

Ground Water Issue Paper: Synthesis Report on State of Understanding of Chlorinated Solvent Transformation

Bruce Pivetz, Ann Keeley*, Eric Weber, Jim Weaver, John Wilson, and Cissy Ma

Contents

1. Objectives and Scope	1
2. Introduction	2
2.1 MNA	2
2.2 Site Characterization and Conceptual Site Model.	2
2.3 Physical and Chemical Properties of the Contaminants.	2
2.4 Contaminant Transport and Physical Attenuation Processes	4
2.5 Geochemical Conditions.	5
2.6 Contaminant Natural Attenuation Rates	6
3. Biotic Chlorinated Solvent Transformation Pathways and Processes	7
3.1 Introduction to Biotic Transformations	7
3.2 PCE and TCE	9
3.3 TCA	24
3.4 Dioxane	25
4. Abiotic Transformations	27
4.1 PCE and TCE	29
4.2 TCA	33
4.3 Dioxane	35
5. Summary of Biotic and Abiotic Transformations	35
6. Modeling applications and conceptualizations for chlorinated solvent transformations	37
6.1 Historical Background	37
6.2 Types of Models	37
6.3 Parameter Measurement in the Field	38
6.4 Model Application	38
7. References	41

Figures

Figure 1.1. Elements of a conceptual site model for monitored natural attenuation.	3
Figure 3.1. Bacterial species involved in dechlorination processes.	23
Figure 3.2. Enzymes involved in dechlorination processes.	23
Figure 4.1. Formation of abiotic reductants as a function of iron and sulphate reducing zones.	29
Figure 4.2. Reaction Scheme illustrating the degradation pathways for PCE.	30
Figure 4.3. Reaction scheme illustrating the degradation pathways for TCA	34

Tables

Table 1. Contaminant physical and chemical properties.	4
Table 2a. Microbial Metabolic Processes	8
Table 2b. Reactions and Subsurface Conditions	8
Table 3a. Compilation of compilations of chlorinated solvent	11
Table 3b. Chlorinated solvent biotic transformation	21
Table 4.1. Surface area-normalized rate constants	31

1. OBJECTIVES AND SCOPE

Chlorinated solvents are altered by biotic and abiotic processes. Biotic transformation can include reductive dechlorination, cometabolism, and limited oxidation. Abiotic transformation is less well understood but may play a role at some sites. Transformations may be limited such that endpoints fall short of complete degradation of the solvent to innocuous compounds. Determination of which endpoints are reached, the processes of transformation, and the needed site data are critical for assessing and modeling transport, and deciding on monitored natural attenuation (MNA) as a remedy.

This Issue Paper summarizes the biotic and abiotic transformations of several important chlorinated solvents. It briefly describes the factors that affect the transformation mechanisms, as well as the measurements necessary to distinguish among the mechanisms. It serves as a guide for developing an advanced ground-water transport model, with governing equations for simulating these processes in models. The primary audience is the EPA remedial project managers (RPMs). The Issue Paper is intended to provide RPMs with a basic understanding of the fundamentals and terminology of chlorinated solvent transformation in the context of MNA.

The focus of this document is on three chlorinated solvents used at industrial and dry-cleaning facilities: tetrachloroethene (PCE), trichloroethene (TCE), and 1,1,1-trichloroethane (TCA). It also discusses their degradation (“daughter”) products: 1,2-dichloroethene (DCE) [primarily *cis*-1,2-dichloroethene (*cis*-DCE)], vinyl chloride (VC), 1,1-dichloroethene (1,1-DCE), 1,1-dichloroethane (1,1-DCA), and chloroethane (CA). It also covers 1,4-dioxane (dioxane), which is present as a stabilizer in some chlorinated solvent preparations [it was primarily used to stabilize TCA (Mohr 2001)]. These chlorinated solvents are among the most commonly encountered contaminants at many of the worst contaminated sites, and PCE is the primary contaminant found at dry-cleaner sites. TCE is also found at dry-cleaner sites as a degradation product of PCE, and as the initial contaminant at older dry cleaning sites as it was the dry-cleaning agent used for a few decades starting about 1930.

* Corresponding author: National Risk Management Research Laboratory, U.S. Environmental Protection Agency, 919 Kerr Research Drive, Ada, OK 74820, USA
Tel.: 1.580.436.8890 fax: 1.580.436.8614
Email: keeley.ann@epa.gov (A. Keeley)

2. INTRODUCTION

Understanding and modeling the fate (transformation) and transport of chlorinated solvents at contaminated sites, as well as their remediation through the use of MNA, requires a thorough recognition of transformation processes to form a strong foundation for conceptual modeling. This introductory section presents brief discussions of these topics.

2.1 MNA

The U.S. EPA (1999) provided clarification of its policy on the application of MNA as a remedy for contaminated sites, and defines this alternative as *“the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods”*. Natural attenuation (NA) processes that degrade or destroy contaminants are preferred over other processes (e.g., dilution and volatilization) that merely attenuate (i.e., diminish contaminant concentrations) contaminant mass (U.S. EPA, 1999). By definition, MNA does not include the use of any active remedial technologies; however, at most sites MNA is very likely to be just one component of the overall remedial strategy as it may be applied to only certain portions of the site, and/or after active technologies have been implemented. Thus, when investigating, modeling, or evaluating MNA it is imperative to take into consideration other remedial activities that have previously occurred or are currently taking place. Guidance documents have been used for implementing MNA in ground water (Wiedemeier et al., 1998, 1999; U.S. EPA, 1999; National Research Council, 2000).

2.2 Site Characterization and Conceptual Site Model.

Information about the subsurface contamination, geology, hydrogeology, geochemistry, and microbiology collected during site characterization is assembled into a conceptual site model (Figure 1.1). The conceptual site model (CSM) is *“a three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and*

the transport and fate of those contaminants” (U.S. EPA, 1999). The elements of site characterization and the process of preparing a CSM for MNA of volatile organic compounds (VOCs; including chlorinated solvents) are described in Pivetz et al. (2012).

Defining the plume in three dimensions and understanding the geochemical and microbiological environment are necessary parts of establishing the CSM. Identifying and defining the most significant ground-water and contaminant flow path(s), and quantifying flow velocities, are critical for estimating chlorinated solvent attenuation rates. Characterization of the subsurface geochemistry is also important. Microbiological characterization and confirmation of the presence of specific bacterial strains is likely to be important to fully evaluate MNA for PCE, TCE, TCA, and dioxane, since effective bioattenuation of each of these depends on the presence of specific microbes. Monitoring should be extensive enough in three dimensions to be able to understand the differing conditions that are likely to occur in different portions of the site and plume. Monitoring should be conducted for a long enough period (likely several years) in order to estimate rates of attenuation at a given location.

Development of the CSM and modeling of the plume migration, attenuation, and duration requires knowledge of physical characteristics of the subsurface, and activities and changes at the site. According to Pivetz et al. (2012), information related to the ground-water and contaminant velocities, the lithology (which impacts contaminant transport and sorption such as back-diffusion), seasonal changes impacting ground-water levels, longer-term changes (e.g., droughts), and the role and impacts of active remedial technologies (especially source removal activities) should be collected during site characterization.

2.3 Physical and Chemical Properties of the Contaminants.

Table 1 presents the most significant physical and chemical properties, and their values, of the chlorinated solvents that impact the fate and transport of these compounds in the subsurface. One set of values is provided in the table; however, it should

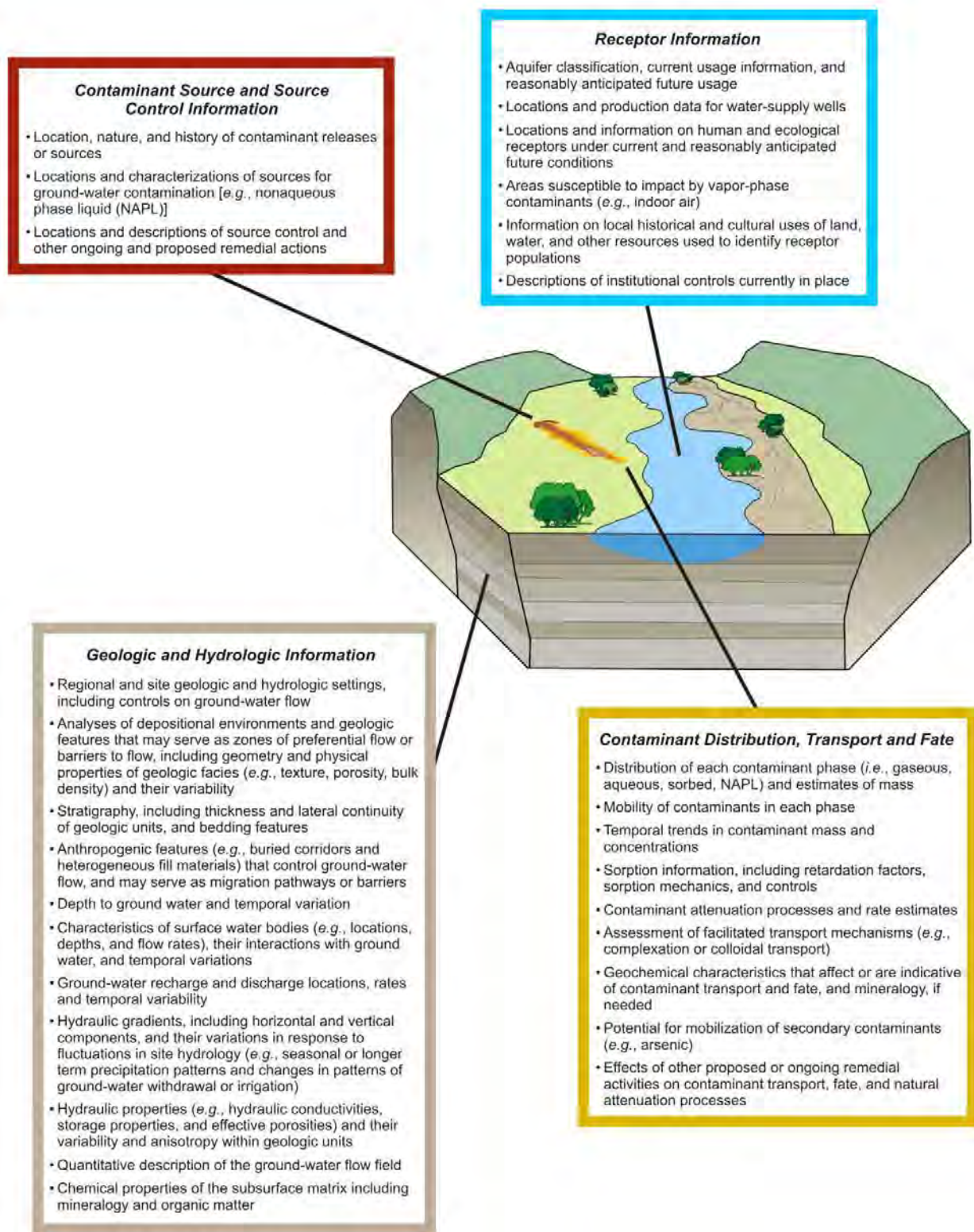


Figure 1.1. Elements of a conceptual site model for monitored natural attenuation.

Table 1. Contaminant physical and chemical properties.

Properties:	PCE ¹ C ₂ Cl ₄ (Cl ₂ C=CCl ₂)	TCE ¹ C ₂ HCl ₃ (HCIC=CCl ₂)	Cis-DCE ¹ C ₂ H ₂ Cl ₂ (HCIC=CCIH)	VC ¹ C ₂ H ₃ Cl (H ₂ C=CCIH)	TCA ¹ Cl ₃ CH ₃ (CCl ₃ CH ₃)	1,1-DCA ¹ C ₂ H ₄ Cl ₂ (HCl ₂ C-CH ₃)	CA ¹ C ₂ H ₅ Cl (CH ₃ -CH ₂ -Cl)	Dioxane ^{1,2} (C ₄ H ₈ O ₂)
Molecular weight (g mole ⁻¹)	165.83	131.4	96.95	62.5	133.4	98.97	64.52	88.11
Water solubility at 25 °C (mg L ⁻¹)	150	1070	3500	2763	1500	5500	5740	Miscible
Contaminant density as a NAPL (g mL ⁻¹)	1.6227	1.465	1.2837	0.9106	1.3390	1.1747	0.9214	1.0329
Log soil/water partition coefficient (Log K _{ow})	3.40	2.42	1.86	1.36	2.49	1.79	1.43	-0.27
Vapor pressure at 20 or 25 °C (mm Hg)	18.47	74	180	2530	124	1.82	1008	38.1
Henry's Law Constant at 25 °C (atm m ³ mol ⁻¹)	1.8 x 10 ⁻²	1.1 x 10 ⁻²	4.08 x 10 ⁻³	2.78 x 10 ⁻²	6.3 x 10 ⁻³	4.4 x 10 ⁻²	1.11 x 10 ⁻²	5 x 10 ⁻⁶

References

¹ATSDR: Toxicological Profiles for each compound²Mahendra and Alvarez-Cohen (2006)

be noted that the values of these properties can vary, depending on the conditions and how the values were measured.

2.4 Contaminant Transport and Physical Attenuation Processes

The attenuation of contaminant concentrations with time and distance from a source area (i.e., natural attenuation) can be due to *“a variety of physical, chemical, or biological processes that... include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants”* (U.S. EPA, 1999). Detailed discussion of these processes can be found in the following contaminant hydrogeology reference books: Freeze and Cherry (1979), Fetter (1993),

and Domenico and Schwartz (1998). This document focuses on the destructive processes: biotic transformations (biodegradation) and abiotic transformations (degradation through chemical reactions). However, confirming and quantifying the impacts of these destructive processes (and calculation and understanding of attenuation rates) requires an understanding of how the other, non-destructive, processes impact the site and the data collected for the MNA evaluation. All of the contaminants in this document are subject to advection, dispersion, and dilution. Chlorinated solvent concentrations will be relatively low in ground water due to a low solubility. Dioxane, however, is miscible with water, meaning ground-water concentrations can be quite high. This means that sorption will be negligible for dioxane,

whereas, the chlorinated solvent contaminants will be slightly to moderately sorbed. Volatilization from shallow ground water can occur with the chlorinated solvents; however, volatilization is unimportant for dioxane due to its very low Henry's Law constant. None of these contaminants are subject to radioactive decay. All of these contaminant fate and transport processes and properties need to be recognized and quantified in order to model contaminant ground-water migration and to quantify the effectiveness of NA. This includes understanding the relative significance of each of the processes.

2.5 Geochemical Conditions.

Biotic and abiotic transformations of the chlorinated solvents will be influenced by the subsurface soil and ground-water geochemical conditions, which may vary with time and location. Most significantly, which oxidation-reduction (redox) reactions occur in the subsurface will determine whether or not a particular contaminant is transformed, and the extent and rate of its transformation. Identification of different zones of different redox conditions and processes will help indicate where particular transformations are or are not occurring. The main redox reactions (terminal e^- accepting processes, or TEAPs), their final or terminal e^- acceptors (TEAs), and their reaction products that occur or are found in the subsurface are:

- Aerobic respiration: the TEA is oxygen (O_2), and CO_2 is produced.
- Nitrate reduction (denitrification): the TEA is nitrate (NO_3^-), and N_2 is produced.
- Manganese reduction: the TEA is manganese(IV) (Mn^{+4}), and manganese(II) (Mn^{+2}) is produced.
- Iron(III) reduction: the TEA is iron(III) (Fe^{+3}), and iron(II) (Fe^{+2}) is produced.
- Sulfate reduction: the TEA is sulfate (SO_4^{2-}), and hydrogen sulfide (H_2S) is produced.
- Methanogenesis: the TEA is carbon dioxide (CO_2), and methane (CH_4) is produced.

The TEAPs generally occur in the order given above. After dissolved oxygen is depleted and the subsurface becomes anaerobic, the TEAPs shift to denitrification, then iron(III) reduction and sulfate reduction, and ultimately to methanogenesis. However, although one

TEAP may be relatively predominant, several of the TEAPs may occur simultaneously in close proximity to each other. The occurrence of any one given TEAP depends on the supply of the terminal e^- acceptor and the appropriate microbial community.

As discussed below in section 3.1.1, the bacteria that biodegrade chlorinated solvents obtain their energy during microbiologically mediated oxidation-reduction reactions in which electrons transfer between compounds that act as electron (e^-) donors (co-contaminants or naturally occurring carbon) and e^- acceptors (the chlorinated solvents). This reductive dechlorination (which is a major anaerobic biodegradation pathway for chlorinated solvents) uses the chlorinated solvents as e^- acceptors. Its occurrence and rate varies depending on the geochemical conditions brought about during the TEAPs discussed above, as well as whether the requisite microbes for dechlorination use the chlorinated solvents or the TEAs as their e^- acceptors.

The predominant redox condition and zone (i.e., correlating to a specific microbial TEAP) can also be identified through subsurface dissolved hydrogen (H_2) measurements (Lovley et al. 1994), as indicated by the following ranges:

- Denitrification: <0.1 nM H_2
- Iron(III) reduction: 0.2 - 0.8 nM H_2
- Sulfate reduction: 1 - 4 nM H_2
- Methanogenesis: 5 - 20 nM H_2

Measurement of the TEAs and/or their reduced products in ground water can indicate what processes are occurring. Relevant or potentially important geochemical parameters include soil total organic carbon (TOC); dissolved organic carbon (DOC); oxidation-reduction potential (ORP); dissolved oxygen; (DO); nitrate; manganese (Mn(II)/Mn(IV)); iron (Fe(II)/Fe(III)); sulfate; hydrogen sulfide; carbon dioxide; (CO_2); methane, ethane, and ethene; dissolved hydrogen; pH; alkalinity; temperature; conductivity; additional major ions such as Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , CO_3^{2-} , and HCO_3^- ; minerals present; and concentrations of metals and metalloids. Not all these parameters will need to be measured nor will be useful in many cases. Specific

geochemical parameters are discussed below for individual chlorinated solvents when relevant to the transformation.

