In general it is not as readily biodegraded as toluene but appears to be biodegraded at a similar rate as ethylbenzene and the other xylene isomers. As with the other BTEX compounds, preference is given to field and *in situ* microcosm studies and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies (Table 12) alone ranged from 0 to 0.21/day with a mean value of 0.025/day. This mean rate constant changes to 0.021/day when only field/*in situ* microcosm studies in common with other xylenes are considered.

In order to determine an appropriate lower limit for the recommended range, studies reporting no biodegradation were examined more closely to determine whether this was a reasonable value. o-Xylene was not biodegraded in three field and five *in situ* microcosm studies. Barbaro et al. (1992) reported the partial biodegradation of o-xylene in a field study with the presence of nitrate (by the 1 m piezometer fence); these conditions resulted in a first-order rate constant of 0.026/day. At the same site but without the presence of nitrate, o-xylene was not biodegraded by the 5 m fence which corresponded to a time of 56 days. Therefore, this site is capable of biodegrading o-xylene, but the rate may be much slower without the addition of nitrate. Acton and Barker (1992) reported that o-xylene was not biodegraded at an aquifer site impacted by the North Bay landfill during an injection experiment that ran for 51 days. Reinhard et al. (1984) however, reported that o-xylene was biodegraded at the same site although a rate constant could not be calculated from the data in this paper. A continuous field injection experiment by Rugge et al. (1995) reported no biodegradation of o-xylene by the 2 m fence over an injection period of 8 months; the flow path encountered methanogenic, sulfate-reducing and iron-reducing conditions. Other compounds such as benzene, toluene, trichloroethylene, and 1,1,1-trichloroethane were also not biodegraded although one might expect that both toluene and the chlorinated aliphatic compounds would be in this environment.

In addition to the field studies, o-xylene was not biodegraded in five *in situ* microcosm studies; three of these were reported at the Vejen city landfill. The *in situ* microcosm studies by Nielsen et al. (1992) reported no biodegradation for benzene, toluene, o-xylene, naphthalene, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene; only carbon tetrachloride was degraded under these anaerobic conditions. Lyngkilde et al. (1992) reported no biodegradation of benzene, toluene or o-xylene under anaerobic conditions. Neither laboratory microcosms nor *in situ* microcosm experiments by Lyngkilde et al. (1995B) showed biodegradation of o-xylene at distances up to 350 m from the landfill site; however, naphthalene, biphenyl, trichloroethylene were also not biodegraded and toluene was possibly degraded at only one of ten sites. Evidence that o-xylene could be biodegraded at the Vejen landfill site was reported in a field study by Lyngkilde & Christensen (1992); a rate constant of 0.029/day for o-xylene was calculated from this data. Finally, o-xylene was not biodegraded in *in situ* microcosms at Rocky Point, NC (Hunt et al. 1995; Rifai et al. 1995; Barlaz et al. 1995) but biodegradation was reported both in laboratory microcosm studies and a field study (with a rate constant of 0.0021/day) at this site by another author (Rifai et al. 1995). After a review of the papers reporting no biodegradation of o-xylene, there does not appear to be substantive evidence that this

compound is not biodegraded at any of the studied sites. Therefore, a lower limit of biodegradation was set at the lowest reported field study rate constant.

Several authors reported that biodegradation of o-xylene in the laboratory proceeded only in the presence of other carbon sources. As field studies were reported for sites which had been contaminated with a mixture of compounds, this possible dependence on other carbon sources was not seen. One *in situ* microcosm study by Hunt et al. (1995) showed that o-xylene was not biodegraded until toluene was added. Barbaro et al. (1992) reported that the possible recalcitrance of the xylene isomers (o-xylene particularly) at the 5 m piezometer fence monitoring site in both non-acclimated and acclimated field injection experiments may have been due to concentrations of other organic compounds which may have been too low to support the growth of a microbial population required to degrade xylene under denitrifying conditions. Hutchins (1991; 1991A; 1993), in laboratory microcosm experiments, showed that o-xylene present as the sole carbon source in non-acclimated aquifer material was recalcitrant; however, once toluene was added, o-xylene was biodegraded. It was thought that o-xylene was possibly degraded through co-metabolic mechanisms under nitrate-reducing conditions. When aquifer material was obtained from a contaminated site, *i.e.* it had an acclimated microbial population, this dependence on the presence of toluene was not seen and o-xylene was biotransformed following a lag period (Hutchins 1991). Evans et al. (1991) reported that the depletion of o-xylene, but not m- or p-xylene, is enhanced during the active transformation of toluene in nitrate-reducing enrichment culture experiments. Thus, it is possible that if o-xylene is present at a spill site alone or if other compounds are degraded more quickly in an aquifer environment leaving it as the only carbon source, o-xylene may be more recalcitrant than suggested by the collected first-order rate constants.

Mean first-order rate constant values for nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic studies are 0.040/day, 0.0078/day, 0.065/day, and 0.021/day, respectively, suggesting that the rate constant values are fairly similar for most redox conditions. These numbers are reported for all summarized studies where only a single redox condition was present. Many field studies reported multiple redox conditions along a single flow path and thus, were not included in this redox analysis.

A range of recommended values seems most appropriate for this compound with the lower limit equal to 0.00082/day (half-life of 845 days), which was the lowest measured field value, to 0.021/day (half-life of 33 days), which is the mean value for the entire field/*in situ* microcosm data set in common with the other xylene isomers. This is expected to give a fairly conservative range of values for the first-order rate constant of o-xylene. If o-xylene is present as the sole carbon source, however, these values may not be representative of the actual rate.

Table 11. All Summarized Studies for o-Xylene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	NO3	Batch reactor	100 ug/L	19			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	130 ug/L				Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	170 ug/L	13			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	200 ug/L	27			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	220 ug/L	15			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	220 ug/L	30			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	280 ug/L	41			Reinhard,M et al. (1991)
Denmark	Meth	Batch reactor, groundwater inoculum	~150 ug/L	90	NB		Lyngkilde,J et al. (1992)
Lower Glatt Valley, Switzerland	NO3	Column	22290 ug/L	6	NB		Kuhn,EP et al. (1988)
Seal Beach, CA	Meth	Column	0.056 umol/g	570	NB		Haag,F et al. (1991)
Seal Beach, CA	Meth	Column	0.056 umol/g	68	NB		Haag,F et al. (1991)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)

Table 11. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
George Air Force Base, CA	NO3/SO4	Field	377 ug/L	153			Wilson,JT et al. (1995A)
Traverse City, MI	NO3	Field	600 ug/L		0-620 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Sampson County, NC	NO3	Field			0.0007-0.0017/day		Borden,RC et al. (1997)
Tibbetts Road Site, Barrington, NH	Fe	Field	240 ug/L	876	0.00082/day		Wilson,BH et al. (1996)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2300 ug/L	70-105	0.0011/day		Wilson,JT et al. (1994B)
Rocky Point, NC	Fe	Field			0.0021/day		Rifai,HS et al. (1995)
Tibbetts Road Site, Barrington, NH	Fe	Field	1400 ug/L	2336	0.0022/day		Wilson,BH et al. (1996)
Patrick AFB, FL	Meth	Field	1390 ug/L	1200	0.003/day		Wiedemeier,TH et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2400 ug/L	70-105	0.004/day		Wilson,JT et al. (1994B)

Table 11. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	Meth	Field		70	0.0043/day		Wilson,BH et al. (1990)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2300 ug/L	35	0.0086/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.009-0.016/day		Barlaz,MA et al. (1993)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2400 ug/L	35	0.015/day		Wilson,JT et al. (1994B)
Hill AFB, Utah	SO4	Field	2300 ug/L	102	0.02/day		Wiedemeier,TH et al. (1995)
CFB Borden aquifer, Ontario, Canada	NO3	Field	551 ug/L	11	0.026/day		Barbaro,JR et al. (1992)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	16 ug/L	71	0.029/day		Lyngkilde,J & Christensen,TH (1992)
	NO3	Field	210-290 ug/L	80	0.041/day		Reinhard,M et al. (1996)
Noordwijk landfill, The Netherlands		Field	100 ug/L	3650	0.063/day		Zoeteman,BCJ et al. (1981)
	SO4	Field	200-300 ug/L	45	0.077/day	17	Reinhard,M et al. (1996)
Seal Beach, CA	SO4	Field	212-319 ug/L	60	0.16/day	17	Beller,HR et al. (1995)
Eglin AFB, FL	Meth	Field	5480 ug/L	35	0.21/day		Wilson,JT et al. (1994A)

Table 11. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Tibbetts Road Site, Barrington, NH	Fe	Field	240 ug/L	3650	>0.0015/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field	37 ug/L	320-640	Biodegrades		Cozzarelli,IM et al. (1994)
Bemidji, MN	Meth/Fe/Mn	Field			Biodegrades		Cozzarelli,IM et al. (1990)
North Bay landfill, Ontario Canada	Meth	Field	720 ug/L		Biodegrades		Reinhard,M et al. (1984)
CFB Borden aquifer, Ontario, Canada	NO3	Field	423 ug/L	56	NB		Barbaro,JR et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~165 ug/L	51	NB		Acton,DW & Barker,JF (1992)
Fredensborg, Denmark	NO3	Groundwater grab sample	30 ug/L	380	NB		Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	30 ug/L	60	NB		Flyvbjerg,J et al. (1993)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	~295 ug/L	85	NB		Morgan,P et al. (1993)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	~295 ug/L	85	NB		Morgan,P et al. (1993)
Rocky Point, NC	Fe	In situ microcosm			NB		Rifai,HS et al. (1995)

Table 11. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	217	NB		Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		123	NB		Hunt,MJ et al. (1995)
Vejen city landfill, Denmark		In situ microcosm	26 ug/L	90	NB		Lyngkilde,J et al. (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	210 ug/L	450			Albrechtsen,HJ et al. (1994)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	0.00020/day		Kao,CM & Borden,RC (1997)
Ft. Bragg, NC	NO3	Lab microcosm	1600 ug/L	250	0.00031/day		Kao,CM & Borden,RC (1997)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth	Lab microcosm			0.0006/day		Barlaz,MA et al. (1993)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	322 ug/L	452	0.0012/day		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada		Lab microcosm	3000 ug/L	62	0.0015/day		Major,DW et al. (1988)
Sampson County, NC	NO3	Lab microcosm	2000 ug/L	200	0.0051/day	50	Borden,RC et al. (1997)
Traverse City, MI	NO3	Lab microcosm	~5000 ug/L	80	0.0066/day	18	Hutchins,SR (1991A)

Table 11. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	NO3	Lab microcosm	~5000 ug/L	80	0.0066/day	18	Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	24100 ug/L	63	0.0083/day		Hutchins,SR et al. (1991)
Norman, OK	Meth	Lab microcosm	257 ug/L	280	0.0087/day	140	Wilson,BH et al. (1986)
Traverse City, MI	NO3	Lab microcosm	~5000 ug/L	80	0.010/day	30	Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~3750 ug/L	49	0.012/day	28	Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	~3650 ug/L	49	0.016/day	28	Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	~1650 ug/L	28	0.02/day		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~1800 ug/L	28	0.021/day		Hutchins,SR (1991A)
Sleeping Bear Dunes Natl Lakeshore, MI	NO3	Lab microcosm	1400 ug/L	132	0.022/day	15	Kao,CM & Borden,RC (1997)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	3000 ug/L	62	0.027/day		Major,DW et al. (1988)
Traverse City, MI	N2O	Lab microcosm	~2300 ug/L	100	0.045/day		Hutchins,SR (1991)
Rocky Point, NC	SO4/Fe	Lab microcosm	2000 ug/L	140	0.0559/day	37	Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	Lab microcosm		120	0.0559/day	37	Hunt,MJ et al. (1995)
Rocky Point, NC	Fe	Lab microcosm	2000-3000 ug/L	400	0.056/day		Rifai,HS et al. (1995)

Table 11. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Traverse City, MI	NO3	Lab microcosm	~12000 ug/L	49	0.061/day	7	Hutchins,SR (1993)
Traverse City, MI	NO3	Lab microcosm	2400 ug/L	13	0.068/day		Hutchins,SR (1992)
Seal Beach, CA	SO4	Lab microcosm	~5000 ug/L	105	0.069/day	80	Edwards,EA et al. (1992)
Traverse City, MI	Meth/Fe	Lab microcosm	410 ug/L	28	0.071/day		Wilson,BH et al. (1990)
Traverse City, MI	NO3	Lab microcosm	~2300 ug/L	100	0.092/day		Hutchins,SR (1991)
Seal Beach, CA	NO3	Lab microcosm	1750 ug/L	4	0.14/day		Ball,HA & Reinhard,M (1996)
Seal Beach, CA	NO3	Lab microcosm	2000 ug/L	4	0.15/day		Ball,HA & Reinhard,M (1996)
Traverse City, MI	NO3	Lab microcosm	~4350 ug/L	15	0.68/day	10	Hutchins,SR (1993)
Traverse City, MI	NO3	Lab microcosm	2500 ug/L	20	130 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Bemidji, MN	Meth/Fe/Mn	Lab microcosm	3122 ug/L	64	>0.0091/day		Cozzarelli,IM et al. (1994)
CFB Borden aquifer, Ontario, Canada	SO4	Lab microcosm	523 ug/L	420	NB		API (1994)
CFB Borden aquifer, Ontario, Canada		Lab microcosm	3000 ug/L	60	NB		Barker,JF et al. (1987)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	318 ug/L	452	NB		Barbaro,JR et al. (1992)

Table 11. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
North Bay landfill, Ontario Canada	Meth	Lab microcosm	126.9 ug/L	187	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/NO3	Lab microcosm	146.3 ug/L	187	NB		Acton,DW & Barker,JF (1992)
Rocky Point, NC	Meth	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Rocky Point, NC	NO3	Lab microcosm	13000 ug/L	270	NB		Kao,CM & Borden,RC (1997)
Seal Beach, CA	SO4	Lab microcosm	1500 ug/L	39	NB		Ball,HA & Reinhard,M (1996)
Traverse City, MI		Lab microcosm	~2400 ug/L	100	NB		Hutchins,SR (1991)
Traverse City, MI	NO3	Lab microcosm	~15000 ug/L	55	NB		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~15000 ug/L	55	NB		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	4880 ug/L	160	NB		Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	4550 ug/L	160	NB		Hutchins,SR et al. (1991)
Vejen city landfill, Denmark	Fe	Lab microcosm	220 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/Fe/NO3	Lab microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)

Table 11. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	NO3	Lab microcosm	21 ug/L	450	NB		Albrechtsen,HJ et al. (1994)

Table 12. Field and *in situ* Microcosm Studies for o-Xylene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
George Air Force Base, CA	NO3/SO4	Field	377 ug/L	153			Wilson,JT et al. (1995A)
Traverse City, MI	NO3	Field	600 ug/L		0-620 ug/L/day		Hutchins,SR & Wilson,JT (1991)
Sampson County, NC	NO3	Field			0.0007-0.0017/day		Borden,RC et al. (1997)
Tibbetts Road Site, Barrington, NH	Fe	Field	240 ug/L	876	0.00082/day		Wilson,BH et al. (1996)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2300 ug/L	70-105	0.0011/day		Wilson,JT et al. (1994B)
Rocky Point, NC	Fe	Field			0.0021/day		Rifai,HS et al. (1995)
Tibbetts Road Site, Barrington, NH	Fe	Field	1400 ug/L	2336	0.0022/day		Wilson,BH et al. (1996)
Patrick AFB, FL	Meth	Field	1390 ug/L	1200	0.003/day		Wiedemeier,TH et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2400 ug/L	70-105	0.004/day		Wilson,JT et al. (1994B)
Traverse City, MI	Meth	Field		70	0.0043/day		Wilson,BH et al. (1990)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2300 ug/L	35	0.0086/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.009-0.016/day		Barlaz,MA et al. (1993)

Table 12. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2400 ug/L	35	0.015/day		Wilson,JT et al. (1994B)
Hill AFB, Utah	SO4	Field	2300 ug/L	102	0.02/day		Wiedemeier,TH et al. (1995)
CFB Borden aquifer, Ontario, Canada	NO3	Field	551 ug/L	11	0.026/day		Barbaro,JR et al. (1992)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	16 ug/L	71	0.029/day		Lyngkilde,J & Christensen,TH (1992)
	NO3	Field	210-290 ug/L	80	0.041/day		Reinhard,M et al. (1996)
Noordwijk landfill, The Netherlands		Field	100 ug/L	3650	0.063/day		Zoeteman,BCJ et al. (1981)
	SO4	Field	200-300 ug/L	45	0.077/day	17	Reinhard,M et al. (1996)
Seal Beach, CA	SO4	Field	212-319 ug/L	60	0.16/day	17	Beller,HR et al. (1995)
Eglin AFB, FL	Meth	Field	5480 ug/L	35	0.21/day		Wilson,JT et al. (1994A)
Tibbetts Road Site, Barrington, NH	Fe	Field	240 ug/L	3650	>0.0015/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field	37 ug/L	320-640	Biodegrades		Cozzarelli,IM et al. (1994)

Table 12. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Bemidji, MN	Meth/Fe/Mn	Field			Biodegrades		Cozzarelli,IM et al. (1990)
North Bay landfill, Ontario Canada	Meth	Field	720 ug/L		Biodegrades		Reinhard,M et al. (1984)
CFB Borden aquifer, Ontario, Canada	NO3	Field	423 ug/L	56	NB		Barbaro,JR et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
North Bay landfill, Ontario Canada	Meth/SO4	Field	~165 ug/L	51	NB		Acton,DW & Barker,JF (1992)
Rocky Point, NC	Fe	In situ microcosm			NB		Rifai,HS et al. (1995)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	217	NB		Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		123	NB		Hunt,MJ et al. (1995)
Vejen city landfill, Denmark		In situ microcosm	26 ug/L	90	NB		Lyngkilde,J et al. (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)

3.1.6. p-Xylene

p-Xylene was biodegraded in nitrate-reducing, sulfate-reducing, methanogenic, and iron-reducing aquifer environments (Table 13). In general it is not as readily biodegraded as toluene but appears to be biodegraded at a similar rate as ethylbenzene and the other xylene isomers. Again, preference is given to field and *in situ* microcosm studies and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies alone (Table 14) ranged from 0 to 0.057/day with a mean value of 0.014/day. This mean rate constant changes to 0.015/day when only field/*in situ* microcosm study papers in common with other xylenes are considered.

In order to determine an appropriate lower limit for the recommended range, studies reporting no biodegradation were examined more closely to determine whether this was a reasonable value. Two field studies report that p-xylene was not biodegraded. A continuous injection experiment by Rugge et al. (1995) reported no biodegradation of p-xylene by the 2 m piezometer fence over an injection period of 8 months; the flow path encountered methanogenic, sulfate-reducing and iron-reducing conditions. Other compounds such as benzene, toluene, trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane were also not biodegraded although one might expect that both toluene and the chlorinated aliphatic compounds would be degraded in this environment. Barbaro et al. (1992) reported the partial anaerobic biodegradation of p-xylene in a field study with the presence of added nitrate (by the 1 m piezometer fence); these conditions resulted in a first-order rate constant of 0.026/day. At the same site but without the presence of added nitrate, p-xylene was not biodegraded by the 5 m fence which corresponded to a time of 56 days. Therefore, this site is capable of biodegrading p-xylene, but the rate may be much slower without the addition of nitrate. After a review of the papers reporting no biodegradation of p-xylene, there does not appear to be substantive evidence that this compound is not biodegraded at any of the studied sites. Therefore, a lower limit of biodegradation was set at the lowest reported field study rate constant.

Similar to other BTEX compounds, the rate of anaerobic biodegradation of p-xylene in aquifer environments may be related to the redox environment. Mean first-order rate constant values for nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic studies are 0.047/day, 0.0050/day, 0.079/day, and 0.015/day, respectively. These numbers are reported for all summarized studies where only a single redox condition was present. Many field studies reported multiple redox conditions along a single flow path and thus, were not included in this redox analysis.

A range of recommended values seems most appropriate for this compound with the lower limit equal to 0.00085/day (half-life of 815 days), which was the lowest measured field value, to 0.015/day (half-life of 46 days), which is the mean value for the entire field/*in situ* microcosm data set in common with the other xylene isomers. This is expected to give a fairly conservative range of values for the first-order rate constant of p-xylene.

Table 13. All Summarized Studies for p-Xylene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	NO3	Batch reactor	120 ug/L				Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	230 ug/L	19			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	370 ug/L	13			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	440 ug/L	27			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	470 ug/L	15			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	470 ug/L	30			Reinhard,M et al. (1991)
Seal Beach, CA	NO3	Batch reactor	610 ug/L	41			Reinhard,M et al. (1991)
Lower Glatt Valley, Switzerland	NO3	Column	22290 ug/L	6	NB		Kuhn,EP et al. (1988)
Seal Beach, CA	Meth	Column	0.053 umol/g	570	NB		Haag,F et al. (1991)
Seal Beach, CA	Meth	Column	0.053 umol/g	68	NB		Haag,F et al. (1991)
George Air Force Base, CA	NO3/SO4	Field	182 ug/L	153			Wilson,JT et al. (1995A)
Tibbetts Road Site, Barrington, NH	Fe	Field	1100 ug/L	876	0.00085/day		Wilson,BH et al. (1996)

Table 13. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Sampson County, NC	NO3	Field			0.0012-0.0035/day		Borden,RC et al. (1997)
Rocky Point, NC	Fe	Field			0.0013/day		Rifai,HS et al. (1995)
Tibbetts Road Site, Barrington, NH	Fe	Field	1400 ug/L	2336	0.0018/day		Wilson,BH et al. (1996)
Swan Coastal Plain, Western Australia	SO4/Fe	Field	3870 ug/L	71	0.0023-0.0083/day		Thierrin,J et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1400 ug/L	70-105	0.0024/day		Wilson,JT et al. (1994B)
Patrick AFB, FL	Meth	Field	1220 ug/L	1200	0.0029/day		Wiedemeier,TH et al. (1995)
Traverse City, MI	Meth	Field		70	0.0043/day		Wilson,BH et al. (1990)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.005-0.014/day		Barlaz,MA et al. (1993)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2100 ug/L	35	0.0051/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1400 ug/L	35	0.0094/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2100 ug/L	70-105	0.0096/day		Wilson,JT et al. (1994B)
Noordwijk landfill, The Netherlands		Field	300 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)

Table 13. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Eglin AFB, FL	Meth	Field	3120 ug/L	35	0.02, 0.08/day		Wilson,JT et al. (1994A)
CFB Borden aquifer, Ontario, Canada	NO3	Field	367 ug/L	11	0.026/day		Barbaro,JR et al. (1992)
Hill AFB, Utah	SO4	Field	1620 ug/L	228	0.032/day	102	Wiedemeier,TH et al. (1995)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	224 ug/L	71	0.057/day		Lyngkilde,J & Christensen,TH (1992)
Tibbetts Road Site, Barrington, NH	Fe	Field	1100 ug/L	3650	>0.0019/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field	122 ug/L	320-640	Biodegrades		Cozzarelli,IM et al. (1994)
North Bay landfill, Ontario Canada	Meth	Field	1100 ug/L		Biodegrades		Reinhard,M et al. (1984)
CFB Borden aquifer, Ontario, Canada	NO3	Field	267 ug/L	56	NB		Barbaro,JR et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	290 ug/L	85	0.0054/day		Morgan,P et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	80 ug/L	380	NB		Flyvbjerg,J et al. (1993)

Table 13. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Fredensborg, Denmark	NO3	Groundwater grab sample	80 ug/L	60	NB		Flyvbjerg,J et al. (1993)
Uiterburen, The Netherlands	NO3	Groundwater grab sample	275 ug/L	85	NB		Morgan,P et al. (1993)
Rocky Point, NC	Fe	In situ microcosm			0.014/day		Rifai,HS et al. (1995)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	130	0.0143/day		Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		251	0.0143/day	121	Hunt,MJ et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth	Lab microcosm			0.0006/day		Barlaz,MA et al. (1993)
Rocky Point, NC	Fe	Lab microcosm	2000-3000 ug/L	400	0.02/day		Rifai,HS et al. (1995)
Traverse City, MI	NO3	Lab microcosm	~9000 ug/L	160	0.023/day	62	Hutchins,SR et al. (1991)
Sampson County, NC	NO3	Lab microcosm	2000 ug/L	260	0.033/day	150	Borden,RC et al. (1997)
Seal Beach, CA	SO4	Lab microcosm	~5000 ug/L	77	0.036/day	30	Edwards,EA et al. (1992)
Traverse City, MI	Meth/Fe	Lab microcosm	440 ug/L	28	0.057/day		Wilson,BH et al. (1990)
Seal Beach, CA	NO3	Lab microcosm	2600 ug/L	25	0.10/day	11	Ball,HA & Reinhard,M (1996)

Table 13. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	NO3	Lab microcosm	2600 ug/L	25	0.10/day	11	Ball,HA & Reinhard,M (1996)
Traverse City, MI	NO3	Lab microcosm	15000 ug/L	39	0.11/day	20	Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	6500 ug/L	56	0.14/day	28	Hutchins,SR et al. (1991)
Seal Beach, CA	SO4	Lab microcosm	2300 ug/L	39	0.17/day	17	Ball,HA & Reinhard,M (1996)
Traverse City, MI	NO3	Lab microcosm	2100 ug/L	13	0.21/day		Hutchins,SR (1992)
Traverse City, MI	NO3	Lab microcosm	6500 ug/L	42	0.24/day	28	Hutchins,SR et al. (1991)
Vejen city landfill, Denmark	NO3	Lab microcosm	100 ug/L	450	Biodegrades		Albrechtsen,HJ et al. (1994)
CFB Borden aquifer, Ontario, Canada	SO4	Lab microcosm	328 ug/L	420	NB		API (1994)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	208 ug/L	452	NB		Barbaro,JR et al. (1992)
CFB Borden aquifer, Ontario, Canada	NO3	Lab microcosm	212 ug/L	452	NB		Barbaro,JR et al. (1992)
Traverse City, MI	NO3	Lab microcosm	19800 ug/L	63	NB		Hutchins,SR et al. (1991)
Traverse City, MI	NO3	Lab microcosm	~26000 ug/L	55	NB		Hutchins,SR (1991A)
Traverse City, MI	NO3	Lab microcosm	~9000 ug/L	160	NB		Hutchins,SR et al. (1991)

Table 13. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	Fe	Lab microcosm	1100 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	920 ug/L	450	NB		Albrechtsen,HJ et al. (1994)

Table 14. Field and *in situ* Microcosm Studies for p-Xylene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
George Air Force Base, CA	NO3/SO4	Field	182 ug/L	153			Wilson,JT et al. (1995A)
Tibbetts Road Site, Barrington, NH	Fe	Field	1100 ug/L	876	0.00085/day		Wilson,BH et al. (1996)
Sampson County, NC	NO3	Field			0.0012-0.0035/day		Borden,RC et al. (1997)
Rocky Point, NC	Fe	Field			0.0013/day		Rifai,HS et al. (1995)
Tibbetts Road Site, Barrington, NH	Fe	Field	1400 ug/L	2336	0.0018/day		Wilson,BH et al. (1996)
Swan Coastal Plain, Western Australia	SO4/Fe	Field	3870 ug/L	71	0.0023-0.0083/day		Thierrin,J et al. (1995)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1400 ug/L	70-105	0.0024/day		Wilson,JT et al. (1994B)
Patrick AFB, FL	Meth	Field	1220 ug/L	1200	0.0029/day		Wiedemeier,TH et al. (1995)
Traverse City, MI	Meth	Field		70	0.0043/day		Wilson,BH et al. (1990)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field			0.005-0.014/day		Barlaz,MA et al. (1993)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2100 ug/L	35	0.0051/day		Wilson,JT et al. (1994B)
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	1400 ug/L	35	0.0094/day		Wilson,JT et al. (1994B)

Table 14. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Sleeping Bear Dunes Natl Lakeshore, MI	Meth/NO3/SO4	Field	2100 ug/L	70-105	0.0096/day		Wilson,JT et al. (1994B)
Rocky Point, NC	Fe	In situ microcosm			0.014/day		Rifai,HS et al. (1995)
Rocky Point, NC	SO4/Fe	In situ microcosm	<500 ug/L	130	0.0143/day		Barlaz,MA et al. (1995)
SE coastal plain, NC	SO4/Fe	In situ microcosm		251	0.0143/day	121	Hunt,MJ et al. (1995)
Noordwijk landfill, The Netherlands		Field	300 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)
Eglin AFB, FL	Meth	Field	3120 ug/L	35	0.02, 0.08/day		Wilson,JT et al. (1994A)
CFB Borden aquifer, Ontario, Canada	NO3	Field	367 ug/L	11	0.026/day		Barbaro,JR et al. (1992)
Hill AFB, Utah	SO4	Field	1620 ug/L	228	0.032/day	102	Wiedemeier,TH et al. (1995)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	224 ug/L	71	0.057/day		Lyngkilde,J & Christensen,TH (1992)
Tibbetts Road Site, Barrington, NH	Fe	Field	1100 ug/L	3650	>0.0019/day		Wilson,BH et al. (1996)
Bemidji, MN	Meth/Fe/Mn	Field	122 ug/L	320-640	Biodegrades		Cozzarelli,IM et al. (1994)

Table 14. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
North Bay landfill, Ontario Canada	Meth	Field	1100 ug/L		Biodegrades		Reinhard,M et al. (1984)
CFB Borden aquifer, Ontario, Canada	NO3	Field	267 ug/L	56	NB		Barbaro,JR et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)

3.2. Chlorinated Aliphatic Compounds

In this section, each chlorinated aliphatic compound is reviewed with an individual summary table listing all reported studies. If sufficient data were available, a second table with information from just the field and *in situ* microcosm studies was included. The amount and quality of the data for these compounds varied greatly, with a large amount of information collected for trichloroethylene and very little information reported on compounds such as 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane. Included in most reviews is a recommended first-order rate constant or range of first-order rate constants, depending on the amount of information located, that could be used for input into the EPACMTP model. Table 15 summarizes both the range and mean of all studies and the field/*in situ* microcosm studies alone for each of the studied chlorinated aliphatic compounds. A few compounds did not have sufficient data available to determine a recommended rate constant; however, these compounds, similar in structure to the other reviewed chlorinated aliphatic compounds, should biodegrade under anaerobic conditions using the same mechanisms that are reviewed below.

