23

Contamination Cleanup: Natural Attenuation and Advanced Remediation Technologies

23.1 NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUND WATER

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23.1.1 INTRODUCTION

Chlorinated solvents were first produced some 100 years ago and came into common usage in the 1940's. Chlorinated solvents are excellent degreasing agents and they are nearly non-flammable and non-corrosive. These properties have resulted in their widespread use in many industrial processes such as cleaning and degreasing rockets, electronics and clothing (used as dry-cleaning agents). Chlorinated solvent compounds and their natural degradation or progeny products have become some of the most prevalent organic contaminants found in the shallow groundwater of the United States. The most commonly used chlorinated solvents are perchloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA), and carbon tetrachloride (CT).[1]

Chlorinated solvents (CS) undergo the same natural attenuation processes as many other ground water contaminants such as advection, dispersion, sorption, volatilization and biodegradation. In addition, CS are subject to abiotic reactions such as hydrolysis and dehydrohalogenation and abiotic reduction reactions. While many of the physical and chemical reactions affecting chlorinated solvents have been extensively studied, their biodegradation is not as well understood as perhaps it is for petroleum hydrocarbons. Researchers are just beginning to understand the microbial degradation of chlorinated solvents with many degradation pathways remaining to be discovered. Unlike petroleum hydrocarbons, which can be oxidized by microorganisms under either aerobic or anaerobic condi-

tions, most chlorinated solvents are degraded only under specific ranges of oxidation-reduction potential. For example, it is currently believed that PCE is biologically degraded through use as a primary growth substrate only under strongly reducing anaerobic conditions.

This chapter is focused on the natural attenuation behavior of CS at the field scale. The first part of the chapter reviews many of the physical, chemical and abiotic natural attenuation processes that attenuate CS concentrations in ground water. Some of these processes have been described in more detail in previous chapters in the handbook and are therefore only reviewed in brief. In the second part of this chapter, we will review the biological processes that bring about the degradation of the most common chlorinated solvents, present conceptual models of chlorinated solvent plumes, and summarize data from field studies with chlorinated solvent contamination.

23.1.2 NATURAL ATTENUATION PROCESSES AFFECTING CHLORINATED SOLVENT PLUMES

Many abiotic mechanisms affect the fate and transport of organic compounds dissolved in ground water. Physical processes include advection and dispersion while chemical processes include sorption, volatilization and hydrolysis. Advection transports chemicals along ground water flow paths and in general does not cause a reduction in contaminant mass or concentration. Dispersion or mixing effects, on the other hand, will reduce contaminant concentrations but will not cause a reduction in the total mass of chemicals in the aquifer. Sorption or partitioning between the aquifer matrix and the ground water, much like dispersion, will not cause a reduction in contaminant mass. Volatilization and hydrolysis both will result in lower concentrations of the contaminant in ground water. The majority of these processes, with the exception of hydrolysis and dehydrohalogenation chemical reactions, do not break down or destroy the contaminants in the subsurface.

Chlorinated solvents are advected, dispersed, and sorbed in ground water systems. They also volatilize although their different components have varying degrees of volatility. Chlorinated solvents additionally hydrolyze and undergo other chemical reactions such as dehydrohalogenation or elimination and oxidation and reduction. These abiotic reactions, as will be seen later in the chapter, are typically not complete and often result in the formation of an intermediate that may be at least as toxic as the original contaminant.