In summary, the biotic transformation of the chlorinated solvents occurs in the subsurface geochemical environment developed under several different terminal e^- accepting processes that occur in a general sequence of aerobic oxidation, denitrification, iron(III) reduction, sulfate reduction, and then methanogenesis. However, several TEAPs may be active at one time within the same general subsurface volume, the predominant TEAP may shift with time, or a given TEAP may not occur. The occurrence and significance of a given TEAP depends on the availability of the relevant electron acceptor.

2.6 Contaminant Natural Attenuation Rates

Calculating the rate of contaminant attenuation in a ground-water plume is important for evaluating plume migration and the time frame to reach a remedial goal. For MNA, attenuation (and contaminant biodegradation) is often described as a first-order decay process (i.e., first-order kinetics; exponential decay):

$$C(t) = C_0 e^{-kt} \quad \text{where} \quad \begin{array}{l} C(t) = \text{concentration at time } t \text{ [M L}^{-3}\text{]} \\ C_0 = \text{initial concentration [M L}^{-3}\text{]} \\ k = \text{rate constant [T}^{-1}\text{]} \\ t = \text{time [T]} \end{array}$$

The rate of degradation is given by:

$$\partial C / \partial t = -kC \quad \text{where} \quad \partial C / \partial t \text{ is the change in concentration at time } t$$

The rate constant (k) is a critical parameter in mathematically modeling fate and transport of a plume. Rate constants for a given process (e.g., biodegradation) are often determined under laboratory conditions, although in NA it is important to determine the rate constant under site-specific field conditions. Rate constant values are sometimes described in terms of half-lives, since they are related through:

$$t_{1/2} = 0.693/k \quad \text{where} \quad \begin{array}{l} t_{1/2} \text{ is the half-life [T]} \\ k = \text{first-order rate constant [T}^{-1}\text{]} \end{array}$$

The overall attenuation rate (i.e., rate constant) representing all transport and attenuation processes at a single point, or along the entire migration pathway of the plume, can be calculated using contaminant concentration data from a sufficient number of monitoring wells that are properly located in the migration pathway of the plume. Attenuation of the source material must also be understood, as contaminant influx into the plume from the source area affects the longevity of the plume. The biodegradation attenuation rate can also be calculated, which represents the contaminant destructive loss due only to biological activity. Further discussion of attenuation rates and methods for their calculation are provided in Suarez and Rifai (1999) and Newell et al. (2002). It should be noted that other kinetic models (e.g., zero order or second order) may be used to better describe biodegradation or other transformations of contaminants. Monod kinetics, as well as the Michaelis-Menten rate law model, is often used to describe laboratory biodegradation data, and a variety of kinetic parameters for these kinetics are determined. Chapelle et al. (2007) discuss the mathematical treatment of the biotransformation sink term and kinetics, including substrate and electron (e^-) acceptor utilization as described by Monod kinetics. Alvarez-Cohen and Speitel (2001) provide a comprehensive discussion of the kinetics involved in aerobic cometabolism of chlorinated solvents.

Biodegradation and plume attenuation rates (and rate constants) have been determined from both laboratory and field studies at contaminated sites. Literature compilations of rates and rate constants from numerous sites often do not provide the entire set of related geochemical, hydrogeological, microbiological, and anthropogenic conditions, so it may be difficult to fully understand the conditions that impacted the rates. Studies where rates and rate constants have been calculated at chlorinated solvent sites may not have been published in the peer-reviewed literature, rather, in gray literature such as site remediation reports. Laboratory biodegradation rates should be viewed with caution, as they generally represent much more optimum conditions than found in the field.

Modeling the potential for NA processes to

successfully remediate a chlorinated solvent site depends strongly on knowledge of the rate of biotic transformation of the solvent(s). Biodegradation rates and/or rate constants can be calculated from site-specific measurements, or estimated using previous knowledge and experience as reflected in the NA literature.

3. BIOTIC CHLORINATED SOLVENT TRANSFORMATION PATHWAYS AND PROCESSES

3.1 Introduction to Biotic Transformations

3.1.1 Biodegradation

In situ biodegradation of chlorinated solvents (i.e., biotic transformations) is due primarily to subsurface bacteria (fungi-mediated biodegradation that may occur in the unsaturated zone will not occur in the saturated conditions of ground water). For growth, bacteria require a carbon source and energy (as well as water and mineral nutrients) from a substrate(s) (i.e., the compound(s) providing the carbon and/or energy). Heterotrophic bacteria (the majority of bacteria) that biodegrade chlorinated solvents obtain their carbon from either naturally occurring compounds or other contaminants. The energy is obtained from the energy released during microbiologically mediated oxidation-reduction reactions in which electrons transfer between compounds that act as e^- donors and e^- acceptors. The e^- acceptors can be dissolved oxygen (O_2), some naturally occurring inorganic compounds (NO_3^- , Mn^{+4} , Fe^{+3} , SO_4^{2-} , CO_2), or some chlorinated solvents. In growth-supporting biodegradation, the contaminant is used as a primary substrate by the bacteria. Complete biodegradation of the contaminant to CO_2 is termed mineralization. Contaminants may also be biodegraded through cometabolism, in which the degradation is non-growth-supporting for the bacteria bringing about the transformation (the degradation of the contaminant occurs as a fortuitous event as the bacteria use some other substrate and the appropriate enzymes are induced). It is important to realize that a transformation of a contaminant to an end product often involves a number of intermediate compounds and types of reactions, some of which may not be identified and/or have short persistence.

Reductive dechlorination of PCE and TCE does not involve any persistent or significant intermediates before the daughter products DCE and VC are formed.

Early research on biodegradation of chlorinated solvents was published by Vogel et al. (1987), Vogel and McCarty (1987), Sims et al. (1991), Bouwer (1993), McCarty and Semprini (1993), and Vogel (1993). MNA microbial processes were discussed in Azadpour-Keeley et al. (1999), a comprehensive examination of MNA of petroleum hydrocarbons and chlorinated solvents is found in Wiedemeier et al. (1999), and a comprehensive review of chlorinated solvent MNA is found in Rifai et al. (2001). More recent reviews of subsurface biodegradation of VOCs under intrinsic conditions include Field and Sierra-Alvarez (2004), Lawrence (2006), Aulenta et al. (2006), Chapelle et al. (2007), and Bradley and Chapelle (2010).

The literature frequently group chlorinated solvents biotransformation in a variety of ways: (a) based on the chemical reaction involved, (b) whether the contaminant was reduced or oxidized, (c) whether or not a chlorine was removed, (d) whether the subsurface conditions were aerobic or anaerobic, (e) whether the subsurface conditions were oxidizing or reducing, or (f) by the microbiological metabolic process involved. Since the same degradative phenomenon may be referred to in different ways by different practitioners, it is useful to review and understand the varied terminology, as well as the basic microbial processes. Table 2a indicates the biotic transformations of the contaminants, categorized by the microbial processes that occur. Table 2b also indicates these biotic transformations, but categorized by the reactions that occur. A detailed discussion of relevant terminology is provided in Bradley and Chapelle (2010). The broad term “reductive dechlorination” as commonly used in MNA literature is usually meant to signify only the specific microbially-mediated process (via halorespiration, also known as chlororespiration) resulting in removal of one chloride ion from the chlorinated compound under anaerobic (reducing) conditions and its replacement by a hydrogen atom. However, as indicated by Table 2a and b, other

Table 2a. Microbial Metabolic Processes Involved in Biotic Transformations of the Chlorinated Solvents.								
	PCE	TCE	DCE	VC	TCA	1,1-DCA	CA	Dioxane
A. Contaminant as primary substrate: Growth-supporting. 1. Halorespiration: Anaerobic (anoxic); reductive dechlorination driven by H ₂ as an electron donor; chlorinated solvent used as electron acceptor; halogen removed (dehalogenation). 2. Respiration/Oxidation: Contaminant used as electron donor. a. Oxidic respiration: Direct aerobic oxidation. Oxygen is the terminal electron acceptor. b. Anoxic respiration: Direct anaerobic oxidation Inorganic ions other than oxygen are the terminal electron acceptors.	Yes	Yes	Yes	Yes	Yes	Yes	No	NA
B. Cometabolism: Non-growth supporting; contaminant fortuitously degraded with the presence of another, primary, substrate. 1. Aerobic cometabolism, Cometabolic oxidation, or Cooxidation: An oxidation reaction; not a significant naturally occurring process in the subsurface. 2. Anaerobic cometabolism: A reductive dechlorination (for the chlorinated solvents); occurs, but an uncommon and/or slow occurrence; the more effective anaerobic reductive dechlorination via halorespiration is not cometabolic.	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes
	Yes	Yes	Yes	Yes	Yes	Yes	No	No

Table 2b. Reactions and Subsurface Conditions Involved in Biotic Transformations of the Chlorinated Solvents.								
	PCE	TCE	DCE	VC	TCA	1,1-DCA	CA	Dioxane
A. Aerobic oxidation: a. Direct aerobic oxidation: Oxidic respiration. Oxygen is the terminal electron acceptor. b. Indirect aerobic oxidation: Aerobic cometabolism. An oxidation reaction; not a significant naturally occurring process in the subsurface.	No	No	Yes	Yes	No	Yes	Yes	Yes
	No	Yes	Yes	Yes	Yes	Yes	Yes	No
B. Anaerobic oxidation: Anoxic respiration. Inorganic ions other than oxygen are the terminal electron acceptors.	No	No	Yes	Yes	No	No	No	Maybe
C. Anaerobic reduction: Reductive dechlorination 1. Halorespiration: Anaerobic (anoxic); reductive dechlorination driven by H ₂ as an electron donor; chlorinated solvent used as electron acceptor; halogen removed; growth-supporting. 2. Anaerobic cometabolism: A reductive dechlorination, but an uncommon and/or slow occurrence; the more effective anaerobic reductive dechlorination via halorespiration is not cometabolic	Yes	Yes	Yes	Yes	Yes	Yes	No	NA
	Yes	Yes	Yes	Yes	Yes	Yes	No	NA

<p>3. Hydrogenolysis: A biotic and abiotic anaerobic reductive reaction; substitution of a hydrogen atom for chlorine on the molecule; a reductive dechlorination; halogens removed (for chlorinated solvents). When hydrogenolysis is thought of in terms of being strictly an abiotic reaction, it is likely, however, to depend on the presence of microbes to create the conditions conducive to the reaction (Wiedemeier et al., 1999).</p> <p>3a. Biotic hydrogenolysis</p> <p>3b. Abiotic hydrogenolysis</p> <p>4. Dihaloelimination (dichloroelimination): An anaerobic reductive reaction; removal of two adjacent halogen atoms, leaving a double bond between the respective carbon atoms (forming an alkene from an alkane); halogens removed (dehalogenation); a reductive dechlorination. When dihaloelimination is thought of in terms of being strictly an abiotic reaction, it is likely, however, to depend on the presence of microbes to create the conditions conducive to the reaction (Wiedemeier et al., 1999).</p>	Yes	Yes	Yes	Yes	Yes	Yes	NA
	Maybe	Maybe			Maybe	Yes	NA
	Maybe	Maybe			Maybe		NA

microbial processes and chemical reactions can also be reductive dechlorinations.

3.1.2 General Factors Influencing Subsurface Biodegradation and NA

Subsurface microbes catalyze redox reactions in ground water which alters the redox potential and impacts the occurrence and rate of biotic transformations of contaminants.

Under anaerobic environments, reducing compounds, such as organic carbon, are fermented to produce H₂ which serves as e⁻ donor for Dehalococcoides and other dechlorinating bacteria (Duhamel et al., 2002). Research has demonstrated that under strongly reducing conditions in the presence of sufficient supply of bioavailable natural organic carbon, complete reductive dechlorination of PCE was observed (Thomas et al., 2013). Therefore, dissolved H₂ concentrations could also be measured and used to indicate the predominant microbially catalyzed redox reactions and conditions in anoxic ground water (Lovley et al., 1994). There may be competition for H₂ or other electron donor, or for electron acceptor, between different microbial species carrying out one or more of these processes, which can affect the occurrence and extent of contaminant transformation by a particular species.

The concentration of a target contaminant can also impact the occurrence and rate of biodegradation. At high enough concentrations, the contaminant may be toxic to the microbes that degrade it, and low concentrations may be insufficient to support growth of the microbe. A co-existing contaminant may be toxic or detrimental to a biodegradative process carried out by specific bacteria.

At some sites, PCE, TCE, and TCA may be present as a dense non-aqueous phase liquid (DNAPL) that acts as a continual source of dissolved solvent as it dissolves into the ground water. High dissolved concentrations resulting from dissolution of the DNAPL contaminant constituent may inhibit or prevent biodegradation. The presence of a source, and especially DNAPL, impacts the determination of attenuation rate constants, and the source decay needs to be considered (Newell et al., 2002).

3.2 PCE and TCE

3.2.1 Processes and pathways

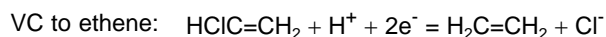
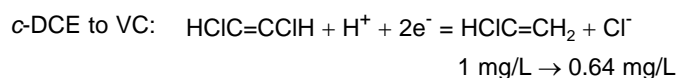
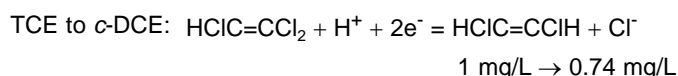
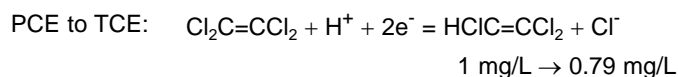
Biotransformation of PCE and TCE is discussed together, since they share many similar processes (Table 2a and b).

The major biodegradation route of PCE and TCE is through reductive dechlorination, a process known as “halorespiration”. During this growth-supporting

microbial process, H₂ is directly used as an e⁻ donor and the chlorinated solvent serve as the e⁻ acceptor. The H₂ is produced during biodegradation of other organic compounds, either naturally occurring organic carbon or organic contaminants such as petroleum hydrocarbons (Wiedemeier et al., 1999). PCE or TCE loses a chlorine atom and is reduced. PCE and TCE degradation products from reductive dechlorination are DCE and the more toxic VC; however, the desired end products are ethene, ethane, and ultimately CO₂.

This biotransformation sequence may slow or stop at DCE, with build-up of DCE concentrations (known as “DCE stall”). In some cases, VC formed from DCE may persist, if reducing conditions are not strong enough. However, VC is biodegraded under aerobic conditions more than the other chlorinated ethenes, raising the possibility of its biodegradation as it moves downgradient into a more aerobic environment. DCE and VC can be biotically transformed through several different mechanisms under either aerobic or anaerobic conditions (Table 3).

Relevant coupled redox half reactions (modified from Wiedemeier et al., 1998) for the PCE/TCE reductive dechlorination sequence, and associated stoichiometric concentration changes are:



The predominant biotic transformation of the parent compounds PCE and TCE that occurs and that is desirable for remediation through NA is the reductive dechlorination sequence PCE → TCE → DCE → VC → non-toxic end products. However, sufficient electron donors need to be present, along with the requisite microbes. If not, the reductive dechlorination sequence will be incomplete and result in persistence of one or more of the contaminants.

3.2.2 Factors influencing transformation to desired end product

The primary factors affecting the transformation of PCE and TCE to innocuous end products (i.e., CO₂ and Cl⁻), and without accumulation of *c*-DCE and/or VC, are (1) the presence of sufficient e⁻ donor to drive the redox conditions to the most efficient reductive dechlorination processes, and (2) the presence of the microbes necessary for the complete transformation.

The predominant redox condition affects the occurrence, type, and efficiency of the biotransformation reaction which will occur for the chlorinated ethenes. A highly reducing condition may be necessary for efficient reductive dechlorination of VC to ethene. Halorespiration is most efficient under sulfate-reducing and methanogenesis, less efficient under iron-reducing, and questionable under manganese-reducing conditions (Bradley and Chapelle, 2010). Halorespiration does not occur under aerobic or nitrate-reducing conditions (North Wind, 2003), but TCE reductive dechlorination to *cis*-DCE can occur under iron-reducing conditions (Bradley and Chapelle, 2010). At contaminated sites where either geochemical conditions are not appropriate for complete anaerobic biodegradation of chlorinated ethenes or *Dehalococcoides ethenogenes* microorganisms capable of carrying out the transformation to ethene are not present, direct aerobic biodegradation of VC offers a remedial solution for persistent VC plumes that are not amenable to the anaerobic process of reductive dechlorination.

The final e⁻ donor (H₂) for the halorespiration process to occur is produced through fermentation of organic compounds. As discussed earlier, sufficient e⁻ donors must also be available for the redox conditions to reach those in which reductive dechlorination occurs. At many sites, the initial e⁻ donor (from which the H₂ ultimately comes from) is not identified, unless there is a petroleum hydrocarbon (i.e., e⁻ donor) plume commingled with the chlorinated solvent plume. Otherwise, the e⁻ donor may be simply identified as dissolved TOC.

The presence of the appropriate microbes, specifically *Dehalococcoides ethenogenes* (DHC), is required for

Table 3a. Compilation of compilations of chlorinated solvent biotic transformation first-order rate constants.