Biodegradation of organic compounds most often occurs when bacteria catalyze the breakdown of these molecules and then recover some of this chemical energy as ATP (adenosine triphosphate) which is absolutely necessary for maintenance of the bacterial cell. ATP is generated through a series of oxidation-reduction reactions (the electron transport chain) where electrons are sequentially transferred from one compound, the electron donor, to an electron acceptor. The final or terminal electron acceptor in aerobic respiration is oxygen; the equivalent for anaerobic respiration is usually nitrate, iron(III), manganese (IV), sulfate, or carbon dioxide. The BTEX compounds are biodegraded through their use as an electron donor (used as a carbon substrate) by the degrading microbial population in order to produce energy in the form of ATP. Their degradation is considered to be limited by the availability of electron acceptors (and not electron donors) in the aquifer. Electron acceptors such as carbon dioxide, sulfate, and iron(III) are generally present in more than sufficient quantities in most aquifers for these reactions to proceed. The biodegradation of highly chlorinated aliphatic compounds in anaerobic groundwater environments differs from the BTEX compounds as the chlorinated compounds themselves are used as electron acceptors.

Under natural, anaerobic conditions, the highly chlorinated aliphatic compounds are thought to biodegrade mainly through their use as an electron acceptor during a process called reductive dechlorination. Reductive dechlorination involves the removal of a chlorine atom and its replacement with hydrogen; this results in the sequential loss of chlorine atoms from the chlorinated compound. For a compound such as tetrachloroethylene, this sequence is generally as follows: degradation to trichloroethylene, dichloroethylene (most often cis-1,2-dichloroethylene), vinyl chloride and finally to ethene and ethane. It is currently believed that the complete degradation of tetrachloroethylene or trichloroethylene in the natural environment requires the activity of mixed microbial populations; however, a recently isolated bacterial strain was shown to completely biodegrade tetrachloroethylene to ethene (Maymo-Gatell et al. 1997). Importantly, reductive dechlorination does not result in the production of energy for the microorganism. Because the chlorinated compound is used as an electron acceptor, an electron donor (or carbon substrate) is required to produce energy for the bacterial cell.

Electron donors can be anything from natural organic carbon present in the aquifer to compounds present as co-contaminants (*e.g.* landfill leachate, BTEX compounds). A problem may exist if the aquifer system is depleted of electron donors before reductive dechlorination of the contaminant(s) is complete; in this case, reductive dechlorination of the chlorinated compound will stop (Wiedemeier et al. 1996B). While reductive dechlorination has been shown under nitrate-reducing (Ala & Domenico 1992) and iron-reducing conditions (Wilson BH et al. 1996), the rate of this process is expected to be slower than under stronger reducing environments such as methanogenic and sulfate-reducing groundwater environments. There is evidence that the strength of the reducing environment may affect the ability of a system to reductively dechlorinate a highly chlorinated compound completely through to ethene. Methanogenic environments often complete this sequence whereas nitrate- or iron-reducing environments may only proceed to the formation of dichloroethylene (Chapelle 1996). This is of concern as compounds such as tetrachloroethylene, trichloroethylene and carbon tetrachloride, which tend to disappear fairly rapidly in a strong reducing environment, often produce unwanted transformation products as the result of incomplete reductive dechlorination processes. These products include chloroform, dichloromethane, cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,1-dichloroethene, vinyl chloride, 1,1-dichloroethane, and chloroethane. Reductive dechlorination of chlorinated aliphatic compounds does not occur under aerobic conditions; highly oxidized (and highly chlorinated) compounds such as tetrachloroethylene, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene are expected to be recalcitrant under aerobic conditions. Cometabolic degradation of trichloroethylene to carbon dioxide by methanotrophs present in aerobic aquifer environments (Kastner 1991) is a major exception to this observation. Vinyl chloride, trans-dichloroethylene and cis-dichloroethylene are biodegraded even more readily than trichloroethylene by these bacteria (Semprini et al. 1992).

In addition to biodegradation via reductive dechlorination, less chlorinated aliphatic compounds may also biodegrade in anaerobic aquifer systems by acting as an electron donor [compounds such as vinyl chloride (Bradley & Chapelle 1996) and possibly dichloromethane (McCarty & Semprini 1994)]. Similar to the BTEX compounds, these compounds can biodegrade via oxidation reactions in nitrate- and iron-reducing redox environments. These chlorinated compounds are also biodegraded by reductive dechlorination in methanogenic and sulfate-reducing environments. Rate constants reported for methanogenic and sulfate-reducing groundwater environments are expected to be lower for these compounds when compared to the more highly chlorinated compounds but higher under nitrate- and iron-reducing environments, again, when they are compared to the more highly chlorinated compounds.

The determination of biodegradation for a chlorinated aliphatic compound during a field study differs somewhat from that of the BTEX compounds. During reductive dechlorination along a flow path, chloride is generated and must be accounted for when chloride is used as a conservative tracer. This is accomplished by calculating a mass balance for chloride including both organic and ionic species (demonstrated by Wiedemeier et al. 1996B). Another common method used to demonstrate biodegradation of a chlorinated compound at a particular site is to measure daughter products such as dichloroethylene which are not commonly produced and would only be present through the

biodegradation of more highly chlorinated compounds. The presence of daughter products can also lead to some confusion in the interpretation of a site where a spill of several chlorinated compounds has occurred. Vinyl chloride, trichloroethylene, and chloroform are both commonly used industrial compounds as well as reductive dechlorination products from more chlorinated compounds. Daughter products from the reductive dechlorination of tetrachloroethylene, such as trichloroethylene and dichloroethylene, would initially increase as they are first produced and then decrease in concentration further downgradient as they are either used as an electron acceptor or oxidized themselves. If the spill included both tetrachloroethylene and trichloroethylene, trichloroethylene concentrations might appear to increase downgradient from the initial spill due to its production as a metabolite and would not necessarily signify recalcitrance of trichloroethylene at this site. Some authors published net biodegradation rate constants which accounted for both the production and biodegradation of these compounds.

As mentioned briefly above, the redox condition is very important in the degradation of the chlorinated aliphatic compounds. This is a result of the two different mechanisms used to biodegrade the chlorinated aliphatic compounds. Highly chlorinated compounds are mainly biodegraded via reductive dechlorination (compound used as an electron acceptor), a process requiring a strong reducing environment; whereas, less highly chlorinated compounds may be biodegraded either via reductive dechlorination or by oxidation (compound used as an electron donor) depending on the redox environment. Therefore, compounds such as tetrachloroethylene and carbon tetrachloride, which are highly oxidized and highly chlorinated, will biodegrade more quickly by reductive dechlorination than a less oxidized and less highly chlorinated compound such as vinyl chloride. Sulfate-reducing and methanogenic conditions are expected to result in the reduction of the more highly chlorinated compounds and aerobic or nitrate-reducing conditions may be more suitable for the oxidative degradation of the less chlorinated compounds (Vogel 1994). While sufficient data were not available to determine rate constants for each redox condition, most field/*in situ* studies of the chlorinated aliphatic compounds tended to be from methanogenic or sulfate-reducing aquifer environments. The summary table for the chlorinated aliphatic compounds (Table 15) shows carbon tetrachloride with the largest average first-order rate constant of the compounds which were studied. Average rate constant values determined for 1,2-dichloroethane, dichloromethane, tetrachloroethylene, trichloroethylene and vinyl chloride are fairly similar, differing by less than an order of magnitude. An average rate constant for 1,1,1-trichloroethane for all studies was lower than that calculated for just field/*in situ* studies. As this is only one of two reviewed chlorinated aliphatic compounds to undergo abiotic hydrolysis reactions within an environmentally relevant time period (Table 16), this suggests that field studies may not have accounted for these hydrolysis reactions. Average rate constant data for chloroform was minimal, only one field study reported a first-order rate constant. This may have resulted in an average field/*in situ* rate constant value which appears to be high when compared to other chlorinated aliphatic compounds. Again, insufficient data was published to determine a degradation rate constant for either 1,1,2-trichloroethane or 1,1,2,2-tetrachloroethane; however, the evidence collected for the remainder of the chlorinated aliphatic compounds indicates that these compounds should also be susceptible to reductive dechlorination in an anaerobic aquifer environment.

One issue of concern was left unresolved in most cases during the literature search of this set of compounds. Very little information was collected on the biodegradation of these compounds in nitrate-reducing aquifer environments. As stated above, the highly chlorinated compounds are not expected to biodegrade readily under this condition as reductive dechlorination requires a strong reducing environment. Only tetrachloroethylene had data giving a rate constant under nitrate-reducing conditions; a half-life of about ten years was reported. The inclusion of these data had a marked effect on the mean value used as the upper limit to tetrachloroethylene's first-order rate constant range. If similar information for the other highly chlorinated compounds had been available, the mean value for these compounds would be expected to be substantially lower than that reported. Therefore, a qualifier is given at the end of each highly chlorinated compound stating that the range which was determined from the available data is not expected to be representative for nitrate-reducing conditions.

Table 15. Summary Table of First-Order Anaerobic Biodegradation Rate Constants for the Chlorinated Aliphatic Compounds

Compound	Range, all studies	Mean, all studies	Range, field/*in situ* studies	Mean, field/*in situ* studies
Carbon Tetrachloride	0-1.73[ab]	0.34 n=15	0-1.73	0.37 n=9
Chloroform	0.004-0.25	0.080 n=12	0.030	0.030 n=1
1,2-Dichloroethane	0.0042-0.011	0.0076 n=2	0.0042-0.011	0.0076 n=2
Dichloromethane	0.0064	0.0064 n=1	0.0064	0.0064 n=1
1,1,2,2-Tetrachloroethane	I.D.[c]	I.D.	I.D.	I.D.
Tetrachloroethylene	0-0.41	0.027 n=36	0-0.034	0.0029 n=16
1,1,1-Trichloroethane	0-0.059	0.010 n=28	0-0.059	0.016 n=15
1,1,2-Trichloroethane	I.D.	I.D.	I.D.	I.D.
Trichloroethylene	0-0.19	0.011 n=78	0-0.00611	0.0025 n=47
Vinyl Chloride	0-0.12	0.018[d] n=27	0-0.0845	0.0073 n=19

[a]First-order rate constants in units of $days^{-1}$

[b]Studies reporting "biodegrades" or zero-order rate constants were assigned a value equal to the mean of the positive rate constant values.

[c]Insufficient data to determine a biodegradation rate constant

[d]Mean for all studies without three laboratory studies by Bradley & Chapelle (1996) where FeEDTA was added resulting in increased rates of biodegradation equals 0.0078/day; the redefined range would be 0-0.0845/day.

Table 16. Abiotic Hydrolysis Half-Lives for Several Chlorinated Aliphatic Compounds

Compound	Hydrolysis Half-Life (in years)	Reference
Carbon Tetrachloride	40.5	Jeffers,PM et al. (1989)
Chloroform	1849	Jeffers,PM et al. (1989)
1,2-Dichloroethane	72	Jeffers,PM et al. (1989)
Dichloromethane	704	Mabey,W & Mill,T (1978)
1,1,2-Trichloroethane	139	Jeffers,PM et al. (1989)
1,1,1-Trichloroethane	1.1	Jeffers,PM et al. (1989)
1,1,2,2-Tetrachloroethane	0.4	Jeffers,PM et al. (1989)
Tetrachloroethylene	$9.9X10^{+8}$	Jeffers,PM et al. (1989)
Trichloroethylene	$1.3X10^{+6}$	Jeffers,PM et al. (1989)
Vinyl Chloride	>10	Kollig,HP (1990)

3.2.1. Carbon Tetrachloride

The carbon in this compound is present in its most oxidized state (chlorine is present as the only substituent) and thus the only biological anaerobic transformation process possible is reduction (McCarty & Reinhard 1993). The main reaction pathway leading to the anaerobic degradation of carbon tetrachloride is through reductive dechlorination with chloroform formed as the initial reaction product followed by dichloromethane. As with the other chlorinated aliphatic compounds with sufficient information, preference is given to field and *in situ* microcosm studies and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies (Table 15) alone ranged from 0 to 1.73/day with a mean value of 0.37/day. The high value of 1.73/day results from a field experiment where the groundwater was injected with high concentrations of acetate in order to enhance biotransformation of carbon tetrachloride (Semprini et al. 1992). If this value is ignored, the mean adjusted value for the field/*in situ* studies becomes 0.18/day.

Six different field and *in situ* microcosm studies reported in the database show that carbon tetrachloride degrades quickly under methanogenic, sulfate-reducing and iron-reducing conditions (Table 17). Two of these studies investigate the degradation of this compound under nitrate-reducing conditions and report either 1) carbon tetrachloride degradation increased as the nitrate concentrations decreased (Semprini et al. 1992) or 2) no biodegradation of carbon tetrachloride was reported over a 180 day period under nitrate-reducing conditions but that biodegradation occurred readily under methanogenic, sulfate-reducing and iron-reducing conditions along the same plume of contamination (Nielsen et al. 1995B). This suggests that either biodegradation of carbon tetrachloride does not occur under nitrate-reducing conditions or that the rate of biodegradation is much slower than for other anaerobic environments where the reducing potential is higher.

The redox conditions of the aquifer are expected to play an important role in the degradation of carbon tetrachloride as with all of the chlorinated aliphatics. As this compound is in a highly oxidized state (highly chlorinated), methanogenic conditions are expected to give the highest rate constant values with sulfate-reducing and iron-reducing conditions giving somewhat lower average rate constant values. There is insufficient published data however, to determine a value for each redox environment. Therefore, a range of recommended values seems most appropriate for this compound with the lower limit equal to 0.0037/day (half-life of 187 days), which was the lowest measured field value (reported for iron-reducing conditions), to 0.18/day (half-life of 4 days), which is the mean adjusted value for the field/*in situ* microcosm data set. It is not possible to determine an appropriate rate constant from this data for nitrate-reducing conditions at this time, although it is expected that the rate will be markedly slower than the recommended range of rate constants given above as reductive dechlorination either may not occur or will occur slowly under this redox environment. Therefore, the above range of recommended values will not be representative if the redox potential of the aquifer under study is classified as nitrate-reducing.

Table 17. All Summarized Studies for Carbon Tetrachloride

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		Biodegrades		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		Biodegrades		Lyngkilde,J et al. (1992)
Moffett Field Naval Air Station, CA	NO3/SO4	Field	45 ug/L	1.8	1.73/day		Semprini,L et al. (1992)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	Biodegrades		Rugge,K et al. (1995)
Moffett Field Naval Air Station, CA	NO3/SO4	Field			Biodegrades		Semprini,L et al. (1990)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	28	0.11/day		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L	12-30	0.15-0.49/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	19	0.21/day		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Fe	In situ microcosm	150 ug/L	60	<0.0037/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Fe	In situ microcosm	150 ug/L	10-60	>0.0037->0.23/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)

Table 17. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	Meth	Lab microcosm	150 ug/L	10	>0.23/day		Nielsen,PH et al. (1995B)
Biscayne aquifer, southern Florida		Lab microcosm	4000 ug/L	14	Biodegrades		Parsons,F et al. (1985)
Vejen city landfill, Denmark	Fe	Lab microcosm	150 ug/L	60	Biodegrades		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Fe/NO3/Mn	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995B)

3.2.2. Chloroform

Only four different studies were located reporting the biodegradation potential of chloroform in an aquifer environment (Table 18). Based on the current literature, chloroform is expected to biodegrade under anaerobic conditions. Limited field data for this compound resulted in the use of rate constants from laboratory microcosm studies in order to offer a range of first-order rate constant values recommended for input into the EPACMTP model. First-order rate constants for all studies (Table 15) ranged from 0.004 to 0.25/day with a mean value of 0.080/day.

The only field study to report first-order rate constant data indicates that chloroform is biodegraded at a wastewater injection site (Roberts et al. 1982). During the injection period no biodegradation was reported for any of the chlorinated aliphatic compounds. However, once injection stopped, chloroform was biodegraded after a 20-30 day lag period with a published rate constant of 0.030/day. Chloroform continued to be biodegraded until a plateau of 0.75 Og/L was reached after 150 days.

A laboratory microcosm study by Saunders et al. (1996), using aquifer material from both a northern and a southern site with varying concentrations of chloroform, gave ranges of rate constants from 0.004-0.025/day and 0.033-0.25/day for the southern and northern site, respectively. Laboratory studies of chloroform are able to follow the loss of this compound without complications added often by field studies where chloroform can also be formed as a reaction product from the biodegradation of carbon tetrachloride (Semprini et al. 1992; Parsons et al. 1985). However, these laboratory studies also follow the biodegradation of chloroform in a system where other chlorinated compounds and other compounds in general are not present; this is probably not very representative of field conditions where a spill of multiple compounds has occurred.

Results in the field are expected to be complicated if carbon tetrachloride and chloroform are present in the spill. In this case, there will be two sources of chloroform, that from the original source and that from the reductive dechlorination of carbon tetrachloride. A field study by Barber et al. (1992) concludes that increasing concentrations of chloroform along a contaminant flow path may be due to the biodegradation of another compound. There were no published field studies under these circumstances where a net rate of chloroform biodegradation was calculated.

Given the limited amount of information on the anaerobic biodegradation of chloroform in aquifer environments, a range of rate constants is recommended with the lower limit equal to 0.0004/day (a half-life of 1733 days) which is an order of magnitude lower than the lowest published rate constant (a laboratory microcosm study) and the upper limit equal to 0.03/day (a half-life of 23 days) which represents the sole, reported field study rate constant. Although information on the biodegradation of chloroform under different redox conditions was not available, data for other chlorinated aliphatic compounds suggest that chloroform is expected to biodegrade most rapidly under methanogenic conditions and less rapidly under sulfate-reducing and iron-reducing conditions. Biodegradation of this compound under nitrate-reducing conditions may be slower than the recommended range of rate constants given above as reductive dechlorination either may not occur or will occur slowly under this

redox environment. Therefore, the above range of recommended values will not be representative if the redox potential of the aquifer under study is classified as nitrate-reducing.

Table 18. All Summarized Studies for Chloroform

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Gloucester landfill, Ontario, Canada	SO4	Field	52 ug/L	5000			Lesage,S et al. (1990)
Otis AFB, Sandwich, MA	NO3	Field	<0.2-0.6 ug/L	6667			Barber,LBII (1992)
Palo Alto, CA		Field	20 ug/L	350	0.03/day	20-30	Roberts,PV et al. (1982)
South Carolina		Lab microcosm	168 ug/L		0.004/day	112	Saunders,F et al. (1996)
South Carolina		Lab microcosm	196 ug/L		0.0041/day	112	Saunders,F et al. (1996)
South Carolina		Lab microcosm	3.7 ug/L		0.02/day	56	Saunders,F et al. (1996)
South Carolina		Lab microcosm	184 ug/L		0.025/day	56	Saunders,F et al. (1996)
South Carolina		Lab microcosm	83.0 ug/L		0.025/day	56	Saunders,F et al. (1996)
Wisconsin		Lab microcosm	11.2 ug/L		0.033/day		Saunders,F et al. (1996)
Wisconsin		Lab microcosm	56 ug/L		0.099/day		Saunders,F et al. (1996)
Wisconsin		Lab microcosm	53 ug/L		0.099/day		Saunders,F et al. (1996)
Wisconsin		Lab microcosm	10.7 ug/L		0.12/day		Saunders,F et al. (1996)
Wisconsin		Lab microcosm	155 ug/L		0.25/day	14	Saunders,F et al. (1996)
Wisconsin		Lab microcosm	164 ug/L		0.25/day	14	Saunders,F et al. (1996)

3.2.3. 1,2-Dichloroethane

Only two studies were located reporting the possible biodegradation of 1,2-dichloroethane in an aquifer system (Table 19). A field study by Lee et al. (1996) was undertaken following a 1,2-dichloroethane spill. Reported first-order decay half-lives determined from wells at the site as well as laboratory microcosm studies showing the biodegradation of 1,2-dichloroethane using site material indicate that this compound can be biodegraded in a methanogenic aquifer environment. The second study by Lesage et al. (1990) reports that 1,2-dichloroethane concentrations decrease in wells downgradient from the source. However, without reported conservative tracer data, corrections for abiotic processes could not be made in order to determine whether this loss was due to biotransformation. Possible reaction products of 1,2-dichloroethane biodegradation were also not measured.

Based on these limited data, a range of rate constants taken from the Lee et al. field study is recommended (0.0042-0.011/day; half-lives of 63 to 165 days). However, this range was reported for only a single, methanogenic site and therefore it does not have the same supporting evidence that other compounds with more extensive data have. Biodegradation of this compound under nitrate-reducing conditions may occur more readily than for other more highly chlorinated aliphatic compounds as it is less chlorinated (less oxidized). This indicates that it may be biodegraded via oxidation pathways.

Table 19. All Summarized Studies for 1,2-Dichloroethane

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Gloucester landfill, Ontario, Canada	SO4	Field	14 ug/L	1000			Lesage,S et al. (1990)
Gulf Coast site	Meth	Field			0.0042-0.011/day		Lee,MD et al. (1996)

3.2.4. Dichloromethane (Methylene Chloride)

Only three studies were located that reported the possible biodegradation of dichloromethane at an aquifer site (Table 20). A field study by Fiorenza et al. (1994) at a site contaminated with tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, naphtha, and dichloromethane reports the biodegradation of dichloromethane, most likely to products such as methanol, acetic acid, methane and carbon dioxide. The authors report that if only dispersion and retardation had affected the dichloromethane plume that it would have extended off-site. Instead, the plume was restricted in size and was found only on-site. A second study by Lehmicke et al. (1996) reports that dichloromethane concentrations in the source area decreased by an order of magnitude within five years. Concentrations are even lower 100 m downgradient, below what would be expected due to non-biodegradation processes. This study suggests that acetic acid production, due to biodegradation of dichloromethane, may have provided an electron donor suitable to drive the reductive dechlorination of other more highly chlorinated aliphatic solvents present at this site. The report by Cline and Viste (1985) shows that dichloromethane concentrations decreased as it traveled 80 meters downgradient. However, without reported conservative tracer data, corrections for abiotic processes could not be made in order to determine whether this loss was due to biotransformation.

Based on these limited data, a measured rate constant taken from the Fiorenza et al. field study is recommended as an upper limit (0.0064/day; half-life of 108 days) with a value one order of magnitude lower than this (0.00064/day, half-life of 1083 days) for the lower limit of a recommended first-order rate constant range. However, the measured rate constant was reported for only a single, methanogenic site and therefore this range does not have the same supporting evidence that other compounds with more extensive data have. Biodegradation of this compound under nitrate-reducing conditions may occur more readily than for other more highly chlorinated aliphatic compounds as it is less chlorinated (less oxidized). This indicates that it may be biodegraded via oxidation pathways.

Table 20. All Summarized Studies for Dichloromethane

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Connecticut		Field	100000 ug/L				Cline,PV & Viste,DR (1985)
Wisconsin		Field	230000 ug/L				Cline,PV & Viste,DR (1985)
Hawkesbury, Ontario, Canada	Meth	Field	37000 ug/L	906	0.0064/day		Fiorenza,S et al. (1994)
Oregon		Field	2300000 ug/L		Biodegrades		Lehmicke,LL et al. (1996)

3.2.5. 1,1,2,2-Tetrachloroethane

Abiotic as well as biotic reactions may be important in the fate of 1,1,2,2-tetrachloroethane in the environment. An abiotic hydrolysis half-life of this compound was reported as 0.4 years (Table 16) (Jeffers et al. 1989) with a reaction product of trichloroethylene (Vogel et al. 1987). Very little information on the biodegradation of this compound in an anaerobic aquifer environment was found (Table 21); insufficient information was available to recommend an appropriate rate constant. However, it is likely that this compound does biodegrade, as do all of the highly chlorinated aliphatics, under strong reducing conditions (e.g. methanogenic, sulfate-reducing, and iron-reducing conditions). To supplement the evidence that this compound can be reductively dechlorinated in an aquifer environment, a quick literature search of papers using non-groundwater inocula was also performed.

Only two papers were located reporting the possible degradation of 1,1,2,2-tetrachloroethane in an anaerobic aquifer. Chen et al. (1996) studied the abiotic and biotic transformations of this compound under methanogenic conditions using municipal sludge as an inoculum. However, in this paper, there is some discussion of a spill affecting an aquifer in Tacoma, WA where 1,1,2,2-tetrachloroethane was a major contaminant. Compounds found in groundwater from an extraction well taken from this site include 1,1,2-trichloroethane and trichloroethylene, the dechlorination and dehydrochlorination products of 1,1,2,2-tetrachloroethane transformation, as well as cis- and trans-dichloroethylene which may represent dichloroelimination products of 1,1,2,2-tetrachloroethane as well as reductive products of trichloroethylene. Laboratory studies by the same authors using a municipal sludge inoculum, which had been exposed to chlorinated compounds, show the complete degradation of 1,1,2,2-tetrachloroethane within three to four weeks with the initial formation of trichloroethylene, c-dichloroethylene and t-dichloroethylene. Smaller amounts of 1,1,2-trichloroethane and 1,2-dichloroethane appeared later. Some abiotic transformation of 1,1,2,2-tetrachloroethane to trichloroethylene also occurred.