23.1.2.1 Advection

Advective transport is the transport of solutes by the bulk movement of ground water. Advection is the most important process driving dissolved contaminant migration in the subsurface and is given by:

$$v_x = -\frac{K}{n_e}\frac{dH}{dL} \qquad [23.1.1]$$

where:

V_x	seepage velocity [L/T]
K	hydraulic conductivity [L/T]
n_e	effective porosity [L^3/L^3]
dH/dL	hydraulic gradient [L/L]

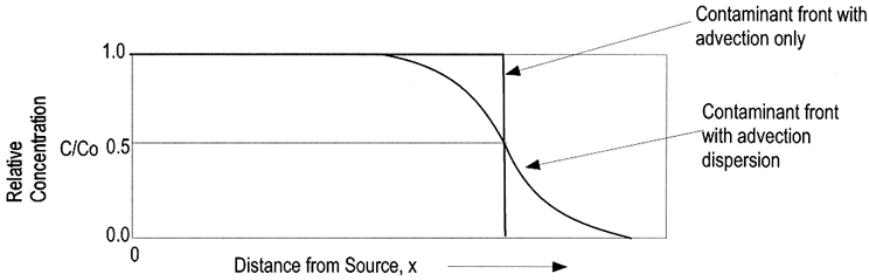

Figure 23.1.1. Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only and from the combined processes of advection and hydrodynamic dispersion. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**. Copyright © 1999 *John Wiley & Sons*. Reprinted by permission of John Wiley & Sons.]

Typical velocities range between 10^{-7} and 10^{3} ft/day^2 with a median national average of 0.24 ft/day. The seepage velocity is a key parameter in natural attenuation studies since it can be used to estimate the time of travel of the contaminant front:

$$t = \frac{x}{v_x} \qquad [23.1.2]$$

where:

x	travel distance (ft or m)
t	time

Solute transport by advection alone yields a sharp solute concentration front as shown in Figure 23.1.1. In reality, the advancing front spreads out due to the processes of dispersion and diffusion as shown in Figure 23.1.1, and is retarded by sorption (Figure 23.1.2) and biodegradation.

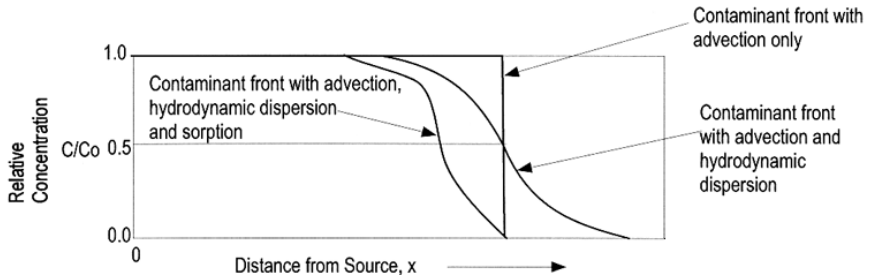

Figure 23.1.2. Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only; from the combined processes of advection and hydrodynamic dispersion; and from the combined processes of advection, hydrodynamic dispersion, and sorption. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

23.1.2.2 Dispersion

Hydrodynamic dispersion causes a contaminant plume to spread out from the main direction of ground water flow. Dispersion dilutes the concentrations of the contaminant, and introduces the contaminant into relatively pristine portions of the aquifer where it mixes with more electron acceptors crossgradient to the direction of ground-water flow. As a result of

dispersion, the solute front travels at a rate that is faster than would be predicted based solely on the average linear velocity of the ground water. Figure 23.1.1 illustrates the effects of hydrodynamic dispersion on an advancing solute front. Mechanical dispersion is commonly represented by the relationship:

$$\textit{Mechanical Dispersion} = \alpha_x v_x \qquad [23.1.3]$$

where:

v_x	average linear ground-water velocity [L/T]
α_x	dispersivity [L]

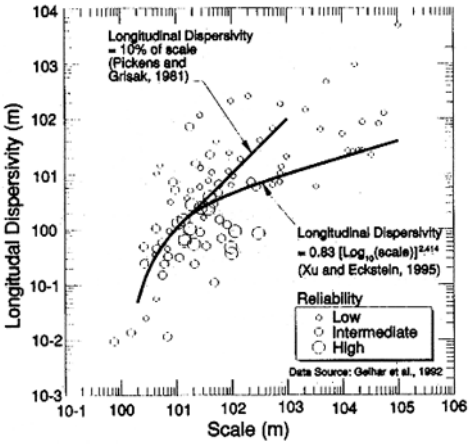

Figure 23.1.3. Relationship between dispersivity and scale. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

Dispersivity represents the spreading of a contaminant over a given length of flow and is characteristic of the porous medium through which the contaminant migrates. It is commonly accepted that dispersivity is scale-dependent, and that at a given scale, dispersivity may vary over three orders of magnitude[3,4] as shown in Figure 23.1.3.