Contaminant: PCE										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Field	Reductive dechlorination	0.0022	0.0025	0.0030	0.0047	0.0066	0.0038	3	Aziz et al. 2000	Table B-1. Used Biochlor with rates from AFCEE database of 24 sites.
Field	Not specified			0.003					Aziz et al. 2000	Table 12. Median of field values. Cites Weidemeier et al. 1999.
Lab	Not specified	0.0381				0.0381			Aziz et al. 2000	Table 12. Range of laboratory values. Cites Weidemeier et al. 1999.
Lab and Field	Anaerobic	0		0.00186		0.071			HydroGeoLogic, Inc. 1999	Table 2.1. Update of Aronson and Howard 1997.
Field	Methanogenic	0.0007		0.0007		0.034	0.0029	5	HydroGeoLogic, Inc. 1999	Table E-12
Lab	Methanogenic	0		0.0084		0.071	0.0265	3	HydroGeoLogic, Inc. 1999	Table D-12
Field	Sulfate reducing	0.0035		0.0041		0.0046	0.0041	2	HydroGeoLogic, Inc. 1999	Table E-12
Lab	Sulfate reducing	0		0.0065		0.013	0.0204	3	HydroGeoLogic, Inc. 1999	Table D-12
Field	Anaerobic						0.0029	16	Lawrence 2006	Table 15. Mean of field/in situ studies. Cites Aronson and Howard 1997.
Lab and Field	Anaerobic	0.0002				0.0029		36	Lawrence 2006	Table 15. Mean or range for all studies. Cites Aronson and Howard 1997.
Field	Not specified	0.0000	0.0005	0.0006	0.0007	0.0027		9	Newell et al. 2006	Table 8. Rate constants are from concentration vs. time at a point.
Lab and Field	All studies	0	0	0.009	0.079	0.410	0.051	50	Suarez and Rifai 1999	Table 8
Field	Aerobic oxidation	0				0	0	3	Suarez and Rifai 1999	Table 7
Lab	Aerobic oxidation	0				0.004	0.001	7	Suarez and Rifai 1999	Table 7
Lab and Field	Aerobic oxidation	0	0	0	0.002	0.004	0.001	10	Suarez and Rifai 1999	Table 8

Table 3a. continued...

Lab	Aerobic cometabolism	0				0.054	0.025	3	Suarez and Rifai 1999	Table 7
Field	Reductive dechlorination	0				0.080	0.010	13	Suarez and Rifai 1999	Table 7
Lab	Reductive dechlorination	0				0.410	0.101	23	Suarez and Rifai 1999	Table 7
Lab and Field	All studies	0	0.002	0.004	0.050	1.96	1.41	61	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: nitrate-reducing						0	3	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: iron-reducing						0.004	2	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: methanogenesis	0	0.013	0.080	0.147	0.410	0.100	22	Suarez and Rifai 1999	Table 8
Field	Anaerobic	0.00019				0.0033	0.0029	16	Weidemeier et al. 1999	Table 6-7. Mean is from field/in situ studies. Min and max are "recommended" rate constants. Cites Aronson and Howard 1997.
Contaminant: TCE										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Field	Reductive dechlorination	0.0008	0.0014	0.0033	0.0066	0.0088	0.0041	10	Aziz et al. 2000	Table B-1. Used Biochlor with rates from AFCEE database of 24 sites.
Field	Not specified			0.003					Aziz et al. 2000	Table 12. Median of field values. Cites Weidemeier et al. 1999.
Lab	Not specified	0.0001				0.3452			Aziz et al. 2000	Table 12. Range of laboratory values. Cites Weidemeier et al. 1999.
Lab and Field	Anaerobic	0.00082		0.0016		0.04			HydroGeoLogic, Inc. 1999	Table 2.1. Update of Aronson and Howard 1997.
Field	Methanogenic	0.0004		0.0006		0.0008	0.0013	6	HydroGeoLogic, Inc. 1999	Table E-15
Lab	Methanogenic	0.0020		0.0145		0.0400	0.0170	4	HydroGeoLogic, Inc. 1999	Table D-15
Field	Sulfate reducing	0.0001		0.0015		0.0071	0.0019	10	HydroGeoLogic, Inc. 1999	Table E-15

Table 3a. continued...

Lab	Sulfate reducing	0		0.0029		0.0110	0.0049	7	HydroGeoLogic, Inc. 1999	Table D-15
Field	Anaerobic						0.0025	30	Lawrence 2006	Table 15. Mean of field/in situ studies. Cites Aronson and Howard 1997.
Lab and Field	Not specified						0.0006	78	Lawrence 2006	Table 15. Mean or range for all studies. Cites Aronson and Howard 1997.
Field	Not specified	-0.0010	-0.0001	0.0003	0.0007	0.0016		13	Newell et al. 2006	Table 8. Rate constants are from concentration vs. time at a point.
Lab and Field	All studies	0				3.130	0.173	86	Suarez and Rifai 1999	Table 7
Field	Aerobic oxidation							2	Suarez and Rifai 1999	Table 7
Lab	Aerobic oxidation	0				0.028	0.006	10	Suarez and Rifai 1999	Table 7
Lab and Field	Aerobic oxidation	0	0	0	0.003	0.028	0.005	11	Suarez and Rifai 1999	Table 8
Field	Aerobic cometabolism	0.105				1.410	0.948	3	Suarez and Rifai 1999	Table 7
Lab	Aerobic cometabolism	0.024				1.650	0.509	14	Suarez and Rifai 1999	Table 7
Lab and Field	Aerobic cometabolism	0.024	0.2	0.26	0.88	1.650	0.586	17	Suarez and Rifai 1999	Table 8
Field	Aerobic/ Anaerobic							1	Suarez and Rifai 1999	Table 7
Field	Reductive dechlorination	0				0.023	0.003	32	Suarez and Rifai 1999	Table 7
Lab	Reductive dechlorination	0				3.130	0.196	24	Suarez and Rifai 1999	Table 7
Field	Anaerobic oxidation								Suarez and Rifai 1999	Table 7
Lab	Anaerobic oxidation								Suarez and Rifai 1999	Table 7
Lab and/or Field	Reductive dechlorination: iron-reducing	0	0.001	0.002	0.004	0.011	0.003	11	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: sulfate-reducing	0.002	0.005	0.008	0.018	0.023	0.011	7	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: methanogenesis	0	0.001	0.004	0.008	0.109	0.015	10	Suarez and Rifai 1999	Table 8

Table 3a. continued...

Lab and/or Field	Reductive dechlorination: mixed						0.001	2	Suarez and Rifai 1999	Table 8
Field	Anaerobic	0.00014				0.0025	0.0025	47	Weidemeier et al. 1999	Table 6-7. Mean is from field/in situ studies. Min and max are "recommended" rate constants. Cites Aronson and Howard 1997.
Contaminant: <i>cis</i> -DCE										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Lab	Not specified	0.0086				0.0256			Aziz et al. 2000	Table 12. Range of laboratory values. Cites Weidemeier et al. 1999.
Lab and Field	All studies	0				1.960	0.004	34	Suarez and Rifai 1999	Table 7
Field	Aerobic cometabolism	0.281				1.960	0.885	3	Suarez and Rifai 1999	Table 7
Lab	Aerobic cometabolism	0.081				0.434	0.187	2	Suarez and Rifai 1999	Table 7
Field	Aerobic/ Anaerobic	0				0.008	0	4	Suarez and Rifai 1999	Table 7
Field	Reductive dechlorination	0				0.130	0.002	17	Suarez and Rifai 1999	Table 7
Lab	Reductive dechlorination	0.001				0.200	0.014	8	Suarez and Rifai 1999	Table 7
Contaminant: DCE										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Field	Reductive dechlorination	0.0003	0.0019	0.0033	0.0060	0.0573	0.0096	9	Aziz et al. 2000	Table B-1. Used Biochlor with rates from AFCEE database of 24 sites.
Field	Not specified	0.0000	0.0000	0.0004	0.0000	0.0005		2	Newell et al. 2006	Table 8. Rate constants are from concentration vs. time at a point.
Contaminant: DCE (not <i>cis</i>)										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Lab and Field	All studies	0				1.150	0.149	27	Suarez and Rifai 1999	Table 7

Table 3a. continued...

Field	Aerobic cometabolism	0.390				1.150	0.720	4	Suarez and Rifai 1999	Table 7
Lab	Aerobic cometabolism	0				0.714	0.196	4	Suarez and Rifai 1999	Table 7
Field	Aerobic/ Anaerobic								Suarez and Rifai 1999	Table 7
Field	Reductive dechlorination	0.001				0.006	0.003	16	Suarez and Rifai 1999	Table 7
Lab	Reductive dechlorination	0.010				0.270	0.101	3	Suarez and Rifai 1999	Table 7
Contaminant: DCE (all isomers)										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Lab and Field	All studies	0	0.002	0.004	0.050	1.96	1.41	61	Suarez and Rifai 1999	Table 8
Lab and Field	Aerobic cometabolism	0	0.081	0.434	0.714	1.96	0.591	13	Suarez and Rifai 1999	Table 8
Lab and Field	Reductive dechlorination: iron-reducing	0	0.001	0.002	0.003	0.005	0.002	8	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: sulfate-reducing						0.045	3	Suarez and Rifai 1999	Table 8
Lab and Field	Reductive dechlorination: methanogenesis	0.002	0.007	0.016	0.058	0.200	0.047	8	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: mixed						0.001	2	Suarez and Rifai 1999	Table 8
Contaminant: VC										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Field	Reductive dechlorination	0.0011	0.0016	0.0047	0.0134	0.0334	0.0099	7	Aziz et al. 2000	Table B-1. Used Biochlor with rates from AFCCE database of 24 sites.
Field	Not specified			0.0079					Aziz et al. 2000	Table 12. Median of field values. Cites Weidemeier et al. 1999.
Lab	Not specified	0.0003				0.01			Aziz et al. 2000	Table 12. Range of laboratory values. Cites Weidemeier et al. 1999.
Lab and Field	Anaerobic	0		0.00405		0.0082			HydroGeoLogic, Inc. 1999	Table 2.1. Update of Aronson and Howard 1997.

Table 3a. continued...

Field	Methanogenic	0.0005		0.002		0.006	0.002	2	HydroGeoLogic, Inc. 1999	Table E-16
Lab	Methanogenic							0	HydroGeoLogic, Inc. 1999	Table D-16
Field	Sulfate reducing	0		0.0008		0.0013	0.0008	1	HydroGeoLogic, Inc. 1999	Table E-16
Lab	Sulfate reducing	0.0057		0.0076		0.0082	0.0076	2	HydroGeoLogic, Inc. 1999	Table D-16
Lab and Field	All studies	0	0.005	0.051	0.163	8.020	0.518	27	Suarez and Rifai 1999	Table 8
Field	Aerobic oxidation								Suarez and Rifai 1999	Table 7
Lab	Aerobic oxidation	0.043	0.064	0.091	0.114	0.125	0.087	4	Suarez and Rifai 1999	Table 8
Field	Aerobic cometabolism	1.500				1.960	1.730	2	Suarez and Rifai 1999	Table 7
Lab	Aerobic cometabolism	0.055				0.576	0.316	2	Suarez and Rifai 1999	Table 7
Lab and Field	Aerobic cometabolism	0.055	0.576	1.500	1.960	8.020	2.422	5	Suarez and Rifai 1999	Table 8
Field	Aerobic/ Anaerobic	0.001				0.009	0.004	3	Suarez and Rifai 1999	Table 7
Field	Reductive dechlorination	0				0.007	0.003	4	Suarez and Rifai 1999	Table 7
Lab	Reductive dechlorination	0				0.520	0.303	4	Suarez and Rifai 1999	Table 7
Lab	Anaerobic oxidation	0.008				0.120	0.049	6	Suarez and Rifai 1999	Table 7
Field and Lab	Anaerobic oxidation: iron- reducing	0.001	0.008	0.012	0.073	0.120	0.042	7	Suarez and Rifai 1999	Table 8
Field	Anaerobic	0.00033				0.0072	0.0079	19	Weidemeier et al. 1999	Table 6-7. Mean is from field/in situ studies. Min and max are "recommended" rate constants. Cites Aronson and Howard 1997.
Contaminant: TCA										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Field	Reductive dechlorination	0.0044	0.0055	0.0066	0.0077	0.0088	0.0066	2	Aziz et al. 2000	Table B-1. Used Biochlor with rates from AFCEE database of 24 sites.
Field	Not specified			0.0159					Aziz et al. 2000	Table 12. Median of field values. Cites Weidemeier et al. 1999.

Table 3a. continued...

Lab	Not specified	0.0099				0.0099			Aziz et al. 2000	Table 12. Range of laboratory values. Cites Weidemeier et al. 1999.
Lab and Field	Anaerobic	0		0.00355		0.041			HydroGeoLogic, Inc. 1999	Table 2.1. Update of Aronson and Howard 1997.
Field	Methanogenic	0		0.011		0.0	0.0182	5	HydroGeoLogic, Inc. 1999	Table E-13
Lab	Methanogenic	0.0034		0.0065		0.015	0.0065	2	HydroGeoLogic, Inc. 1999	Table D-13
Field	Sulfate reducing	0		0.0030		0.010	0.043	3	HydroGeoLogic, Inc. 1999	Table E-13
Lab	Sulfate reducing	0		0.0092		0.015	0.0064	3	HydroGeoLogic, Inc. 1999	Table D-13
Lab	Aerobic, 0.1 and 0.5 mg L ⁻¹ TCA	No biotransformation observed.						1	Klecka et al. 1999	Table 2. Used field soil and ground water.
Lab	Nitrate-reducing, 0.1 and 0.5 mg L ⁻¹ TCA	No biotransformation observed.						1	Klecka et al. 1999	Table 2. Used field soil and ground water.
Lab	Sulfate reducing, 0.1 mg L ⁻¹ TCA						0.0162	1	Klecka et al. 1999	Table 2. Used field soil and ground water. Pseudo-first-order rate constant.
Lab	Sulfate reducing, 0.5 mg L ⁻¹ TCA						0.0035	1	Klecka et al. 1999	Table 2. Used field soil and ground water. Pseudo-first-order rate constant.
Lab	Methanogenic, 0.1 mg L ⁻¹ TCA						0.0142	1	Klecka et al. 1999	Table 2. Used field soil and ground water. Pseudo-first-order rate constant.
Lab	Methanogenic, 0.5 mg L ⁻¹ TCA						0.0033	1	Klecka et al. 1999	Table 2. Used field soil and ground water. Pseudo-first-order rate constant.
Lab and Field	Anaerobic	0.239				0.3013		28	Lawrence 2006	Table 15. Mean or range for all studies. Cites Aronson and Howard 1997.
Field	Not specified	0.0006	0.0007	0.0009	0.0015	0.0017		6	Newell et al. 2006	Table 8. Rate constants are from concentration vs. time at a point.
Lab	Sulfate reducing	0.0003					0.0013	1	Scheutz et al. 2011	Table 3. Pseudo-first-order rate constant. 1,1-DCA was end product.

Table 3a. continued...

Lab	Methanogenic	0.0038				0.0148		1	Scheutz et al. 2011	Table 3. Pseudo-first-order rate constant. 1,1-DCA was end product.
Lab and Field	All studies	0	0	0.010	0.195	2.330	0.261	47	Suarez and Rifai 1999	Table 8
Field	Aerobic oxidation							2	Suarez and Rifai 1999	Table 7
Lab	Aerobic oxidation	0				0.022	0.003	9	Suarez and Rifai 1999	Table 7
Field and Lab	Aerobic oxidation	0	0	0	0	0.022	0.002	11	Suarez and Rifai 1999	Table 8
Field	Aerobic cometabolism								Suarez and Rifai 1999	Table 7
Lab	Aerobic cometabolism	0	0.002	0.013	0.038	1.180	0.247	5	Suarez and Rifai 1999	Table 8
Field	Aerobic/ Anaerobic								Suarez and Rifai 1999	Table 7
Field	Reductive dechlorination	0				0.125	0.029	10	Suarez and Rifai 1999	Table 7
Lab	Reductive dechlorination	0				2.330	0.551	21	Suarez and Rifai 1999	Table 7
Lab and/or Field	Reductive dechlorination: nitrate-reducing	0	0	0	0	0	0	4	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: sulfate-reducing						0.010	2	Suarez and Rifai 1999	Table 8
Lab and/or Field	Reductive dechlorination: methanogenesis	0.003	0.025	0.125	0.880	2.330	0.498	17	Suarez and Rifai 1999	Table 8
Field	Anaerobic	0.0013				0.01	0.016	15	Weidemeier et al. 1999	Table 6-7. Mean is from field/in situ studies. Min and max are "recommended" rate constants. Cites Aronson and Howard 1997.
Contaminant: 1,1-DCA										
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Field	Reductive dechlorination	0.0005	0.0005	0.0008	0.0019	0.0033	0.0014	3	Aziz et al. 2000	Table B-1. Used Biochlor with rates from AFCEE database of 24 sites.
Lab	Not specified	0.0044				0.0096			Aziz et al. 2000	Table 12. Range of laboratory values. Cites Weidemeier et al. 1999.

Table 3a. continued...

Contaminant: DCA (all isomers)											
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes	
		Min	25 th	Median	75 th	Max	Mean	n, number of studies			
Lab and Field	All studies	0	0	0.001	0.014	0.131	0.017	25	Suarez and Rifai 1999	Table 8	
Lab	Aerobic oxidation							2	Suarez and Rifai 1999	Table 7	
Lab	Aerobic cometabolism	0.014	0.019	0.047	0.123	0.131	0.067	5	Suarez and Rifai 1999	Table 8	
Field	Aerobic/ Anaerobic								Suarez and Rifai 1999	Table 7	
Field	Reductive dechlorination	0				0.011	0.002	16	Suarez and Rifai 1999	Table 7	
Lab	Reductive dechlorination	0.028				0.044	0.036	2	Suarez and Rifai 1999	Table 7	
Field	Reductive dechlorination: sulfate-reducing	0	0	0	0.001	0.028	0.003	13	Suarez and Rifai 1999	Table 8	
Field	Reductive dechlorination: methanogenesis						0.006	3	Suarez and Rifai 1999	Table 8	
Contaminant: CA											
No experiments or results reported.											
Contaminant: Dioxane											
Type of Study	Biogeochemical Conditions	First-Order Rate Constants (day ⁻¹)							Reference	Notes	
		Min	25 th	Median	75 th	Max	Mean	n, number of studies			
Field	Methanogenic, <15°C, pH 6-8			0			0	1	HydroGeoLogic, Inc. 1999	Table E-39	
Lab	Aerobic, 4 or 14°C, 50 mg L ⁻¹ dioxane	No significant dioxane biodegradation.							1	Li et al. 2010	Used microcosms without bioaugmentation or substrate addition, to simulate natural attenuation conditions. High concentration simulated source zone.
Lab	Aerobic, 14°C, 500 µg L ⁻¹ dioxane, CB1190 bacterial strain						0.1	1	Li et al. 2010	Used microcosms with bioaugmentation and substrate addition. Low concentration simulated leading edge of plume.	