The paper by Cline and Viste (1985) reports results for a solvent recovery facility in Wisconsin. Concentrations of 1,1,2,2-tetrachloroethane are found only at the water table on-site and by 80 m downgradient are not detectable either at the water table or in the lower wells of piezometer nests at this location. This suggests that biodegradation is possible but without further information, particularly data for a conservative tracer to rule out abiotic or transport processes, it is not possible to determine a rate of biodegradation.

A study by Bouwer and McCarty (1983) used a continuous-flow methanogenic fixed-film laboratory scale column with acetate present as a primary substrate. Under steady state conditions, 1,1,2,2-tetrachloroethane had a 97% removal rate. The initial step in the transformation of 1,1,2,2-tetrachloroethane was reductive dechlorination to 1,1,2-trichloroethane.
Given the very limited groundwater information on 1,1,2,2-tetrachloroethane, it is currently not possible to recommend a rate constant describing this compound's biotransformation in anaerobic groundwater. It is, however, likely that this compound will undergo reductive dechlorination in strong, reducing environments.

Table 21. All Summarized Studies for 1,1,2,2-Tetrachloroethane

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Wisconsin		Field	19000 ug/L				Cline,PV & Viste,DR (1985)
Tacoma, WA		Field	5203 ug/L		Possible		Chen,C et al. (1996)

3.2.6. Tetrachloroethylene

Tetrachloroethylene undergoes sequential reductive dechlorination initially forming trichloroethylene, the dichloroethylene isomers (mainly cis-1,2-dichloroethylene), then vinyl chloride and finally ethene and ethane. The reductive dechlorination of tetrachloroethylene is thought to require the absence of oxygen or nitrate (Ellis et al. 1996). As with the other chlorinated aliphatic compounds with sufficient information, preference is given to field and *in situ* microcosm studies and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies (Table 15) alone ranged from 0 to 0.034/day with a mean value of 0.0029/day.

Four different field/*in situ* microcosm studies reported in the database show that tetrachloroethylene degrades under anaerobic conditions and give sufficient data to determine a rate constant. Another eight studies report that tetrachloroethylene biodegrades at a particular aquifer site, generally by showing the production of reaction products (Table 22). One study reports that tetrachloroethylene was not biodegraded. This was a continuous injection experiment by Rugge et al, 1995, which reported no biodegradation of tetrachloroethylene by the 2 m piezometer fence over an injection period of 8 months; the flow path encountered methanogenic, sulfate-reducing and iron-reducing conditions. Other compounds such as benzene, toluene, trichloroethylene and 1,1,1-trichloroethane were also not biodegraded although one might expect that both toluene and the chlorinated aliphatic compounds would be degraded in this environment.

The redox conditions of the aquifer are expected to play an important role in the degradation of tetrachloroethylene as with all of the chlorinated aliphatics. As this compound is in a highly oxidized state (highly chlorinated), methanogenic conditions are expected to give the highest rate constant values with sulfate-reducing and iron-reducing conditions giving somewhat lower average rate constant values. There is insufficient published data however, to determine a value for each redox environment. Therefore, a range of recommended values again seems most appropriate for this compound with the lower limit equal to 0.00019/day (half-life of 3647 days), which was the lowest measured field value (thought to be under nitrate-reducing conditions), to 0.0029/day (half-life of 239 days), which is the mean value for the field/*in situ* microcosm data set. The lower limit measured under nitrate-reducing conditions is substantially lower than that reported for any other chlorinated aliphatic compound and may represent a realistic baseline for the highly chlorinated compounds under this redox condition.

Table 22. All Summarized Studies for Tetrachloroethylene

Site Name	Redox Regime	Study Type	Initial Concn	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Swan Coastal Plain, Western Australia	NO3	Column	550 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	1000 ug/L	13-14	NB		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	560 ug/L	13-14	NB		Patterson,BM et al. (1993)

Table 22. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn	Time, days	Rate Constant	Lag, days	Reference
Swan Coastal Plain, Western Australia	NO3	Column	540 ug/L	13-14	Possible		Patterson,BM et al. (1993)
Swan Coastal Plain, Western Australia	NO3	Column	590 ug/L	13-14	Possible		Patterson,BM et al. (1993)
Connecticut		Field	2900 ug/L				Cline,PV & Viste,DR (1985)
Rockford, IL		Field					Hamper,MJ & Hill,JA (1989)
Wisconsin		Field	22000 ug/L				Cline,PV & Viste,DR (1985)
Otis AFB, MA	NO3	Field	133.6 ug/L		0.00019/day		Ala,NK & Domenico,PA (1992)
Dover AFB, DE	Meth	Field			0.00068-0.00079/day		Ellis,DE et al. (1996)
Palo Alto, CA		Field	2.5 ug/L	350	0.003/day		Roberts,PV et al. (1982)
Seattle, WA	NO3/Fe/SO4/Meth	Field			0.0035-0.0046/day		Nelson,S (1996)
Cecil Field Naval Air Station, FL	Fe/Meth/SO4	Field	28 ug/L		Biodegrades		Chapelle,FH (1996)
Gloucester landfill, Ontario, Canada	SO4	Field	60 ug/L	1000	Biodegrades		Lesage,S et al. (1990)

Table 22. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn	Time, days	Rate Constant	Lag, days	Reference
Hawkesbury, Ontario, Canada	Meth	Field	160 ug/L	906	Biodegrades		Fiorenza,S et al. (1994)
Niagara Falls, NY	Fe/Mn/Meth/SO4	Field	564-26531 ug/L		Biodegrades		Lee,MD et al. (1995)
North Toronto, Canada	Meth/SO4	Field			Biodegrades		Major,DW et al. (1991)
Victoria, TX	SO4	Field	235 ug/L		Biodegrades		Beeman,RE et al. (1994)
Victoria, TX	SO4	Field	1700 ug/L		Biodegrades		Beeman,RE et al. (1994)
Wurtsmith AFB, MI	Meth/Fe/SO4/NO3	Field	>1500 mg/kg		Biodegrades		Henry,M (1995)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
Vejen city landfill, Denmark	Fe/NO3/Mn	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L	140-160	NB;0.0097-0.034/day		Nielsen,PH et al. (1995B)
Norman, OK	SO4	Lab microcosm	40 ug/L	70	0.00073/day		Suflita,JM et al. (1988)
Dover AFB, DE	Meth	Lab microcosm		84	0.004/day		Lige,JE et al. (1995)
Norman, OK	Meth	Lab microcosm	36 ug/L	70	0.0084/day		Suflita,JM et al. (1988)

Table 22. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn	Time, days	Rate Constant	Lag, days	Reference
Dover AFB, DE	Meth	Lab microcosm		84	0.0123/day		Lige,JE et al. (1995)
Traverse City, MI		Lab microcosm	2217 ug/L	175	0.013/day		Sewell,GW & Gibson,SA (1991)
Biscayne aquifer, southern Florida		Lab microcosm	1463 ug/L	21	0.054/day		Parsons,F et al. (1984)
North Toronto, Canada	Meth/SO4	Lab microcosm	672 ug/L	83	0.13/day		Major,DW et al. (1991)
North Toronto, Canada	Meth/SO4	Lab microcosm	1965 ug/L	83	0.15/day		Major,DW et al. (1991)
North Toronto, Canada	Meth/SO4	Lab microcosm	372 ug/L	83	0.18/day		Major,DW et al. (1991)
North Toronto, Canada	Meth/SO4	Lab microcosm	1641 ug/L	46	0.41/day		Major,DW et al. (1991)
		Lab microcosm	5000 ug/L	>200	Biodegrades		Xu,N & Sewell,GW (1996)
Biscayne aquifer, southern Florida		Lab microcosm	4200 ug/L	14	Biodegrades		Parsons,F et al. (1985)
Traverse City, MI		Lab microcosm	2534 ug/L	200	NB		Sewell,GW & Gibson,SA (1991)
Vejen city landfill, Denmark	Meth/Fe/NO3/Mn	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995B)

3.2.7. 1,1,1-Trichloroethane

Abiotic as well as biotic reactions are important in the environmental fate of 1,1,1-trichloroethane. Without intervention by microbes, 1,1,1-trichloroethane can be abiotically degraded by hydrolysis or dehydrohalogenation to acetic acid and 1,1-dichloroethylene, respectively. The 1,1-dichloroethylene present due to dehydrohalogenation can be further degraded microbially to vinyl chloride. The rate of the hydrolysis reaction is thought to be about four times greater than that of the dehydrohalogenation reaction (McCarty & Reinhard 1993). A hydrolysis half-life of 1.1 years was reported for 1,1,1-trichloroethane at neutral pH and 25°C (Jeffers et al. 1989) (Table 16). If microbial activity is present then 1,1-dichloroethane is formed. This compound can then be reduced to chloroethane and finally to ethanol and HCl.

As with the other chlorinated aliphatic compounds with sufficient information, preference is given to field and *in situ* microcosm studies and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies (Table 15) alone ranged from 0 to 0.059/day with a mean value of 0.016/day. The high value of 0.059/day results from a field experiment where the groundwater was injected with high concentrations of acetate in order to enhance biotransformation of the chlorinated compounds (Semprini et al. 1992). If this value is ignored, the mean adjusted value for the field/*in situ* studies becomes 0.013/day. All summarized studies are presented in Table 23.

Wing (1997) studied the degradation of 1,1,1-trichloroethane in an otherwise uncontaminated aquifer. An overall half-life including both abiotic and biotic processes was measured as 2.3 years and an abiotic half-life alone was reported as 2.9 years. While this study reported a comparatively low rate constant, this was the only experiment which accounted for both abiotic and biotic degradation of 1,1,1-trichloroethane. A field study by Fiorenza et al. (1994) at a site contaminated with tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, naphtha, and dichloromethane reports the biodegradation of 1,1,1-trichloroethane, with both abiotic and biotic reaction products of 1,1-dichloroethylene and 1,1-dichloroethane formed, respectively. Reductive dechlorination appeared to be the major pathway for 1,1,1-trichloroethane degradation as much more 1,1-dichloroethane was measured than 1,1-dichloroethylene. Chloroethane was also reported at this site. However, while plumes of tetrachloroethylene, trichloroethylene, and dichloromethane were contained on-site, the 1,1,1-trichloroethane plume extended off-site, suggesting relatively slower degradation of this compound. Cox et al. (1995) reports low concentrations of 1,1,1-trichloroethane at a spill site but 1,1-dichloroethane and chloroethane were both measured in the groundwater; neither of these compounds were used at the site and represent degradation products due to the reductive dechlorination of 1,1,1-trichloroethane. The authors note however, that the rate of reaction to ethene and ethane in the anaerobic portion of the aquifer does not appear to be fast enough to prevent the transport of some of these chlorinated compounds to the aerobic zone. This should not represent much of a problem if these compounds are chloroethane or vinyl chloride (they are aerobically biodegraded) but could be problematic for the more highly chlorinated compounds.

A field injection experiment by Semprini et al. (1992) initially added both nitrate and acetate to the groundwater. Very little transformation was reported until nitrate concentrations were eliminated on day 52. Rates of degradation were much lower than those reported for carbon tetrachloride. 1,1-Dichloroethane was reported as a transformation product.

Four field/*in situ* microcosm studies are reported giving a result of "no biodegradation". Studies by Nielsen et al. (1995B) and Nielsen and Christensen (1994) show that 1,1,1-trichloroethane was biodegraded under methanogenic conditions but not under nitrate- or iron-reducing conditions suggesting that the redox environment controls this compounds biodegradation. A study by Nielsen et al. (1992) reports no biodegradation of 1,1,1-trichloroethane in the groundwater only section of the *in situ* microcosm. However, the lower section with both sediment and groundwater present had a measured rate constant of 0.022/day. A continuous injection experiment by Rugge et al. (1995) reported no biodegradation of 1,1,1-trichloroethane by the 2 m piezometer fence over an injection period of 8 months; the flow path encountered methanogenic, sulfate-reducing and iron-reducing conditions. Other compounds such as benzene, toluene, tetrachloroethylene and trichloroethylene were also not biodegraded although one might expect that both toluene and the chlorinated aliphatic compounds would be degraded in this environment.

While many of the field studies did not account for the loss of 1,1,1-trichloroethane through abiotic hydrolysis or elimination reactions, rates of biological degradation may be at least an order of magnitude higher than abiotic degradation mechanisms (Klecka et al. 1990). The redox conditions of the aquifer are expected to play an important role in the degradation of 1,1,1-trichloroethane as with all of the chlorinated aliphatics. As this compound is in a highly oxidized state (highly chlorinated), methanogenic conditions are expected to give the highest rate constant values with sulfate-reducing and iron-reducing conditions giving somewhat lower average rate constant values. There is insufficient published data however, to determine a value for each redox environment. Therefore, a range of recommended values seems most appropriate for this compound with the lower limit equal to 0.0013/day (half-life of 533 days), which was the lowest measured field value (unreported redox condition), to 0.013/day (half-life of 53 days), which is the mean adjusted value for the field/*in situ* microcosm data set. It is not possible to determine an appropriate rate constant from this data for nitrate-reducing conditions at this time, although it is expected that the rate will be substantially less. Laboratory microcosm studies by Klecka et al. (1990) report no biodegradation of 1,1,1-trichloroethane under either aerobic or nitrate-reducing conditions over a 720 day period. Under methanogenic or sulfate-reducing conditions using the same aquifer sediment, this compound was readily biodegraded. Higher concentrations of acetic acid were measured for methanogenic microcosms whereas higher concentrations of carbon dioxide were reported for the sulfate-reducing microcosms. The authors believed that the acetic acid produced was not only due to abiotic hydrolysis mechanisms but also possibly to the participation of microbial halidohydrolases, which also can directly participate in a hydrolytic substitution reaction resulting in the formation of acetic acid. Therefore, the above range of recommended values will not be representative if the redox potential of the aquifer under study is classified as nitrate-reducing.

Table 23. All Summarized Studies for 1,1,1-Trichloroethane

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Connecticut		Field	3700 ug/L				Cline,PV & Viste,DR (1985)
Wisconsin		Field	270000 ug/L				Cline,PV & Viste,DR (1985)
Santa Clara, CA		Field			0.00018/day		Wing,MR (1997)
Hawkesbury, Ontario, Canada	Meth	Field	5500 ug/L	906	0.0013/day		Fiorenza,S et al. (1994)
Palo Alto, CA		Field	10 ug/L	350	0.003/day		Roberts,PV et al. (1982)
Moffett Field Naval Air Station, CA	NO3/SO4	Field	50 ug/L	1.8	0.059/day		Semprini,L et al. (1992)
Gloucester landfill, Ontario, Canada	SO4	Field	193 ug/L	1000	Biodegrades		Lesage,S et al. (1990)
Moffett Field Naval Air Station, CA	NO3/SO4	Field			Biodegrades		Semprini,L et al. (1990)
Sacramento, CA	Meth/NO3	Field	<5 ug/L		Biodegrades		Cox,E et al. (1995)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)

Table 23. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	Fe	In situ microcosm	150 ug/L	50	0.010/day		Nielsen,PH & Christensen,TH (1994)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	90	0.022/day		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L	75-105	0.029-0.046/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L	90	0.041/day	30	Nielsen,PH & Christensen,TH (1994)
Vejen city landfill, Denmark	Fe/NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	90	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	NO3	In situ microcosm	150 ug/L		NB		Nielsen,PH & Christensen,TH (1994)
Dover AFB, DE	Meth	Lab microcosm		84	0.0022/day		Lige,JE et al. (1995)
Dover AFB, DE	Meth	Lab microcosm		84	0.0026/day		Lige,JE et al. (1995)
Norman, OK	Meth	Lab microcosm	500 ug/L	424	0.0034/day		Klecka,GM et al. (1990)
Norman, OK	SO4	Lab microcosm	500 ug/L	732	0.0034/day		Klecka,GM et al. (1990)
Biscayne aquifer, southern Florida		Lab microcosm	3600 ug/L	14	0.0099/day		Parsons,F et al. (1985)

Table 23. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Norman, OK	Meth	Lab microcosm	100 ug/L	168	0.015/day		Klecka,GM et al. (1990)
Norman, OK	SO4	Lab microcosm	100 ug/L	169	0.015/day		Klecka,GM et al. (1990)
Vejen city landfill, Denmark	Meth	Lab microcosm	150 ug/L	60	<0.0037/day		Nielsen,PH et al. (1995B)
Traverse City, MI	Meth/Fe	Lab microcosm	570 ug/L	665	Biodegrades		Wilson,BH et al. (1990)
Norman, OK	NO3	Lab microcosm	500 ug/L	720	NB		Klecka,GM et al. (1990)
Vejen city landfill, Denmark	Fe/NO3/Mn	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995B)

3.2.8. 1,1,2-Trichloroethane

Very little information on the biodegradation of this compound in an anaerobic aquifer environment was found (Table 24); insufficient information was available to recommend an appropriate rate constant. To supplement the evidence that this compound can be reductively dechlorinated in an aquifer environment, a quick literature search of papers using non-groundwater inocula was also performed.

The only located study in an aquifer environment is a paper by Cline and Viste (1985) which reports results for a solvent recovery facility in Wisconsin. Concentrations of 1,1,2,-trichloroethane are found only 80 m downgradient from the source location, at depth. While these authors list this compound as a parent compound, it is possible that 1,1,2-trichloroethane is present as a biotransformation product of 1,1,2,2-tetrachloroethane which is also found at this site.

Laboratory studies by Chen et al. (1996), using a municipal sludge inoculum which had been exposed to chlorinated compounds, show the complete degradation of 1,1,2-trichloroethane within one to two weeks with the initial formation of 1,2-dichloroethane, vinyl chloride and traces of ethene.

Unlike 1,1,1-trichloroethane, 1,1,2-trichloroethane is not expected to rapidly hydrolyze abiotically in groundwater. Measured half-lives range from 47 (Kollig 1990) to 139 years (Jeffers et al. 1989) under neutral conditions at 25°C.

Given the very limited anaerobic biodegradation information on 1,1,2-trichloroethane, it is currently not possible to recommend a rate constant describing this compounds biotransformation in anaerobic groundwater. However, it is likely that this compound does biodegrade, as do all of the highly chlorinated aliphatics, under strong reducing conditions (e.g. methanogenic, sulfate-reducing, and iron-reducing conditions).

Table 24. All Summarized Studies for 1,1,2-Trichloroethane

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Wisconsin		Field	<10 ug/L				Cline,PV & Viste,DR (1985)

3.2.9. Trichloroethylene

Trichloroethylene undergoes sequential reductive dechlorination initially forming the dichloroethylene isomers (mainly cis-1,2-dichloroethylene), then vinyl chloride and finally ethene and ethane. The reductive dechlorination of trichloroethylene is thought to require the absence of oxygen or nitrate (Ellis et al. 1996). As with the other chlorinated aliphatic compounds with sufficient information, preference is given to field and *in situ* microcosm studies and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies (Table 15) alone ranged from 0 to 0.013/day with a mean value of 0.0025/day. The mean value of 0.010/day reported for all studies appears to be affected by rate constants determined in several experiments by Haston et al. (1994) where different carbon sources were added to aquifer material contaminated with trichloroethylene. All summarized studies for this compound are reported in Table 25.

Field studies from 16 different aquifer sites show that trichloroethylene degrades under anaerobic conditions (Table 26). Most data is from either the St. Joseph site in Michigan (biodegradation rate constants from this site range from 0.00069 to 0.00611/day) or Picatinny Arsenal in New Jersey (biodegradation rate constants from this site range from 0.00014 to 0.013/day). Only a few studies report that trichloroethylene is not biodegraded in an anaerobic aquifer environment. A continuous injection experiment by Rugge et al. (1995), reported no biodegradation of tetrachloroethylene by the 2 m piezometer fence over an injection period of 8 months; the flow path encountered methanogenic, sulfate-reducing and iron-reducing conditions. Other compounds such as benzene, toluene, tetrachloroethylene and 1,1,1-trichloroethane were also not biodegraded although one might expect that both toluene and the chlorinated aliphatic compounds would be degraded in this environment. *In situ* microcosm studies by Nielsen et al. (1992) did not show biodegradation of several other compounds such as toluene, o-xylene, tetrachloroethylene, and naphthalene, which are generally considered to be biodegradable, over a 95 day period; only carbon tetrachloride and 1,1,1-trichloroethane were anaerobically biodegraded in this study. Both *in situ* microcosm and laboratory studies by Nielsen et al. (1995B), at the same site as Nielsen et al. (1992), reported that trichloroethylene was not biodegraded. Multiple *in situ* microcosms were placed along the contaminant plume in different redox zones; even in methanogenic sites, this compound was not biodegraded while other chlorinated aliphatic compounds, such as 1,1,1-trichloroethane, carbon tetrachloride and tetrachloroethylene, were. Study length in these experiments appears to be considerably less than that reported for many of the field studies suggesting that insufficient time was allowed to show trichloroethylene degradation.

Trichloroethylene can be present in a groundwater environment either as an original component of a spill or as a reductive dechlorination product of tetrachloroethylene. Because the production of trichloroethylene at a site which has been contaminated with both tetrachloroethylene and trichloroethylene depends on the degradation rate of tetrachloroethylene, rate constants determined in the field may be best estimated as net rate coefficients which include both the production of trichloroethylene and then its degradation (Weaver et al. 1995). When a comparison of the gross rate

of decay of vinyl chloride, not including its production, and a net rate of decay, accounting for both production and biodegradation of this compound at the St. Joseph site, was determined, the net rate was lower than the gross rate (Weaver et al. 1996). Other authors determined rate constants in the field using conservative tracer data (Wiedemeier et al. 1996B) or by calculating a mass balance of chlorine (Wilson JT et al. 1995B).

Chapelle (1996) reports that the completeness of the sequential dechlorination of trichloroethylene to less chlorinated compounds is dependent on the redox conditions. Under mildly reducing conditions, nitrate-reducing or iron-reducing conditions, the transformation of trichloroethylene may stop at the dichloroethylene isomers. Under sulfate-reducing or methanogenic conditions, these compounds are more likely to dechlorinate to either vinyl chloride or ethene.

The redox conditions of the aquifer are expected to play an important role in the degradation of trichloroethylene as with all of the chlorinated aliphatics. As this compound is in a highly oxidized state (highly chlorinated), methanogenic conditions are expected to give the highest rate constant values with sulfate-reducing and iron-reducing conditions giving somewhat lower average rate constant values. There is insufficient published data however, to determine a value for each redox environment. Therefore, a range of recommended values again seems most appropriate for this compound with the lower limit equal to 0.00014/day (half-life of 4950 days), which was the lowest measured field value, to 0.0025/day (half-life of 277 days), which is the mean value for the field/*in situ* microcosm data set.

Table 25. All Summarized Studies for Trichloroethylene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
St. Joseph site, MI	Meth/SO4	Column	3324 ug/L	42	0.005/day		Haston,ZC et al. (1994)
St. Joseph site, MI	Meth/SO4	Column	3114 ug/L	42	0.020/day		Haston,ZC et al. (1994)
St. Joseph site, MI	Meth/SO4	Column	3389 ug/L	42	0.024/day		Haston,ZC et al. (1994)
St. Joseph site, MI	Meth/SO4	Column	3206 ug/L	42	0.046/day		Haston,ZC et al. (1994)
St. Joseph site, MI	Meth/SO4	Column	3902 ug/L	42	0.060/day		Haston,ZC et al. (1994)
St. Joseph site, MI	Meth/SO4	Column	3140 ug/L	42	0.092/day		Haston,ZC et al. (1994)
St. Joseph site, MI	Meth/SO4	Column	3416 ug/L	42	>0.19/day		Haston,ZC et al. (1994)
Offutt AFB, Nebraska		Column	640 ug/L		Biodegrades		LaPat-Polasko,LT et al. (1995)
Connecticut		Field	39000 ug/L				Cline,PV & Viste,DR (1985)
Wisconsin		Field	250000 ug/L				Cline,PV & Viste,DR (1985)

Table 25. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		3385	-0.00082/day		Wiedemeier,TH et al. (1996A)
Tacoma, WA		Field	2890 ug/L	2008	0.00014-0.00024/day		Silka,LR & Wallen,DA (1988)
Picatinny Arsenal, NJ	SO4/Fe	Field	15-16 ug/L		0.00014-0.0071/day		Ehlke,TA et al. (1994)
Otis AFB, MA	NO3	Field	94.5 ug/L		0.00017/day		Ala,NK & Domenico,PA (1992)
Tacoma, WA		Field	2890 ug/L	2008	0.00019-0.0024/day		Silka,LR & Wallen,DA (1988)
Dover AFB, DE	Meth	Field			0.00045-0.00079/day		Ellis,DE et al. (1996)
Eielson Air Force Base, AK		Field	40.1 kg	420	0.0005/day		Dupont,RR et al. (1996)
Cape Canaveral Air Station, FL	Fe/Meth/SO4	Field			0.00059-0.00079/day		Swanson,M et al. (1996)
St. Joseph site, MI	Meth/SO4	Field			0.00069-0.0016/day		Rifai,HS et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	7411 ug/L	2336	0.00082/day		Weaver,JW et al. (1996)

Table 25. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Picatinny Arsenal, NJ	Fe/Meth/SO4	Field	1900 ug/L	1132	0.00086/day		Imbrigiotta,TE et al. (1996)
St. Joseph site, MI	Meth/SO4	Field	6500 ug/L	2373	0.0010/day		Wilson,JT et al. (1995B)
St. Joseph site, MI	Meth/SO4	Field	0.0067 kg/cu m	2380	0.0011/day		Wilson,JT et al. (1994C)
Tibbetts Road Site, Barrington, NH	Fe	Field	200 ug/L	2336	0.0011/day		Wilson,BH et al. (1996)
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		692	0.0014/day		Wiedemeier,TH et al. (1996A)
Tibbetts Road Site, Barrington, NH	Fe	Field	710 ug/L	3650	0.0015/day		Wilson,BH et al. (1996)
St. Joseph site, MI	Meth/SO4	Field			0.0016-0.0033/day		Rifai,HS et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	7411 ug/L	2336	0.0016/day		Weaver,JW et al. (1995)
Tibbetts Road Site, Barrington, NH	Fe	Field	710 ug/L	876	0.0016/day		Wilson,BH et al. (1996)
Picatinny Arsenal, NJ	SO4/Fe	Field			0.0017-0.0029/day		Ehlke,TA & Imbrigiotta,TE (1996)

Table 25. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Eielson Air Force Base, AK		Field			0.0020-0.0064/day		Gorder,KA et al. (1996)
St. Joseph site, MI	Meth/SO4	Field			0.0023-0.0047/day		Rifai,HS et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	15 ug/L	1971	0.0025/day		Wilson,JT et al. (1995B)
Eielson Air Force Base, AK		Field	90000 ug/L		0.0026/day		Dupont,RR et al. (1996)
Picatinny Arsenal, NJ	SO4/Fe	Field		1533	0.0027/day		Wilson,JT et al. (1995B)
Palo Alto, CA		Field	10 ug/L	350	0.003/day		Roberts,PV et al. (1982)
Picatinny Arsenal, NJ	SO4/Fe	Field	10000 ug/L	475	0.0033/day		Wilson,JT et al. (1995B)
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		2487	0.0033/day		Wiedemeier,TH et al. (1996A)
St. Joseph site, MI	Meth/SO4	Field	0.000504 kg/cu m	1015	0.0034/day		Wilson,JT et al. (1994C)
St. Joseph site, MI	Meth/SO4	Field	520 ug/L	1022	0.0036/day		Wilson,JT et al. (1995B)
Picatinny Arsenal, NJ	SO4/Fe	Field	25000 ug/L	730	0.0038/day		Wilson,JT et al. (1995B)