Several approaches can be used to estimate longitudinal dispersivity, α_x, at the field scale. One technique involves conducting a tracer test but this method is time consuming and costly. Another method commonly used in solute transport modeling is to start with a longitudinal dispersivity of 0.1 times the plume lengths.[5-7] This assumes that dispersivity varies linearly with scale. Xu and Eckstein[8] proposed an alternative approach. They evaluated the same data presented by Gelhar et al.[4] and, by using a weighted least-squares method, developed the following relationship for estimating dispersivity:

$$\alpha_x = 0.83\left(\log_{10} L_p\right)^{2.414} \qquad [23.1.4]$$

where:

α_x	longitudinal dispersivity [L]
L_p	plume length [L]

Both relationships are shown on Figure 23.1.3.

In addition to estimating longitudinal dispersivity, it may be necessary to estimate the transverse and vertical dispersivities (α_T and α_Z, respectively) for a given site. Commonly, α_T is estimated as $0.1\alpha_x$ (based on data[4]), or as $0.33\alpha_x$.[9,10] Vertical dispersivity (α_Z) may be estimated as $0.05\alpha_x$,[9] or as 0.025 to $0.1\alpha_x$.[10]

23.1.2.3 Sorption

Many organic contaminants, including chlorinated solvents, are removed from solution by sorption onto the aquifer matrix. Sorption of dissolved contamination onto the aquifer ma-

trix results in slowing (retardation) of the contaminant relative to the average advective ground-water flow velocity and a reduction in dissolved organic concentrations in ground water. Sorption can also influence the relative importance of volatilization and biodegradation.[11] Figure 23.1.2 illustrates the effects of sorption on an advancing solute front. Sorption is a reversible reaction; at given solute concentrations, some portion of the solute is partitioning to the aquifer matrix and some portion is also desorbing, and reentering solution.

Sorption can be determined from bench-scale experiments. These are typically performed by mixing water-contaminant solutions of various concentrations with aquifer materials containing various amounts of organic carbon and clay minerals. The solutions are then sealed with no headspace and left until equilibrium between the various phases is reached. The amount of contaminant left in solution is then measured.

The results are commonly expressed in the form of a sorption isotherm or a plot of the concentration of chemical sorbed (μg/g) versus the concentration remaining in solution (μg/L). Sorption isotherms generally exhibit one of three characteristic shapes depending on the sorption mechanism. These isotherms are referred to as the Langmuir isotherm, the Freundlich isotherm, and the linear isotherm (a special case of the Freundlich isotherm). The reader is referred to ref. 1 for more details on sorption isotherms.

Since sorption tends to slow the transport velocity of contaminants dissolved in ground water, the contaminant is said to be "retarded." The coefficient of retardation, R, is defined as:

$$R = \frac{v_x}{v_c} \qquad [23.1.5]$$

where:

R	coefficient of retardation
v_x	average linear ground-water velocity parallel to ground-water flow
v_c	average velocity of contaminant parallel to ground-water flow

The ratio v_x/v_c describes the relative velocity between the ground water and the dissolved contaminant. The coefficient of retardation for a dissolved contaminant (for saturated flow) assuming linear sorption is determined from the distribution coefficient using the relationship:

$$R = 1 + \frac{\rho_b K_d}{N} \qquad [23.1.6]$$

where:

R	coefficient of retardation [dimensionless]
ρ_b	bulk density of aquifer [M/L^3]
K_d	distribution coefficient [L^3/M]
N	porosity [L^3/L^3]

The bulk density, ρ_b, of a soil is the ratio of the soil mass to its field volume. In sandy soils, ρ_b can be as high as 1.81 g/cm^3, whereas, in aggregated loams and clayey soils, ρ_b can be as low as 1.1 g/cm^3.