Table 3a. continued...

Lab	Aerobic, 14°C, 500 µg L ⁻¹ dioxane, DVS 5a1 bacterial strain						0.4	1	Li et al. 2010	Used microcosms with bioaugmentation and substrate addition. Low concentration simulated leading edge of plume.
-----	---	--	--	--	--	--	-----	---	----------------	--

Notes:

1. Rows without rate constant data indicate biogeochemical conditions where no data was provided, and are left in for comparison to other conditions.
2. Description of biogeochemical conditions is as specific as was reported in the cited Reference.

Table 3b. Chlorinated solvent biotic transformation zero-order rates.										
Contaminant: PCE										
Type of Study	Biogeochemical Conditions	Zero-Order Rate ($\mu\text{g L}^{-1} \text{day}^{-1}$)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies or rates		
Lab	Reductive dechlorination	13	288	577	1040	19800	1863	29	Suarez and Rifai 1999	Table 6
Contaminant: TCE										
Type of Study	Biogeochemical Conditions	Zero-Order Rate ($\mu\text{g L}^{-1} \text{day}^{-1}$)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies or rates		
Lab	Reductive dechlorination	314	511	760	1297	7490	1740	7	Suarez and Rifai 1999	Table 6
Contaminant: cis-DCE										
Type of Study	Biogeochemical Conditions	Zero-Order Rate ($\mu\text{g L}^{-1} \text{day}^{-1}$)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies or rates		
Lab	Reductive dechlorination	13	183	511	1318	16958	1854	18	Suarez and Rifai 1999	Table 6
Contaminant: DCE (not cis)										
Type of Study	Biogeochemical Conditions	Zero-Order Rate ($\mu\text{g L}^{-1} \text{day}^{-1}$)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies or rates		
Lab	Reductive dechlorination	9	23	250	1385	3470	850	8	Suarez and Rifai 1999	Table 6
Contaminant: VC										
Type of Study	Biogeochemical Conditions	Zero-Order Rate ($\mu\text{g L}^{-1} \text{day}^{-1}$)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies or rates		
Lab	Reductive dechlorination	2	6	11	75	495	107	9	Suarez and Rifai 1999	Table 6
Contaminant: Dioxane										
Type of Study	Biogeochemical Conditions	Zero-Order Rate ($\mu\text{g L}^{-1} \text{day}^{-1}$)							Reference	Notes
		Min	25 th	Median	75 th	Max	Mean	n, number of studies		
Lab	Aerobic, 14°C, 500 $\mu\text{g L}^{-1}$ dioxane						1.4	1	Li et al. 2010	Used microcosms without bioaugmentation or substrate addition, to simulate natural attenuation conditions. Low concentration simulated leading edge of plume.

the complete reductive dechlorination sequence of PCE to ethene (Figure A). A detailed discussion of the role of DHC is provided by Maymó-Gatell (1997). If DHC is not present, other microbes may partially dechlorinate the PCE and/or TCE to DCE and/or VC. If yet other appropriate microbes are present, the products of the PCE and/or TCE dechlorination (i.e., *c*-DCE and/or VC) could be further dechlorinated. Extreme pH or temperatures out of the range suitable for efficient microbial activity may inhibit PCE and/or TCE biotransformation. A pH range of between pH 5 and 9 has been cited (Wiedemeier et al., 1999) for reductive transformation, as a screening measure.

Co-contaminants or interfering compounds may have an inhibiting effect on biotransformation of a target chlorinated solvent. These compounds may include solvent stabilizers [e.g., up to about 5% 1,4-dioxane in TCA, or a large number of compounds up to a total of about 1% in TCE (Mohr 2001)]. During biodegradation of PCE, Aulenta et al. (2006) reported that the presence of a co-contaminant 1,1,2,2-tetrachloroethane (TCA) negatively impacted the dechlorination of VC to ethene by DHC species. Carbon tetrachloride (CT), but not the TCA, however, inhibited PCE and VC biodegradation by the same culture, even though it was able to cometabolize both CT and TCA (literature cited by Aulenta et al., 2006). TCA completely inhibited dechlorination of VC to ethene in presence of a TCE-dechlorinating culture as reported by Duhamel et al. (2002) and similarly, the reductive dechlorination of PCE, TCE, *cis*-DCE, and/or VC was partially or completely inhibited by chloroform (CF) with a dechlorinating culture related to DHC (Duhamel et al., 2002).

3.2.3 Geochemical conditions and contaminant concentrations (required measurements)

Geochemical conditions (e.g., redox conditions) strongly influence which transformation processes will occur and to what extent, as discussed above. The naturally occurring e^- acceptor(s) supply can also impact the biotransformation process due to competition with the chlorinated ethene e^- acceptor. The contaminant concentration may become important in terms of microbial toxicity and e^-

acceptor supply as mentioned in section 3.1.2. Aulenta et al. (2006) identified some PCE- and TCE-dehalorespiring bacterial strains that are inhibited by PCE concentrations over 0.1 to 0.7 mmol L⁻¹.

3.2.4 Indicator species - biological (required measurements)

Dehalococcoides ethenogenes strain 195 (DHC) is recognized (Maymó-Gatell, 1997; Maymó-Gatell et al., 1999) as being capable of completely degrading PCE to ethene, through the intermediate products TCE, *cis*-DCE, *trans*-DCE, VC, and 1,1-DCE. Other *Dehalococcoides* strains and known microbial consortia (Wiedemeier et al., 1998; and Aulenta et al., 2006) that are capable of biotransforming portions of the chlorinated ethene degradation sequence are identified in Figure 3.1. Mixed cultures that can reductively dechlorinate DCE and VC are also described by Bradley and Chapelle (2010). Molecular biological tools (MBTs) are available to examine the presence of degradative enzymes (*tceA*, *vcrA*, and *bvcA*) (Figure 3.2). *vcrA* activity is required for complete degradation of PCE to ethene through an energy yielding pathway. A combination of *tceA* and *bvcA* may lead to complete degradation; however, through cometabolic reactions that are usually slower than that observed for *vcrA*. Molecular biological tools are described in depth in ITRC (2011).

3.2.5 Rates of transformation

The presentation, analysis, and use of biotransformation rate data is complicated by the manner in which these data are presented in the literature, since the kinetics of chlorinated ethene solvent biotransformation in field and laboratory studies has been described using Monod kinetics, Michaelis-Menten kinetics, zero-order rates, and by first-order rate constants (Rifai et al., 2001; Aulenta et al., 2006). Rate information resulting from laboratory microbial degradation experiments may be described using different parameters than the simple first-order rates and rate constants that can be derived from field measurements. Further, summaries of kinetic parameter values from the literature often are not accompanied by a full range of geochemical and hydrogeological parameter values that could help in understanding or modeling MNA at a field site.

Microbiology of Reductive Dechlorination of Chloroethenes

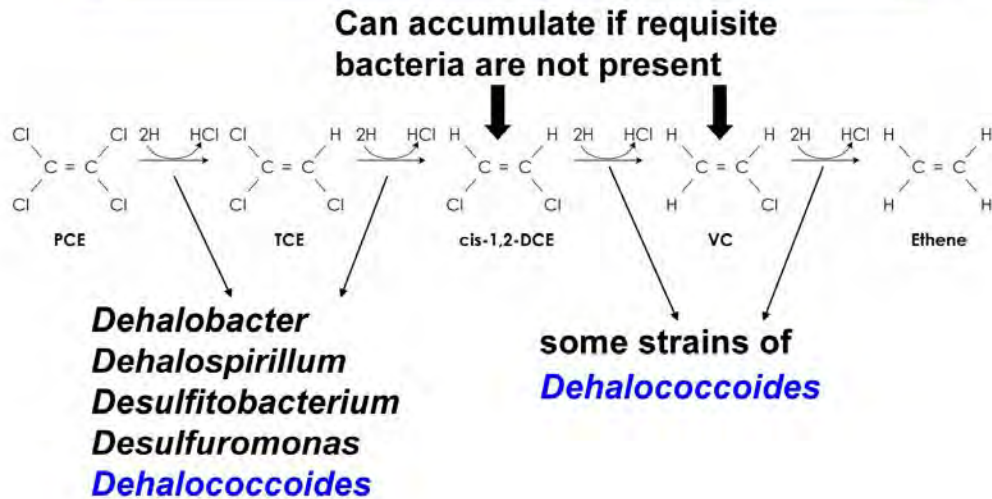


Figure 3.1. Bacterial species involved in dechlorination processes.

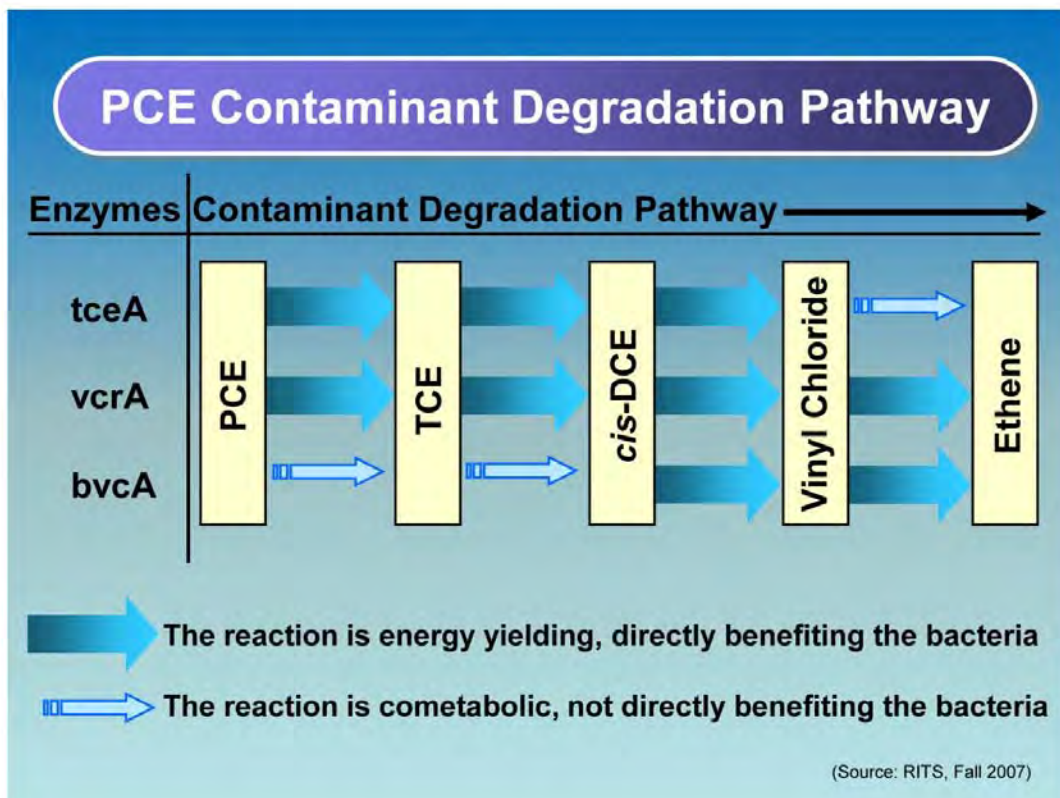


Figure 3.2. Enzymes involved in dechlorination processes.

Table 3a provides a sample of first-order rate constants from a number of literature compilations, as well as from some individual studies. Table 3b provides some zero-order rates.

3.2.6 Case studies

TCE is found at 1034 National Priority List (NPL, Superfund) Sites, while PCE is found at 938 NPL sites (ATSDR, 2011). The great majority of these sites where remedial activities have occurred have used “active” remedial technologies, rather than the “passive” MNA technology. Where MNA has been used, it has almost always been a component of the overall remedy, in combination with other technologies used prior to MNA or for other portions of the site. It is difficult to identify many sites where MNA has been the sole remedial technology (although the 23 PCE, TCE, or TCA sites evaluated by Newell et al. (2006), were reported to have not had any other remediation or source depletion activities). For many sites, this means that the NA processes may have been likely to be impacted by the other activities. Nonetheless, there have been numerous sites where successful, comprehensive MNA studies have been conducted and extensive information obtained on the NA processes and rates (whether or not MNA was ultimately selected and was successful as a remedy). The discussions throughout this document have alluded to MNA sites; the references cited can be referred to for further information on these studies. A sampling of sites includes the Twin Cities Army Ammunition Plant Superfund Site, MN for TCE and TCA; Air Force Plant 44, Tucson International Airport Area Superfund Site, Tucson, AZ for TCE and TCA; Picatinny Arsenal, NJ for TCE; Altus AFB, Altus, OK for TCE; Plattsburgh AFB, Plattsburgh, NY for TCE; Dover AFB Superfund Site, Area 6, Dover, DE; Lakehurst NAES Superfund Site, Lakehurst, NJ; Moffett Field Superfund Site, CA; St. Joseph Superfund Site, MI; and England AFB, LA.

3.3 TCA

3.3.1 Processes and pathways

Biotic transformation of TCA has many similarities with biotic transformation of PCE and TCE. This section focuses on significant differences in processes for TCA.

The biotransformation processes for TCA are shown in Table 3, with the most significant process being reductive dechlorination via growth-supporting halo-respiration (i.e., with TCA as the electron acceptor) (Scheutz et al, 2011). Under anaerobic methanogenic conditions, TCA is reductively dechlorinated (relatively faster) to 1,1-DCA, which is then dechlorinated (relatively slower) to chloroethane (CA). Either of the two degradation products can be the end product, depending on the subsurface microbiological and/or geochemical conditions, although CA has been observed to be the most common end product (Scheutz et al., 2011). Some mineralization of each of these compounds may occur, although it is likely to be minor (Vogel and McCarty, 1987; Scheutz et al., 2011).

Aerobic and anaerobic cometabolic dechlorination of TCA and 1,1-DCA can occur, but are not significant in terms of using MNA as a remedy for TCA (Scheutz et al, 2011). Direct aerobic oxidation of CA (but not TCA or 1,1-DCA) has been reported (Scheutz et al., 2011).

3.3.2 Factors influencing transformation to desired end product

The factors affecting the transformation of TCA to innocuous end products (i.e., ethene, or ultimately to CO₂ and Cl⁻), without accumulation of CA are somewhat different than the factors that impact PCE and TCE degradation to those end products. While the presence of sufficient e⁻ donor to drive the subsurface to methanogenic conditions and the appropriate microbes are necessary for transformation of the individual contaminant, there is not one sole set of conditions where complete dechlorination of TCA to innocuous end products occurs (as with methanogenic conditions and the presence of DHC for PCE dechlorination). TCA to CA dechlorination will occur under one set of conditions (methanogenic with the presence of the appropriate *Dehalobacter* bacteria), while CA will be degraded to the desired end products under a different set of conditions, through aerobic oxidation in the presence of sufficient dissolved oxygen and the appropriate aerobic microbes (Scheutz et al., 2011). Known microbial cultures are unable to completely dechlorinate TCA to ethane (Scheutz et al., 2011).

The presence of CT and TCA inhibited the biotransformation of each other under anaerobic methanogenic conditions (Adamson and Parkin, 1999).

3.3.3 Geochemical conditions and contaminant concentrations (required measurements)

As with PCE and TCE, the redox conditions will strongly influence what transformation processes will occur and their extent. Since the TCA reductive dechlorination product CA can be aerobically oxidized, identification of downgradient zones of sufficient dissolved oxygen, and the evaluation of the migration pathway of the CA, will be important to help assure that this degradation product does not persist.

3.3.4 Indicator species - biological (required measurements)

As with PCE and TCE, the presence of suitable microbes with the ability to transform TCA is necessary, specifically, the appropriate *Dehalobacter* species for the reductive dechlorination of TCA to 1,1-DCA and/or CA.

3.3.5 Rates of transformation

TCA halorespiration (and anaerobic cometabolic transformation) has been described using pseudo-first-order kinetics (Scheutz et al., 2011), and with Michaelis-Menten model parameters and first-order rate constants (Rifai et al., 2001). Table 3a provides a sample of first-order rate constants from a number of literature compilations, as well as from some individual studies. Table 3b provides some zero-order rates.

3.3.6 Case studies

TCA is found at 791 NPL Sites (ATSDR, 2011). Many of these sites that have TCA also have PCE and/or TCE. One well-studied TCA site is the Twin Cities Army Ammunition Plant, MN (e.g., Wilson 2010). Scheutz et al. (2011) discuss TCA biotransformation under enhanced reductive dechlorination (ERD) at 18 sites where both TCA and chloroethenes were found, and four sites with just TCA. Although these sites used the active remedial technology of ERD, and not MNA, baseline data was collected prior to ERD implementation and indicated the potential for some

anaerobic dechlorination of the TCA via NA. Further information on these, and other sites, can be found in the cited references and may be available in a web appendix to this document.

3.4 Dioxane

3.4.1 Processes and pathways

Dioxane biodegradation occurs through oxidation, under aerobic conditions, in both growth-supporting (i.e., as primary substrate) and non-growth-supporting (i.e., cometabolic) processes involving certain monooxygenase enzymes. Three bacterial strains and one fungus have been identified that use dioxane for growth, while a larger number of bacteria and one fungus have been reported to degrade dioxane in the presence of an alternate substrate (i.e., non-growth-supporting; cometabolic) such as methane. The dioxane degradation pathway proceeds to complete mineralization. The initial degradation step is rate-limiting, with subsequent degradation steps being fast. Intermediate degradation products have been identified (including ethylene glycol); however, these products are further degraded and mineralization ultimately occurs (Mahendra and Alvarez-Cohen, 2006; Mahendra et al., 2007; Mora and Chiang, 2011). This suggests that undesirable degradation products will not occur or persist.

Dioxane biodegradation in laboratory experiments was described by Monod kinetics (Mahendra and Alvarez-Cohen, 2006) and by either zero-order kinetics for “natural attenuation” treatment or first order for bioaugmented treatments (Li et al., 2010), as shown in Table 3a and b..