Table 25. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Picatinny Arsenal, NJ	SO4/Fe	Field	25000 ug/L	244-733	0.0043-0.011/day		Wilson,BH et al. (1991)
Picatinny Arsenal, NJ	SO4/Fe	Field	10000 ug/L	156-467	0.0043-0.013/day		Wilson,BH et al. (1991)
St. Joseph site, MI	Meth/SO4	Field	30.1 ug/L	2740	0.0047/day		Weaver,JW et al. (1996)
St. Joseph site, MI	Meth/SO4	Field	864 ug/L	1438	0.0047/day		Weaver,JW et al. (1996)
St. Joseph site, MI	Meth/SO4	Field	30.1 ug/L	2740	0.00557/day		Weaver,JW et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	864 ug/L	1438	0.00611/day		Weaver,JW et al. (1995)
Gloucester landfill, Ontario, Canada	SO4	Field	505 ug/L	1000	Biodegrades		Lesage,S et al. (1990)
Hawkesbury, Ontario, Canada	Meth	Field	1500 ug/L	906	Biodegrades		Fiorenza,S et al. (1994)
Sacramento, CA	Meth/NO3	Field	1400 ug/L		Biodegrades		Cox,E et al. (1995)
St. Joseph site, MI	Meth/SO4	Field			Biodegrades		Semprini,L et al. (1995)

Table 25. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Upstate NY	Meth/SO4	Field			Biodegrades		Major,DW et al. (1995)
Victoria, TX	SO4	Field	95 ug/L		Biodegrades		Beeman,RE et al. (1994)
Victoria, TX	SO4	Field	535 ug/L		Biodegrades		Beeman,RE et al. (1994)
Wurtsmith AFB, MI	Meth/Fe/SO4/NO3	Field	>1500 mg/kg		Biodegrades		Henry,M (1995)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
Western United States		Groundwater inoculum	1000 ug/L	150	NB		Sonier,DN et al. (1994)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)
		Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
		Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
		Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
		Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)

Table 25. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
		Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
	SO4	Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
	SO4	Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
	SO4	Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
	SO4	Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
	SO4	Lab microcosm	15766 ug/L	180			Odom,JM et al. (1995)
Merced, CA		Lab microcosm	7.75 ug/L	30	0.000086/day		Cox,EE et al. (1994)
Picatinny Arsenal, NJ	SO4/Fe	Lab microcosm	1100000 ug/L		0.00057-0.005/day		Ehlke,TA & Imbrigiotta,TE (1996)
Picatinny Arsenal, NJ	SO4/Fe	Lab microcosm	980 ug/L	147	0.0011/day		Wilson,BH et al. (1991)
Picatinny Arsenal, NJ	SO4/Fe	Lab microcosm	360 ug/L	147	0.0017/day		Wilson,BH et al. (1991)
Norman, OK	Meth	Lab microcosm	155 ug/L	280	0.0020-0.024/day	112	Wilson,BH et al. (1986)
Dover AFB, DE	Meth	Lab microcosm		84	0.0026/day		Lige,JE et al. (1995)
Picatinny Arsenal, NJ	SO4/Fe	Lab microcosm	340 ug/L	147	0.0029/day		Wilson,BH et al. (1991)
Everglades, FL		Lab microcosm	5000 ug/L	180	0.0077/day		Barrio-Lage,G et al. (1987)

Table 25. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Everglades, FL		Lab microcosm	2700 ug/L	625	0.0082-0.011/day		Barrio-Lage,G et al. (1987)
Tibbetts Road Site, Barrington, NH	Fe	Lab microcosm	299 ug/L	294	0.010/day		Wilson,BH et al. (1996)
Vero Beach, FL	Meth/Fe/SO4	Lab microcosm	2750 ug/L	750	0.011-0.021/day		Barrio-Lage,G et al. (1987)
Dover AFB, DE	Meth	Lab microcosm		84	0.0122/day		Lige,JE et al. (1995)
Piedmont province, North Carolina	Meth	Lab microcosm	1100 ug/L	222	>0.038/day	110	Johnston,JJ et al. (1996)
Piedmont province, North Carolina	Meth	Lab microcosm	900 ug/L	218	>0.040/day	108	Johnston,JJ et al. (1996)
Piedmont province, North Carolina	Meth	Lab microcosm	2000-3000 ug/L	306	Biodegrades	41-208	Johnston,JJ et al. (1996)
Traverse City, MI	Meth/Fe	Lab microcosm	540 ug/L	665	Biodegrades		Wilson,BH et al. (1990)
Biscayne aquifer, southern Florida		Lab microcosm	3700 ug/L	14	Biodegrades		Parsons,F et al. (1985)

Table 25. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Picatinny Arsenal, NJ	SO4/Fe	Lab microcosm	430 ug/L	147	NB		Wilson,BH et al. (1991)
Vejen city landfill, Denmark	Meth/Fe/NO3/Mn	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995B)
		Lab microcosm	15766 ug/L	180	NB		Odom,JM et al. (1995)
		Lab microcosm	15766 ug/L	180	NB		Odom,JM et al. (1995)
	SO4		15766 ug/L	180	NB		Odom,JM et al. (1995)
	SO4		15766 ug/L	180	NB		Odom,JM et al. (1995)

Table 26. Field and *in situ* Microcosm Studies for Trichloroethylene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Connecticut		Field	39000 ug/L				Cline,PV & Viste,DR (1985)
Wisconsin		Field	250000 ug/L				Cline,PV & Viste,DR (1985)
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		3385	-0.00082/day		Wiedemeier,TH et al. (1996A)
Tacoma, WA		Field	2890 ug/L	2008	0.00014-0.00024/day		Silka,LR & Wallen,DA (1988)
Picatinny Arsenal, NJ	SO4/Fe	Field	15-16 ug/L		0.00014-0.0071/day		Ehlke,TA et al. (1994)
Otis AFB, MA	NO3	Field	94.5 ug/L		0.00017/day		Ala,NK & Domenico,PA (1992)
Tacoma, WA		Field	2890 ug/L	2008	0.00019-0.0024/day		Silka,LR & Wallen,DA (1988)
Dover AFB, DE	Meth	Field			0.00045-0.00079/day		Ellis,DE et al. (1996)
Eielson Air Force Base, AK		Field	40.1 kg	420	0.0005/day		Dupont,RR et al. (1996)
Cape Canaveral Air Station, FL	Fe/Meth/SO4	Field			0.00059-0.00079/day		Swanson,M et al. (1996)
St. Joseph site, MI	Meth/SO4	Field			0.00069-0.0016/day		Rifai,HS et al. (1995)

Table 26. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
St. Joseph site, MI	Meth/SO4	Field	7411 ug/L	2336	0.00082/day		Weaver,JW et al. (1996)
Picatinny Arsenal, NJ	Fe/Meth/SO4	Field	1900 ug/L	1132	0.00086/day		Imbrigiotta,TE et al. (1996)
St. Joseph site, MI	Meth/SO4	Field	6500 ug/L	2373	0.0010/day		Wilson,JT et al. (1995B)
St. Joseph site, MI	Meth/SO4	Field	0.0067 kg/cu m	2380	0.0011/day		Wilson,JT et al. (1994C)
Tibbetts Road Site, Barrington, NH	Fe	Field	200 ug/L	2336	0.0011/day		Wilson,BH et al. (1996)
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		692	0.0014/day		Wiedemeier,TH et al. (1996A)
Tibbetts Road Site, Barrington, NH	Fe	Field	710 ug/L	3650	0.0015/day		Wilson,BH et al. (1996)
St. Joseph site, MI	Meth/SO4	Field			0.0016-0.0033/day		Rifai,HS et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	7411 ug/L	2336	0.0016/day		Weaver,JW et al. (1995)
Tibbetts Road Site, Barrington, NH	Fe	Field	710 ug/L	876	0.0016/day		Wilson,BH et al. (1996)
Picatinny Arsenal, NJ	SO4/Fe	Field			0.0017-0.0029/day		Ehlke,TA & Imbrigiotta,TE (1996)

Table 26. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Eielson Air Force Base, AK		Field			0.0020-0.0064/day		Gorder,KA et al. (1996)
St. Joseph site, MI	Meth/SO4	Field			0.0023-0.0047/day		Rifai,HS et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	15 ug/L	1971	0.0025/day		Wilson,JT et al. (1995B)
Eielson Air Force Base, AK		Field	90000 ug/L		0.0026/day		Dupont,RR et al. (1996)
Picatinny Arsenal, NJ	SO4/Fe	Field		1533	0.0027/day		Wilson,JT et al. (1995B)
Palo Alto, CA		Field	10 ug/L	350	0.003/day		Roberts,PV et al. (1982)
Picatinny Arsenal, NJ	SO4/Fe	Field	10000 ug/L	475	0.0033/day		Wilson,JT et al. (1995B)
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		2487	0.0033/day		Wiedemeier,TH et al. (1996A)
St. Joseph site, MI	Meth/SO4	Field	0.000504 kg/cu m	1015	0.0034/day		Wilson,JT et al. (1994C)
St. Joseph site, MI	Meth/SO4	Field	520 ug/L	1022	0.0036/day		Wilson,JT et al. (1995B)
Picatinny Arsenal, NJ	SO4/Fe	Field	25000 ug/L	730	0.0038/day		Wilson,JT et al. (1995B)

Table 26. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Picatinny Arsenal, NJ	SO4/Fe	Field	25000 ug/L	244-733	0.0043-0.011/day		Wilson,BH et al. (1991)
Picatinny Arsenal, NJ	SO4/Fe	Field	10000 ug/L	156-467	0.0043-0.013/day		Wilson,BH et al. (1991)
St. Joseph site, MI	Meth/SO4	Field	30.1 ug/L	2740	0.0047/day		Weaver,JW et al. (1996)
St. Joseph site, MI	Meth/SO4	Field	864 ug/L	1438	0.0047/day		Weaver,JW et al. (1996)
St. Joseph site, MI	Meth/SO4	Field	30.1 ug/L	2740	0.00557/day		Weaver,JW et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	864 ug/L	1438	0.00611/day		Weaver,JW et al. (1995)
Gloucester landfill, Ontario, Canada	SO4	Field	505 ug/L	1000	Biodegrades		Lesage,S et al. (1990)
Hawkesbury, Ontario, Canada	Meth	Field	1500 ug/L	906	Biodegrades		Fiorenza,S et al. (1994)
Sacramento, CA	Meth/NO3	Field	1400 ug/L		Biodegrades		Cox,E et al. (1995)
St. Joseph site, MI	Meth/SO4	Field			Biodegrades		Semprini,L et al. (1995)
Upstate NY	Meth/SO4	Field			Biodegrades		Major,DW et al. (1995)
Victoria, TX	SO4	Field	95 ug/L		Biodegrades		Beeman,RE et al. (1994)

Table 26. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Victoria, TX	SO4	Field	535 ug/L		Biodegrades		Beeman,RE et al. (1994)
Wurtsmith AFB, MI	Meth/Fe/SO4/NO3	Field	>1500 mg/kg		Biodegrades		Henry,M (1995)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	21	NB		Rugge,K et al. (1995)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)

3.2.10. Vinyl Chloride

In an anaerobic aquifer environment, vinyl chloride is expected to biodegrade using both reductive dechlorination, forming ethene and methane as transformation products, and oxidation pathways. As it is less oxidized (fewer chlorine atoms) than the other more highly chlorinated aliphatic compounds, the rate of reductive dechlorination should be comparatively slower. However, biodegradation under nitrate-reducing and iron-reducing conditions may be more rapid than for compounds such as tetrachloroethylene and trichloroethylene as this compound can be oxidatively biodegraded. Vinyl chloride is also biodegraded in aerobic environments (Bradley & Chapelle 1996). As with the other chlorinated aliphatic compounds with sufficient information, preference is given to field and *in situ* microcosm studies (Table 27) and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies (Table 15) alone ranged from 0 to 0.0845/day with a mean value of 0.0073/day.

Vinyl chloride can be present in a groundwater environment either as an original component of a spill or as a reductive dechlorination product of other more chlorinated aliphatic compounds such as tetrachloroethylene or trichloroethylene. Chapelle (1996) reports that the completeness of the sequential dechlorination of tetrachloroethylene or trichloroethylene to less chlorinated compounds is dependent on the redox conditions. Under mildly reducing conditions, nitrate-reducing or iron-reducing conditions, the transformation of tetrachloroethylene or trichloroethylene may stop at the dichloroethylene isomers. Under sulfate-reducing or methanogenic conditions, these compounds are more likely to completely biodegrade to either vinyl chloride or ethene. This appears to be substantiated by reports that vinyl chloride appears to accumulate along plumes of tetrachloroethylene or trichloroethylene contamination where reductive dechlorination is occurring under methanogenic conditions (Weaver et al. 1995; Wilson et al. 1995). In iron- or nitrate-reducing environments, vinyl chloride does not appear to accumulate to such an extent; it may biodegrade to carbon dioxide using oxidative pathways.

Because the production of vinyl chloride at a site which has been contaminated with trichloroethylene or tetrachloroethylene depends on the degradation rate of trichloroethylene and the dichloroethylene isomers, rate constants determined in the field may be best estimated as net rate coefficients which include both the production of vinyl chloride and then its degradation (Weaver et al. 1995). A comparison of the gross rate of decay of vinyl chloride, not including its production, and a net rate of decay, accounting for both production and biodegradation of this compound at the St. Joseph site, shows that the net rate is lower than the gross rate (0.00041-0.0071/day compared to 0.0071-0.055/day, respectively) (Weaver et al. 1996). Other authors determined rate constants in the field using conservative tracer data (Wiedemeier et al. 1996B) or by calculating a mass balance of chlorine (Wilson JT et al. 1995B).

Field studies from five different aquifer sites show that vinyl chloride degrades under anaerobic conditions. Most data is from the St. Joseph site in Michigan; biodegradation rate constants from this site alone range from 0.00033 to 0.0845/day. While no biodegradation is reported along one of three

flowpath segments (the segment closest to the source) at the Plattsburg AFB the other two segments report rate constants for vinyl chloride ranging from 0.0012-0.0013/day.

The redox conditions of the aquifer are expected to play an important role in the degradation of vinyl chloride as with all of the chlorinated aliphatics. As this compound is in a more reduced state than other more chlorinated compounds, methanogenic conditions are expected to give comparatively lower rate constant values with sulfate-reducing and iron-reducing conditions giving somewhat higher average rate constant values. There is insufficient published data however, to determine a value for each redox environment. Therefore, a range of recommended values seems most appropriate for this compound with the lower limit equal to 0.00033/day (half-life of 2100 days), which was the lowest measured field value (reported for methanogenic/sulfate-reducing conditions), to 0.0073/day (half-life of 95 days), which is the mean value for the field/*in situ* microcosm data set. It is not possible to determine an appropriate rate constant from this data for nitrate-reducing conditions at this time, although it is possible that the rate of biodegradation may be higher.

Table 27. All Summarized Studies for Vinyl Chloride

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
		Column			Biodegrades		Barrio-Lage,GA et al. (1990)
		Column			Biodegrades		Barrio-Lage,GA et al. (1990)
		Column			Biodegrades		Barrio-Lage,GA et al. (1990)
		Column			Biodegrades		Barrio-Lage,GA et al. (1990)
		Column			Biodegrades		Barrio-Lage,GA et al. (1990)
St. Joseph site, MI	Meth/SO4	Field			0.00033-0.00067/day		Rifai,HS et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	998 ug/L		0.00041/day		Weaver,JW et al. (1996)
St. Joseph site, MI	Meth/SO4	Field	930 ug/L	2373	0.00049/day		Wilson,JT et al. (1995B)
Dover AFB, DE	Meth	Field			0.00086-0.0010/day		Ellis,DE et al. (1996)
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		692	0.0012/day		Wiedemeier,TH et al. (1996A)
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		3385	0.0013/day		Wiedemeier,TH et al. (1996A)

Table 27. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
St. Joseph site, MI	Meth/SO4	Field			0.0016-0.0033/day		Rifai,HS et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	473 ug/L		0.0021/day		Weaver,JW et al. (1996)
St. Joseph site, MI	Meth/SO4	Field	450 ug/L	1022	0.0024/day		Wilson,JT et al. (1995B)
St. Joseph site, MI	Meth/SO4	Field	998 ug/L	2336	0.004740.0147 /day		Weaver,JW et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	106 ug/L	1971	0.0060/day		Wilson,JT et al. (1995B)
St. Joseph site, MI	Meth/SO4	Field	97.7 ug/L		0.0071/day		Weaver,JW et al. (1996)
St. Joseph site, MI	Meth/SO4	Field			0.0076-0.016/day		Rifai,HS et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	473 ug/L	1438	0.00921-0.0135/day		Weaver,JW et al. (1995)
St. Joseph site, MI	Meth/SO4	Field	97.7 ug/L	2740	0.0319-0.0845/day		Weaver,JW et al. (1995)
Cecil Field Naval Air Station, FL	Fe/Meth/SO4	Field	2.5 ug/L		Biodegrades		Chapelle,FH (1996)
Victoria, TX	SO4	Field	186-310 ug/L		Biodegrades		Beeman,RE et al. (1994)

Table 27. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Victoria, TX	SO4	Field	30 ug/L		Biodegrades		Beeman,RE et al. (1994)
Plattsburg AFB, Plattsburg, NY	NO3/Fe/SO4/Meth	Field		2487	NB		Wiedemeier,TH et al. (1996A)
	Meth	Lab microcosm	2000 ug/L	180 days	0.00005/day		Barrio-Lage,GA et al. (1990)
Plattsburg AFB, Plattsburg, NY		Lab microcosm	1063 ug/L	3.5	0.0057/day		Bradley,PM & Chapelle,FH (1996)
Cecil Field, Jacksonville, FL		Lab microcosm	1063 ug/L	3.5	0.0082/day		Bradley,PM & Chapelle,FH (1996)
Plattsburg AFB, Plattsburg, NY		Lab microcosm	1063 ug/L	3.5	0.0082/day		Bradley,PM & Chapelle,FH (1996)
Cecil Field, Jacksonville, FL	Fe	Lab microcosm	1063 ug/L	3.5	0.051/day		Bradley,PM & Chapelle,FH (1996)
Plattsburg AFB, Plattsburg, NY	Fe	Lab microcosm	1063 ug/L	3.5	0.098/day		Bradley,PM & Chapelle,FH (1996)
Plattsburg AFB, Plattsburg, NY	Fe	Lab microcosm	1063 ug/L	3.5	0.12/day		Bradley,PM & Chapelle,FH (1996)

3.3. Phenols

In this section, each compound is reviewed with an individual summary table listing all reported studies. Both non-chlorinated and chlorinated phenol compounds were included in this section. These two types of compounds are expected to have different degradation pathways and are expected to respond to the prevailing redox environment differently. The amount and quality of the data for these compounds varied, with a fairly large amount of information collected for phenol and very little information reported for 2,4,6-trichlorophenol. Included in most reviews is a recommended first-order rate constant range that could be used for input into the EPACMTP model. Table 28 summarizes both the range and mean of all studies and the field/*in situ* microcosm studies alone for each of the studied phenol compounds.

Table 28. Summary Table of the First-Order Anaerobic Biodegradation Rate Constants for the Phenol Compounds

Compound	Range, all studies	Mean, all studies	Range, field/*in situ* studies	Mean, field/*in situ* studies
Phenol	0-1.15[ab]	0.16 n=30	0-0.032	0.015 n=4
o-Cresol	0-0.31	0.063 n=18	0-0.034	0.017 n=2
m-Cresol	0-0.54	0.21 n=19	0.033	0.033 n=1
p-Cresol	0->0.50	0.13 n=13	0.048	0.048 n=1
2,4-Dichlorophenol	0-0.12	0.037 n=14	0-<0.027	0.014 n=2
2,4,6-Trichlorophenol	I.D.[c]	I.D.	I.D.	I.D.
Pentachlorophenol	0-0.076	0.023 n=9	0.0019	0.0019 n=1

[a]First-order rate constants in units of days^{-1}

[b]Studies reporting "biodegrades" or zero-order rate constants were assigned a value equal to the mean of the positive rate constant values.

[c]Insufficient data to determine a recommended biodegradation rate constant

3.3.1. Phenol

Several mechanisms for the degradation of phenol have been published. Carboxylation of the aromatic ring is suggested as the initial step under both nitrate- and iron-reducing conditions (Tschech & Fuchs 1987; Lovley & Lonergan 1990). A second mechanism results in the initial transformation of phenol to cyclohexanol, then to cyclohexanone followed by ring cleavage (Bakker 1977). Phenol is used as an electron donor during both mechanisms and thus the degradation of this compound may be promoted under weaker reducing environments. Limited field/*in situ* microcosm data for this compound resulted in the analysis and use of rate constants from laboratory microcosm studies in order to offer a range of first-order rate constant values recommended for input into the EPACMTP model. First-order rate constants for all studies (Table 28) ranged from 0 to 1.15/day with a mean value of 0.16/day.

Phenol was reported as not biodegraded in several studies (Table 29). In order to determine whether zero was a reasonable value for the lower limit of the recommended rate constant range, these studies were examined in further detail. Klecka et al. (1990B) reports that laboratory microcosms incubated under anaerobic conditions were unable to biodegrade phenol, o-cresol and naphthalene over an 84 day period at 10°C, whereas these compounds were readily biodegraded in aerobic microcosms within 30 days. Field results for this site however, showed the complete removal of all indicator compounds (including phenol) within 100 m. Because this was a shallow groundwater site, oxygen was present in the groundwater except within the contaminant plume. The lack of biodegradation in the anaerobic microcosms was thought to be due to the use of aquifer sediment collected from an aerobic location and not to an inability of this site to anaerobically biodegrade phenol. A study by Nielsen et al. (1995A) reports no biodegradation of phenol in several *in situ* microcosms placed along a contaminant plume in a landfill-leachate impacted aquifer. The result of no biodegradation was obtained for mainly methanogenic regions of the plume; fairly rapid biodegradation was reported in both iron-reducing and nitrate-reducing regions often following a lag period of 30-70 days. Haag et al. (1991) reports that phenol was not biodegraded during a column study; only toluene was degraded of the eight to nine compounds (including the BTEX compounds, chlorobenzene and naphthalene) initially added. It is possible that toluene was preferentially used as a carbon donor and that in a column study, the toluene concentration never became low enough to permit biodegradation of the other compounds, including phenol.

It is generally accepted that phenol is biodegraded under anaerobic conditions and several studies show that it is biodegraded under methanogenic, sulfate-reducing, iron-reducing, and nitrate-reducing conditions. Field studies by Godsy et al. (1983; 1992), Troutman et al. (1984), Goerlitz et al. (1985), and Klecka et al. (1990B) for three contaminated sites, St. Louis Park, MN, Cliff-Dow Chemical Company, MI, and Pensacola, FL, present varying levels of information. Goerlitz et al. (1985) observed methanogenic degradation of phenol in a shallow groundwater aquifer at Pensacola, FL which was contaminated with wood-preserving wastes. Phenol, initially present at concentrations of up to 10400 Og/L, was not detected at a second monitoring well only ~140 m downgradient. Troutman et al. (1984), at the same methanogenic aquifer site, showed that phenol was biodegraded; it was postulated that a lack of degradation during the first 450 feet of the flow path may have resulted from inhibitory

concentrations of pentachlorophenol which was also present in the contaminant plume. Laboratory studies by the same authors show that pentachlorophenol at concentrations of 450 Og/L or greater seem to inhibit methanogenesis. Godsy et al. (1992) present evidence of biodegradation suitable for the calculation of a first-order rate constant (rate constant of 0.032/day). In addition, laboratory microcosm studies by the same authors also indicate that phenol is rapidly biodegraded at this site (rate constant of 0.068/day with a lag period of 40-50 days). At the Cliff-Dow site, as previously discussed, phenol was not biodegraded in anaerobic microcosms yet the authors concluded that the complete loss of phenol *in situ*, within 100 m downgradient of the source, was probably due to anaerobic degradation. Godsy et al. (1983) reports that phenol is nearly completely biodegraded under methanogenic conditions over a 143 m distance in a shallow aquifer at St. Louis Park, MN; the biodegradation of phenol was confirmed in laboratory studies using groundwater from this site.

Given the limited amount of field/*in situ* microcosm data on the anaerobic biodegradation of phenol in aquifer environments, a range of rate constants is recommended with the lower limit equal to 0.0013/day (a half-life of 533 days) which is an order of magnitude less than the lowest reported rate constant for a laboratory microcosm study. A lower value, reported for a groundwater grab sample study, was not used as it is believed that most of the microbial activity is associated with the aquifer sediment (Holm et al, 1992); groundwater grab sample studies are expected to have lower rate constant values than comparable laboratory microcosm studies which include aquifer sediment. A value equal to 0.032/day (a half-life of 22 days) which represents the sole, reported field study rate constant is proposed as the upper limit to the recommended range.

Table 29. All Summarized Studies for Phenol

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		Biodegrades		Lyngkilde,J et al. (1992)
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Archer, FL		Column	4500 ug/L		1.15/day		Lin,CH (1988)
Norman, OK	Meth	Column			Biodegrades		Suflita,JM & Miller,GD (1985)
Seal Beach, CA	Meth	Column	0.021-0.50 umol/g	570	NB		Haag,F et al. (1991)
Pensacola, FL	Meth	Field	80-10400 ug/L	87-260	Biodegrades		Goerlitz,DF et al. (1985)
Pensacola, FL	Meth	Field	26010 ug/L	125	0.032/day		Godsy,EM et al. (1992)
Pensacola, FL	Meth	Field	5210 ug/L	250	Biodegrades		Troutman,DE et al. (1984)
St. Louis Park, MN	Meth	Field	2050 ug/L		Biodegrades		Godsy,EM et al. (1983)
West Valley, NY	NO3/SO4	Groundwater grab sample	5800 ug/L	60	0.0029/day		Francis,AJ (1982)
St. Louis Park, MN	Meth	Groundwater grab sample	2050 ug/L	56	0.012/day		Godsy,EM et al. (1983)

Table 29. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Fredensborg, Denmark	NO3	Groundwater grab sample	2000 ug/L	25	0.42/day	18	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	1900 ug/L	20	0.43/day	17	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	2000 ug/L	10	0.52/day	5	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	2000 ug/L		Biodegrades	60	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	2000 ug/L		Biodegrades	20	Flyvbjerg,J et al. (1993)
Vejen city landfill, Denmark	Fe	In situ microcosm	150 ug/L	110-130	>0.027/day	0-70	Nielsen,PH et al. (1995A)
Vejen city landfill, Denmark	Fe	In situ microcosm	150 ug/L		NB		Nielsen,PH et al. (1995A)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L		NB		Nielsen,PH et al. (1995A)
Vejen city landfill, Denmark	NO3/Mn	In situ microcosm	150 ug/L		Possible		Nielsen,PH et al. (1995A)
Pensacola, FL	Meth	Lab microcosm	5140 ug/L	70	0.013/day		Troutman,DE et al. (1984)
Norman, OK	SO4	Lab microcosm	28000-47000 ug/L	90	0.051/day		Gibson,SA & Suflita,JM (1986)

Table 29. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Pensacola, FL	Meth	Lab microcosm	19000 ug/L	95	0.068/day	40	Godsy,EM et al. (1992)
Pensacola, FL	Meth	Lab microcosm	20000 ug/L	90	0.071/day	30	Arvin,E et al. (1989)
Newport News, VA	Meth/SO4	Lab microcosm	100000 ug/L	29	0.10/day		Morris,MS (1988)
Newport News, VA	NO3	Lab microcosm	105000 ug/L	29	0.10/day		Morris,MS (1988)
Pensacola, FL	Meth	Lab microcosm	41000 ug/L	80	0.13/day	50	Godsy,EM et al. (1992A)
Dumfries, VA		Lab microcosm	50000 ug/L	43	0.20/day		Smith,JA & Novak,JT (1987)
Norman, OK	Meth	Lab microcosm	28000-47000 ug/L	90	>0.11/day		Gibson,SA & Suflita,JM (1986)
Cliff-Dow Chemical Co., Marquette, MI		Lab microcosm	500 ug/L	84	NB		Klecka,GM et al. (1990A)
Vejen city landfill, Denmark	Meth/Fe/NO3	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995A)

3.3.2. o-Cresol

The methyl group on the aromatic ring of o-cresol provides a site for an initial oxidative attack by water-derived oxygen (Grbic-Galic 1990). This results in the production of o-hydroxybenzoate. Unlike p-cresol, which forms p-hydroxybenzoate and then decarboxylates this intermediate to enter the phenol pathway, o-hydroxybenzoate is O-oxidized through a pathway similar to that for benzoate via 3-methylbenzoyl coenzyme A (Tschech & Schink 1986). o-Cresol is used as an electron donor during this pathway and thus the degradation of this compound may be promoted under weaker reducing environments. Limited field data for this compound resulted in the analysis and use of rate constants from laboratory microcosm studies in order to offer a range of first-order rate constant values recommended for input into the EPACMTP model. First-order rate constants for all studies (Table 28) ranged from 0 to 0.31/day with a mean value of 0.063/day.

o-Cresol was reported as not biodegraded in several studies (Table 30). In order to determine whether zero is a reasonable value for the lower limit of the recommended rate constant range, these studies were examined in further detail. Klecka et al. (1990B) reports that laboratory microcosms incubated under anaerobic conditions were unable to biodegrade phenol, o-cresol and naphthalene over an 84 day period at 10°C, whereas these compounds were readily biodegraded in aerobic microcosms within 30 days. Field results for this site however, showed the complete removal of all indicator compounds (including o-cresol) within 100 m. Because this was a shallow groundwater site, oxygen was present in the groundwater except within the contaminant plume. The lack of biodegradation in the anaerobic microcosms was thought to be due to the use of aquifer sediment collected from an aerobic location and not to an inability of this site to anaerobically biodegrade o-cresol. A study by Nielsen et al. (1995A) reports no biodegradation of o-cresol in a series of *in situ* microcosms placed along a contaminant plume in a landfill-leachate impacted aquifer. The result of no biodegradation was surprising to the authors as conditions ranging from methanogenic to nitrate-reducing were present along the plume. o-Cresol was also not biodegraded during companion laboratory microcosm studies using aquifer sediment collected along the plume. Three of four laboratory microcosm studies by Flyvbjerg et al. (1993) report the biodegradation of o-cresol. The study not showing biodegradation was incubated at 10°C without added nitrate. The companion study which was incubated at 20°C without added nitrate had a reported lag period of 235 days. A column study showed the biodegradation of both m- and p-cresol but not o-cresol over the six day retention time; this column was adapted to m-xylene and thus may not have developed a microbial population that could initiate the biodegradation pathway of o-cresol during this short period of time (Kuhn et al. 1988).