The distribution coefficient is a measure of the sorption/desorption potential and characterizes the tendency of an organic compound to be sorbed to the aquifer matrix. The

higher the distribution coefficient, the greater the potential for sorption to the aquifer matrix. The distribution coefficient, K_d, is given by:

$$K_d = \frac{C_a}{C_l} \qquad [23.1.7]$$

where:

K_d	distribution coefficient (slope of the sorption isotherm, mL/g).
C_a	a sorbed concentration (mass contaminant/mass soil or µg/g)
C_l	dissolved concentration (mass contaminant/volume solution or µg/mL)

Several researchers have found that if the distribution coefficient is normalized relative to the aquifer matrix total organic carbon content, much of the variation in observed K_d values between different soils is eliminated.[12-19] Distribution coefficients normalized to total organic carbon content are expressed as K_{oc}. The following equation gives the expression relating K_d to K_{oc}:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad [23.1.8]$$

where:

K_{oc}	soil sorption coefficient normalized for total organic carbon content
K_d	distribution coefficient
f_{oc}	fraction total organic carbon (mg organic carbon/mg soil)

Table 23.1.1 presents calculated retardation factors for several LNAPL and DNAPL related chemicals as a function of the fraction of organic carbon content of the soil. It can be seen from Table 23.1.1 that R can vary over two orders of magnitude at a site depending on the chemical in question and the estimated value of porosity and soil bulk density.

Table 23.1.1. Calculated retardation factors for several chlorinated solvent-related chemicals

Compound	log(K_{oc})	Fraction of organic compound in aquifer (f_{oc})			
		0.0001	0.001	0.01	0.1
Carbon tetrachloride	2.67	1.2	3.3	24.0	231.2
1,1,1-TCA	2.45	1.1	2.4	14.9	139.7
PCE	2.42	1.1	2.3	13.9	130.4
1,1- or 1,2-DCA	1.76	1.0	1.3	3.8	29.3
trans 1,2-DCE	1.42	1.0	1.1	2.3	13.9
cis 1,2-DCE	1.38	1.0	1.1	2.2	12.8
TCE	1.26	1.0	1.1	1.9	10.0
Chloroethane	1.25	1.0	1.1	1.9	9.8
Dichloromethane	1.23	1.0	1.1	1.8	9.4
Vinyl chloride	0.06	1.0	1.0	1.1	1.6

Notes: Units of f_{oc}: g naturally-occurring organic carbon per g dry soil. Assumed porosity and bulk density: 0.35 and 1.72, respectively. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

23.1.2.4 One-dimensional advection-dispersion equation with retardation

In one dimension, the advection-dispersion equation is given by:

$$R\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad [23.1.9]$$

where:

v_x	average linear ground-water velocity [L/T]
R	coefficient of retardation [dimensionless]
C	contaminant concentration [M/L^3]
D_x	hydrodynamic dispersion [L^2/T]
T	time [T]
x	distance along flow path [L]

23.1.2.5 Dilution (recharge)

Ground water recharge can be defined as the entry into the saturated zone of water made available at the water-table surface.[20] Recharge may therefore include precipitation that infiltrates through the vadose zone and water entering the ground-water system due to discharge from surface water bodies (i.e., streams and lakes). Recharge of a water table aquifer has two effects on the natural attenuation of a dissolved contaminant plume. Additional water entering the system due to infiltration of precipitation or from surface water will contribute to dilution of the plume, and the influx of relatively fresh, electron acceptor-charged water will alter geochemical processes and in some cases facilitate additional biodegradation.