3.4.2 Factors influencing transformation to desired end product

A variety of bacterial strains were able to use potential co-contaminants as growth substrates for the cometabolism of dioxane under laboratory conditions, including toluene, tetrahydrofuran (THF), MTBE, and methane (Mahendra and Alvarez-Cohen, 2006). Although acetylene inhibited biodegradation of dioxane as a growth substrate, after its removal and when an alternate substrate was supplied, the ability to biodegrade dioxane was restored (Mahendra and Alvarez-Cohen, 2006).

Li et al. (2010) simulated natural attenuation conditions in laboratory microcosms to investigate dioxane biodegradation at temperatures (4 and 14 °C) that are lower than the typical laboratory conditions (>20 °C). They also studied the impact of dioxane concentration, using higher concentrations (50 mg L⁻¹) to represent a source zone, and lower concentrations (500 µg L⁻¹) to represent the leading edge of a plume. No significant biodegradation occurred at either temperature with the higher 50 mg L⁻¹ dioxane concentration. However, at the lower 500 µg L⁻¹ dioxane concentration, significant biodegradation was observed, with dioxane decreasing from 500 to 130 µg L⁻¹ in six months.

3.4.3 Geochemical conditions and contaminant concentrations - required measurements

Dioxane biodegradation occurs under aerobic conditions, requiring the presence of molecular oxygen (Mahendra and Alvarez-Cohen, 2006), although Mohr et al. (2010) cited laboratory studies in one investigation that anaerobic biodegradation of dioxane occurred under iron-reducing conditions. Field measurements and identification of the aerobic and anaerobic zones at a site are likely to indicate where dioxane biodegradation is possible.

A wider variety of microbes are capable of dioxane cometabolism than use it as a primary growth substrate (Mahendra and Alvarez-Cohen, 2006). Therefore, the identification of a primary substrate source, such as methane, THF, or other cyclic ethers (Mora and Chiang, 2011) should provide additional supporting evidence for the potential occurrence of NA via biotic transformation.

For all the compounds discussed in this document, the contaminant concentration at a number of longitudinal locations in a plume is an obvious measurement, not only for calculation of attenuation rates, but also in terms of potential toxicity issues. There appears to be very limited literature on microbial toxicity due to high dioxane concentrations; however, Li et al. (2010) reported that significant dioxane biodegradation occurred at 500 µg L⁻¹, but not at 50 mg L⁻¹. The number of measurement locations is site-specific.

3.4.4 Indicator species - required biological measurements

Research has suggested that dioxane is biodegraded by *Pseudonocardia dioxanivorans* CB1190, *Pseudonocardia benzenivorans* B5, and *Rhodococcus* strain 219 as a sole source of carbon and energy (Mahendra and Alvarez-Cohen, 2006). As apparent, only a limited number of microbes are capable of utilizing dioxane as a growth substrate. Thus, the identification of the known dioxane-degrading microbes and even more significantly, confirmation of their monooxygenase enzymatic activity is the most important evidence for potential MNA at a specific site. As indicated earlier, dioxane can also be cometabolized by a larger number of bacterial species, so the identification of those bacteria could be advantageous.

3.4.5 Rates of transformation

There has been very little investigation, determination, or reporting of dioxane biotic transformation rates under field conditions. Mohr et al. (2010) summarize laboratory research and present Monod kinetic parameter values for 1,4-dioxane biodegradation, including those in Mahendra and Alvarez-Cohen (2006).

A zero-order rate of 1.4 ± 0.02 µg L⁻¹ day⁻¹ was calculated for biodegradation of 500 µg L⁻¹ dioxane at 14 °C in laboratory microcosms containing soil and ground water from a dioxane-contaminated site, under simulated natural attenuation conditions (i.e., no biostimulation or bioaugmentation) (Li et al., 2010).

3.4.6 Case studies

Dioxane has not been the primary or sole target for MNA at contaminated sites, and has seldom been included in the evaluation of MNA at chlorinated solvent sites. The limited literature on dioxane and MNA at contaminated sites is summarized below.

3.4.6.1. Mohr et al. (2010) presented seven case studies of dioxane site investigations and remediation. MNA does not appear to have been considered for all or most of the sites. Each site had some active remedial technology implemented. The off-site plume beyond a ground-water extraction system at one site may have been considered for MNA; however, it was believed that any NA would

be via dispersion, diffusion, and dilution rather than via dioxane transformation.

3.4.6.2. Biotic NA of a very large dioxane plume at a site near Wilmington, NC was hypothesized by Chiang et al. (2008). The dioxane plume was the result of releases during chemical manufacturing activities at the site; the dioxane was not associated with chlorinated solvents. Chiang et al. (2008) stated that the results from a calibrated model, and dioxane concentration declines observed during long-term monitoring, indicated that *“the rate of dioxane attenuation...cannot be explained solely due to nonbiological and abiotic attenuation mechanisms”*, which suggested that there were biological *“degradation mechanisms that have limited the migration rate and size of the plume”*. They also stated that the *“extent of negative ORP and ferrous iron”* correlated with the locations of reduction in dioxane concentrations, *“suggesting the potential for biological attenuation”*. However, no direct evidence such as intermediate products or presence of dioxane-degrading microbes were observed. Jenkins et al. (2009) discussed the weaknesses in Chiang et al.’s (2008) use of limited data and modeling as the primary evidence of in situ biodegradation, concluding that this site was not likely to be a good candidate for MNA. The inappropriate or premature conclusion that NA via biodegradation was occurring at this site indicates the need for a robust site characterization and collection of the appropriate parameters.

3.4.6.3. An investigation of NA was conducted for a large dilute TCE and 1,4-dioxane plume at the Air Force Plant 44, Tucson International Airport Area Superfund Site, Tucson, AZ. Both TCE and TCA had been used at the site; however, the main contaminants were the TCE (maximum of 520 $\mu\text{g L}^{-1}$) and dioxane (maximum of 1,110 $\mu\text{g L}^{-1}$), which was present due to the use of TCA. The site ground water was aerobic, with low TOC. The plumes appeared to be shrinking, and MNA was considered for part of the site remedial strategy (Mora and Chiang, 2011). Pump-and-treat, with reinjection of the treated ground water around the plume perimeter, was started in 1987 (Chiang

et al., 2012); thus, the site has an active remedial strategy that complicates calculation of dioxane attenuation rates due solely to NA.

Site ground-water samples were tested using stable isotope probing (SIP) with ^{13}C -dioxane baited bio-traps. Phospholipid fatty acid analysis (PLFA) indicated that ^{13}C was incorporated into microbial biomass, detection of ^{13}C in CO_2 indicated that some dioxane was mineralized, and quantitative real time polymerase chain reaction (qPCR) indicated the presence of the necessary bacteria and enzymes. Enzyme activity probe analysis indicated that the necessary toluene oxygenase enzymes were present and active. This was the first field study to directly indicate the natural biodegradation of dioxane in the context of subsurface NA; however, the analyses used in the study were unable to address the determination of attenuation rates (Mora and Chiang, 2011; Chiang et al., 2012).

4. ABIOTIC TRANSFORMATIONS

The following discussion provides an overview of current understanding of the pathways and geochemical conditions controlling the abiotic transformation of the contaminants of interest: PCE, TCE, and 1,1,1-TCA. This discussion will not address 1,4-dioxane due to the fact that there is no evidence in the literature indicating that it is susceptible to abiotic degradation.

The transformation of chlorinated solvents in the subsurface is inextricably linked to a set of complex biological, chemical and geochemical processes. Overall transformation rate constants for chlorinated solvents represent a contribution from both abiotic and biological processes:

$$k_{\text{trans}} = k_{\text{abiotic}} + k_{\text{biol}}$$

Each of the rate constants represents the relative contribution of degradation processes, which depending on the chlorinated solvent, can include both abiotic reduction and hydrolysis.

$$k_{\text{abiotic}} = k_{\text{red}} + k_{\text{hyd}}$$

The relative contribution of these terms is dependent on the inherent reactivity of the chlorinated solvent and the geochemical conditions of the aquatic ecosystem of interest. The inherent reactivity is a reflection of the strength of C-Cl bonds and the reactivity of the abiotic reductants and nucleophiles present in the aquatic system of interest.

As discussed below, the relative contributions of k_{red} and k_{hyd} is dependent on the structure of the chlorinated solvent. PCE and TCE, are susceptible to only abiotic reduction (i.e., $k_{abiotic} = k_{red}$), whereas the abiotic degradation 1,1,1-TCA is susceptible to both abiotic reduction and hydrolysis. The rate constant for hydrolysis is dependent on the neutral and acid- and base-catalyzed processes described by:

$$k_{hyd} = k_{base}[\text{substrate}][\text{OH}^-] + k_n[\text{substrate}] + k_{acid}[\text{substrate}][\text{H}^+]$$

Consequently, based on values for the individual rate constants, which can be measured relatively easily in the laboratory, and the pH of the reaction system of interest, it is a fairly straight forward process to calculate the overall hydrolysis rate constant, k_{hyd} .

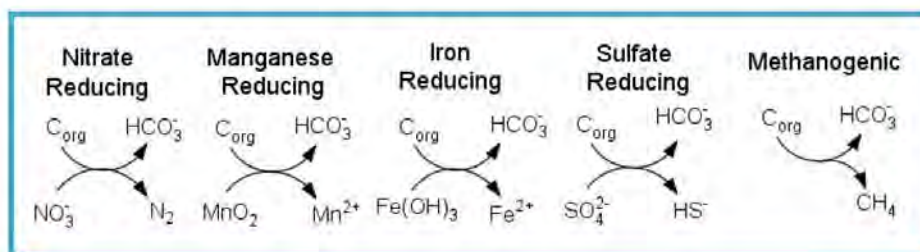
The situation for predicting rate constants for abiotic reduction is much more challenging, primarily due to the fact that numerous abiotic reductants may contribute to the overall rate constant, k_{red} , the formation and reactivity of which will vary as a function of geochemical conditions. Furthermore, our knowledge base at this point is dependent primarily on laboratory studies of abiotic model systems and anaerobic microcosms designed to mimic naturally occurring conditions in the subsurface. The extent to which these results apply to natural systems not fully understood at this time.

The formation of abiotic reductants in anaerobic aquifer systems is the result of the biologically-

mediated oxidation of bioavailable organic matter resulting in the reduction of various e^- acceptors (e.g., Fe(III) oxides and sulfate) as described by Terminal Electron Accepting Processes (TEAPs). The resulting redox zones in anaerobic subsurfaces can be mapped by the measurement of solution phase species (e.g., Mn^{2+} , Fe^{2+} , H_2S and CH_4) resulting from reduction of the e^- acceptors (Bjerg, Ruggie et al. 1995; Chapelle, McMahon et al. 1995; Jeong and Hayes 2007; Himmelheber, Taillefert et al. 2008; Himmelheber, Thomas et al. 2008). Additional information concerning the determination of redox zones in anaerobic aquifers is provided from the measurement of dissolved H_2 concentrations based on a gas stripping procedure (Lovley, Chapelle et al. 1994). Each TEAP has a H_2 -utilizing efficiency resulting in characteristic concentrations of dissolved H_2 (i.e., $< 0.1 \text{ nM H}_2$ for Nitrate reducing zones; 0.2 to 0.8 nM H_2 for iron reducing zones; 1 to 4 nM H_2 sulfate reducing zones, and 5 to 15 nM H_2 methanogenic (Lovley and Goodwin 1988).

This concept provides a useful construct for the subsequent discussion of the formation of abiotic reductants in anaerobic subsurface systems. Although laboratory studies can be designed to mimic specific redox zones, their occurrence in natural systems is often complex with overlapping and/or completely mixed redox zones. One result of this scenario is the difficulty in identifying the predominant chemical reductants in these complex systems.

These reactive forms are primarily reactive surfaces such as surface complexed Fe(II) and reactive minerals such as green rusts and iron sulfides, all of which form as the result of reactions of high concentrations of ferrous iron and sulfide. These abiotic reductants that are known to form as a function of iron and sulfate redox zones are illustrated in Figure 4.1.



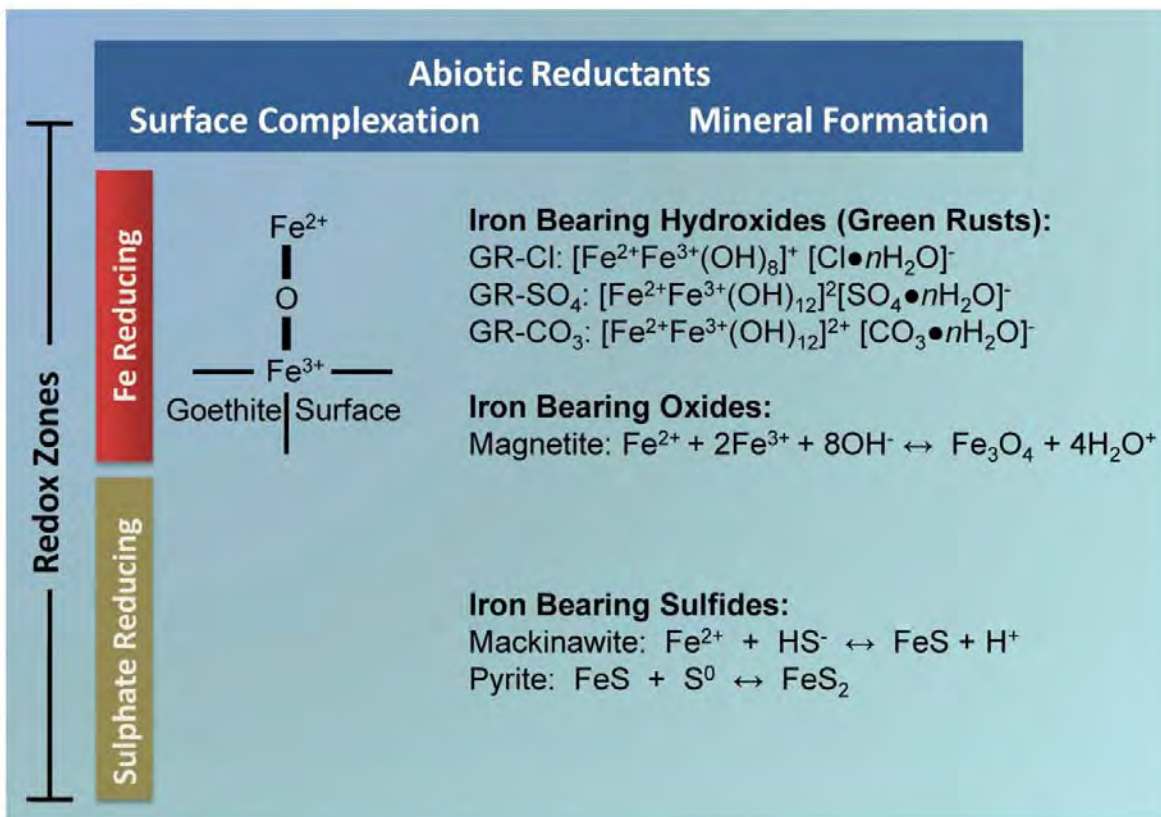


Figure 4.1. Formation of abiotic reductants as a function of iron and sulphate reducing zones.

4.1 PCE and TCE

4.1.1 Processes and Pathways

The abiotic reduction of chlorinated solvents has received much attention over the past decade due to the observations that:

- Abiotic reduction pathways result in reaction products that are of much less concern than those based on biologically-mediated reductive transformations
- The toxic reaction products formed from the biologically-mediated process are susceptible to abiotic degradation
- Lower concentrations of the targeted chlorinated solvents can be achieved in remediation scenarios by maximizing geochemical conditions for abiotic degradation

The abiotic reductions of PCE and TCE have been demonstrated in a number of abiotic model systems and anaerobic microcosms designed to mimic iron-reducing and sulfate-reducing zones in anaerobic systems. Figure 4.2 illustrates the pathways for both the abiotic and biologically-mediated reduction

of PCE and TCE. The abiotic pathway occurs predominantly through reductive elimination resulting in the formation of the reactive intermediate dichloroacetylene (Lee and Batchelor 2002). Subsequent hydrogenolysis of dichloroacetylene results in the formation of acetylene through the reactive intermediate, chloroacetylene, which is reduced further to ethane and ethene, all of which are relatively innocuous degradation products (Butler and Hayes 2001; Lee and Batchelor 2002). In contrast, the biologically-mediated pathway is dominated by hydrogenolysis (i.e., the replacement of a Cl group with an H) to form TCE. Sequential hydrogenolysis of TCE gives *cis*-1,2-DCE and subsequently VC, both of which are susceptible to abiotic reduction resulting in the formation of acetylene, ethene, and ethane.