Biodegradation of o-cresol has been shown under methanogenic, sulfate-reducing, and nitrate-reducing conditions. Field studies by Godsy et al. (1983; 1992), Troutman et al. (1984), Goerlitz et al. (1985), and Klecka et al. (1990B) for three contaminated sites, St. Louis Park, MN, Cliff-Dow Chemical Company, MI, and Pensacola, FL, present varying levels of information. Goerlitz et al. (1985) observed methanogenic degradation of o-cresol in a shallow groundwater aquifer at Pensacola, FL which was contaminated with wood-preserving wastes. o-Cresol, initially present at concentrations of

up to 7100 Og/L, was present at only 40 Og/L at a second monitoring well only ~140 m downgradient. Troutman et al. (1984), at the same methanogenic aquifer site, showed that o-cresol was biodegraded; it was postulated that a lack of degradation during the first 450 feet of the flow path may have resulted from inhibitory concentrations of pentachlorophenol which was also present in the contaminant plume. Laboratory studies by the same authors show that pentachlorophenol at concentrations of 450 Og/L or greater seem to inhibit methanogenesis. Godsy et al. (1992) present evidence of biodegradation suitable for the calculation of a first-order rate constant (rate constant of 0.034/day). In addition, laboratory microcosm studies by the same authors also indicate that o-cresol is rapidly biodegraded at this site (rate constant of 0.032/day with a lag period of 100 days). At the Cliff-Dow site, as previously discussed, o-cresol was not biodegraded in anaerobic microcosms yet the authors concluded that the complete loss of o-cresol *in situ*, within 100 m downgradient of the source, was probably due to anaerobic degradation. Godsy et al. (1983) report that o-cresol is biodegraded under methanogenic conditions over a 143 m distance in a shallow aquifer at St. Louis Park, MN; the biodegradation of o-cresol could not be confirmed in laboratory studies using groundwater from this site, possibly due to a problem with the laboratory method. The cresols were degraded completely to carbon dioxide and methane with acetate formed transiently during this process.

Given the limited amount of field/*in situ* microcosm data on the anaerobic biodegradation of o-cresol in aquifer environments, a range of rate constants is recommended with the lower limit equal to 0.0005/day (a half-life of 1386 days) which is an order of magnitude less than the lowest reported rate constant (for a laboratory microsom study) and the upper limit equal to 0.034/day (a half-life of 20 days) which represents the sole, reported field study rate constant.

Table 30. All Summarized Studies for o-Cresol

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		Biodegrades		Lyngkilde,J et al. (1992)
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Lower Glatt Valley, Switzerland	NO3	Column	21630 ug/L	6	NB		Kuhn,EP et al. (1988)
Pensacola, FL	Meth	Field	13270 ug/L	125	0.034/day		Godsy,EM et al. (1992)
Pensacola, FL	Meth	Field	4270 ug/L	250	Biodegrades		Troutman,DE et al. (1984)
Pensacola, FL	Meth	Field	100-7100 ug/L		Biodegrades		Goerlitz,DF et al. (1985)
St. Louis Park, MN	Meth	Field	2240 ug/L		Biodegrades		Godsy,EM et al. (1983)
Fredensborg, Denmark	NO3	Groundwater grab sample	650 ug/L	98	0.17/day	80	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	650 ug/L	26	0.31/day	23	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	650 ug/L		Biodegrades	120	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	650 ug/L	235	NB		Flyvbjerg,J et al. (1993)

Table 30. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
St. Louis Park, MN	Meth	Groundwater grab sample	2070 ug/L	56	NB		Godsy,EM et al. (1983)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995A)
Pensacola, FL	Meth	Lab microcosm	4330 ug/L	70	0.0050/day		Troutman,DE et al. (1984)
Pensacola, FL	Meth	Lab microcosm	8500 ug/L	185	0.032/day	100	Godsy,EM et al. (1992)
Pensacola, FL	Meth	Lab microcosm	9000 ug/L	175	0.034/day	100	Arvin,E et al. (1989)
Pensacola, FL	Meth	Lab microcosm	36000 ug/L	145	0.070/day	75	Godsy,EM et al. (1992A)
Norman, OK	Meth	Lab microcosm	16223-21630 ug/L		Biodegrades	>90	Smolenski,WJ & Suflita,JM (1987)
Norman, OK	SO4	Lab microcosm	16223-21630 ug/L		Biodegrades	>100	Smolenski,WJ & Suflita,JM (1987)
Cliff-Dow Chemical Co., Marquette, MI		Lab microcosm	500 ug/L	84	NB		Klecka,GM et al. (1990A)
Vejen city landfill, Denmark	Meth/Fe/NO3	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995A)

3.3.3. m-Cresol

Unlike o- and p-cresol, the methyl group on the aromatic ring of m-cresol is not initially oxidized before ring cleavage; radiolabel studies show that the methyl group is mainly converted to methane whereas in p-cresol this group forms carbon dioxide. m-Cresol is initially carboxylated forming o-methyl-p-hydroxybenzoate which then is thought to undergo ring cleavage followed by O-oxidation to acetate (Grbic-Galic 1990). Limited field data for this compound resulted in the analysis and use of rate constants from laboratory microcosm studies in order to offer a range of first-order rate constant values recommended for input into the EPACMTP model. First-order rate constants for all studies (Table 28) ranged from 0 to 0.54/day with a mean value of 0.21/day.

m-Cresol was reported as not biodegraded in one study (Table 31). In order to determine whether zero is a reasonable value for the lower limit of the recommended rate constant range, this study was examined in further detail. Ramanand and Suflita (1991) report that m-cresol, present as the sole carbon source, is biodegraded under nitrate- and sulfate-reducing conditions but not under methanogenic conditions. The incubation period was six days which may not have been sufficiently long to determine biodegradation under a methanogenic environment. This redox regime is expected to give the lowest rate constant when compared to other, weaker redox conditions as m-cresol acts as an electron donor (it is oxidized) during its biotransformation.

Biodegradation of m-cresol has been shown under methanogenic, sulfate-reducing, and nitrate-reducing conditions. Field studies by Godsy et al. (1983; 1992), Troutman et al. (1984), Goerlitz et al. (1985) for two contaminated sites, St. Louis Park, MN and Pensacola, FL, present varying levels of information. Goerlitz et al. (1985) observed methanogenic degradation of m-cresol in a shallow groundwater aquifer at Pensacola, FL which was contaminated with wood-preserving wastes. m-Cresol, initially present at concentrations of up to 13730 Og/L, was present at only 50 Og/L at a second monitoring well only ~140 m downgradient. Troutman et al. (1984), at the same methanogenic aquifer site, showed that m-cresol was biodegraded; it was postulated that a lack of degradation during the first 450 feet of the flow path may have resulted from inhibitory concentrations of pentachlorophenol which was also present in the contaminant plume. Laboratory studies by the same authors show that pentachlorophenol at concentrations of 450 Og/L or greater seem to inhibit methanogenesis. Godsy et al. (1992) present evidence of biodegradation *in situ* suitable for the calculation of a first-order rate constant (rate constant of 0.033/day). In addition, laboratory microcosm studies by the same authors also indicate that m-cresol is rapidly biodegraded at this site (rate constant of 0.029/day with a lag period of 100 days). Godsy et al. (1983) report that m-cresol is biodegraded under methanogenic conditions over a 143 m distance in a shallow aquifer at St. Louis Park, MN; the biodegradation of m-cresol was confirmed in laboratory studies using groundwater from this site. The cresols were degraded completely to carbon dioxide and methane with acetate formed transiently during this process.

Given the limited amount of field/*in situ* microcosm data on the anaerobic biodegradation of m-cresol in aquifer environments, a range of rate constants is recommended with the lower limit equal to

0.00029/day (a half-life of 2390 days) which is an order of magnitude less than the lowest reported rate constant (for a laboratory microsom study) and the upper limit equal to 0.033/day (a half-life of 21 days) which represents the sole, reported field study rate constant.

Table 31. All Summarized Studies for m-Cresol

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Lower Glatt Valley, Switzerland	NO3	Column	21630 ug/L	6	>0.50/day		Kuhn,EP et al. (1988)
Pensacola, FL	Meth	Field	26650 ug/L	125	0.033/day		Godsy,EM et al. (1992)
Pensacola, FL	Meth	Field	10890 ug/L	250	Biodegrades		Troutman,DE et al. (1984)
Pensacola, FL	Meth	Field	150-13730 ug/L		Biodegrades		Goerlitz,DF et al. (1985)
St. Louis Park, MN	Meth	Field	5690 ug/L		Biodegrades		Godsy,EM et al. (1983)
St. Louis Park, MN	Meth	Groundwater grab sample	5222 ug/L	56	0.066/day		Godsy,EM et al. (1983)
Fredensborg, Denmark	NO3	Groundwater grab sample	780 ug/L	37	0.20/day	25	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	780 ug/L	12	0.34/day	5	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	780 ug/L		Biodegrades	60	Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	780 ug/L		Biodegrades	20	Flyvbjerg,J et al. (1993)
Pensacola, FL	Meth	Lab microcosm	10960 ug/L	70	0.0029/day		Troutman,DE et al. (1984)
Pensacola, FL	Meth	Lab microcosm	18500 ug/L	220	0.029/day	100	Arvin,E et al. (1989)

Table 31. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Pensacola, FL	Meth	Lab microcosm	17500 ug/L	220	0.029/day	100	Godsy,EM et al. (1992)
Pensacola, FL	Meth	Lab microcosm	32000 ug/L	50	0.17/day	20	Godsy,EM et al. (1992A)
Norman, OK	NO3	Lab microcosm	27254 ug/L	6	0.52/day	2	Ramanand,K & Suflita,JM (1991)
Norman, OK	SO4	Lab microcosm	24983 ug/L	6	0.54/day	2	Ramanand,K & Suflita,JM (1991)
Norman, OK	Meth	Lab microcosm	16223-21630 ug/L		Biodegrades	46-90	Smolenski,WJ & Suflita,JM (1987)
Norman, OK	SO4	Lab microcosm	16223-21630 ug/L		Biodegrades	43	Smolenski,WJ & Suflita,JM (1987)
Norman, OK	Meth	Lab microcosm	29092 ug/L	6	NB		Ramanand,K & Suflita,JM (1991)

3.3.4. p-Cresol

The methyl group on the aromatic ring of p-cresol provides a site for an initial oxidative attack by water-derived oxygen (Grbic-Galic 1990). This results in the production of p-hydroxybenzoate. Unlike o-cresol, which forms o-hydroxybenzoate and then is O-oxidized through a pathway similar to that for benzoate (Tschech & Schink 1986), p-cresol forms p-hydroxybenzoate which is then decarboxylated and enters the phenol pathway. p-Cresol is used as an electron donor during this pathway and thus the degradation of this compound may be promoted under weaker reducing environments. Limited field data for this compound resulted in the analysis and use of rate constants from laboratory microcosm studies in order to offer a range of first-order rate constant values recommended for input into the EPACMTP model. First-order rate constants for all studies (Table 28) ranged from 0 to >0.50/day with a mean value of 0.13/day.

p-Cresol was reported as not biodegraded in one study (Table 32). In order to determine whether zero is a reasonable value for the lower limit of the recommended rate constant range, this study was examined in further detail. Haag et al. (1991) reports that p-cresol was not biodegraded during a column study; only toluene was degraded of the eight to nine compounds (including the BTEX compounds, chlorobenzene and naphthalene) initially added. It is possible that toluene was preferentially used as a carbon donor and that in a column study, the toluene concentration never became low enough to permit biodegradation of the other compounds, including p-cresol.

Biodegradation of p-cresol has been shown under methanogenic, sulfate-reducing, and nitrate-reducing conditions. Field studies by Godsy et al. (1992) and Goerlitz et al. (1985) for a contaminated site at Pensacola, FL, present varying levels of information. Goerlitz et al. (1985) observed methanogenic degradation of p-cresol in a shallow groundwater aquifer at Pensacola, FL which was contaminated with wood-preserving wastes. p-Cresol, initially present at concentrations of up to 6170 Og/L, was not present at a second monitoring well only ~140 m downgradient. Godsy et al. (1992) present evidence of biodegradation suitable for the calculation of a first-order rate constant (rate constant of 0.048/day). In addition, laboratory microcosm studies by the same authors also indicate that p-cresol is rapidly biodegraded at this site (rate constant of 0.035/day with a lag period of 100 days). The cresols were degraded completely to carbon dioxide and methane with acetate formed transiently during this process.

Given the limited amount of field/*in situ* microcosm data on the anaerobic biodegradation of p-cresol in aquifer environments, a range of rate constants is recommended with the upper limit equal to 0.048/day (a half-life of 14 days) which represents the sole, reported field study rate constant. A lower limit of 0 0037/day (half-life of 19 days), which is an order of magnitude less than the lowest reported rate constant (for a laboratory microsom study) was not thought to be a good lower estimate upon comparison with the lower limits recommended for the other two cresol isomers. There is no evidence to support that this isomer biodegrades more rapidly than the m- or o-cresol isomers. Therefore, to obtain a value consistent with the other cresol isomers, a lower limit of 0.0004/day is proposed; this was determined by taking the average of the two lower limits of m- and o-cresol.

Table 32. All Summarized Studies for p-Cresol

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Lower Glatt Valley, Switzerland	NO3	Column	21630 ug/L	6	>0.50/day		Kuhn,EP et al. (1988)
Seal Beach, CA	Meth	Column	0.063 umol/g	14	NB		Haag,F et al. (1991)
Pensacola, FL	Meth	Field	11970 ug/L	125	0.048/day		Godsy,EM et al. (1992)
Pensacola, FL	Meth	Field	70-6170 ug/L		Biodegrades		Goerlitz,DF et al. (1985)
Florida		Groundwater grab sample		45	Biodegrades		Delfino,JJ et al. (1989)
Pensacola, FL	Meth	Lab microcosm	8000 ug/L	180	0.035/day	100	Godsy,EM et al. (1992)
Pensacola, FL	Meth	Lab microcosm	8000 ug/L	185	0.037/day	100	Arvin,E et al. (1989)
Pensacola, FL	Meth	Lab microcosm	81113 ug/L	70	0.038/day		Beller,HR et al. (1991)
Pensacola, FL	Meth	Lab microcosm	25000 ug/L	110	0.11/day	75	Godsy,EM et al. (1992A)
Norman, OK	Meth	Lab microcosm	16223-21630 ug/L		Biodegrades	46	Smolenski,WJ & Suflita,JM (1987)
Norman, OK	Meth	Lab microcosm	16223-21630 ug/L	10	Biodegrades		Smolenski,WJ & Suflita,JM (1987)
Norman, OK	SO4	Lab microcosm	16223-21630 ug/L		Biodegrades	<10	Smolenski,WJ & Suflita,JM (1987)

Table 32. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Norman, OK	SO4	Lab microcosm	16223-21630 ug/L	10	Biodegrades		Smolenski,WJ & Suflita,JM (1987)

3.3.5. 2,4-Dichlorophenol

Suflita and Miller's data (1985) show that the initial step in the degradation of a chlorophenol is sequential reductive dechlorination, as outlined above for the chlorinated aliphatic compounds. Using mass spectral data, it was determined that the ortho chlorine was initially removed. Complete dechlorination was necessary before the phenol ring could be attacked (Suflita & Miller 1985). It is thought that the processes of reductive dechlorination and ring cleavage are carried out by separate microbial populations, one group using the chlorinated compound as an electron acceptor (reductive dechlorination) and the other using the remaining phenol group as an electron donor (oxidative degradation). The process of reductive dechlorination is expected to occur readily under strong reducing conditions such as methanogenic and sulfate-reducing redox environments but not under aerobic and possibly not under nitrate-reducing conditions. Oxidative degradation of the remaining phenol is expected to occur under any anaerobic redox condition but most rapidly under nitrate-reducing conditions. Limited field data for this compound resulted in the analysis and use of rate constants from laboratory microcosm studies in order to offer a range of first-order rate constant values recommended for input into the EPACMTP model. First-order rate constants for all studies (Table 28) ranged from 0 to 0.12/day with a mean value of 0.037/day.

2,4-Dichlorophenol was reported as not biodegraded in several studies (Table 33). To determine whether zero is a reasonable value for the lower limit of the recommended rate constant range, these studies were examined in further detail. 2,4-Dichlorophenol was not biodegraded in either methanogenic or nitrate-reducing groundwater inoculum studies by Lyngkilde et al. (1992). Many other compounds were not biodegraded in this system as well, including toluene, o-xylene, and several chlorinated aliphatic compounds. These results are surprising but possibly reflect that only groundwater and not sediment was present in the sample. Nielsen et al. (1995A) at the same site, reports that *in situ* microcosm columns placed in the iron-reducing or nitrate-reducing region of the contaminant plume did not show biodegradation of 2,4-dichlorophenol; however, two of three *in situ* microcosm columns placed in the methanogenic region reported slow biotransformation of this compound (<80% transformation in two months). A column study by Suflita and Miller (1985) reports rapid biodegradation of 2,4-dichlorophenol under methanogenic conditions and no biodegradation of this compound under non-methanogenic conditions (added sulfate inhibited methanogenesis). This suggests that biodegradation under "weaker" reducing conditions (sulfate-reducing conditions) is either much slower or does not occur.

Given the limited amount of field/*in situ* microcosm data on the anaerobic biodegradation of 2,4-dichlorophenol in aquifer environments, a range of rate constants is recommended with the lower limit equal to 0.00055/day (a half-life of 126 days; sulfate-reducing conditions) which is an order of magnitude less than the lowest reported rate constant (for a laboratory microsom study) and the upper limit equal to 0.027/day (a half-life of 26 days; methanogenic conditions) which represents one *in situ* microcosm study rate constant. Redox conditions are expected to be very important during the initial steps of biodegradation of this compound. Reductive dechlorination will occur most readily under methanogenic conditions and the collected data support this view. It is not known whether 2,4-dichlorophenol will biodegrade under iron- or nitrate-reducing conditions; the available data suggests

that it does not or that the rate is much slower than that for the stronger reducing environments. Therefore, the above range of recommended values will not be representative if the redox potential of the aquifer under study is classified as nitrate- or iron-reducing.

Table 33. All Summarized Studies for 2,4-Dichlorophenol

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Forlev, Denmark	Meth	Column	2860 ug/L		0.015/day		Kjeldsen,P et al. (1990)
Forlev, Denmark	Meth	Column	2860 ug/L		0.017/day		Kjeldsen,P et al. (1990)
Archer, FL		Column	4500 ug/L		0.070/day		Lin,CH (1988)
Norman, OK	Meth	Column	67900 ug/L	56	0.090/day		Suflita,JM & Miller,GD (1985)
Norman, OK		Column	67900 ug/L	91	NB		Suflita,JM & Miller,GD (1985)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L	60	<0.027/day		Nielsen,PH et al. (1995A)
Vejen city landfill, Denmark	Fe/NO3	In situ microcosm	150 ug/L		NB		Nielsen,PH et al. (1995A)
Norman, OK	SO4	Lab microcosm	48900-81500 ug/L	90	0.0055/day		Gibson,SA & Suflita,JM (1986)
Newport News, VA	Meth/SO4	Lab microcosm	70000 ug/L	23	0.12/day		Morris,MS (1988)
Newport News, VA	NO3	Lab microcosm			200 mM/d/g		Morris,MS (1988)

Table 33. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Norman, OK	Meth	Lab microcosm	48900-81500 ug/L	90	>0.12/day		Gibson,SA & Suflita,JM (1986)
Vejen city landfill, Denmark	Fe/NO3	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995A)
Vejen city landfill, Denmark	Meth	Lab microcosm	150 ug/L	150-180	Possible		Nielsen,PH et al. (1995A)

3.3.6. 2,4,6-Trichlorophenol

Suflita and Miller's data (1985) show that the initial step in the degradation of a chlorophenol is sequential reductive dechlorination, as outlined above for the chlorinated aliphatic compounds. Using mass spectral data, it was determined that the ortho chlorine was initially removed. Complete dechlorination was necessary before the phenol ring could be attacked (Suflita & Miller 1985). Very little information on the biodegradation of 2,4,6-trichlorophenol in an anaerobic aquifer environment was found (Table 34); insufficient information was available to recommend a first-order rate constant although this compound is expected to be recalcitrant. To supplement the evidence that this compound could be reductively dechlorinated in an aquifer environment, a quick literature search of papers using non-groundwater inocula was also performed.

The only located study in an aquifer environment is a paper by Valo et al. (1984) which reports that 2,4,6-trichlorophenol is present in groundwater contaminated by two sawmills using wood-preservative. 2,4,6-Trichlorophenol was one of three major components of this preservative. Unfortunately, concentrations of this compound were so low at this site (from 0 to 0.12 Og/L) that it was not possible to determine if biodegradation of 2,4,6-trichlorophenol was occurring.

Smith and Novak (1987) report the biodegradation of 2,4,6-trichlorophenol in unsaturated soil incubated under anaerobic conditions; initial concentrations of 20 to 60 mg/L were nearly completely biodegraded within 30 to 70 days. Studies using saturated soils (*i.e.* aquifer sediments) were not completed for this compound. However, in the same study, when saturated soils were incubated under the same conditions with 2-chlorophenol, the rate of degradation was much slower than for 2-chlorophenol in the unsaturated soil microcosms. Therefore, 2,4,6-trichlorophenol may biodegrade in groundwater; however, the rate of biodegradation may be considerably lower than that published for other, non-groundwater, environments. Two of three marine sediment samples collected from sites in Sweden/Norway were able to reductively dechlorinate 2,4,6-trichlorophenol (Abrahamsson & Klick 1991). One author reports that the dechlorination of 2,4,6-trichlorophenol, using a sewage inoculum, may be pH dependent with optima from a pH of 8 to 8.8 (Armenante et al. 1993). This result was repeated using river sediment by Chang et al. (1995); 2,4,6-trichlorophenol was optimally dechlorinated at a pH of 8. The process of dechlorination was inhibited by the addition of nitrate, but not by sulfate, and the addition of a carbon source enhanced the biodegradation of this compound.

Given the very limited anaerobic biodegradation information on 2,4,6-trichlorophenol, it is currently not possible to recommend a rate constant describing the biotransformation of this compound in anaerobic groundwater. However, it is possible that this compound is reductively dechlorinated, particularly under strong reducing conditions (e.g. methanogenic and sulfate-reducing conditions) when sufficient organic carbon is present.

Table 34. All Summarized Studies for 2,4,6-Trichlorophenol

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Central Finland		Field	5.67 ug/L				Valo,R et al. (1984)

3.3.7. Pentachlorophenol

Biodegradation of pentachlorophenol by reductive dechlorination has been reported in flooded soil and anaerobic sediment environments but much less often in aquifer environments. A common pathway via initial ortho dechlorinations followed by para dechlorination to 3,5-dichlorophenol has been reported for various microbial consortia (Mikesell & Boyd 1986; Nicholson et al. 1992) but initial meta or para dechlorination has also been seen (Hendriksen et al. 1992). Often, dechlorination is not complete and daughter products, the di-, tri-, and tetrachlorophenols result. It is thought that the processes of reductive dechlorination and ring cleavage are carried out by separate microbial populations, one group using the chlorinated compound as an electron acceptor (reductive dechlorination) and the other using the remaining phenol group as an electron donor (oxidative degradation). The process of reductive dechlorination is expected be most likely under strong reducing conditions such as methanogenic and sulfate-reducing redox environments but not under aerobic and possibly not under nitrate-reducing conditions. Oxidative degradation of the remaining phenol is expected to occur under any anaerobic redox condition but most rapidly under nitrate-reducing conditions. Pentachlorophenol can also be biodegraded through aerobic pathways (Davis A et al. 1994). First-order rate constants for all studies (Table 28) ranged from 0 to 0.076/day with a mean value of 0.037/day.

Results from all summarized studies for this compound are presented in Table 35. Field studies for three different aquifer sites suggest that biodegradation of pentachlorophenol may be site-specific, mainly dependent on the concentration of pentachlorophenol present at the site, the microbial population, and the redox conditions. As technical formulations contain high concentrations of mineral spirits or diesel fuel, degradation of pentachlorophenol should not be limited by electron donor availability. Operating practices at an industrial site resulted in the contamination of soil and groundwater with pentachlorophenol present in a mineral oil solution (Fu & O'Toole 1990). While the authors attribute the degradation of pentachlorophenol at this site during treatment to reductive dechlorination (increased chloride concentrations downgradient), the reported redox environment is nitrate-reducing. This is surprising as one would not expect pentachlorophenol to undergo reductive dechlorination readily under nitrate-reducing conditions. The treatment process included the addition of alternate electron acceptors as well as chemical agents and nutrients to encourage biodegradation at this site. Groundwater beneath a wood treatment facility at Dania, FL was contaminated with pentachlorophenol (Davis A et al. (1994). Daughter products, 3,4-dichlorophenol, 3,5-dichlorophenol, and 3-chlorophenol (chosen because they are not present in technical formulations of pentachlorophenol) were measured along the contaminant flow path. The authors report that dichlorophenol and chlorophenol concentrations are much higher, representing greater biodegradation of pentachlorophenol, in samples containing low concentrations of pentachlorophenol than they are in high pentachlorophenol concentration samples. This indicates that pentachlorophenol can be toxic or at least inhibitory to microbial populations; these authors observe a biocidal threshold at pentachlorophenol concentrations greater than 20000 Og/L. Biodegradation of the plume tended to occur at the periphery where pentachlorophenol concentrations are generally lower (oxygen may also be present). Troutman et al. (1984) report that pentachlorophenol is inhibitory to methanogenesis in a Pensacola, FL aquifer at concentrations above 450 Og/L based on laboratory studies. Field studies,

showing inhibition of other phenolic compounds along the contaminant plume until pentachlorophenol concentrations decrease, are consistent with the laboratory studies. In a study of the same site, Godsy et al. (1992) report that pentachlorophenol decreases in proportion to the conservative tracer indicating that this compound is not biodegraded along this flow path.