Wiedemeier et al.[1] present the following relationship for estimating the amount of dilution caused by recharge:

$$C_L = C_o \exp - \left[\frac{RW\left(\frac{L}{V_D}\right)}{WThV_D} \right] \qquad [23.1.10]$$

eliminating the width and rearranging, gives:

$$C_L = C_o \exp\left(-\frac{RL}{Th(V_D)^2} \right) \qquad [23.1.11]$$

where:

C_L	concentration at distance L from origin assuming complete mixing of recharge with groundwater (mg/L)
C_o	concentration at origin or at distance L = 0 (mg/L)
R	recharge mixing with groundwater (ft/yr)
W	width of area where recharge is mixing with groundwater (ft)
L	length of area where recharge is mixing with groundwater (ft)
Th	thickness of aquifer where groundwater flow is assumed to completely mix with recharge (ft)
V_D	Darcy velocity of groundwater (ft/yr)

23.1.2.6 Volatilization

Volatilization causes contaminants to transfer from the dissolved phase to the gaseous phase. In general, factors affecting the volatilization of contaminants from ground water into soil gas include the contaminant concentration, the change in contaminant concentration with depth, the Henry's Law constant and diffusion coefficient of the compound, mass transport coefficients for the contaminant in both water and soil gas, sorption, and the temperature of the water.[21]

The Henry's Law constant of a chemical determines the tendency of a contaminant to volatilize from ground water into the soil gas. Henry's Law states that the concentration of a contaminant in the gaseous phase is directly proportional to the compound's concentration in the liquid phase and is a constant characteristic of the compound:[11]

$$C_a = HC_l \qquad [23.1.12]$$

where:

H	Henry's Law constant (atm m^3/mol)
C_a	concentration in air (atm)
C_l	concentration in water (mol/m^3)

Values of Henry's Law constants for selected chlorinated solvents are given in Table 23.1.2. As indicated in the table, values of H for chlorinated compounds also vary over several orders of magnitude. Chlorinated solvents have low Henry's Law constants, with the exception of vinyl chloride. Volatilization of chlorinated solvents compounds from ground water is a relatively slow process that generally can be neglected when modeling biodegradation.

Table 23.1.2. Physical properties for chlorinated compounds

Constituent	CAS #	Molecular weight		Diffusion coefficients				log K_{oc} (@20-25°C)	
				in air		in water		Partition log(L/kg)	Ref
		M_W, g/mol	Ref	D_{air}, cm^2/s	Ref	D_{wat}, cm^2/s	Ref		
Bromodichloromethane	75-27-4	163.8	22	2.98E-02	22	1.06E-05	22	1.85	22
Carbon tetrachloride	56-23-5	153.8	22	7.80E-02	22	8.80E-06	22	2.67	22
Chlorobenzene	108-90-7	112.6	22	7.30E-02	22	8.70E-06	22	2.46	22
Chloroethane	75-00-3	64.52	22	1.50E-01	22	1.18E-05	22	1.25	22
Chloroform	67-66-3	119.4	22	1.04E-01	22	1.00E-05	22	1.93	22
Chloromethane	74-87-3	51	23	1.28E-01	22	1.68E-04	b	1.40	28
Chlorophenol, 2-	95-57-8	128.6	22	5.01E-02	22	9.46E-06	22	2.11	22
Dibromochloromethane	124-48-1	208.29	22	1.99E-02	22	1.03E-05	22	2.05	22
Dichlorobenzene, (1,2)(-o)	95-50-1	147	22	6.90E-02	22	7.90E-06	22	3.32	22
Dichlorobenzene, (1,4)(-p)	106-46-7	147	22	6.90E-02	22	7.90E-06	22	3.33	22
Dichlorodifluoromethane	75-71-8	120.92	22	5.20E-02	22	1.05E-05	22	2.12	22