4.1.2 Factors influencing transformation to desired end product

The desired end products for the reductive transformation of PCE and TCE are those for which all of the Cl groups have been removed (i.e.,

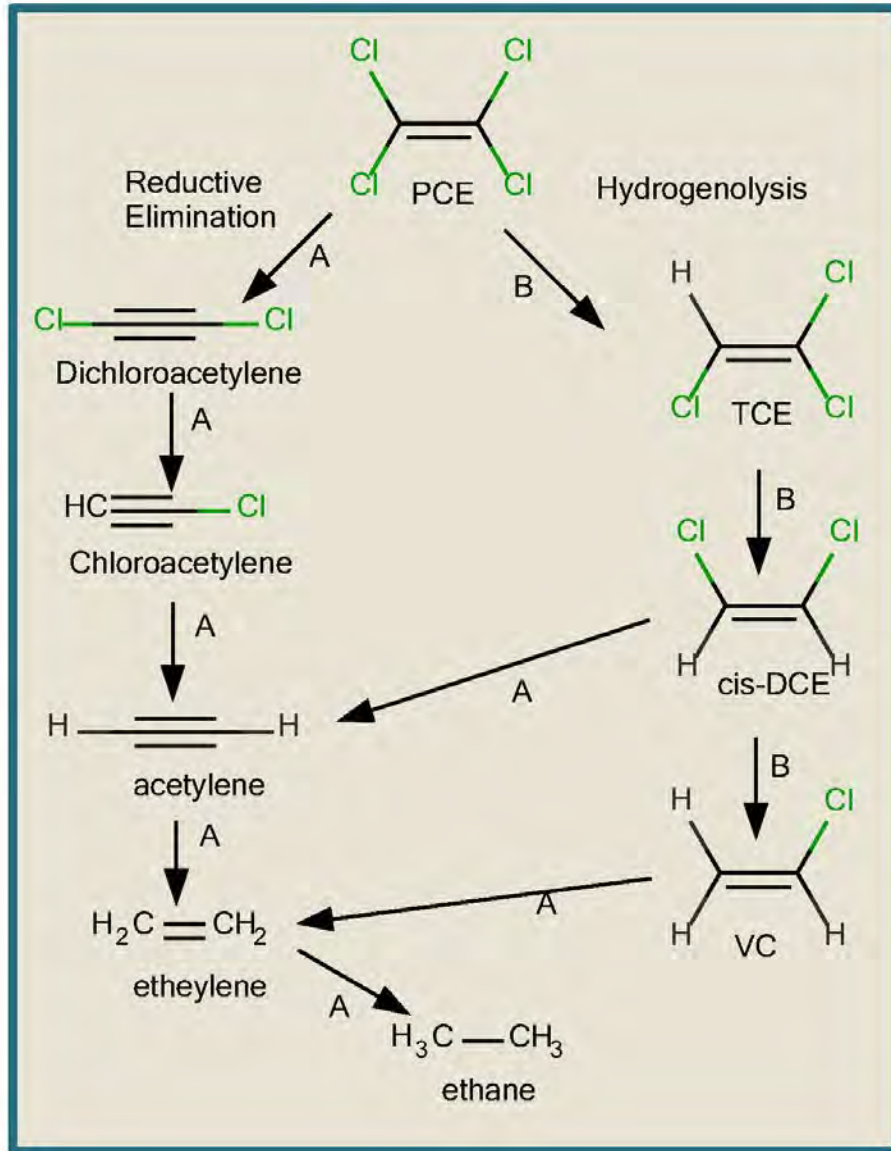


Figure 4.2. Reaction Scheme illustrating the degradation pathways for PCE in anaerobic systems and the predominant processes controlling each of the transformation steps: A = abiotic degradation pathway, B = biotic degradation pathway.

acetylene, ethene, and ethane). Consequently, conditions that maximize the potential for abiotic reduction, as discussed below, will favor the formation of these desired end products. pH is also a factor in determining the formation of the desired end products as higher values (>8) increase rates of abiotic transformations (see Table 4.1) and is thought to inhibit the growth of dechlorinating bacteria.

4.1.3 Geochemical conditions

Our understanding of the geochemical conditions controlling the abiotic reduction of PCE and TCE is the result of laboratory based studies of abiotic model systems and anaerobic microcosms. In total these studies indicate that subsurface conditions defined as iron and sulfate reducing will promote abiotic reduction of PCE and TCE as a result of

Table 4.1. Surface area-normalized rate constants, k_{sa} , with units of $\text{Lm}^{-2}\text{day}^{-1}$, for PCE, TCE, *cis*-DCE and VC measured in anoxic model studies and anaerobic microcosms.

Exp #	Reaction System	PCE	TCE	<i>cis</i> -DCE	VC	Reference
1	FeS, pH 7	$(6.3 \pm 1.6) \times 10^{-5}$		NR	NR	Butler, Elizabeth 2009
2	FeS, pH 8	$(5.3 \pm 0.5) \times 10^{-4}$	$(1.6 \pm 0.2) \times 10^{-4}$	NR	NR	Butler, Elizabeth 2009
3	FeS, pH 9	$(1.21 \pm 0.1) \times 10^{-3}$	$(6.4 \pm 0.8) \times 10^{-4}$	NR	NR	Butler, Elizabeth 2009
4	GR-Cl, pH 8	$(5.6 \pm 1.4) \times 10^{-6}$	$(2.9 \pm 0.61) \times 10^{-5}$	NR	NR	Butler, Elizabeth 2009
5	FeS ₂ , pH 8	$(1.6 \pm 1.0) \times 10^{-6}$	$(6.4 \pm 1.5) \times 10^{-5}$	NR	NR	Butler, Elizabeth 2009
6	GR-SO ₄ , pH 8	NC	NC	NR	NR	Butler, Elizabeth 2009
7	Fe ₃ O ₄ , pH 8	NC	NC	NR	NR	Butler, Elizabeth 2009
8	Fe(II)/goethite, pH 8	NC	NC	NR	NR	Butler, Elizabeth 2009
9	Microcosm, pH 7	$(1.8 \pm 1.2) \times 10^{-4}$	$(6.2 \pm 5.7) \times 10^{-4}$	NR	NR	Butler, Elizabeth 2009
10	Microcosm, pH 8	$(9.1 \pm 1.6) \times 10^{-4}$	$(1.7 \pm 1.9) \times 10^{-3}$	NR	NR	Butler, Elizabeth 2009
12	FeS ₂	2.0×10^{-5}	2.5×10^{-5}	1.3×10^{-5}	2.27×10^{-5}	Leite, 2002
13	Fe ₃ O ₄	8.4×10^{-7}	7.2×10^{-7}	5.6×10^{-7}	5.6×10^{-7}	Lee, 2002
14	FeS, pH=8.3	$(7.6 \pm 1.0) \times 10^{-4}$	$(2.1 \pm 0.1) \times 10^{-3}$	NR	NR	Jeong, 2007
15	FeS, pH=8.3 (0.04 M FeCl ₂)	$(3.8 \pm 0.3) \times 10^{-3}$	$(2.0 \pm 0.1) \times 10^{-2}$	NR	NR	Jeong, 2007

the formation of high concentrations of Fe(II) and (S-II), and the subsequent formation of reactive minerals as illustrated in Figure 4.1. Under most field conditions, both abiotic and biologically-mediated reduction of PCE and TCE will occur. The relative rates of these processes will depend on the abundance of dechlorination bacteria and the mass loadings of reactive minerals.

4.1.4 Indicator species (chemical)

Indicator species (i.e., indicators of reactivity) for abiotic reductions are those that will reflect the reactivity of various abiotic reductants due to formation and subsequent reactions of ferrous iron and sulfide. This can include direct measures of the reactive species (e.g., mass loadings of iron sulfides) or measures of species that are not reactive, but

may reflect the reactivity of the abiotic reductants (e.g., aqueous phase concentration of ferrous iron and sulfide). The direct measure of solid-phase reactive species is challenging at best and is based primarily on laboratory methods involving sequential extraction methods. These extraction methods will provide measures of weakly bound Fe(II) (i.e., surface complexed Fe(II) and strongly bound Fe(II), acid-soluble sulfur, and chromium-extractable sulfur (CrES), which provide measures of reactive Fe(II) and S(-II) bearing minerals (Kostka and Luther III, 1994; Heron, Bjerg et al. 1995).

By comparison, the measurement of aqueous phase ferrous iron, sulfide and hydrogen concentrations are quite feasible. Additionally, these parameters have been measured for the principal aquifers in the U.S. and are available in the USGS National Water Quality Data Base. Although studies to determine the efficacy of soluble ferrous iron and sulfide as indicators of reactivity for abiotic reductive dehalogenation have not yet been reported, aqueous phase concentrations of ferrous iron measured in iron-reducing sediments were shown to correlated strongly with the rates for the abiotic reduction measured for a nitro aromatic probe chemical in 21 iron-reducing sediments collected from a diverse set of sites across the country.

When given enough time for reactions to proceed to their maximum extent, reductive capacities are defined by the amount of oxidant reduced. For PCE reductions by active mineral reactions, reductive capacities were found to correlate with the Fe(II) content (Lee and Batchelor 2003).

Also, an increase in reduction rate constants for PCE and TCE in FeS systems treated with increasing concentrations of Fe(II) has been reported, which was attributed to an increase in the presence of different types of solid-bound Fe phases with Fe(II).

4.1.5 Rates of transformation

Rate constants for abiotic reduction of PCE and TCE have been measured in laboratory based abiotic model systems and anaerobic microcosms designed to mimic iron and sulfate reducing zones in natural subsurface conditions. Abiotic degradation rate constants for PCE and TCE measured in situ have not

been reported. A summary of pseudo-first-order rate constants generated from these studies are summarized in Table 4.1. These data are grouped according to the study in which they were generated. Comparison of rate constants generated from different studies is somewhat problematic primarily due to the differences in procedures used to generate the reactive minerals resulting in materials with varying reactivity. Analysis of the rate constants measured within a given study does allow for a number of general observations as reported below.

4.1.6 Normalization of rate constants to account for partitioning

Rate constants for the abiotic transformation of PCE and TCE in Table 4.1 were normalized for the effects of partitioning among the gas, aqueous, and solid phases according to:

$$k_{m,corr} = \frac{k_m}{F_i}$$

where F_i , the partitioning factor, is defined as:

$$1 + K_{i,s} + H_i \left(\frac{V_g}{V_{aq}} \right)$$

$K_{i,s}$ is calculated as follows:

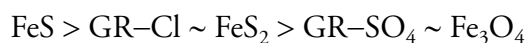
$$K_{i,s} = K_{i,d} \frac{m_s}{V_{aq}}$$

where $K_{i,d}$ is the solid/water distribution coefficient, and f_{oc} is the weight fraction of organic matter in the solid phase. $K_{i,d}$ can be estimated from the empirical relationship $K_{i,d} = K_{i,oc} f_{oc}$.

These rate constants, which have been adjusted for partitioning, were subsequently normalized to the surface areas of the various reactive mineral phases, providing surface normalized rate constants, k_{sa} , with units of $L m^{-2} day^{-1}$. The normalization of rate constants for partitioning and surface area allow for the direct comparison of reduction rates for PCE and TCE measured in the various experimental systems.

General observations based on the kinetic data reported in Table 4.1:

- Rates for the abiotic reduction of PCE and TCE increase with pH. PCE reduction by FeS increased by approximately an order of magnitude with each pH unit (Exps. 1, 2 and 3). Similar results were observed for the microcosm studies (Exps. 9 and 10).
- Based on results of model studies of individual reactive minerals (Exps, 2, 4, 5, 6, 7 and 8), their relative reactivities can be assigned as follows:



The contribution of any one of these reductants to the rate of abiotic reduction will depend on the concentration and surface area of the reductant.

- The pathways for abiotic reduction as illustrated in Figure 4.2 follow the same pathway (i.e., reductive elimination) regardless of the relative contributions of these abiotic reductants,
- Half-lives for biodegradation (~10 days, not shown) of PCE and TCE in the anaerobic microcosms were shorter than those measured in abiotic systems of reactive minerals, 900 to 5,000 days for PCE and 500-1,000 days for TCE. The half-lives for abiotic reduction were calculated from rate constants that were mass normalized to FeS surface areas (Exps 9 and 10).
- Abiotic degradation, though slower than biodegradation rates, can be significant when biodegradation is not complete leading to the formation of cis-DCE and VC (Exps 12 and 13).

Extrapolation of laboratory based generated rate constants to field conditions

Lee and Batchelor have proposed a method for extrapolating first-order rate constants measured in model systems of reactive iron sulfides to aquifers containing the reactive iron sulfide (Lee and Batchelor 2002). The following example is based on the reduction kinetics measured for TCE in a suspension of GR-SO₄. A number of assumptions are required for this extrapolation:

- The initial reductive capacity concentration (C_{RC}^0) in the aquifer can be calculated by assuming that green rusts represents 1% of the iron content of

the soil

- Based on the assumption that iron content is 2.6%, a bulk density 1.4 kg/L, and a porosity of 0.40, the mass of iron per volume water can be calculated as 91 g/L
- Assuming that GR-SO₄ is 52.6% iron, the green rust concentration can be calculated as 1.73 g/L
- Based on measured rate constants in the GR-SO₄ model systems, the calculated value for C_{RC}^0 is 0.0225 mM
- Assuming a soil organic fraction of 0.005 and an organic carbon partition coefficient of 206 L/kg, a partition coefficient of 4.66 can be calculated for TCE

Based on these assumptions, the following equation was then used to calculate a pseudo-first-order rate constant of 0.0037 day⁻¹, which gives an apparent half-life of 190 days in the simulated aquifer for the reduction of TCE by GR-SO₄:

$$k_1 = \frac{(k / P_{CE}) (C_{RC}^0)}{1 / K + C_{RC}^0}$$

Where k is the experimentally determined pseudo-first-order rate constant measured in the GR-SO₄ model system, P_{CE} is the partition coefficient for partitioning to the gas, aqueous and solid phases, K is the sorption coefficient, and C_{RC}^0 is the initial reductive capacity concentration.

This same approach was used to extrapolate results from laboratory studies of PCE in suspensions of pyrite and magnetite to estimate half lives for PCE of 13 days by pyrite and 608 days by magnetite under field conditions (Lee and Batchelor 2003). These results suggest that pyrite formed under sulfate reducing conditions has the potential to significantly contribute to the abiotic reduction of PCE.

4.2 TCA

4.2.1 Processes and Pathways

Relative to PCE and TCE, studies of the abiotic degradation of TCA are limited. Figure 4.3 illustrates the pathways for both the abiotic hydrolysis and reduction, and biologically-mediated reduction of

TCA based on our knowledge of the existing process science (Vogel and McCarty 1987; Haag and Mill 1988; Butler and Hayes 2000; Gander, Parkin et al. 2002). In the case of TCA, base-catalyzed hydrolysis results in the formation of 1,1-DCE through elimination and acetic acid through nucleophilic substitution (Haag and Mill 1988). Hydrogenolysis mediated by both abiotic and biologically mediated processes results in the formation of 1,1-DCA, and subsequently CA, which is susceptible to hydrolysis to form ethanol. Laboratory studies have demonstrated that the formation of acetic acid occurs at a rate ~5 times faster than the formation of 1,1-DCE (Haag, Mill et al. 1986). Although product recoveries are typically quite low (< 10%) for the formation of 1,1-DCA in FeS suspensions, 1,1-DCA was the only product observed (Butler and Hayes 2000; Gander, Parkin et al. 2002). With the addition of a methanogenic consortium to the FeS suspensions,

product recovery of 1,1-DCA increased to ~46% (Gander, Parkin et al. 2002).

4.2.2 Factors influencing transformation to desired end product

Of the three transformation pathways for TCA illustrated in Figure 4.3, it is abiotic hydrolysis that results in formation of the degradation product (i.e., acetic acid) of least concern. Because the hydrolysis of TCA is base catalyzed, increases in pH will increase the rate of TCA hydrolysis; however the rate of elimination, which leads to the formation of 1,1-TCE, will also increase with pH.

4.2.3. Geochemical conditions

The abiotic reduction of TCA in mackinawite (FeS) suspensions suggest that sulfate-reducing conditions will favor the abiotic reduction of TCA (Butler and Hayes 2000; Gander, Parkin et al. 2002).

4.2.4 Rates of transformation

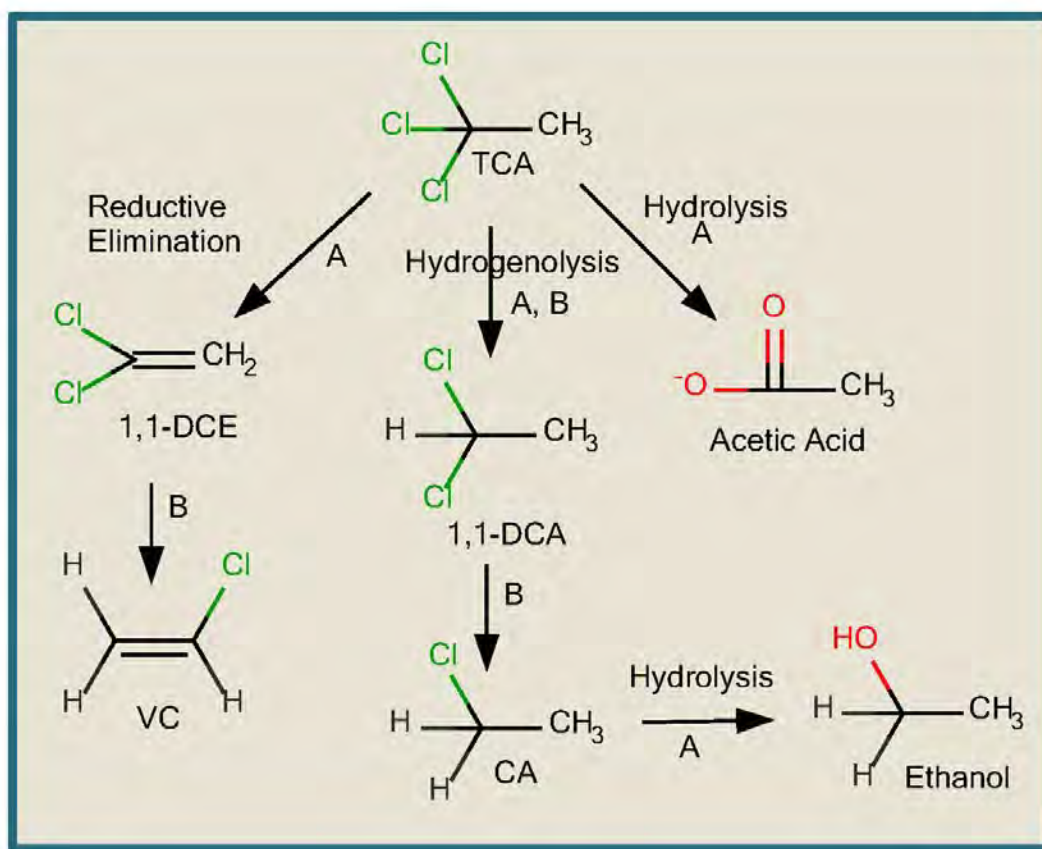


Figure 4.3. Reaction scheme illustrating the degradation pathways for TCA in anaerobic systems and the predominant processes controlling each of the transformation steps: A = abiotic degradation pathway, B = biotic degradation pathway.