There is very little data suggesting that pentachlorophenol can be biodegraded in an anaerobic aquifer environment; most of the positive evidence comes from a single study where active remediation of the site was occurring (Fu & O'Toole 1990). Much of the literature reports that this compound actually may inhibit the microbial population to the extent that other compounds will not be biodegraded. If pentachlorophenol is found at inhibitory concentrations, biodegradation of itself as well as any other contaminant also present may be compromised. Until further work is completed, including the determination of concentration thresholds for this compound in groundwater environments as well as the effect of the redox condition on the biodegradation of pentachlorophenol, a rate constant value describing this compound in anaerobic groundwater cannot be recommended.

Table 35. All Summarized Studies for Pentachlorophenol

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Wausau, WI	NO3	Batch reactor	13200 ug/kg	84	0.019-0.034/day		Fu,K & O'Toole,R (1990)
Archer, FL		Column	4500 ug/L		0.076/day		Lin,CH (1988)
Forlev, Denmark	Meth	Column	1000 ug/L	218-236	Possible		Kjeldsen,P et al. (1990)
Central Finland		Field	23.3 ug/L				Valo,R et al. (1984)
Dania site, FL		Field	12-230000 ug/L		Biodegrades		Davis,A et al. (1994)
Wausau, WI	NO3	Field	1280-25100 ug/kg	180	Biodegrades		Fu,K & O'Toole,R (1990)
Wausau, WI	NO3	Field	23500-54600 ug/kg	180	Biodegrades		Fu,K & O'Toole,R (1990)
Pensacola, FL	Meth	Field	620 ug/L	125	NB		Godsy,EM et al. (1992)
Conroe, TX		Lab microcosm		56	NB		Thomas,JM et al. (1989)
Pensacola, FL	Meth	Lab microcosm	450 ug/L	70	NB		Troutman,DE et al. (1984)
Pensacola, FL	Meth	Lab microcosm	900 ug/L	70	NB		Troutman,DE et al. (1984)
Conroe, TX		Lab microcosm		56	Possible		Thomas,JM et al. (1989)

3.4. Freons

3.4.1. Trichlorofluoromethane (CFC-11)

Like carbon tetrachloride, the carbon in trichlorofluoromethane is present in its most oxidized state (chlorine/fluorine only are present as substituents) and thus the only biological anaerobic transformation process possible is reduction. The main reaction pathway leading to the anaerobic degradation of trichlorofluoromethane is via reductive dehalogenation with chlorine as the initial leaving group; this results in fluorodichloromethane as the initial reaction product (Vogel et al. 1987). The one carbon-fluoride bond provides greater stability to this molecule than that shown for carbon tetrachloride which has four carbon-chlorine bonds. This should result in lower transformation rates for trichlorofluoromethane when compared to carbon tetrachloride. This compound is not expected to biodegrade aerobically and can be used in aerobic aquifers, because of its stability, to date shallow groundwater (Dunkle et al. 1993). It is expected that in highly reducing groundwater with significant amounts of carbon present, trichlorofluoromethane will biodegrade.

Several studies report the biodegradation of trichlorofluoromethane (Table 36). Sonier et al. (1994) show that trichlorofluoromethane is biodegraded to HCFC-21 (fluorodichloromethane) under sulfate-reducing conditions in the presence of an added carbon source (acetate). Using a groundwater inoculum from a site contaminated with trichloroethylene and trichlorofluoromethane, they showed that degradation rates of trichlorofluoromethane increased during respike experiments (from 0.2 Og/L/day to 37 Og/L/day). Trichlorofluoromethane degradation did not occur when acetate was not present; similar to the chlorinated aliphatic compounds, the presence of an electron donor is necessary for biodegradation of this compound to proceed. Nitrate addition did not promote the degradation of this compound (Sonier et al. 1994B).

Semprini et al. (1992) report the enhanced biodegradation of trichlorofluoromethane in a field study using added acetate (as a carbon substrate/electron donor) and nitrate and sulfate (as potential electron acceptors); this aquifer was contaminated with 1,1,1-trichloroethane, trichlorofluoromethane and 1,1,2-trichloro-1,2,2-trifluoroethane. Within 2 m of the injection site, 68% of the added trichlorofluoromethane was biodegraded. Increased rates of biodegradation occurred when nitrate was removed from the injection mixture with an increase in the slope of the biotransformation curve by a factor of two.

Cook et al. (1995) determine that trichlorofluoromethane is biodegraded during a groundwater recharge study. Using vertical sampling profiles of an aquifer site in Ontario, Canada, a rate constant of 0.0016/day was reported (half-life of 433 days). This value is recommended as the upper limit of a rate constant range; a lower limit of 0.00016/day (half-life of 4331 days), representing a rate one order of magnitude lower than this field value is proposed. While another, higher rate constant was published for a field study (Semprini et al. 1992), it was not felt to be representative as both a carbon source and electron acceptors were added to enhance biodegradation. As the proposed rate constant is derived from only a single value from one study at one site it does not have the same supporting evidence that

other compounds with more extensive data. Biodegradation is expected to occur most rapidly under methanogenic conditions; conversely, there is not enough information to determine whether this compound can biodegrade under either iron- or nitrate-reducing conditions although it is expected that the rate of degradation will be substantially lower. Therefore, the range recommended above may not be representative if the redox potential of the aquifer under study is classified as nitrate-reducing. In addition, the published studies for trichlorofluoromethane all use very low concentrations of this chlorofluorocarbon. It is not known if higher concentrations will affect the biodegradation rate of this compound.

Table 36. All Summarized Studies for Trichlorofluoromethane (CFC-11)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Central Oklahoma		Field					Busenberg,E & Plummer,LN (1992)
Delmarva Peninsula, US	SO4	Field					Dunkle,SA et al. (1993)
San Antonio, TX		Field	35 ug/L				Thompson,GM & Hayes,JM (1979)
Sturgeon Falls, Ontario		Field	725 pg/kg		0.0016/day		Cook,PG et al. (1995)
Moffett Field Naval Air Station, CA	NO3/SO4	Field	3 ug/L	1.8	0.63/day		Semprini,L et al. (1992)
Moffett Field Naval Air Station, CA	NO3/SO4	Field			Biodegrades		Semprini,L et al. (1990)
Western United States	SO4	Groundwater inoculum	9.8 ug/L	52	0.051/day		Sonier,DN et al. (1994)
Western United States	SO4	Groundwater inoculum	500 ug/L	40	0.063/day		Sonier,DN et al. (1994)
		Groundwater inoculum			Biodegrades		Sonier,DN et al. (1994A)
Western United States	SO4	Groundwater inoculum	3.5 ug/L	5	Biodegrades		Sonier,DN et al. (1994)

3.4.2. Dichlorodifluoromethane (CFC-12)

Like carbon tetrachloride, the carbon in dichlorodifluoromethane is present in its most oxidized state (chlorine/fluorine only are present as substituents) and thus the only biological anaerobic transformation process possible is reduction. The main reaction pathway leading to the anaerobic degradation of dichlorodifluoromethane is via reductive dehalogenation with chlorodifluoromethane most likely formed as the initial reaction product. The two carbon-fluoride bonds provides greater stability to this molecule than that shown for trichlorofluoromethane (CFC-11) which has three carbon-chlorine bonds; this should result in lower transformation rates for dichlorodifluoromethane when compared to trichlorofluoromethane. This compound is not expected to biodegrade aerobically and is used in aerobic aquifers, because of its stability, to date shallow groundwater (Busenberg & Plummer 1992).

Two aquifer recharge field studies report that dichlorodifluoromethane does not appear to be biodegraded in anaerobic groundwater (Table 37). Busenberg and Plummer (1992) report that groundwater samples taken from anoxic sites in an essentially aerobic Oklahoma aquifer did not show obvious depletion of either trichlorofluoromethane or dichlorodifluoromethane. Cook et al. (1995) determined that dichlorodifluoromethane was not biodegraded during analysis of vertical sampling profiles for an aquifer site in Ontario, Canada. Trichlorofluoromethane was shown to biodegrade at the same site by these authors.

It is possible that dichlorodifluoromethane will biodegrade slowly in highly reducing groundwater with significant amounts of carbon present; however, the current literature does not provide sufficient information to make the recommendation of a rate constant for this compound possible at this time. The added stability of an another carbon-fluorine bond, when compared to trichlorofluoromethane, is expected to result in a rate of biodegradation even slower than that reported for trichlorofluoromethane. Biodegradation is expected to occur most rapidly under methanogenic conditions; conversely, there is not enough information to determine whether dichlorodifluoromethane can biodegrade under either iron- or nitrate-reducing conditions although it is expected that the rate of degradation will be substantially lower.

Table 37. All Summarized Studies for Dichlorodifluoromethane (CFC-12)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Central Oklahoma		Field					Busenberg,E & Plummer,LN (1992)
Sturgeon Falls, Ontario		Field	411 pg/kg		NB		Cook,PG et al. (1995)

3.4.3. 1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)

The two carbon atoms in 1,1,2-trichloro-1,2,2-trifluoroethane are present in their most oxidized state (chlorine/fluorine only are present as substituents) and thus the only biological anaerobic transformation process possible is reduction. The main reaction pathway leading to the anaerobic degradation of 1,1,2-trichloro-1,2,2-trifluoroethane is via reductive dehalogenation with 1,2-dichloro-1,2,2-trifluoroethane formed as an initial reaction product of biodegradation; chlorotrifluoroethene is formed abiotically by a dichloroelimination reaction (Lesage et al. 1992). The three carbon-fluoride bonds as well as the total number of halogenated substituents suggest that the rate of biodegradation will be much lower than that reported for less halogenated and more chlorinated compounds (Lesage et al. 1992); this should result in lower transformation rates for 1,1,2-trichloro-1,2,2-trifluoroethane when compared to trichlorofluoromethane (CFC-11). This compound is not expected to biodegrade aerobically and is used in aerobic aquifers, because of its stability, to date shallow groundwater (Cook et al. 1995).

All summarized studies are presented in Table 38. Lesage and others have published much of the known work on the anaerobic degradation of 1,1,2-trichloro-1,2,2-trifluoroethane in groundwater based on the well-researched Gloucester Landfill in Canada (Lesage et al. 1990; Lesage et al. 1992; Lesage et al. 1993). Based on the identification of daughter products 1,2-dichloro-1,2,2-trifluoroethane and, in much smaller quantities, 1,1,2-trichloro-1,2-difluoroethane, field data suggest that at this site 1,1,2-trichloro-1,2,2-trifluoroethane is biodegrading slowly (Lesage et al. 1990). However, the rate of this biodegradation is slow and 1,1,2-trichloro-1,2,2-trifluoroethane is now the compound present at this site in the highest concentration (the rate of its degradation is less than that of tetrachloroethylene). The authors state that without historical disposal data, the quantitative loss of this compound over time cannot be measured.

Semprini et al. (1992) report the enhanced biodegradation of 1,1,2-trichloro-1,2,2-trifluoroethane in a field study using added acetate (as a carbon substrate/electron donor) and nitrate and sulfate (as potential electron acceptors); this aquifer was contaminated with 1,1,1-trichloroethane, trichlorofluoromethane and 1,1,2-trichloro-1,2,2-trifluoroethane. Within 2 m of the injection site, 20% of the added 1,1,2-trichloro-1,2,2-trifluoroethane was biodegraded during a 67 day injection period. Increased rates of biodegradation occurred when nitrate was removed from the injection mixture.

Cook et al. (1995) determined that 1,1,2-trichloro-1,2,2-trifluoroethane was not biodegraded during analysis of vertical sampling profiles for an aquifer site in Ontario, Canada. Trichlorofluoromethane was reported to be biodegraded at the same site in this paper.

It is likely that in highly reducing groundwater with significant amounts of carbon present, 1,1,2-trichloro-1,2,2-trifluoroethane will biodegrade very slowly; however, the current literature does not provide sufficient information to make the recommendation of a rate constant for this compound possible at this time. While a rate constant was published for a field study (Semprini et al. 1992), it was not felt to be representative as both a carbon source and electron acceptors were added to enhance

biodegradation. Biodegradation is expected to occur most rapidly under methanogenic conditions; there is not enough information currently available to determine whether this compound can biodegrade under either iron- or nitrate-reducing conditions, although it is expected that the rate of degradation will be substantially lower. Use of the rate constants determined by Lesage et al. (1992;1993) for a series of landfill leachate laboratory studies is not recommended; these studies do provide, however, evidence that 1,1,2-trichloro-1,2,2-trifluoroethane can biodegrade under methanogenic conditions.

Table 38. All Summarized Studies for 1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Moffett Field Naval Air Station, CA	NO3/SO4	Field	6 ug/L	1.8	0.11/day		Semprini,L et al. (1992)
Gloucester landfill, Ontario, Canada	SO4	Field	200 ug/L	1000	Biodegrades		Lesage,S et al. (1990)
Moffett Field Naval Air Station, CA	NO3/SO4	Field			Biodegrades		Semprini,L et al. (1990)
Sturgeon Falls, Ontario		Field			NB		Cook,PG et al. (1995)
Guelph, Ontario, Canada		Groundwater grab sample	>2500 ug/L	60	0.039/day		Lesage,S et al. (1993)
	Meth	Groundwater grab sample	1500 ug/L	40	0.099/day		Lesage,S et al. (1992)
	Meth	Groundwater grab sample	1500 ug/L	29	0.14/day		Lesage,S et al. (1992)
Guelph, Ontario, Canada		Groundwater grab sample	1500 ug/L	90	0.14/day		Lesage,S et al. (1993)
Guelph, Ontario, Canada		Groundwater grab sample			Biodegrades		Lesage,S et al. (1989)

3.5. Ketones

3.5.1. Acetone

Very limited data were located for acetone (Table 39) requiring the use of laboratory microcosm studies in order to provide a recommended rate constant range suitable for input into the EPACMTP model. However, as there is no evidence suggesting that this compound cannot biodegrade anaerobically (indeed all evidence suggests that it biodegrades very rapidly), it is very likely that acetone will readily biodegrade in anaerobic groundwater.

Acetone, at an initial concentration of 50 ppm C, is completely biodegraded in laboratory microcosm studies within 85 and 244 days for nitrate- and sulfate-reducing conditions, respectively (Mormile et al. 1994). Biodegradation was accompanied by 100% and 76% reduction in nitrate and sulfate concentrations, respectively, as well. A second laboratory microcosm study reported a 25 day lag period before biodegradation of acetone began; a zero-order rate constant of 12000 Og/L/day suggests a zero-order half-life of about four days (Suflita & Mormile (1993). Eighty-nine percent of the theoretical methane was recovered during this process. This zero-order rate constant was approximated to a first-order rate constant for use in the EPACMTP model; the approximation has a first-order half-life of about two days showing that this conversion is not a conservative process.

A field study by Major et al. (1994), indicates rapid biodegradation of acetone in a methanogenic/sulfate-reducing bedrock aquifer contaminated with chlorinated solvents. The authors observe that the distribution of acetone is much less than that of the other chlorinated compounds although the mobility of acetone is expected to be the same as the groundwater flow; this provides qualitative evidence that acetone is biodegraded in this environment.

The only study reporting a rate constant for the biodegradation of acetone is a laboratory microcosm study. As laboratory microcosm rate constant data are generally faster than their field study counterparts it is not possible to recommend this value as a single overall rate constant for input into the EPACMTP model. Instead, recognizing the ready biodegradability of this compound, a range of values with an order of magnitude less than the converted zero-order rate constant determined for the laboratory study (0.037/day, sulfate-reducing conditions, half-life of 19 days) used as an upper limit with the lower limit another order of magnitude less than this estimated value (0.0037/day, half-life of 187days) is proposed. It is likely that acetone will biodegrade more rapidly in a nitrate-reducing environment than in stronger reducing environments. The laboratory study used to determine a rate constant range measured biodegradation for acetone alone; in the presence of other compounds as at a spill site, this range may be lower although it is likely that this compound will still be a preferred carbon source.

Table 39. All Summarized Studies for Acetone

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Finger Lakes region, NY	Meth/SO4	Field			Biodegrades		Major,DW et al. (1994)
Norman, OK	Meth/SO4	Lab microcosm	81000 ug/L		12000 ug/L/day	25	Suflita,JM & Mormile,MR (1993)
Empire, MI	NO3	Lab microcosm	81000 ug/L	85	Biodegrades		Mormile,MR et al. (1994)
Empire, MI	SO4	Lab microcosm	81000 ug/L	244	Biodegrades		Mormile,MR et al. (1994)

3.5.2. Methyl Ethyl Ketone

Methyl ethyl ketone is expected to readily biodegrade in anaerobic groundwater environments. Very limited data were located for this compound (Table 40) requiring the use of laboratory microcosm studies in order to provide a recommended rate constant range suitable for input into the EPACMTP model. However, as there is no evidence suggesting that this compound cannot biodegrade anaerobically, indeed all evidence suggests that it biodegrades very rapidly, it is very likely that methyl ethyl ketone will readily biodegrade in anaerobic groundwater.

Methyl ethyl ketone, at an initial concentration of 50 ppm C, is completely biodegraded in laboratory microcosm studies within 85 and 244 days for nitrate- and sulfate-reducing conditions, respectively (Mormile et al. 1994). Biodegradation was accompanied by 100% reduction in both nitrate and sulfate concentrations, respectively, as well. A second laboratory microcosm study reported a 15 to 20 day lag period before biodegradation of methyl ethyl ketone began; a zero-order rate constant of 14000 Og/L/day suggests a half-life of about three days (Suflita & Mormile (1993). Ninety percent of the theoretical methane was recovered during this process. This zero-order rate constant was approximated to a first-order rate constant for use in the EPACMTP model; the approximation has a first-order half-life of about 1.3 days showing that this conversion is not a conservative process.

The only study reporting a rate constant for the biodegradation of methyl ethyl ketone is a laboratory microcosm study. As laboratory microcosm rate constant data are generally faster than their field study counterparts it is not possible to recommend this value as a single overall rate constant for input into the EPACMTP model. Instead, recognizing the ready biodegradability of this compound, a range of values with an order of magnitude less than the converted zero-order rate constant determined for the laboratory study (0.054/day, sulfate-reducing conditions, half-life of 13 days) used as an upper limit with the lower limit another order of magnitude less than this estimated value (0.0054/day, half-life of 128 days) is proposed. It is likely that methyl ethyl ketone will biodegrade more rapidly in a nitrate-reducing environment than in stronger reducing environments. The laboratory study used to determine a rate constant range measured biodegradation for methyl ethyl ketone alone; in the presence of other compounds as at a spill site, this range may be lower although it is likely that this compound will still be a preferred carbon source.

Table 40. All Summarized Studies for Methyl Ethyl Ketone

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Norman, OK	Meth/SO4	Lab microcosm	75000 ug/L		14000 ug/L/day	15-20	Suflita,JM & Mormile,MR (1993)
Empire, MI	NO3	Lab microcosm	75000 ug/L	85	Biodegrades		Mormile,MR et al. (1994)
Empire, MI	SO4	Lab microcosm	75000 ug/L	244	Biodegrades		Mormile,MR et al. (1994)

3.5.3. Methyl Isobutyl Ketone

Unlike the simpler ketones, acetone and methyl ethyl ketone, the more highly branched methyl isobutyl ketone is expected to be relatively resistant to biodegradation. Very limited data were located for this compound (Table 41) requiring the use of laboratory microcosm studies in order to provide a recommended rate constant range suitable for input into the EPACMTP model.

Methyl isobutyl ketone, at an initial concentration of 50 ppm C, in laboratory microcosm studies was completely biodegraded under sulfate-reducing conditions within 244 days (Mormile et al. 1994). However, as biodegradation was not accompanied by a significant loss in sulfate (only 4% of the theoretical (expected) amount was used), there was little evidence for methane production, and the production of reaction products could not be correlated to the loss of this compound, it is not known whether methyl isobutyl ketone was actually biodegraded in this study. Under nitrate-reducing conditions, methyl isobutyl ketone was biodegraded with only a trace amount left after 85 days; the rate of biodegradation was reportedly one order of magnitude slower than that of acetone and methyl ethyl ketone. A second laboratory microcosm study reported a 21 to 28 day lag period before biodegradation of methyl isobutyl ketone began; a zero-order rate constant of 65 Og/L/day suggests a half-life of about 531 days (Suflita & Mormile (1993). Forty-six percent of the theoretical methane was recovered during this process. This zero-order rate constant was approximated to a first-order rate constant for use in the EPACMTP model; the approximation has a first-order half-life of about 533 days which is close to the half-life proposed for the zero-order rate constant.

The only study reporting a rate constant for the biodegradation of methyl isobutyl ketone is a laboratory microcosm study. As laboratory microcosm rate constant data are generally faster than their field study counterparts it is not possible to recommend this value as a single overall rate constant for input into the EPACMTP model. Instead, a range of values with an order of magnitude less than the converted zero-order rate constant determined for the laboratory study (0.00013/day, sulfate-reducing conditions, half-life of 5330 days) used as an upper limit with the lower limit another order of magnitude less than this estimated value (0.000013/day, half-life of 53308 days) are proposed. The laboratory study used to determine a rate constant range measured biodegradation for methyl isobutyl ketone alone; in the presence of other compounds as at a spill site, this range may be lower. This ketone is not expected to be a preferred carbon source at a site containing multiple compounds. Redox conditions are expected to be important. Based on the limited data published, methyl isobutyl ketone appears to be biodegraded more rapidly in a nitrate-reducing environment and much less rapidly in sulfate-reducing and methanogenic groundwater.

Table 41. All Summarized Studies for Methyl Isobutyl Ketone

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Norman, OK	Meth/SO4	Lab microcosm	69000 ug/L		65 ug/L/day	21-28	Suflita,JM & Mormile,MR (1993)
Empire, MI	SO4	Lab microcosm	69000 ug/L	244	NB		Mormile,MR et al. (1994)
Empire, MI	NO3	Lab microcosm	69000 ug/L	85	Possible		Mormile,MR et al. (1994)

3.6. Organic Acids

3.6.1. Acetic Acid

Acetic acid is expected to be readily biodegraded in anaerobic groundwaters with the formation of methane and carbon dioxide. The summary of all located studies is presented in Table 42. Limited field/*in situ* microcosm data were located for this compound requiring the use of laboratory microcosm studies in order to provide a range of recommended rate constant values suitable for input into the EPACMTP model.

Godsy et al. (1992) report that acetic acid concentrations increase along a flow path at a creosote contaminated site at Pensacola, FL; this is attributed to the formation of this compound as an intermediate in the biodegradation of compounds found in the water-soluble fraction (C_3-C_6 volatile fatty acids, the cresol isomers, and several quinolinone compounds). Therefore, while acetic acid appears to persist during downgradient movement, this is most likely due to the production of this compound during the biodegradation of other, more complex, molecules and not because it is inherently non-biodegradable.

Chapelle and Lovley (1990) report that oxidation of radiolabeled acetic acid was faster in the sandy sediments and slower in the clayey sediments of a deep anaerobic aquifer (considered to be highly oligotrophic) in a series of laboratory microcosm studies. In general, microcosms constructed from aquifer sediment collected at very low depths (>240 m depth) also show little biodegradation of acetic acid; radiolabeled glucose was still utilized in these microcosms, although at much reduced rates.

Acetate is one of two major fermentation products as well as a common intermediate from the biodegradation of many, more complex, compounds. Competition among microorganisms under iron-reducing, sulfate-reducing or methanogenic conditions for this readily used carbon source often controls the spatial and temporal distribution of the anaerobic redox environment (Lovley & Phillips 1987). Lovley & Phillips (1987) suggest that iron-reducers may maintain acetic acid and hydrogen concentrations below that which would induce populations of sulfate-reducers or methanogens to increase. While limited data were located in the literature for this compound, it is very likely that this simple organic acid will be biodegraded in anaerobic groundwater. A rate constant of 0.00071/day (half-life of 976 days), which is an order of magnitude less than the lowest positive laboratory microcosm value, is recommended as a lower limit and 0.075/day (half-life of 9 days) which is the mean value for all studies, as the upper limit of a recommended rate constant range describing anaerobic biodegradation of acetic acid in groundwater.

Table 42. All Summarized Studies for Acetic Acid

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Wilmington, DE	Meth/Fe/SO4	Field	9350000 ug/L	730-1460			Leenheer,JA et al. (1976)
Pensacola, FL	Meth	Field	45140 ug/L	150	Biodegrades		Godsy,EM et al. (1992)
West Valley, NY	NO3/SO4	Groundwater grab sample	Not quantified	60	NB		Francis,AJ (1982)
Myrtle Beach, SC	SO4	Lab microcosm	108 ug/L		0.0071/day		Chapelle,FH & Lovley,DR (1990)
Florence, SC	Fe	Lab microcosm	48 ug/L		0.019/day		Chapelle,FH & Lovley,DR (1990)
Myrtle Beach, SC	SO4	Lab microcosm	108 ug/L	0.8	0.26/day		Chapelle,FH & Lovley,DR (1990)
Florence, SC	Fe	Lab microcosm	60 ug/L		0.32/day		Chapelle,FH & Lovley,DR (1990)
Florence, SC	Fe	Lab microcosm		77	<0.000068/day		Chapelle,FH & Lovley,DR (1990)
Florence, SC	Fe	Lab microcosm	30 ug/L	77	<0.000068/day		Chapelle,FH & Lovley,DR (1990)
Myrtle Beach, SC	SO4	Lab microcosm		77	<0.000068/day		Chapelle,FH & Lovley,DR (1990)
Myrtle Beach, SC	SO4	Lab microcosm		77	<0.000068/day		Chapelle,FH & Lovley,DR (1990)
Myrtle Beach, SC	SO4	Lab microcosm		77	<0.000068/day		Chapelle,FH & Lovley,DR (1990)

Table 42. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Myrtle Beach, SC	SO4	Lab microcosm	84 ug/L	77	<0.000068/day		Chapelle,FH & Lovley,DR (1990)
Baltimore, MD		Lab microcosm	1000 ug/L		Biodegrades		Durant,ND et al. (1994)
Norman, OK	Meth	Lab microcosm	15015-30030 ug/L	365	Biodegrades		Adrian,NR & Suflita,JM (1994)

3.6.2. Phenylacetic Acid

This simple organic acid is expected to be readily used as a carbon source (electron donor) by the microorganisms present in the aquifer. Anaerobic biodegradation of phenylacetic acid may proceed through the intermediary, mandelic acid, followed by decarboxylation to benzoic acid and then ring cleavage (Dietrich et al. 1989). The summary of all located studies is presented in Table 43.