Constituent	CAS #	Molecular weight		Diffusion coefficients				log K_{oc} (@20-25°C)	
				in air		in water		Partition log(L/kg)	Ref
		M_W, g/mol	Ref	D_{air}, cm^2/s	Ref	D_{wat}, cm^2/s	Ref		
Dichloroethane, 1,1-	75-34-3	98.96	22	7.42E-02	22	1.05E-05	22	1.76	22
Dichloroethane, 1,2-	107-06-2	98.96	22	1.04E-01	22	9.90E-06	22	1.76	22
Dichloroethene, cis-1,2-	156-59-2	96.94	22	7.36E-02	22	1.13E-05	22	1.38	c
Dichloroethene, 1,2-trans	156-60-5	96.94	22	7.07E-02	22	1.19E-05	22	1.46	22
Dichloromethane	75-09-2	85	22	1.01E-01	22	1.17E-05	22	1.23	22
Tetrachloroethane, 1,1,2,2-	79-34-5	168	22	7.10E-02	22	7.90E-06	22	0.00	22
Tetrachloroethene	127-18-4	165.83	22	7.20E-02	22	8.20E-06	22	2.43	28
Trichlorobenzene, 1,2,4-	120-28-1	181.5	22	3.00E-02	22	8.23E-06	22	3.91	22
Trichoroethane, 1,1,1-	71-55-6	133.4	22	7.80E-02	22	8.80E-06	22	2.45	22
Trichloroethane, 1,1,2-	79-00-5	133.4	22	7.80E-02	22	8.80E-06	22	1.75	28
Trichloroethene	79-01-6	131.4	24	8.18E-02	a	1.05E-04	b	1.26	d
Trichlorofluoromethane	75-69-4	137.4	22	8.70E-02	22	9.70E-06	22	2.49	22
Vinyl chloride	75-01-4	62.5	22	1.06E-01	22	1.23E-05	22	0.39	26

[a]Calculated diffusivity using the method of Fuller, Schettler, and Giddings [from Reference 25]
[b]Calculated diffusivity using the method of Hayduk and Laudie and the reference 25
[c]Calculated using Kenaga and Goring K_{ow}/solubility regression equation from reference 25 and K_{ow} data from reference 26, log (S, mg/L) = 0.922 log(K_{ow}) + 4.184 d
[d]Back calculated from solubility [see note c, based on K_{ow} from reference 26 and method from reference 27, log(K_{oc}) = 0.00028 + 0.938 log (K_{ow})]

23.1.2.7 Hydrolysis and dehydrohalogenation

Hydrolysis and dehydrohalogenation reactions are the most thoroughly studied abiotic attenuation mechanisms. In general, the rates of these reactions are often quite slow within the range of normal ground-water temperatures, with half-lives of days to centuries.[29,30] Hydrolysis is a substitution reaction in which a compound reacts with water, and a halogen substituent is replaced with a hydroxyl (OH^-) group resulting in the formation of alcohols and alkenes after:[31,32]

$$RX + HOH \rightarrow ROH + HX \qquad [23.1.13]$$

$$H_3C\text{-}CH_2X \rightarrow H_2C{=}CH_2 + HX \qquad [23.1.14]$$

The likelihood that a halogenated solvent will undergo hydrolysis depends in part on the number of halogen substituents. More halogen substituents on a compound will decrease the chance for hydrolysis reactions to occur,[29] and will therefore decrease the rate of the reaction. In addition, bromine substituents are more susceptible to hydrolysis than chlo-

rine substituents;[29] for example, 1,2-dibromoethane is subject to significant hydrolysis reactions under natural conditions. McCarty[33] lists TCA (1,1,1-trichloroethane) as the only major chlorinated solvent that can be transformed chemically through hydrolysis (as well as elimination) leading to the formation of 1,1-DCE (l,1-dichlorethene) and acetic acid.