Based on the limited process science available, the abiotic reduction of TCA is controlled primarily by the presence of FeS in aquifer systems. The overall rate term is characterized by a second-order rate term:

$$\frac{d[TCA]}{dt} = -k_{FeS} \{FeS\}[TCA]$$

where {FeS} is the surface area concentration given by the product of the mass concentration (S, g L⁻¹). The second-order rate constant, k_{FeS} (L m⁻²d⁻¹) is defined as:

$$k_{FeS} = \frac{k_{obs}}{\{FeS\}}$$

The k_{FeS} determined by Gander, et. al. (Gander, Parkin et al. 2002) of 0.26 L m⁻² d⁻¹, compares quite well to the rate constant of 0.47 L m⁻² d⁻¹ reported by Butler and Hayes (Butler and Hayes 2000).





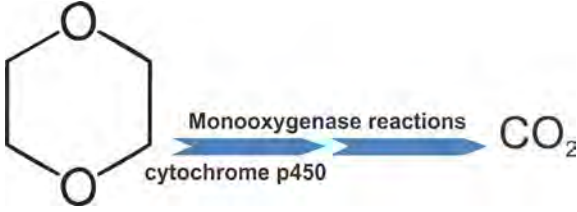
4.3 Dioxane

1,4-Dioxane (1,4-Diethyleneoxide), often called dioxane because the 1,2 and 1,3 isomers of dioxane are rare, is a heterocyclic organic compound. It is a colorless liquid with a faint sweet odor similar to that of diethyl ether. It is classified as an ether and is used as a solvent for fats, greases, and resins and in various products including paints, lacquers, glues, cosmetics, and fumigants. As a miscible compound, 1,4-Dioxane is conservatively transported with no significant known abiotic degradation pathway.

5. SUMMARY OF BIOTIC AND ABIOTIC TRANSFORMATIONS

Chlorinated solvents are altered by intrinsic biotic and abiotic processes. Transformations may be as such that endpoints fall short of complete degradation to innocuous compounds. The determination of which endpoints are reached, the processes of transformation, and the needed site data are critical for assessing and modeling transport, and deciding on Monitored Natural Attenuation (MNA) as a remedy. MNA is a component of 22% of all Record of Decision (ROD) in Superfund sites. Therefore, relevancy of MNA research to OSWER and others in terms of reducing uncertainty over field processes and better remedial decision-making are the expected impacts of this work.

Many sites with chlorinated solvent contamination may never proceed to a contaminant fate and transport modeling stage, and therefore use the data to make statistical inferences. For those sites, a thorough recognition of transformation processes to form a strong foundation for the development of a conceptual site model and integrating site data to conceptualize fate and transport processes without the benefit of a computational model are essential. A quantitative conceptual model, based upon transformation knowledge and field observation provides the framework for understanding and remediating a site. The conceptual model also provides the basis for developing and applying numerical models. This document will briefly describe the process of applying models (Section 6), given the uncertainty in processes and input parameters. It will continue by discussing alternative model formulations and their potential utility. Transformation endpoints are summarized below to facilitate in classification of observed plume behaviors and patterns:

<p>Complete reductive dechlorination</p>  <p>PCE → TCE → DCE → VC → ethene, ethane</p>	<ul style="list-style-type: none"> • PCE, TCE, DCE, VC plumes observed and all decreasing in concentration, mass, and/or extent. • Ethane and ethene detected. • Strong reducing conditions (oxygen, nitrate, sulfate are depleted relative to background wells) • Sufficient electron donor is present. • Requisite microbial community is present. • Presumed mechanism is reductive dechlorination.
<p>Incomplete/limited reductive dechlorination</p>  <p>PCE → TCE → DCE or PCE → TCE → DCE → VC</p>	<ul style="list-style-type: none"> • PCE, TCE, DCE plumes or PCE, TCE, DCE, VC plumes observed. • DCE and/or VC persist. • Weak reducing conditions (sulfate reduction and/or methanogenesis is not occurring) and/or requisite microbial community is not present. • Presumed mechanism is reductive dechlorination, but stopped by lack of appropriate enzymes
<p>Biotic/abiotic transformations</p>  <p>PCE → TCE</p>	<ul style="list-style-type: none"> • PCE and TCE plumes observed and both decreasing in concentration along the flow path. • No observed DCE or VC plumes observed. • Acetylene observed in ground water. • Strong reducing conditions (oxygen, nitrate, sulfate are depleted relative to background wells) • Sufficient electron donor is present. • Requisite microbial community is present. • Mineralogical analysis would indicate presence of reactive minerals • Presumed mechanisms are reductive dechlorination of PCE to TCE, and abiotic transformation of PCE and TCE.
<p>Degradation of TCA</p>  <p>TCA → 1,1-DCE → CA</p>	<ul style="list-style-type: none"> • TCA, 1,1-DCA, and CA plumes are observed • Presumed mechanisms are reductive dechlorination of TCA to DCA and abiotic transformation of PCE and TCE • No known culture has been found that is capable of complete dechlorination of TCA to ethane.
<p>Degradation of 1,4-dioxane</p>  <p>1,4-dioxane → → CO₂</p>	<ul style="list-style-type: none"> • Presumed mechanism is aerobic respiration, as both growth-supporting and non-growth supporting (i.e., cometabolism). • No evidence available to suggest abiotic transformation.

6. MODELING APPLICATIONS AND CONCEPTUALIZATIONS FOR CHLORINATED SOLVENT TRANSFORMATIONS

6.1 Historical Background

The scientific and conceptual basis for models of ground-water flow and contaminant transport date to the latter part of the 19TH century. Darcy's experiment on flow through porous media had the purpose of designing filters for the City of Dijon's water supply (Darcy, 1856). It is important to note that the experiment was performed on a sand filter, where Darcy selected and prepared a relatively uniform sand and placed it in an artificial environment: the filter. Later the concept of how water flowed through uniform materials was extrapolated to the natural environment (Slichter, 1899), where an important distinction holds: the materials are neither uniform nor deliberately placed (for the most part). Methods to quantify flow to wells (Thiem, 1932; Theis, 1935) used mass conservation along with Darcy's Law were developed in the early 20TH century. Although simplified, these methods were successful for determining flow to wells, largely because the location of materials of differing conductivity is less important for determining flow of water, than it is for transport of contaminants, although this factor was not realized at the time.

Mass conservation is also the main principle underlying the transport of contaminants in aquifers. Here the development of the transport theory in the 1950s (Bear, 1972) followed the development of the theory of heat conduction in uniform materials (Carslaw and Jaeger, 1959). In addition to the similar basis in mass conservation, the original development was for uniform materials. This limitation is understandable because the numerical methods and, more importantly, the computer power to solve problems with heterogeneities did not exist at the time.

6.2 Types of Models

In the most commonly used approaches, the solutions for ground-water flow and contaminant transport are found separately. Thus the distinction is made between ground-water flow models and contaminant transport models. Although in this introduction both

are discussed, contaminant transport is the major focus of this issue paper.

Two broad mathematical approaches have been developed to solve the mass conservation equations for ground-water flow and contaminant transport. The first is the historic method of solving the partial differential equation(s) for mass conservation. These are exact solutions of the equations found through the methods of calculus¹. The solutions apply everywhere throughout the domain, but require restrictive assumptions. For contaminant transport, ground-water flow must be steady (not varying with time) and uniform (not varying with position). It is represented as a simple constant in the analytic solution for contaminant transport. Consequently heterogeneity cannot be included, neither converging flow toward wells nor irregular hydrologic boundaries such as streams and rivers².

The alternative is numerical solution which approximates the solution over a set of points (usually a grid), using approximate solution techniques for the same partial differential equations. Numerical methods are much more flexible than analytic solutions because fewer major constraints are imposed. This does not mean that the numerical methods are not without limitations, but some of the basic and severe constraints imposed on analytic solutions have been overcome.

In the 1970s the first numerical models were developed and made publically-available. Concurrently there has been a parallel effort to develop analytical models. Most developers justify the use of these models as tools to test numerical models, a use to which they are well suited, or as a screening tool. The apparent idea behind screening tools is that because they are simplified, they could be used to perform quick analyses of transport when a full-blown analysis is not warranted or possible. Caution is needed in the

1 Hybrid types have been developed that blur the distinction between the two major types. Most familiar are the analytic element methods which solve the ground-water flow equation analytically over a series of domains, which are then linked to each other through what is essentially a numerical approach.

2 Analytic element methods do have the ability to include irregular boundaries, flow to wells and to a less common degree, heterogeneity. Inclusion of these features would have been part of the motivation for development of the method.

use of simplified or screening models, and for example, several questions need to be answered:

Are the assumptions in the simplified models met by the field sites being screened?

Has it been demonstrated that simplified models are appropriate for screening?

Have sufficient data been collected to support use of the model? (i.e., to avoid a “garbage in/garbage out” situation, have the sites been characterized)

Has the site-specific model (i.e., computer code plus its site data) been shown to represent the specific field site? If not, has an uncertainty analysis been performed?

6.3 Parameter Measurement in the Field

Field methods exist to measure some model parameters in the field, other parameters must be estimated. For example, hydraulic conductivity can be measured by aquifer pumping tests or slug tests. Aquifer pumping tests might be impacted by rain or early termination of pumping. Slug test results might be affected by skin effects and the tests are acknowledged to provide results close to the location of the tested well. In contrast aquifer pumping test results can cover a wider extent of the aquifer. Neither of these methods is free from inaccuracies, nor do they typically produce data that are as spatially refined as needed for detailed simulation.

Other parameters are not directly measured. Porosity is usually taken from literature values on aquifer type and not determined on a site-specific basis. As will be seen below, an approach to chlorinated solvent modeling relies on first-order rate constants. These are not directly measured but are estimated from concentrations in wells across a site measured at various times.

6.4 Model Application

Typical model applications use a combination of measured, estimated and literature parameters as a starting point. Even with the most comprehensive investigation, numerical models could use more data on parameter spatial variability than is available. Because of limitations in the values for the initial parameter values, parameters can be legitimately changed to create a model that represents the field

data on contaminant concentrations. This process is called calibration and is necessary to demonstrate that the model reproduces conditions observed in the field. Because it is essentially a process of interpolation, it does not guarantee that the model will predict future behavior, nor that the chosen parameters uniquely determine the model results. Recent research on calibration shows, in fact, that there is a limit beyond which calibration cannot further refine parameters towards reaching an ideal unique or “correct” parameter set. This limitation derives from limitations in the array of science that supports development and application of models from the historic development of the conceptual basis of the models, through field measurement and application of computer codes.

6.4.1 Model Uses

What then are the best uses of models? There is a near consensus that models are the best tool for integrating the various processes occurring at field sites. A consequence of applying the model can be the understanding of which processes govern transformation at a site. Questions can be asked as: “Does abiotic transformation alone explains the reduction in contaminant mass at this site?”

Recent writing on model application highlights the limitations of presuming certainty from application of environmental models in general. Oreskes (2003) highlights the characteristics of problems where application of environmental models is likely to be highly successful. Two of her examples are planetary motion, where predicted locations of planets can be tested by nightly telescope observation, and weather forecasting where the ability to forecast future weather is known by all to be limited, but the forecasts are valuable none-the-less. In a white paper published by *Ground Water*, Konikow (2011) suggested that the objectives for modeling be redefined.

Beyond understanding site behavior, models are useful for situations where we plan to make future measurements. Some examples are:

- More generally, design of remedial systems where performance data will be collected to track the progress of the remedy
- As a specific example: Prediction of the course of

monitored natural attenuation (MNA) remedies, where by definition monitoring will continue to document the efficacy of remediation

6.4.2 Contaminant transport models

Fate and transport models are classified into two categories:

A. Model with a sequential first-order decay process

- Solute fate and transport model
- Sorption and retardation
- NAPL/water partitioning
- Groundwater flow velocity
- Biodegradation rate-constant

In the anaerobic reductive dehalogenation of chloroethenes, chloroethenes were utilized as respiratory electron acceptors. Bacteria can reductively dechlorinate perchloroethene (PCE) to trichloroethene (TCE), *cis*-dichloroethene (*cis*-DCE), vinyl chloride (VC), and finally ethane (ETH). The ultimate electron donor used in the process is H₂ generated from the fermentation substrates, often mediated by mixed culture.

The sequential dechlorination is described in the following pathway:



Each of the five solute (PCE and its daughter products) simultaneous transport and degradation is described by one-dimensional advection-dispersion equation with first-order degradation kinetics. It is assumed that the yield coefficients are based on stoichiometric relations.

$$R_{PCE} \frac{\partial C_{PCE}}{\partial t} = D_{s,i} \frac{\partial^2 C_{PCE}}{\partial x^2} - v_s \frac{\partial C_{PCE}}{\partial x} - k_{PCE} C_{PCE}$$

$$R_{TCE} \frac{\partial C_{TCE}}{\partial t} = D_{s,i} \frac{\partial^2 C_{TCE}}{\partial x^2} - v_s \frac{\partial C_{TCE}}{\partial x} - Y_{TCE/PCE} k_{PCE} C_{PCE} - k_{TCE} C_{TCE}$$

$$R_{DCE} \frac{\partial C_{DCE}}{\partial t} = D_{s,i} \frac{\partial^2 C_{DCE}}{\partial x^2} - v_s \frac{\partial C_{DCE}}{\partial x} - Y_{DCE/TCE} k_{TCE} C_{TCE} - k_{DCE} C_{DCE}$$

$$R_{VC} \frac{\partial C_{VC}}{\partial t} = D_{s,i} \frac{\partial^2 C_{VC}}{\partial x^2} - v_s \frac{\partial C_{VC}}{\partial x} - Y_{VC/DCE} k_{DCE} C_{DCE} - k_{VC} C_{VC}$$

$$R_{ETH} \frac{\partial C_{ETH}}{\partial t} = D_{s,i} \frac{\partial^2 C_{ETH}}{\partial x^2} - v_s \frac{\partial C_{ETH}}{\partial x} - Y_{ETH/VC} k_{VC} C_{VC} - k_{ETH} C_{ETH}$$

C_{PCE}, C_{TCE}, C_{DCE}, C_{VC}, C_{ETH} – aqueous concentrations (mg/L)

k_{PCE}, k_{TCE}, k_{DCE}, k_{VC}, k_{ETH} – first-order degradation rates (day⁻¹)

Y_{TCE/PCE}, Y_{DCE/TCE}, Y_{VC/DCE}, Y_{ETH/VC} – yield coefficients (mg/mg)

Kinetic constants for the sequential degradation of PCE

constant	value (day ⁻¹)	
k _{PCE}	0.005	PCE degradation constant
k _{TCE}	0.003	TCE degradation constant
k _{DCE}	0.002	DCE degradation constant
k _{VC}	0.001	VC degradation constant

coefficient value (mg/mg)

Y _{TCE/PCE}	0.7920	TCE/PCE stoichiometric yield
Y _{DCE/TCE}	0.7377	DCE/TCE stoichiometric yield
Y _{VC/DCE}	0.6445	VC/DCE stoichiometric yield

B. Model with competitive inhibition and a sequential double-Monod kinetic process

To account for limitations imposed by electron donor and electron acceptor availability, the double-Monod kinetic expression was used as the biokinetic models.

The model simulates the microbial transformation of the seven solutes (PCE, TCE, DCE, VC, ETH, H₂ and CH₄), the growth and decay of three microbial populations: PCE/TCE dechlorinators (dech1), DCE/VC dechlorinators (dech2), and hydrogenotrophic methanogens (meth) (or maybe homoacetogens). A one-dimensional transport model is described with dispersion, advection, and rate-limited sorption and desorption, reductive dechlorination kinetics with competitive inhibition and microbial growth and decay.

$$R_1 \frac{\partial C_{PCE}}{\partial t} = D_{s,i} \frac{\partial^2 C_{PCE}}{\partial x^2} - v_s \frac{\partial C_{PCE}}{\partial x} - k_{PCE,dech1} X_{dech1} \left(\frac{C_{PCE}}{K_{s,PCE,dech1} \left(1 + \frac{C_{TCE}}{K_{s,TCE,dech1}} \right) + C_{PCE}} \right) \times \left(\frac{C_{H_2} - C_{H_2,th,dech}}{K_{s,H_2} + (C_{H_2} - C_{H_2,th,dech})} \right)$$

$$R_2 \frac{\partial C_{TCE}}{\partial t} = D_{s,i} \frac{\partial^2 C_{TCE}}{\partial x^2} - v_s \frac{\partial C_{TCE}}{\partial x} - k_{TCE,dech1} X_{dech1} \left(\frac{C_{TCE}}{K_{s,TCE,dech1} \left(1 + \frac{C_{PCE}}{K_{s,PCE,dech1}} \right) + C_{TCE}} \right) \times \left(\frac{C_{H_2} - C_{H_2,th,dech}}{K_{s,H_2,dech1} + (C_{H_2} - C_{H_2,th,dech})} \right)$$

$$R_3 \frac{\partial C_{DCE}}{\partial t} = D_{s,i} \frac{\partial^2 C_{DCE}}{\partial x^2} - v_s \frac{\partial C_{DCE}}{\partial x} - k_{DCE,dech2} X_{dech2} \left(\frac{C_{DCE}}{K_{s,DCE,dech2} \left(1 + \frac{C_{VC}}{K_{s,VC,dech2}} \right) + C_{DCE}} \right) \times \left(\frac{C_{H_2} - C_{H_2,th,dech}}{K_{s,H_2,dech2} + (C_{H_2} - C_{H_2,th,dech})} \right)$$

$$R_4 \frac{\partial C_{VC}}{\partial t} = D_{s,i} \frac{\partial^2 C_{VC}}{\partial x^2} - v_s \frac{\partial C_{VC}}{\partial x} - k_{VC,dech2} X_{dech2} \left(\frac{C_{VC}}{K_{s,VC,dech2} \left(1 + \frac{C_{DCE}}{K_{s,DCE,dech2}} \right) + C_{VC}} \right) \times \left(\frac{C_{H_2} - C_{H_2,th,dech}}{K_{s,H_2,dech2} + (C_{H_2} - C_{H_2,th,dech})} \right)$$

Beyond understanding site behavior, models are useful for situations where we plan to make future measurements. This Issue Paper will form the basis for simulating chlorinated solvent transformation along streamlines using biotic or abiotic processes as appropriate.