A field study by Cozzarelli et al. (1995) showed phenylacetic acid and benzoic acid concentrations decreasing over time in an area of the aquifer controlled by nitrate-reducing conditions. Because the aquifer was impacted by a gasoline spill, these organic acids were both produced during the biodegradation of the hydrocarbons and then utilized by the indigenous microbial population. A net rate for these two processes was not determined for phenylacetic acid in the field. However, biodegradation of phenylacetic acid was faster in comparison to other organic acids with more substituents such as di- or tri-methylbenzoic acid or o-toluic acid. Laboratory microcosm studies by the same authors support the biodegradation of phenylacetic acid under nitrate-reducing conditions, with complete mineralization by 30 to 35 days. No biodegradation of this compound was shown under sulfate- or iron-reducing conditions (where these two electron acceptors were added to the microcosm); the authors state that the time scale of the laboratory study was short and that degradation may have been too slow to be observed during this experiment.

A field study by Reinhard et al. (1984) observes that phenylacetic acid concentrations decrease downgradient in a landfill-impacted plume to a greater extent than that shown for total organic carbon concentrations. This was presented as evidence that this compound was being removed via biodegradation at this site.

Very limited data were located in the literature for this compound. Only one good rate constant value from a nitrate-reducing laboratory microcosm was published (0.12/day); under sulfate- and iron-reducing and methanogenic conditions the rate of degradation of phenylacetic acid is expected to be much slower. In addition, laboratory microcosm rate constant data are generally faster than their field study counterparts. Instead, recognizing the ready biodegradability of this compound, a range of values with an order of magnitude less than the sole published rate constant measured in a laboratory study (0.012/day, half-life of 58 days) used as an upper limit with the lower limit another order of magnitude less than this estimated value (0.0012/day, half-life of 578 days) is proposed.

Table 43. All Summarized Studies for Phenylacetic Acid

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Woolrich landfill, Waterloo, Ontario		Field	>10000 ug/L		Biodegrades		Reinhard,M et al. (1984)
West Valley, NY	NO3/SO4	Groundwater grab sample	13600 ug/L	60	0.0029/day		Francis,AJ (1982)
Atlantic City, NJ	NO3/SO4/Fe	Lab microcosm	24500 ug/L	35	Possible		Cozzarelli,IM et al. (1995)
Atlantic City, NJ	NO3	Lab microcosm	23150 ug/L	32	0.12/day		Cozzarelli,IM et al. (1995)
Atlantic City, NJ	Fe	Lab microcosm	21790 ug/L	35	NB		Cozzarelli,IM et al. (1995)
Atlantic City, NJ	SO4	Lab microcosm	23830 ug/L	35	NB		Cozzarelli,IM et al. (1995)

3.7. Polyaromatic Compounds

3.7.1. Acenaphthene

Acenaphthene, a tricyclic compound, appears to be slowly biodegraded in anaerobic groundwaters based on the published data; it should be noted though, that all published work for this compound has been conducted at a Pensacola, FL site. The summary of all located studies is presented in Table 44. First-order rate constants for all studies ranged from 0 to 0.0043/day.

In laboratory microcosm studies by Mrakovic and Grbic-Galic (1992), using creosote contaminated groundwater from the Pensacola site, acenaphthene was degraded to acenaphthenol. Sharak-Genthner et al. (1997) also report that acenaphthene was biodegraded slowly with 78% still remaining after 28 weeks under methanogenic conditions in laboratory microcosms. Rates of methane production were inhibited with the addition of any of the polyaromatic hydrocarbons suggesting that the initial concentrations these authors used were inhibitory to the microbial population found in the aquifer material. Only one field study provided sufficient information for the calculation of a rate constant. While Godsy et al. (1992) report that the polyaromatic hydrocarbons are not biodegraded along their monitored flow path, a concentration of 520 Og/L was reported at site 3, close to the source, and at site 4, approximately 123 m downgradient, the corrected concentration of acenaphthene was 305 Og/L suggesting that some biodegradation may have occurred. The conservative tracer used for this correction was 3,5-dimethylphenol.

There is very little information published on the anaerobic biodegradation of this compound in groundwater. In general, the polyaromatic hydrocarbons are thought to be resistant to anaerobic biodegradation, with rates under aerobic conditions much higher. The authors of the single field study at the Pensacola site report that this compound is not biodegraded during downgradient movement from the source. Given this background, a qualified rate constant range is proposed with a lower limit of zero and an upper limit of 0.0043/day (half-life of 161 days), which is a SRC calculated value obtained from the sole field study. A lower limit of zero was chosen based on the general recalcitrance of polyaromatic compounds under anaerobic conditions as well as the limited amount of data available on this compound.

Table 44. All Summarized Studies for Acenaphthene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Gas Works Park, Seattle, WA		Field	40 ug/L				Turney,GL & Goerlitz,DF (1990)
Pensacola, FL	Meth	Field	520 ug/L	125	0.0043/day		Godsy,EM et al. (1992)
Pensacola, FL	Meth	Lab microcosm	4600 ug/L	112	0.0022/day		Sharak-Genthner,BR et al. (1997)
Pensacola, FL	SO4	Lab microcosm	10024 ug/L		Biodegrades		Mrakovic,I & Grbic-Galic,D (1992)
Pensacola, FL	Meth/NO3/SO4	Lab microcosm	8700 ug/L	365	NB		Sharak-Genthner,BR et al. (1997)

3.7.2. Fluorene

Fluorene appears to be slowly biodegraded in anaerobic groundwaters based on the published data. The summary of all located studies is presented in Table 45. First-order rate constants for all studies ranged from 0 to 0.306/day. A range of qualified rate constant values taken from field studies are provided for input into the EPACMTP model.

Two field studies report sufficient data for the determination of first-order rate constants. Bedient et al. (1984) and Wilson, JT et al. (1985) both report very slow rates of biodegradation for fluorene at a former creosote waste plant in Conroe, TX. This aquifer has a slow flow velocity and thus the residence time of the contaminated groundwater is quite long. Goerlitz et al. (1985) observes that fluorene concentrations, initially present at up to 610 Og/L at a site near to the source, is not detected at a site approximately 120 m downgradient. Sorption of the PAH compounds to the aquifer sediment was insignificant. Biodegradation of fluorene was possible at this site although conservative tracer data were not available in order to correct for abiotic and transport processes.

There is very little information published on the anaerobic biodegradation of this compound in groundwater. In general, the polyaromatic hydrocarbons are thought to be resistant to anaerobic biodegradation, with rates under aerobic conditions much higher. Given this background, a qualified rate constant range is proposed with a lower limit of 0 to 0.00088/day (half-life of 788 days), which is the mean of the two field study values. A lower limit of zero was chosen based on the general recalcitrance of polyaromatic compounds under anaerobic conditions as well as the limited amount of data available on this compound.

Table 45. All Summarized Studies for Fluorene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Gas Works Park, Seattle, WA		Field	20 ug/L				Turney,GL & Goerlitz,DF (1990)
North Bay landfill, Ontario Canada	Meth	Field	1.7 ug/L				Reinhard,M et al. (1984)
Pensacola, FL	Meth	Field	420-610 ug/L	87-260			Goerlitz,DF et al. (1985)
Conroe,TX		Field	123.8 ug/L	15000	0.00030/day		Bedient,PB et al. (1984)
Conroe,TX		Field	120-230 ug/L	2963	0.0013-0.0016/day		Wilson,JT et al. (1985)
Conroe, TX		Groundwater grab sample			0.306/day		Ward,CH et al. (1986)
Pensacola, FL	Meth/NO3/SO4	Lab microcosm	17500 ug/L	365	NB		Sharak-Genthner,BR et al. (1997)

3.7.3. 1-Methylnaphthalene

1-Methylnaphthalene appears to be recalcitrant in anaerobic groundwaters based on the published data. The summary of all located studies is presented in Table 46. First-order rate constants for all studies ranged from 0 to 0.0047/day. A range of qualified rate constant values taken from field studies are provided for input into the EPACMTP model.

Five field studies for four different locations are presented. Papers by Bedient et al. (1984) and Wilson, JT et al. (1985) both report very slow rates of biodegradation of 1-methylnaphthalene for a former creosote waste plant in Conroe, TX. This aquifer has a very slow flow velocity and thus the residence time of the contaminated groundwater is quite long. While biodegradation of 1-methylnaphthalene is shown along a 39 m flow path from the Vejen City landfill in Denmark, concentrations are so low (initially 6 Og/L) that the biodegradation rate constant may not be as accurate as that determined for the Conroe, TX site. No biodegradation was reported for two other, methanogenic, sites, the North Bay landfill in Canada and a former wood-preserving plant in Pensacola, FL. This may have been due to much shorter residence times (faster flow velocity) along the plume when compared to the Conroe, TX site. For example, a total residence time of 150 days is reported at the Pensacola, FL site. However, the flow path from the North Bay landfill study was over 600 m and while the flow velocity for this site was not reported, this distance probably represents a significant period of time. Limited biodegradation of 1-methylnaphthalene was reported in laboratory microcosms using aquifer sediment from the Pensacola site with a loss of 41% in 16 weeks in methanogenic microcosms; no further biodegradation was observed from week 16 to 30 (Sharak-Genthner et al. 1997).

There is very little information published on the anaerobic biodegradation of this compound in groundwater. In general, the polyaromatic hydrocarbons are thought to be resistant to anaerobic biodegradation, with rates under aerobic conditions much higher. A qualified rate constant range is proposed with a lower limit of 0 and an upper limite of 0.00043/day (half-life of 1611 days), which is the average field value for the Conroe site. While the Vejen city landfill site reported a higher rate constant, for reasons stated above this value was not thought to be as accurate. Greatest weight has been given to the studies completed in Conroe, TX as the residence time for these studies is very long, permitting the measurement of very low rates of anaerobic biodegradation. A lower limit of zero was chosen based on the general recalcitrance of polyaromatic compounds under anaerobic conditions as well as the limited amount of data available on this compound.

Table 46. All Summarized Studies for 1-Methylnaphthalene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Lower Glatt Valley, Switzerland	NO3	Column	24200 ug/L	6	NB		Kuhn,EP et al. (1988)
Gas Works Park, Seattle, WA		Field	30 ug/L				Turney,GL & Goerlitz,DF (1990)
Pensacola, FL	Meth	Field	300-790 ug/L	87-260			Goerlitz,DF et al. (1985)
Conroe,TX		Field	217.6 ug/L	15000	0.00031/day		Bedient,PB et al. (1984)
Conroe,TX		Field	220-370 ug/L	2963	0.00040-0.00068/day		Wilson,JT et al. (1985)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	6 ug/L	30	0.057/day		Lyngkilde,J & Christensen,TH (1992)
North Bay landfill, Ontario Canada	Meth	Field	18 ug/L		NB		Reinhard,M et al. (1984)
Pensacola, FL	Meth	Field	410 ug/L	150	NB		Godsy,EM et al. (1992)
Pensacola, FL	Meth	Lab microcosm	5900 ug/L	112	0.0047/day		Sharak-Genthner,BR et al. (1997)
Pensacola, FL	Meth/NO3/SO4	Lab microcosm	17500 ug/L	365	NB		Sharak-Genthner,BR et al. (1997)
Vejen city landfill, Denmark	Fe	Lab microcosm	120 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	80 ug/L	450	NB		Albrechtsen,HJ et al. (1994)

Table 46. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	NO3	Lab microcosm	11 ug/L	450	NB		Albrechtsen,HJ et al. (1994)

3.7.4. Naphthalene

While anaerobic degradation of naphthalene has been reported in the literature, the metabolic pathways that are used during this process are still unknown. Biodegradation of this compound occurs fairly rapidly under aerobic conditions (Sutherland et al. 1995). As with other reviewed compounds having sufficient information, preference is given to field and *in situ* microcosm studies and a range of values for the first-order rate constant are recommended for input into the EPACMTP model. First-order rate constants for field and *in situ* microcosm studies alone ranged from 0 to 0.043/day with a mean value of 0.0072/day. A mean value of 0.014/day was reported for all studies. Results from all summarized studies are presented in Table 47.

Biodegradation of naphthalene was reported in several field studies. Ehrlich et al. (1982) report that concentrations of naphthalene decreased from about 20 mg/L to 7 mg/L (corrected using chloride as a conservative tracer) 430 m downgradient from the source at St. Louis Park, MN. While laboratory studies showed no biodegradation of this compound, the authors believe that naphthalene is anaerobically biodegraded at this site. Roberts et al. (1980) report that naphthalene is biodegraded during a wastewater injection project in California. An initial lag phase followed by rapid degradation of naphthalene suggests that an acclimated population has developed. The authors do not, however, report the oxygen conditions at this site. Naphthalene was shown to biodegrade following source removal at a site contaminated with manufactured gas plant wastes (EPRI 1993). Biodegradation was suggested as oxygen conditions were depleted in areas of high naphthalene concentrations and were high at the edges of the plume; the loss of naphthalene at this site may be due to aerobic degradation. At an upstate New York site, the persistence of naphthalene at a coal tar burial site was believed to be due to oxygen limitation (Madsen et al. 1996). Laboratory microcosms run under methanogenic, nitrate- and sulfate-reducing conditions did not show any biodegradation of radiolabeled naphthalene in 16 days. Field data were most strongly correlated to oxygen concentrations. Biodegradation of naphthalene was shown at a site in Conroe, TX during an injection experiment (Borden and Bedient 1987) with a loss of 65%; the naphthalene plume at the site is significantly smaller than the chloride plume, also indicating that biodegradation is most likely occurring *in situ.* A microbial population which was acclimated to naphthalene had previously been reported at this site. Laboratory experiments conducted by the same authors show mineralization of radiolabeled naphthalene ranging from 3.8 to 34.3% after 24 hours. Papers by Bedient et al. (1984) and Wilson, JT et al. (1985) both report slow rates of biodegradation of naphthalene at the same site in Conroe, TX. This aquifer has a very slow flow velocity and thus the residence time of the contaminated groundwater is quite long. Godsy et al. (1992) reports that naphthalene is not biodegraded in methanogenic groundwater at a wood-preserving plant in Pensacola, FL.

A range of values describing the anaerobic biodegradation of this compound is given with the lower limit equal to 0 (*e.g.* this compound is not biodegraded anaerobically), which was the lowest measured field/*in situ* microcosm value, to 0.0072/day (half-life of 96 days), which is the mean value for the entire field/*in situ* microcosm data set. While anaerobic biodegradation of naphthalene has been positively shown at Conroe, TX, other studies reporting biodegradation at a field site may be observing

aerobic biodegradation. Many anaerobic laboratory microcosm studies, where oxygen conditions can be strictly controlled, report that naphthalene is not biodegraded. Therefore, until further information on other anaerobic groundwater sites is published, a value of zero as the lower limit is proposed.

Table 47. All Summarized Studies for Naphthalene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Lower Glatt Valley, Switzerland	NO3	Column	21790 ug/L	6	NB		Kuhn,EP et al. (1988)
Seal Beach, CA	Meth	Column	0.052 umol/g	570	NB		Haag,F et al. (1991)
Seal Beach, CA	Meth	Column	0.052 umol/g	68	NB		Haag,F et al. (1991)
Gas Works Park, Seattle, WA		Field	160 ug/L				Turney,GL & Goerlitz,DF (1990)
North Bay landfill, Ontario Canada	Meth	Field	150 ug/L				Reinhard,M et al. (1984)
Pensacola, FL	Meth	Field	600-15600 ug/L	200-600			Goerlitz,DF et al. (1985)
Conroe,TX		Field	649.3 ug/L	15000	0.00018/day		Bedient,PB et al. (1984)
Conroe,TX		Field	650-1600 ug/L	2963	0.0015-0.0021/day		Wilson,JT et al. (1985)

Table 47. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Noordwijk landfill, The Netherlands		Field	30 ug/L	3650	0.0063/day		Zoeteman,BCJ et al. (1981)
Swan Coastal Plain, Western Australia	SO4/Fe	Field	1200 ug/L	71	0.017-0.043/day		Thierrin,J et al. (1995)
Vejen city landfill, Denmark	Meth/SO4/Fe	Field	24 ug/L	71	0.026/day		Lyngkilde,J & Christensen,TH (1992)
		Field			Possible		EPRI (1993)
Conroe, TX		Field		4-6	Biodegrades		Borden,RC & Bedient,PB (1987)
Santa Clara Valley, CA		Field	0.91 ug/L	0.5	Biodegrades		Roberts,PV et al. (1980)
Pensacola, FL	Meth	Field	9380 ug/L	150	NB		Godsy,EM et al. (1992)
Upstate New York		Field		21	NB		Madsen,EL et al. (1996)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	190 ug/L	21	Possible		Rugge,K et al. (1995)
St. Louis Park, MN	Meth	Field	15500 ug/L		Possible		Ehrlich,GG et al. (1982)
Conroe, TX		Groundwater grab sample			0.307/day		Ward,CH et al. (1986)
Florida		Groundwater grab sample		90	NB		Delfino,JJ et al. (1989)

Table 47. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Fredensborg, Denmark	NO3	Groundwater grab sample	500 ug/L	200	NB		Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	NO3	Groundwater grab sample	500 ug/L	60	NB		Flyvbjerg,J et al. (1993)
Fredensborg, Denmark	SO4	Groundwater grab sample	500 ug/L	235	NB		Flyvbjerg,J et al. (1993)
New York		Groundwater grab sample	500-1000 ug/L	6	NB		Madsen,EL et al. (1991)
New York		Groundwater grab sample	500-1000 ug/L	6	Possible		Madsen,EL et al. (1991)
Vejen city landfill, Denmark	Fe	In situ microcosm	75 ug/L	48	0.0050/day		Nielsen,PH & Christensen,TH (1994)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	78	Biodegrades		Acton,DW & Barker,JF (1992)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L	90	NB		Nielsen,PH & Christensen,TH (1994)
Vejen city landfill, Denmark	Meth	In situ microcosm	120 ug/L	94	NB		Nielsen,PH et al. (1992)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	NO3	In situ microcosm	150 ug/L	80	NB		Nielsen,PH & Christensen,TH (1994)

Table 47. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Pensacola, FL	Meth	Lab microcosm	10000 ug/L	112	0.0057/day		Sharak-Genthner,BR et al. (1997)
Conroe, TX		Lab microcosm		21	Biodegrades		Thomas,JM et al. (1989)
Conroe, TX		Lab microcosm		8	Biodegrades		Thomas,JM et al. (1989)
Bemidji,MN	Meth/Fe/Mn	Lab microcosm	1282 ug/L	45	NB		Baedecker,MJ et al. (1993)
Cliff-Dow Chemical Co., Marquette, MI		Lab microcosm	500 ug/L	84	NB		Klecka,GM et al. (1990A)
North Bay landfill, Ontario Canada		Lab microcosm	131.8 ug/L	187	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	NO3	Lab microcosm	148.5 ug/L	187	NB		Acton,DW & Barker,JF (1992)
Pensacola, FL	Meth/NO3/SO4	Lab microcosm	58300 ug/L	365	NB		Sharak-Genthner,BR et al. (1997)
Upstate New York	Meth	Lab microcosm		16	NB		Madsen,EL et al. (1996)
Upstate New York	NO3	Lab microcosm		16	NB		Madsen,EL et al. (1996)
Upstate New York	SO4	Lab microcosm		16	NB		Madsen,EL et al. (1996)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	Fe	Lab microcosm	260 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/Fe/NO3	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	240 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	NO3	Lab microcosm	22 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Baltimore, MD		Lab microcosm	1000 ug/L		Possible		Durant,ND et al. (1994)
Conroe, TX		Lab microcosm		3	Possible		Thomas,JM et al. (1989)

3.7.5. Phenanthrene

Phenanthrene appears to be recalcitrant in anaerobic groundwaters based on the published data. The summary of all located studies is presented in Table 48. First-order rate constants for all studies ranged from 0 to 0.354/day for a study run with limited oxygen. There is insufficient evidence for the anaerobic biodegradation of this compound in groundwater therefore, a rate constant is not recommended for input into the EPACMTP model.

Biodegradation of phenanthrene was reported in two studies. Ward et al. (1986) show that phenanthrene is fairly rapidly biodegraded under conditions of limited oxygen (1.8 mg/L dissolved oxygen). However, oxygen concentrations which are this "high" are not generally considered to be indicative of anaerobic conditions. Thomas et al. (1989) reported 28.5% and 23.1% mineralization of phenanthrene in 19 days in laboratory microcosms using heavily contaminated and slightly contaminated sediment, respectively, from the saturated zone at the Conroe, TX site. Aquifer material collected from a pristine area of the aquifer did not mineralize this compound over the same period of time. These experiments were not conducted under strictly anaerobic conditions, the vial was filled to the top and capped with a teflon lined septum; presumably, anaerobic conditions were attained fairly rapidly; however, the reported biodegradation may have been due to the oxygen initially present. In a field study, Goerlitz et al. (1985) observes that phenanthrene concentrations, initially present at up to 780 Og/L at a site near the source, is not detected at a site approximately 120 m downgradient. Sorption of the PAH compounds to the aquifer sediment was insignificant. Biodegradation of phenanthrene was possible at this site although conservative tracer data were not available in order to correct for abiotic and transport processes.

There is very little information published on the anaerobic biodegradation of this compound in groundwater. In general, the polyaromatic hydrocarbons are thought to be resistant to anaerobic biodegradation, with rates under aerobic conditions much higher. Based on the published studies, the current literature does not provide sufficient information to make the recommendation of a rate constant for phenanthrene possible at this time.

Table 48. All Summarized Studies for Phenanthrene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Gas Works Park, Seattle, WA		Field	60 ug/L				Turney,GL & Goerlitz,DF (1990)
Pensacola, FL	Meth	Field	760-780 ug/L	87-260			Goerlitz,DF et al. (1985)
Conroe, TX		Groundwater grab sample			0.354/day		Ward,CH et al. (1986)
New York		Groundwater grab sample	500-1000 ug/L	6	NB		Madsen,EL et al. (1991)
New York		Groundwater grab sample	500-1000 ug/L	6	Possible		Madsen,EL et al. (1991)
Conroe, TX		Lab microcosm		19	Biodegrades		Thomas,JM et al. (1989)
Conroe, TX		Lab microcosm		21	Biodegrades		Thomas,JM et al. (1989)
Pensacola, FL	Meth/NO3/SO4	Lab microcosm	29100 ug/L	365	NB		Sharak-Genthner,BR et al. (1997)
Conroe, TX		Lab microcosm		7	Possible		Thomas,JM et al. (1989)

3.8. Miscellaneous

3.8.1. 1,1'-Biphenyl

Limited data for this compound suggest that 1,1'-biphenyl may be resistant to biodegradation under anaerobic conditions in groundwater. 1,1'-Biphenyl has been reported to biodegrade fairly rapidly under aerobic conditions however (Saeger et al. 1988). A summary of all located studies is presented in Table 49.

Biodegradation was reported for a methanogenic laboratory microcosm study using contaminated aquifer sediment from the American Creosote Works site in Pensacola, FL (Sharak-Genthner et al. 1997). 1,1'-Biphenyl concentrations decreased by 34% in 16 weeks but no further biodegradation was observed between 16 and 28 weeks when the experiment was ended. Two field studies possibly show the degradation of 1,1'-biphenyl. Bedient et al. (1984) report a very slow rate of biodegradation of 1,1'-biphenyl for a former creosote waste plant in Conroe, TX. This aquifer has a very slow flow velocity and thus the residence time of the contaminated groundwater is quite long. The initial concentration of 1,1'-biphenyl was low (3 Og/L) for a study by Zoeteman et al. (1981); thus, the loss of this compound over the measured flow path is not thought to be very accurate. No biodegradation of 1,1'-biphenyl was seen in *in situ* microcosms placed along a 350 m flow path in an aquifer contaminated by the Vejen city landfill, Denmark as well as in laboratory microcosms constructed with sediment from this aquifer (Nielsen et al. 1995B). This flow path included methanogenic, sulfate-reducing, iron-reducing, and nitrate-reducing conditions. Compounds such as benzene, o-xylene, naphthalene, and trichloroethylene were also not biodegraded.

Information provided in a study by Monsanto Company, using non-groundwater samples, was used to supplement the information above (Saeger et al. 1988). During a 12 week anaerobic ecocore microcosm study, using sewage lagoon sediment-water, radiolabeled biphenyl was not shown to biodegrade in 24 samples (including samples with added nitrate, and samples with added glucose) under either nitrate-reducing or methanogenic conditions.

The evidence so far indicates that 1,1'-biphenyl will be persistent in anaerobic groundwater environments; if biodegradation occurs, the rate is expected to be slow. Therefore, a qualified rate constant range of 0 to 0.00032/day (half-life of 2166 days) is proposed. A lower limit of zero was chosen based on the general recalcitrance of this structure under anaerobic conditions as well as the limited amount of data available on 1,1'-biphenyl.

Table 49. All Summarized Studies for 1,1'-Biphenyl

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		NB		Lyngkilde,J et al. (1992)
Gas Works Park, Seattle, WA		Field	10 ug/L				Turney,GL & Goerlitz,DF (1990)
Pensacola, FL	Meth	Field	360 ug/L	87-260			Goerlitz,DF et al. (1985)
Conroe,TX		Field	61.9 ug/L	15000	0.00032/day		Bedient,PB et al. (1984)
Noordwijk landfill, The Netherlands		Field	3 ug/L	3650	0.019/day		Zoeteman,BCJ et al. (1981)
Vejen city landfill, Denmark	Meth/Fe/NO3	In situ microcosm	150 ug/L	90-180	NB		Nielsen,PH et al. (1995B)
Pensacola, FL	Meth	Lab microcosm	3000 ug/L	112	0.0037/day		Sharak-Genthner,BR et al. (1997)
Pensacola, FL	Meth/NO3/SO4	Lab microcosm	8700 ug/L	365	NB		Sharak-Genthner,BR et al. (1997)
Vejen city landfill, Denmark	Meth/Fe/NO3	Lab microcosm	150 ug/L	150-180	NB		Nielsen,PH et al. (1995B)

3.8.2. Cumene

Very limited data for this compound suggest that cumene may biodegrade under anaerobic conditions in groundwater. Only one relevant paper was found during this literature search. A summary of the studies in this paper is presented in Table 50.

An *in situ* microcosm study at the North Bay landfill site in Canada (a methanogenic aquifer with high carbon loading) showed that cumene was biodegraded both without the addition of an electron acceptor and when sulfate was added at site 2 but not at site 1. Site 1 differed from site 2 by having higher alkalinity, a higher concentration of total hydrocarbons present, and a higher dissolved organic carbon content. While no biodegradation of cumene was reported for accompanying laboratory microcosm studies, this result was obtained for all compounds studied (including BTEX and chlorobenzene) and may not accurately reflect the biodegradation potential of this compound.

The current literature does not provide sufficient information to make the recommendation of a rate constant for this compound possible at this time. The evidence so far indicates that cumene may biodegrade in anaerobic groundwater environments.

Table 50. All Summarized Studies for Cumene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
North Bay landfill, Ontario Canada	Meth	In situ microcosm	150 ug/L	80	Biodegrades		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	80	Biodegrades		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	Meth/SO4	In situ microcosm	150 ug/L	105	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada		Lab microcosm	114.2 ug/L	187	NB		Acton,DW & Barker,JF (1992)
North Bay landfill, Ontario Canada	NO3	Lab microcosm	130.8 ug/L	187	NB		Acton,DW & Barker,JF (1992)

3.8.3. Dioxane

Very limited data for this compound suggest that dioxane may be resistant to biodegradation under anaerobic conditions in groundwater. A summary of all located studies is presented in Table 51.

A field study conducted in Seymour, IN showed that 1,4-dioxane has traveled nearly the distance expected based on transport modeling (Nyer et al. 1991). Another compound, tetrahydrofuran, which does biodegrade, although slowly, and has a similar retardation factor to 1,4-dioxane, was shown to have traveled only 34% of the theoretical distance expected. Other compounds which were also reviewed, including benzene and phenol, were found to have traveled only a small percentage of the theoretical distance based on their retardation factor (8 and 0%, respectively), suggesting that significant biodegradation had occurred. The authors suggest that benzene, phenol, and tetrahydrofuran only start to disappear once they have exited the area covered with an interim cap and may be exposed to some oxygen at this point. Lesage et al. (1990) reports that dioxane does not appear to be biodegraded at a landfill site based on observations that its concentration has not changed significantly over time in monitoring wells. Francis (1982) reports a change in concentration of 1,4-dioxane of 4% in laboratory studies using leachate from a low-level radioactive waste disposal site as the medium.