Locations of the halogen substituent on the carbon chain may also have some effect on the rate of reaction. The rate also may increase with increasing pH; however, a rate dependence upon pH is typically not observed below a pH of 11.[34,35] Rates of hydrolysis may also be increased by the presence of clays, which can act as catalysts.[29] Other factors that impact the level of hydrolysis include dissolved organic matter, and dissolved metal ions. Hydrolysis rates can generally be described using first-order kinetics, particularly in solutions in which water is the dominant nucleophile.[29] A listing of half-lives for abiotic hydrolysis and dehydrohalogenation of some chlorinated solvents is presented in Table 23.1.3. Note that no distinctions are made in the table as to which mechanism is operating; this is consistent with the references from which the table has been derived.[29,36]

Table 23.1.3. Approximate half-lives of abiotic hydrolysis and dehydrohalogenation reactions involving chlorinated solvents

Compound	Half-Life (years)	Products
Chloromethane	no data	
Dichloromethane	704[34]	
Chloroform	3500,[34] 1800[37]	
Carbon tetrachloride	41[37]	
Chloroethane	0.12[29]	ethanol
1,1-Dichloroethane	61[37]	
1,2-Dichloroethane	72[37]	
1,1,1-Trichloroethane	1.7,[34] 1.1,[37] 2.5[38]	acetic acid, 1,1-DCE
1,1,2-Trichloroethane	140,[37] 170[34]	1,1-DCE
1,1,1,2-Tetrachloroethane	47,[37] 380[34]	TCE
1,1,2,2-Tetrachloroethane	0.3,[29] 0.4,[37] 0.8[34]	1,1,2-TCA, TCE
Tetrachloroethene	0.7,[40]* 1.3E+06[37]	
Trichloroethene	0.7,[40]* 1.3E+06[37]	
1,1-Dichloroethene	1.2E+10[37]	
1,2-Dichloroethene	2.1E+10[37]	

*Butler and Barker[36] indicate that these values may reflect experimental difficulties and that the longer half-life [as calculated by Jeffers et al.[37]] should be used. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, Na**tural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

One common chlorinated solvent for which abiotic transformations have been well studied is 1,1,1-TCA. 1,1,1-TCA may be abiotically transformed to acetic acid through a series of substitution reactions, including hydrolysis. In addition, 1,1,1-TCA may be reductively dehalogenated to form 1,1-DCA and then chloroethane (CA), which is then hydrolyzed to ethanol[38] or dehydrohalogenated to vinyl chloride.[37]

Dehydrohalogenation is an elimination reaction involving halogenated alkanes in which a halogen is removed from one carbon atom, followed by the subsequent removal of a hydrogen atom from an adjacent carbon atom. In this two-step reaction, an alkene is produced. Contrary to the patterns observed for hydrolysis, the likelihood that dehydrohalogenation will occur increases with the number of halogen substituents. It has been suggested that under normal environmental conditions, monohalogenated aliphatics apparently do not undergo dehydrohalogenation, and these reactions are apparently not likely to occur.[29,41] However, Jeffers et al.[37] report on the dehydrohalogenation of CA to VC. Polychlorinated alkanes have been observed to undergo dehydrohalogenation under normal conditions and extremely basic conditions.[29] As with hydrolysis, bromine substituents are more reactive with respect to dehydrohalogenation.

Dehydrohalogenation rates may also be approximated using pseudo-first-order kinetics. The rates will not only depend upon the number and types of halogen substituent, but also on the hydroxide ion concentration. Under normal pH conditions (i.e., near a pH of 7), interaction with water (acting as a weak base) may become more important.[29] Transformation rates for dehydrohalogenation reactions are presented in Table 23.1.3.

The organic compound 1,1,1-TCA is also known to undergo dehydrohalogenation.[38] In this case, TCA is transformed to 1,1-DCE, which is then reductively dehalogenated to VC. The VC is then either reductively dehalogenated to ethene or consumed as a substrate in an aerobic reaction and converted to CO_2. In a laboratory study, Vogel and McCarty[38] reported that the abiotic conversion of 1,1,1-TCA to 1,1-DCE has a rate constant of about 0.04 $year^{-1}$. Jeffers et a1.[37] reported that the tetrachloroethanes and pentachloroethanes degrade to TCE and PCE via dehydrohalogenation, respectively. Jeffers et al.[37] also report that CA may degrade to VC.