7. REFERENCES

- Adamson, D.T., and G.F. Parkin. 1999. Biotransformation of mixtures of chlorinated aliphatic hydrocarbons by an acetate-grown methanogenic enrichment culture. *Water Research* 33(6):1482-1494.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1990. Toxicological Profile for 1,1-Dichloroethane. U.S. Department of Health and Human Services, Public Health Service, ATSDR.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1996. Toxicological Profile for 1,2-Dichloroethene. U.S. Department of Health and Human Services, Public Health Service, ATSDR.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1997. Toxicological Profile for Tetrachloroethylene. U.S. Department of Health and Human Services, Public Health Service, ATSDR.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1997. Toxicological Profile for Trichloroethylene. U.S. Department of Health and Human Services, Public Health Service, ATSDR.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1998. Toxicological Profile for Chloroethane. U.S. Department of Health and Human Services, Public Health Service, ATSDR.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2006. Toxicological Profile for Vinyl Chloride. U.S. Department of Health and Human Services, Public Health Service, ATSDR.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2006. Toxicological Profile for 1,1,1-Trichloroethane. U.S. Department of Health and Human Services, Public Health Service, ATSDR.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2007. Draft Toxicological Profile for 1,4-Dioxane. U.S. Department of Health and Human Services, Public Health Service, ATSDR.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2011. A detailed data Table for the "2011 Priority List of Hazardous Substances" that will be the subject of toxicological profiles. Accessed on December 19, 2012 at: http://www.atsdr.cdc.gov/SPL/resources/ATSDR_2011_SPL_Detailed_Data_Table.pdf
- Alvarez-Cohen, L. and G.E. Speitel Jr. 2001. Kinetics of aerobic cometabolism of chlorinated solvents. *Biodegradation* 12:105-126.
- Aulenta, F., M. Majone, and V. Tandoi. 2006. Enhanced anaerobic bioremediation of chlorinated solvents: environmental factors influencing microbial activity and their relevance under field conditions. *J. Chem. Technol. Biotechnol.* 81:1463-1474.
- Azadpour-Keeley, A., H.H. Russell, and G.W. Sewell. 1999. Microbial Processes Affecting Monitored Natural Attenuation of Contaminants in the Subsurface - Ground Water Issue. EPA/540/S-99/001. US Environmental Protection Agency, National Risk Management Research Laboratory, Subsurface Protection and Remediation Division, Robert S. Kerr Environmental Research Center, Ada, OK.
- Bear, J. 1972. *Dynamics of Fluids in Porous Media*. Dover Publications, New York, New York. 764 pp.
- Bjerg, P.L., K. Rügge, J.K. Pedersen, and T.H. Christensen. 1995. Distribution of redox-sensitive groundwater quality parameters downgradient of a landfill (Grindsted, Denmark). *Environ. Sci. Technol.* 29 (5):1387-1394.
- Bouwer, E.J. 1993. Bioremediation of Chlorinated Solvents Using Alternate Electron Acceptors. Section 8 in *In-Situ Bioremediation of Ground Water and Geological Materials: A Review of Technologies*. EPA/600/R-93/124. U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK.
- Butler, E.C., and K.F. Hayes. 2000. Kinetics of the transformation of halogenated aliphatic compounds by iron sulfide. *Environ. Sci. Technol.* 34(3):422-429.
- Butler, E.C., and K.F. Hayes. 2001. Factors influencing rates and products in the transformation of trichloroethylene by iron sulfide and iron metal. *Environ. Sci. Technol.* 35(19):3884-3891.
- Bradley, P.M., and F.H. Chapelle. 2010. Biodegradation of Chlorinated Ethenes. Chapter 3 In: *In Site Remediation of Chlorinated Solvent Plumes*. Stroo, H., and C.H. Ward (Eds.). Springer, New York, NY.
- Carlsaw, H.S., and J.C. Jaeger. 1959. *Conduction of Heat in Solids*. Oxford University Press.
- Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky. 1995. Deducing the Distribution of Terminal Electron-Accepting Processes in Hydrologically Diverse Groundwater Systems. *Water Resources Research*. 31(2):359-371.
- Chapelle, F.H., J. Novak, J. Parker, B.G. Campbell, and M.A. Widdowson. 2007. A Framework for Assessing the Sustainability of Monitored Natural Attenuation. U.S. Geological Survey. Circular 1303. 35 pp.

- Chiang, D.S.-Y., E.W. Glover Jr., J. Peterman, J. Harrigan, B. DiGuseppi, and D.S. Woodward. 2008. Evaluation of natural attenuation at a 1,4-dioxane-contaminated site. *Remediation* (Winter 2008), pp. 19-37.
- Chiang, S.-Y.D., R. Mora, W.H. Diguseppi, G. Davis, K. Sublette, P. Gedalanga, and S. Mahendra. 2012. Characterizing the intrinsic bioremediation potential of 1,4-dioxane and trichloroethene using innovative environmental diagnostic tools. *J. Environmental Monitoring* 14:2317-2326.
- Darcy, H. 1856. *Les Fontaines Publiques de la Ville de Dijon*. Dalmont, Paris.
- Domenico, P.A., and F.W. Schwartz. 1998. *Physical and Chemical Hydrogeology, Second Edition*. John Wiley & Sons, Inc., New York, NY. 506 pp.
- Duhamel, M., S.D. Wehr, L. Yu, H. Rizvi, D. Seepersad, S. Dworatzek, E.E. Cox, and E.A. Edwards. 2002. Comparison of anaerobic dechlorinating enrichment cultures maintained on tetrachloroethene, trichloroethene, cis-dichloroethene and vinyl chloride. *Water Research* 36:4193-4202.
- Fetter, C.W. 1993. *Contaminant Hydrogeology*. MacMillan Publishing Company, New York, NY. 458 pp.
- Field, J.A., and R. Sierra-Alvarez. 2004. Biodegradability of chlorinated solvents and related chlorinated aliphatic compounds. *Rev. Environ. Science Bio. Technol.* 3:185-254.
- Freeze, R.A., and J.A. Cherry. 1979. *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, NJ. 604 pp.
- Gander, J.W., G.F. Parkin, and M.M. Scherer. 2002. Kinetics of 1,1,1-trichloroethane transformation by iron sulfide and a methanogenic consortium. *Environ. Sci. Technol.* 36(21):4540-4546.
- Haitjema, H., 1995. *Modeling with the Analytic Element Method*, Academic Press.
- Haag, W.R., and T. Mill. 1988. Some reactions of naturally occurring nucleophiles with haloalkanes in water. *Environ. Toxicol. Chem.* 7(11):917-924.
- Haag, W. R., T. Mill, and A. Richardson. 1986. Effect of subsurface sediment on hydrolysis reactions. *192nd National Meeting of the American Chemical Society, Division of Environmental Chemistry*. Vol. 26.
- Heron, G., P.L. Bjerg, and T.H. Christensen. 1995. Redox Buffering in Shallow Aquifers Contaminated by Leachate. *Intrinsic Bioremediation - Bioremediation* 3(1):143-151. Battelle Press, Columbus, OH
- Himmelheber, D.W., M. Taillefert, K.D. Pennell, and J.B. Hughes. 2008. Spatial and Temporal Evolution of Biogeochemical Processes Following In Situ Capping of Contaminated Sediments. *Environ. Sci. Technol.* 42(11):4113-4120.
- Himmelheber, D.W., S.H. Thomas, F.E. Löffler, M. Taillefert, and J.B. Hughes. 2008. Microbial colonization of an in situ sediment cap and correlation to stratified redox zones. *Environ. Sci. Technol.* 43(1):66-74.
- ITRC (Interstate Technology & Regulatory Council). 2011. *Environmental Molecular Diagnostics Fact Sheets*. EMD-1. Washington, D.C.: Interstate Technology & Regulatory Council, Environmental Molecular Diagnostics Team. <http://www.itrcweb.org/Documents/EMD1.pdf>
- Jenkins, D.N., J.E. Bentkowski, W.N. O'Steen, and K. Wischkaemper. 2009. Comments Regarding Dora Sheau-Yun Chiang et al.'s "Evaluation of Natural Attenuation at a 1,4-Dioxane-Contaminated Site" (*Remediation*, 19[1], 19 - 37). *Remediation* (Autumn 2009), pp. 141-143.
- Jeong, H.Y. and K.F. Hayes. 2007. Reductive dechlorination of tetrachloroethylene and trichloroethylene by mackinawite (FeS) in the presence of metals: reaction rates. *Environ. Sci. Technol.* 41(18):6390-6396
- Konikow, L.F. 2011. The Secret to Successful Solute-Transport Modeling. *Ground Water*. 49(2):144-159. doi: 10.1111/j.1745-6584.2010.00764.x.
- Kostka, J.E., and G.W. Luther III. 1994. Partitioning and speciation of solid phase iron in saltmarsh sediments. *Geochimica et Cosmochimica Acta* 58(7):1701-1710.
- Lawrence, S.J. 2006. Description, Properties, and Degradation of Selected Volatile Organic Compounds Detected in Ground Water - A Review of Selected Literature. U.S. Department of the Interior, USGS and ATSDR, U.S. Department of Health and Human Services. USGS Open-File Report 2006 - 1338.
- Lee, W., and B. Batchelor. 2002. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 2. Green rust. *Environ. Sci. Technol.* 36(24):5348-5354.
- Lee, W., and B. Batchelor. 2003. Reductive capacity of natural reductants. *Environ. Sci. Technol.* 37(3):535-541.
- Li, M., S. Fiorenza, J.R. Chatham, S. Mahendra, and P.J.J. Alvarez. 2010. 1,4-Dioxane biodegradation at low temperatures in Arctic groundwater samples. *Water Research* 44(9):2894-2990.
- Lovley, D.R., F.H. Chapelle, and J.C. Woodward. 1994. Use of dissolved H₂ concentrations to determine distribution of microbially catalyzed redox reactions in anaerobic groundwater. *Environ. Sci. Technol.* 28: 1205-1210.

- Lovley, D.R., F.H. Chapelle, and J.C. Woodward. 1994. Use of dissolved H₂ concentrations to determine distribution of microbially catalyzed redox reactions in anaerobic groundwater. *Environ. Sci. Technol.* 28: 1205-1210.
- Lovley, D.R., and S. Goodwin. 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. *Geochimica et Cosmochimica Acta.* 52:2993-3003.
- Mahendra, S., and L. Alvarez-Cohen. 2006. Kinetics of 1,4-dioxane biodegradation by monooxygenase-expressing bacteria. *Environ. Sci. Technol.* 40(17):5435-5442.
- Mahendra, S., C. J. Petzold, E. E. Baidoo, J. D. Keasling, and L. Alvarez-Cohen. 2007. Identification of the intermediates of in vivo oxidation of 1,4-dioxane biodegradation by monooxygenase-containing bacteria. *Environ. Sci. Technol.* 41(21):7330-7336.
- Maymó-Gatell, X. 1997. "Dehalococcoides ethenogenes" Strain 195, A Novel Eubacterium that Reductively Dechlorinates Tetrachloroethene (PCE) to Ethene. Report AL/EQ-TR-1997-0029. Air Force Research Laboratory, Tyndall AFB, FL. Find link for document at: <http://www.dtic.mil/docs/citations/ADA357948>
- Maymó-Gatell, X., T. Anguish, and S.H. Zinder. 1999. Reductive dechlorination of chlorinated ethenes and 1,2-dichloroethane by "Dehalococcoides ethenogenes" 195. *Appl. Environ. Microbiol.* 65(7):3108-3113.
- McCarty, P.L., and L. Semprini. 1993. Ground-Water Treatment for Chlorinated Solvents. Section 5 in In-Situ Bioremediation of Ground Water and Geological Materials: A Review of Technologies. EPA/600/R-93/124. U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK.
- Mohr, T.K.G. 2001. 1,4-Dioxane and other Solvent Stabilizers, White Paper, June 14, 2001. Santa Clara Valley Water District, San Jose, CA. Available at <http://www.valleywater.org/WorkArea/DownloadAsset.aspx?id=2686>
- Mohr, T.K.G., J.A. Stickney, and W.H. DiGuseppi. 2010. *Environmental Investigation and Remediation, 1,4-Dioxane and Other Solvent Stabilizers.* CRC Press, Bacon Raton, FL. 520 pp.
- Mora, R., and D. Chiang. 2011. TCE and 1,4-Dioxane MNA: Revealing Intrinsic Biodegradation of TCE and 1,4-Dioxane Using Advanced Tools. Presentation at the "Advanced Tools for In-Situ Green Remediation" Conference, June 10, 2011.
- National Research Council. 2000. *Natural Attenuation for Ground Water Remediation.* National Academy Press, Washington DC. Find links to read free on-line at: http://www.nap.edu/catalog.php?record_id=9792
- Newell, C.J., I. Cowie, T.M. McGuire, and W.W. McNab Jr. 2006. Multiyear temporal changes in chlorinated solvent concentrations at 23 monitored natural attenuation sites. *J. Environ. Engineer* 132(6):653-663.
- Newell, C.J., H.S. Rifai, J.T. Wilson, J.A. Connor, J.A. Aziz, and M.P. Suarez. 2002. *Calculations and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies.* EPA/540/S-02/500. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH.
- North Wind, Inc. 2003. DCE/VC Stall at Natural Attenuation Sites: Strategies for Mitigation during Natural Attenuation or Bioremediation of Chlorinated Ethenes. Remediation Innovative Technology Seminar (RITS) (Fall 2003), Naval Facilities Engineering Command (NAVFAC).
- Oreskes, N. 2003. The Role of Quantitative Models in Science. In: C.D. Canham, J.J. Cole, and W.K. Lauenroth (eds.). *Models in ecosystem science.* Chapter 2. Princeton University Press, Princeton, NJ.
- Pivetz, B.E., D. Abshire, W. Brandon, S. Mangion, B. Roberts, B. Stuart, L. Vanderpool, S.D. Acree, and B. Wilson. 2012. Framework for Site Characterization for MNA of VOCs in Ground Water. EPA 600/R-12/712. U.S. EPA, Office of Research and Development, National Risk Management Research Laboratory.
- Pope, D.F., S.D. Acree, H. Levine, S. Mangion, J. van Ee, K. Hurt, and B. Wilson. 2004. *Performance Monitoring of MNA Remedies for VOCs in Ground Water.* EPA/600/R-04/027. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. Find link for document under "Year" tab at: <http://www.epa.gov/nrmrl/gwerd/publications.html>
- Rifai, H.S., C.J. Newell, and T.H. Wiedemeier. 2001. Natural Attenuation of Chlorinated Solvents in Ground Water. In: *Handbook of Solvents.* Chemtec Publishing. pp. 1571-1616.
- Science, C.D. Canham, J. J. Cole, and W. K. Lauenroth, eds., Princeton University Press, 13-31.
- Scheutz, C., N.D. Durant, M.H. Hansen, and P.L. Bjerg. 2011. Natural and enhanced anaerobic degradation of 1,1,1-trichloroethane and its degradation products in the subsurface: a critical review. *Water Research* 45(9):2701-2723.
- Sims, J.L., J.M. Suffita, and H.H. Russell. 1991. Reductive Dehalogenation of Organic Contaminants in Soils and Ground Water - Ground Water Issue. EPA/540/4-90/054. US Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory.

- Slichter, C. S. 1899. Theoretical investigation of the motion of ground waters. U.S. Geol. Surv. 19th Ann. Rept. pt. 2, pp. 295–384.
- Suarez, M.P., and H.S. Rifai. 1999. Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater. *Bioremediation J.* 3(4):337-362.
- Theis, C.V. 1935. The relation between the lowering of the piezometric surface and the rate and duration of discharge of a well using groundwater storage. *Transactions of the American Geophysical Union* 2:519-524.
- Thiem, G. 1906. Hydrologische methoden (in German). Leipzig: J. M. Gebhardt. p. 56.
- Thomas, L.K., M.A. Widdowson, F.H. Chapelle, J.T. Novak, J.E. Boncal, and C.A. Lebron. 2013. Distribution of potentially bioavailable natural organic carbon in aquifer sediments at a chloroethene-contaminated site. *J. Environ. Eng.* 139:54-60.
- U.S. EPA. 1999. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites.* OSWER Directive 9200.4-17P. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington DC. <http://www.epa.gov/swerst1/directiv/d9200417.pdf>
- Vogel, T.M. 1993. Natural Bioremediation of Chlorinated Solvents. Section 10 in *In-Situ Bioremediation of Ground Water and Geological Materials: A Review of Technologies.* EPA/600/R-93/124. U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK.
- Vogel, T.M., and P.L. McCarty. 1987. Abiotic and biotic transformations of 1,1,1-trichloroethane under methanogenic conditions. *Environ. Sci. Technol.* 21(12):1208-1213.
- Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformation of halogenated aliphatic compounds. *Environ. Sci. Technol.* 21(8):722-736.
- Wiedemeier, T.H., M.A. Swanson, D.E. Moutoux, E.K. Gordon, J.T. Wilson, B.H. Wilson, D.H. Kampbell, P.E. Haas, R.N. Miller, J.E. Hansen, and F.H. Chapelle. 1998. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water.* EPA/600/R-98/128. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. Find link for document under “Year” tab at: <http://www.epa.gov/nrmrl/gwerd/publications.html>
- Wiedemeier, T.H., H.S. Rifai, C.J. Newell, and J.T. Wilson. 1999. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface.* John Wiley & Sons, Inc., New York, NY.
- Wilson, J.T. 2010. Monitored Natural Attenuation of Chlorinated Solvent Plumes. Chapter 11 *In: In Site Remediation of Chlorinated Solvent Plumes.* Stroo, H., and C.H. Ward (Eds.). Springer, New York, NY.