The current literature does not provide sufficient information to make the recommendation of a rate constant for this compound possible at this time. The evidence so far indicates that dioxane will be persistent in anaerobic groundwater environments.

Table 51. All Summarized Studies for Dioxane

Site Name	Site Type	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Gloucester landfill, Ontario, Canada	Laboratory waste disposal site	Field	330 ug/L				Lesage,S et al. (1990)
Seymour, Indiana		Field		3583	NB		Nyer,EK et al. (1991)
West Valley, NY	Low level radioactive waste disposal site	Groundwater grab sample	Not quantified	60	Possible		Francis,AJ (1982)

3.8.4. Methanol

Based on the current literature, methanol is expected to readily biodegrade under anaerobic conditions (Table 52). Limited field data for this compound resulted in the use of rate constants from laboratory microcosm studies in order to offer a range of first-order rate constant values recommended for input into the EPACMTP model. First-order rate constants for all studies ranged from 0.0022 to 0.88/day with a mean value of 0.087/day.

A field study by Major et al. (1994), indicates rapid biodegradation of methanol in a methanogenic/sulfate-reducing bedrock aquifer contaminated with chlorinated solvents. Methanol probably acts as an electron donor (carbon source) at this site, thereby promoting the biodegradation of the chlorinated compounds. The authors observe that the distribution of methanol is much less than that of the other chlorinated compounds although the mobility of methanol is expected to be same as the groundwater flow; this provides qualitative evidence that methanol is biodegraded in this environment.

Laboratory microcosm studies by Novak et al. (1985) at two aquifer sites indicate rapid biodegradation of methanol at concentrations of up to 100 mg/L. At higher concentrations the rate of degradation slows somewhat with complete degradation requiring several hundred instead of 30 to 90 days. The addition of BTEX to microcosm samples did not affect the biodegradation rate of methanol.

Hickman et al. (1990) report that aquifer sediment collected from eight different sites was able to fairly readily biodegrade methanol. Rates of biodegradation appeared to vary between sites with certain sites consistently reporting faster rates than others. The faster sites were characterized by rapid biodegradation rates and enhanced biodegradation if electron acceptors were added; these sites were often found to have sufficient flux of water, nutrients, and organic matter and to have a diverse microbial community. "Slow" sites were characterized by a slow flux of water, nutrients, and organic matter; biodegradation rates were not enhanced but actually inhibited by the addition of electron acceptors (nitrate or sulfate) suggesting that methanogenesis was the main redox condition at these sites.

Methanol was not biodegraded in a laboratory microcosm study by the API (1994) at the CFB Borden site in Canada. These microcosms were constructed from sediment from an aerobic region of the aquifer although the authors believe that sulfate-reducers were present in this sediment as well. In addition, BTEX compounds were added at concentrations of 10 (15% methanol added, ~1000 mg/L) to 15.5 mg/L (85% methanol added, 7400 mg/L) . These concentrations may have been high enough to significantly slow the rate of biodegradation such that degradation of methanol was not detected. However, the work reported by Novak et al. (1985) suggest that inhibition of the biodegradation rate is seen only once methanol concentrations are greater than 100 mg/L.

While limited field data were located in the literature for this compound, it is very likely that this simple organic compound will be biodegraded in anaerobic groundwater. A range of rate constants is recommended with the lower limit equal to 0.00022/day (a half-life of 3150 days) which is an order of

magnitude less than the lowest reported rate constant for a laboratory microcosm study and the upper limit equal to 0.087/day (a half-life of 8 days) which is the mean value for all studies. At very high concentrations of methanol the rate of biodegradation is expected to decrease substantially.

Table 52. All Summarized Studies for Methanol

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Finger Lakes region, NY	Meth/SO4	Field			Biodegrades		Major,DW et al. (1994)
Virginia		Lab microcosm	700000 ug/L	78	0.0022/day		Novak,JT et al. (1985)
Virginia		Lab microcosm	800000 ug/L	78	0.0039/day		Novak,JT et al. (1985)
Dumfries, VA	NO3	Lab microcosm	91000 ug/L	162	0.0051/day		Wilson,WG & Novak,JT (1988)
Virginia		Lab microcosm	800000 ug/L	78	0.0089/day		Novak,JT et al. (1985)
Dumfries, VA	SO4	Lab microcosm	85000 ug/L	50	0.016/day		Hickman,GT et al. (1990)
Upstate NY	SO4	Lab microcosm	520000 ug/L	162	0.016/day	30	Novak,JT et al. (1985)
Dumfries, VA	NO3	Lab microcosm	106000-140000 ug/L	63-168	0.020-0.052/day		Wilson,WG & Novak,JT (1988)
Dumfries, VA		Lab microcosm	113000 ug/L	110	0.028/day		Wilson,WG & Novak,JT (1988)
Dumfries, VA		Lab microcosm	97000 ug/L	108	0.029/day		Hickman,GT et al. (1990)
Dumfries, VA		Lab microcosm	96000 ug/L	105	0.030/day		Wilson,WG & Novak,JT (1988)

Table 52. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Dumfries, VA		Lab microcosm	92000 ug/L	50	0.036/day		Hickman,GT et al. (1990)
Dumfries, VA	SO4	Lab microcosm	91000 ug/L	80	0.039/day		Wilson,WG & Novak,JT (1988)
Dumfries, VA	SO4	Lab microcosm	91000 ug/L	80	0.039/day		Wilson,WG & Novak,JT (1988)
Virginia		Lab microcosm	70000 ug/L	65	0.043/day		Novak,JT et al. (1985)
Dumfries, VA	NO3	Lab microcosm	105000 ug/L	57	0.053/day		Wilson,WG et al. (1986)
Dumfries, VA		Lab microcosm	115000 ug/L	78	0.054/day		Wilson,WG et al. (1986)
Newport News, VA	SO4	Lab microcosm	84000 ug/L	11.5	0.065/day		Hickman,GT et al. (1990)
Wayland, NY		Lab microcosm	80000 ug/L	32	0.067/day		Hickman,GT et al. (1990)
Newport News, VA		Lab microcosm	95000 ug/L	10.5	0.071/day		Hickman,GT et al. (1990)
Virginia		Lab microcosm	88000 ug/L	40	0.072/day		Novak,JT et al. (1985)
Virginia		Lab microcosm	88000 ug/L	40	0.072/day		Novak,JT et al. (1985)
Newport News, VA	Meth/SO4	Lab microcosm	100000 ug/L	26	0.089/day		Morris,MS (1988)

Table 52. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Upstate NY	SO4	Lab microcosm	80000 ug/L	62	0.10/day	24	Novak,JT et al. (1985)
Newport News, VA	NO3	Lab microcosm	100000 ug/L	21	0.13/day		Morris,MS (1988)
Newport News, VA	SO4	Lab microcosm	22000 ug/L	8	0.34/day		Morris,MS & Novak,JT (1987)
Newport News, VA	NO3	Lab microcosm	90000 ug/L	3	0.88/day		Hickman,GT et al. (1990)
Norman, OK	Meth/SO4	Lab microcosm	133000 ug/L		19733 ug/L/day	5	Suflita,JM & Mormile,MR (1993)
Philadelphia, PA	Meth	Lab microcosm	1000000 ug/L	61	55000 ug/L/day		White,KD (1986)
Dumfries, VA	SO4	Lab microcosm			Biodegrades		Wilson,WG et al. (1986)
Empire, MI	Meth/SO4	Lab microcosm	50000 ug/L	244	Biodegrades		Mormile,MR et al. (1994)
Empire, MI	NO3	Lab microcosm	50000 ug/L	85	Biodegrades		Mormile,MR et al. (1994)
CFB Borden aquifer, Ontario, Canada	SO4	Lab microcosm	7432000 ug/L	278	NB		API (1994)
CFB Borden aquifer, Ontario, Canada	SO4	Lab microcosm	997000 ug/L	420	NB		API (1994)

3.8.5. Nitrobenzene

Currently, all published data for nitrobenzene in anaerobic groundwater suggests that this compound will biodegrade. It is expected that the nitro group will be initially reduced to the hydroxylamine form and then aniline. The summary of all located studies is presented in Table 53. First-order rate constants for all studies ranged from <0.0037 to >0.23/day. Evidence that nitrobenzene can biodegrade under nitrate-, iron-, and sulfate-reducing, and methanogenic redox conditions was obtained. A range of first-order rate constant values are recommended for input into the EPACMTP model.

A field study by Rugge et al. (1995) shows that nitrobenzene, injected along with 17 other compounds, was almost instantaneously degraded as it entered the aquifer. Methanogenic, sulfate- and iron-reducing conditions are present along the flow path. A second field study at the Vejen city landfill, by Nielsen et al. (1995B), shows that nitrobenzene is transformed the length of the contaminant plume under all redox conditions during an *in situ* microcosm study. Accompanying laboratory microcosm studies from this site also report that this compound is biodegraded, although at lower rates than found in the field. Lag phases for both types of study were very short (<10 days) or absent.

A range of rate constants is recommended with the lower limit equal to 0.0037/day (a half-life of 187 days) which was the lowest reported rate constant for a field/*in situ* microcosm study and the upper limit equal to 0.032/day (a half-life of 22 days) which is the mean value of all reported studies. Biodegradation of nitrobenzene is expected to be rapid; however, the metabolite from this transformation, aniline, may be of greater concern.

Table 53. All Summarized Studies for Nitrobenzene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Denmark	Meth	Batch reactor, groundwater inoculum	200 mg COD/L		Biodegrades		Lyngkilde,J et al. (1992)
Denmark	NO3	Batch reactor, groundwater inoculum	200 mg COD/L		Biodegrades		Lyngkilde,J et al. (1992)
Chriesback, Dubendorf, Switzerland	Fe	Column			20 ug/L/hr		Heijman,CG et al. (1995)
Grindsted landfill, Denmark	Meth/SO4/Fe	Field	75-350 ug/L	10.5	Biodegrades		Rugge,K et al. (1995)
Vejen city landfill, Denmark	Fe	In situ microcosm	150 ug/L	10-60	>0.0037->0.23/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Fe	In situ microcosm	150 ug/L	60	>0.0037/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth	In situ microcosm	150 ug/L	60	>0.0037/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	NO3/Mn	In situ microcosm	150 ug/L	60	Biodegrades		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Fe	Lab microcosm	150 ug/L	60	<0.0037/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Fe	Lab microcosm	150 ug/L	60	<0.0037/day		Nielsen,PH et al. (1995B)

Table 53. (Continued)

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Vejen city landfill, Denmark	NO3/Mn	Lab microcosm	150 ug/L	60	<0.0037/day		Nielsen,PH et al. (1995B)
Vejen city landfill, Denmark	Meth	Lab microcosm	150 ug/L	60	>0.0037/day		Nielsen,PH et al. (1995B)

3.8.6. Pyridine

Pyridine is expected to be resistant to biodegradation in anaerobic groundwaters based on its chemical structure. As with benzene, the aromatic ring of pyridine is electron deficient and therefore it is expected to be resistant to ring cleavage under anaerobic conditions (Ronen et al. 1994). The summary of all located studies is presented in Table 54. First-order rate constants for all studies ranged from 0 to >0.020/day; only laboratory studies were located in the literature.

In laboratory microcosm studies where pyridine was added as a sole carbon source, Kuhn and Suflita (1989) report that pyridine was biodegraded under both sulfate-reducing and methanogenic conditions in 240 days. Very little to no biodegradation occurred in the first three months for either redox condition. A second, methanogenic, microcosm study using aquifer material from the same site, the Norman, OK landfill, shows no biodegradation of pyridine and no production of methane over a period of 365 days. Ronen and Bollag (1992) report the mineralization of pyridine under nitrate-reducing conditions; these studies were run for short incubation periods of up to seven days. After seven days, 10% of the ^{14}C-labeled pyridine was recovered as $^{14}CO_2$.

While biodegradation of pyridine may occur, particularly in nitrate-reducing environments, there is limited quantitative evidence available to provide a recommended rate constant for input into the EPACMTP model. All studies which were located for this compound were laboratory studies where pyridine was present as the sole carbon source. This is expected to result in the measurement of a rate constant for this recalcitrant compound which would be faster than that measured in the field; pyridine is not expected to be a "favored" carbon substrate for the indigenous microbial population. Instead a first-order rate constant range of 0 to 0.0015/day (a half-life of 462 days), which is an order of magnitude less than the lowest reported rate constant, is proposed. A lower limit of zero was chosen based on the general recalcitrance of pyridine under anaerobic conditions as well as the limited amount of data available on this compound.

Table 54. All Summarized Studies for Pyridine

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Norman, OK	SO4	Lab microcosm	15800 ug/L	240	>0.014/day	30	Kuhn,EP & Suflita,JM (1989)
Norman, OK	Meth	Lab microcosm	15800 ug/L	240	>0.020/day	>90	Kuhn,EP & Suflita,JM (1989)
Indianapolis, Indiana	NO3	Lab microcosm	10 ug/g sediment	1.8	NB		Ronen,Z & Bollag,JM (1992)
Norman, OK	Meth	Lab microcosm	19800-39600 ug/L	365	NB		Adrian,NR & Suflita,JM (1994)
Indianapolis, Indiana	NO3	Lab microcosm	0.006-1.014 ug/g sed	1	Biodegrades		Ronen,Z & Bollag,JM (1992)
Indianapolis, Indiana	NO3	Lab microcosm	10 ug/g sediment	4	Biodegrades		Ronen,Z & Bollag,JM (1992)
Indianapolis, Indiana	NO3	Lab microcosm	10 ug/g sediment	7	0.015/day		Ronen,Z & Bollag,JM (1992)

3.8.7. Styrene

Very limited data for this compound suggest that styrene may be resistant to biodegradation under anaerobic conditions in groundwater. A summary of all located studies is presented in Table 55. A study by Grbic-Galic et al. (1990), using methanogenic consortia isolated from anaerobic sludge, suggests a possible route of biodegradation through the addition of water to the unsaturated side-chain; this initially forms 2-phenylethanol and then phenylacetic acid. This compound is readily biodegraded under aerobic conditions (Fu and Alexander 1992). First-order rate constants for all anaerobic groundwater studies ranged from 0 to 0.016/day.

Fu and Alexander (1996), using aquifer material which had never been exposed to styrene, report that more than 40% of the initial concentration remained after 260 days. No metabolites were detected over this time. The aquifer sediment was collected under aerobic conditions. These authors also measured the loss of styrene in waterlogged soils; rapid initial loss was reported, most likely due to the presence of oxygen, followed by a much slower rate of degradation. Nearly 30% of the initial styrene remained after 260 days. They suggest that other studies showing that styrene can be anaerobically biodegraded (Grbic-Galic et al. 1990) indicate that biodegradation of this compound does not absolutely require the presence of oxygen. However, the persistence of styrene in both anaerobic soils and aquifer sediments suggests that toxic products from the biodegradation of this compound may build up and inhibit further metabolism (Fu & Alexander 1996). Persistence of styrene in field conditions is observed by Grossman (1970). He reports that styrene originating from a point source was found in a contaminated aquifer for over two years after the source was removed. While measured rate constants are reported for a series of laboratory studies by Fu and Alexander (1992), the biodegradation which was measured may have been due to initial aerobic biodegradation.

The current literature does not provide sufficient information to make the recommendation of a rate constant for this compound possible at this time. The evidence so far indicates that styrene will be persistent in anaerobic groundwater environments and that styrene or products of its biodegradation may inhibit further biodegradation from occurring.

Table 55. All Summarized Studies for Styrene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Santa Clara Valley, CA		Field	0.18-4.7 ug/L	0.5	NB		Roberts,PV et al. (1980)
Freeville, NY		Groundwater grab sample	1000 ug/L	33	0.016/day	2	Fu,MH & Alexander,M (1992)
Freeville, NY		Lab microcosm	20 ug/L	21	0.00059/day	4	Fu,MH & Alexander,M (1992)
Freeville, NY		Lab microcosm	100 ug/L	21	0.00089/day	4	Fu,MH & Alexander,M (1992)
Freeville, NY		Lab microcosm	1000 ug/L	33	0.0035/day	3	Fu,MH & Alexander,M (1992)
Freeville, NY		Lab microcosm	200 mg/kg	5	NB		Fu,MH & Alexander,M (1996)
Freeville, NY	NO3	Lab microcosm	200 mg/kg	90	NB		Fu,MH & Alexander,M (1996)

3.8.8. 1,3,5-Trimethylbenzene

Based on the current literature, 1,3,5-trimethylbenzene is expected to be recalcitrant under anaerobic conditions. This compound is often used as a conservative tracer during anaerobic field studies of BTEX contaminated sites to correct for attenuation due to dilution along a flow path. Limited data were located (Table 56); however, in almost every case a result of no biodegradation was published. Three field studies report either that this compound was biodegraded with a published rate constant of 0.0039/day or that biodegradation of 1,3,5-trimethylbenzene was possible. As this compound is readily biodegraded under aerobic conditions it may be possible that these reports of biodegradation reflect aerobic biodegradation along the flow path. Dissolved oxygen concentrations are often greater along plume boundaries and aerobic microsites may be present within the aquifer matrix. Unfortunately, laboratory microcosm studies, where oxygen concentrations can be strictly controlled, were reported by only one author with the result of "no biodegradation". Wiedemeier et al. (1995A), the main proponent of the use of these compounds as conservative tracers in anaerobic groundwater, reports that the degree of recalcitrance of the trimethylbenzene isomers is site specific and must be assessed at each potential location. Currently, there is insufficient evidence of anaerobic biodegradation in groundwater and a rate constant can not be recommended. However, 1,3,5-trimethylbenzene is expected to be resistant to anaerobic biodegradation.

Table 56. All Summarized Studies for 1,3,5-Trimethylbenzene

Site Name	Redox Regime	Study Type	Initial Concn.	Time, days	Rate Constant	Lag, days	Reference
Seal Beach, CA	Meth	Column	0.043 umol/g	570	NB		Haag,F et al. (1991)
Seal Beach, CA	Meth	Column	0.043 umol/g	68	NB		Haag,F et al. (1991)
Bemidji, MN	Meth/Fe/Mn	Field			Possible		Cozzarelli,IM et al. (1990)
Swan Coastal Plain, Western Australia	SO4	Field	520 ug/L		0.0039/day		Thierrin,J et al. (1993)
Eglin AFB, FL	Meth	Field	327 ug/L	35	NB		Wilson,JT et al. (1994A)
Hill AFB, Utah	SO4	Field	417 ug/L	250	NB		Wiedemeier,TH et al. (1996)
George Air Force Base, CA	NO3/SO4	Field	38 ug/L	153	Possible		Wilson,JT et al. (1995A)
Vejen city landfill, Denmark	Fe	Lab microcosm	110 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	Meth/SO4	Lab microcosm	90 ug/L	450	NB		Albrechtsen,HJ et al. (1994)
Vejen city landfill, Denmark	NO3	Lab microcosm	11 ug/L	450	NB		Albrechtsen,HJ et al. (1994)

4. DISCUSSION

Biodegradation is determined by the physical, chemical and biological parameters of the environment in which the contaminant is found as well as the physical/chemical properties of the contaminant itself. In general, most of the compounds reviewed will be most affected in an anaerobic aquifer environment by biotic, and not abiotic, transformations. Aquifer environments are often oligotrophic, have low concentrations of dissolved oxygen or a low ability to recharge oxygen into the system once it is used, low temperatures, and relatively low microbial numbers when compared to other environments. These conditions, in general, lead to reduced rates of biodegradation when compared to other environments. Anaerobic biodegradation rates are expected to be mainly dependent on redox conditions, the presence of terminal electron-acceptors, other contaminants and carbon sources, temperature, pH, the presence of inhibitory compounds (*e.g.* pentachlorophenol), the concentration of the contaminant(s), the nutrients present in the aquifer, and the number of microbes present as well as their ability to acclimate to the compound(s) in question. The data reported above are almost invariably for shallow aquifer sites and thus recommended rate constant ranges are not appropriate for deep subsurface sites where microbial numbers are often much lower.

The constructed database, consisting of over 1200 records, represents the published literature on anaerobic biodegradation in groundwater for the chosen 44 compounds as of 1997. Recommended first-order rate constant ranges were developed for each compound that had sufficient data available for this decision (Table 57). Some compounds, such as the BTEX and the chlorinated aliphatic compounds, have been studied at multiple sites in both field and laboratory studies. Recommended rate constants for these compounds have a fairly substantial weight of evidence behind them. Other compounds, such as many of the polyaromatic compounds and the ketones, have relatively little data. In recommending a rate constant range for these compounds, information as to whether this general type of compound biodegraded readily in other anaerobic circumstances was assessed and an overall decision as to the biodegradability of these compounds was made based on scientific judgement. Both acetone and methyl ethyl ketone were rapidly biodegraded in anaerobic studies; there was no evidence that either of these compounds would be resistant to biodegradation. Therefore, for the ketones it was decided to report a rate constant range by converting the available zero-order rate constant to a first-order rate constant. As this is not a conservative approach, a range was recommended which was one to two orders of magnitude less than the converted rate constant. The polyaromatic compounds represented a set of compounds believed to be resistant to biodegradation under anaerobic conditions. Therefore, for this set of compounds a lower limit of zero was used, when a rate constant range was proposed, to recognize that very little data were available and that in some groundwater environments these compounds were not expected to anaerobically biodegrade. Every effort was made to keep the decision-making process as consistent as possible given the large variation in the amount and type of information available for each compound. If the compound had sufficient information, the lowest field/*in situ* microcosm value was set as the lower limit with the mean of all the field/*in situ* microcosm studies used as the upper limit. For compounds with less data, where laboratory studies were used, the lower limit was set at one order of magnitude less than the lowest reported laboratory rate constant and the upper limit was set to either an appropriate field study value or to an order of magnitude less than

the entire data set if suitable field study data were not published. Several variations of this were used depending on the amount and type of data available for a particular compound.

The determination of mean values mainly has context within the compiled data set. The addition of new data and information from new aquifer sites may significantly change these results, particularly for compounds with very little published data. Certain sites tend to be very well studied; however, there is little information as to how biodegradation rates determined from these sites might translate to other, unstudied aquifer locations. Wiedemeier et al. (1996B) suggests that if published rate constant values are used for modeling that the best approach would be to "start with average values and then vary the model input to predict both the best- and worst-case scenarios". However, he also states that this can be done only once the site has been shown to biodegrade the compound of interest.

Several of these compounds appear to be resistant to biodegradation under anaerobic groundwater conditions. Most, if not all, of these recalcitrant compounds are known to biodegrade fairly readily under aerobic conditions. It is possible that in a field situation loss of these compounds may occur due to aerobic biodegradation at the plume periphery. This question is beyond the scope of this report, which was set up to determine rates of anaerobic biodegradation in groundwater systems only; however, the effect of aerobic biodegradation may be significant for these recalcitrant compounds in some groundwater locations.

Table 57. Summary Table of the Recommended Anaerobic Biodegradation Rate Constants

Compound	Recommended Rate Constant	Comments
Benzene	0-0.0036[a]	
Toluene	0.00099-0.059	
Ethylbenzene	0.00060-0.015	
m-Xylene	0.0012-0.016	Lower limit seems slightly high when compared to other xylene isomers.
o-Xylene	0.00082-0.021	
p-Xylene	0.00085-0.015	
Carbon Tetrachloride	0.0037-0.13	Range not appropriate for nitrate-reducing conditions. Expect lower limit to be much less.
Chloroform	0.0004-0.03	Only one field study available. Biodegradation under nitrate-reducing conditions expected to be much lower.
1,2-Dichloroethane	0.0042-0.011	Range reported from a single field study under methanogenic conditions.
Dichloromethane	0.0064	Rate constant reported from a single field study under methanogenic conditions.
1,1,2,2-Tetrachloroethane	I.D.[b]	Not enough data available to recommend a rate constant. However, based on its structure, it is likely that this compound will undergo reductive dechlorination in strong reducing environments.
Tetrachloroethylene	0.00019-0.0033	Lower limit was reported for a field study under nitrate-reducing conditions.
1,1,1-Trichloroethane	0.0013-0.01	Range not appropriate for nitrate-reducing conditions. Expect lower limit to be much less.
1,1,2-Trichloroethane	I.D.	Not enough data available to recommend a rate constant. However, based on its structure, it is likely that this compound will undergo reductive dechlorination in strong reducing environments.
Trichloroethylene	0.00014-0.0025	Lower limit was reported for a field study under unknown redox conditions.

Table 57. (Continued)

Vinyl Chloride	0.00033-0.0072	Lower limit was reported for a field study under methanogenic/sulfate-reducing conditions.
Phenol	0.0013-0.032	Upper limit was taken from the sole field study.
o-Cresol	0.0005-0.034	Upper limit was taken from the sole field study.
m-Cresol	0.00029-0.033	Upper limit was taken from the sole field study.
p-Cresol	0.0004-0.048	Upper limit was taken from the sole field study. Lower limit is the average lower limit from the other two cresol isomers.
2,4-Dichlorophenol	0.00055-0.027	Range may not be appropriate for nitrate-reducing conditions.
2,4,6-Trichlorophenol	I.D.	
Pentachlorophenol	I.D.	Data on compound is conflicting. Pentachlorophenol appears to be inhibitory to the indigenous microbial population at fairly low concentrations.
Trichlorofluoromethane	0.00016-0.0016	All studies conducted with very low concentrations of this compound.
Dichlorodifluoromethane	I.D.	All studies conducted with very low concentrations of this compound.
1,1,2-Dichloro-1,2,2-difluoromethane	I.D.	All studies conducted with very low concentrations of this compound.
Acetone	0.0037-0.037	Converted zero-order rate constant to first-order from the sole study reporting a rate constant.
Methyl Ethyl Ketone	0.0054-0.054	Converted zero-order rate constant to first-order from the sole study reporting a rate constant.
Methyl Isobutyl Ketone	0.00013-0.000013	Converted zero-order rate constant to first-order from the sole study reporting a rate constant.
Acetic Acid	0.00071-0.075	The lower limit, which is an order of magnitude less than the lowest positive laboratory microcosm study, seems very low for this compound. This value is less than the lower value given for phenylacetic acid.

Table 57. (Continued)

Phenylacetic Acid	0.0012-0.012	
Acenaphthene	0-0.0043	Upper limit is value calculated from the sole field study. All reported data were from the Pensacola, FL site.
Fluorene	0-0.00088	
1-Methylnaphthalene	0-0.00043	
Naphthalene	0-0.0072	
Phenanthrene	I.D.	The available data indicate that phenanthrene is recalcitrant.
1,1'-Biphenyl	0-0.00032	
Cumene	I.D.	The available data suggest that cumene may biodegrade in anaerobic groundwater.
Dioxane	I.D.	The available data indicate that dioxane is recalcitrant.
Methanol	0.00022-0.087	The lower limit, which is an order of magnitude less than the lowest laboratory microcosm study, seems very low for this compound.
Nitrobenzene	0.0037-0.032	The product of biotransformation is aniline.
Pyridine	0-0.0015	
Styrene	I.D.	The available data indicate that styrene is recalcitrant.
1,3,5-Trimethylbenzene	I.D.	The available data indicate that 1,3,5-trimethylbenzene is recalcitrant, but that biodegradation may be site-specific.

[a]First-order rate constant in units of $days^{-1}$

[b]Insufficient data to determine a recommended biodegradation rate constant

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