23.1.2.8 Reduction reactions

Two abiotic reductive dechlorination reactions that may operate in the subsurface are hydrogenolysis and dihaloelimination. Hydrogenolysis is the simple replacement of a chlorine (or another halogen) by a hydrogen, while dihaloelimination is the removal of two chlorines (or other halogens) accompanied by the formation of a double carbon-carbon bond. While these reactions are thermodynamically possible under reducing conditions, they often do not take place in the absence of biological activity.[36,42-45] In general, microbes may produce reductants that facilitate such reactions in conjunction with minerals in the aquifer matrix. Moreover, the reducing conditions necessary to produce such reactions are most often created as a result of microbial activity. It is therefore not clear if some of these reactions are truly abiotic, or if because of their reliance on microbial activity to produce reducing conditions or reactants, they should be considered to be a form of cometabolism. In some cases, truly abiotic reductive dechlorination has been observed;[46,47] however, the conditions that favor such reactions may not occur naturally.

23.1.3 BIODEGRADATION OF CHLORINATED SOLVENTS

The biodegradation of organic chemicals can be grouped into two broad categories:

1) use of the organic compound as a primary growth substrate, and

2) cometabolism.

The use of chlorinated solvents as a primary growth substrate is probably the most important biological mechanism affecting them in the subsurface. Some chlorinated solvents are used as electron donors and some are used as electron acceptors when serving as pri-

mary growth substrates (meaning the mediating organism obtains energy for growth). When used as an electron donor, the chlorinated solvent is oxidized. Oxidation reactions can be aerobic or anaerobic. Conversely, when used as an electron acceptor, the chlorinated solvent is reduced via a reductive dechlorination process called halorespiration. It is important to note that not all chlorinated solvents can be degraded via all of these reactions. In fact, vinyl chloride is the only chlorinated solvent known to degrade via all of these pathways.

Chlorinated solvents can also be degraded via cometabolic pathways. During cometabolism, microorganisms gain carbon and energy for growth from metabolism of a primary substrate, and chlorinated solvents are degraded fortuitously by enzymes present in the metabolic pathway. Cometabolism reactions can be either oxidation or reduction reactions (under aerobic or anaerobic conditions), however based on data from numerous field sites, it does not appear that cometabolic oxidation will be a significant process in plumes of chlorinated solvents. Anaerobic reductive dechlorination can also occur via cometabolism. The process of cometabolic reductive dechlorination, however, is "sufficiently slow and incomplete that a successful natural attenuation strategy typically cannot completely rely upon it".[48]

The types of biodegradation reactions that have been observed for different chlorinated solvents are presented in Table 23.1.4. The remainder of this section will focus on describing the various mechanisms shown in Table 23.1.4.

Table 23.1.4. Biological degradation processes for selected chlorinated solvents

Compound	Halorespiration	Direct aerobic oxidation	Direct anaerobic oxidation	Aerobic cometabolism	Anaerobic cometabolism
PCE	X				X
TCE	X			X	X
DCE	X	X	X	X	X
Vinyl chloride	X	X	X	X	X
1,1,1-TCA	X			X	X
1,2-DCA	X	X		X	X
Chloroethane		X		X	
Carbon tetrachloride	X				X
Chloroform	X			X	X
Dichloromethane		X	X	X	

[From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

23.1.3.1 Halorespiration or reductive dechlorination using hydrogen

Reductive dechlorination is a reaction in which a chlorinated solvent acts as an electron acceptor and a chlorine atom on the molecule is replaced with a hydrogen atom. This results in the reduction of the chlorinated solvent. When this reaction is biological, and the organism is utilizing the substrate for energy and growth, the reaction is termed halorespiration. Only

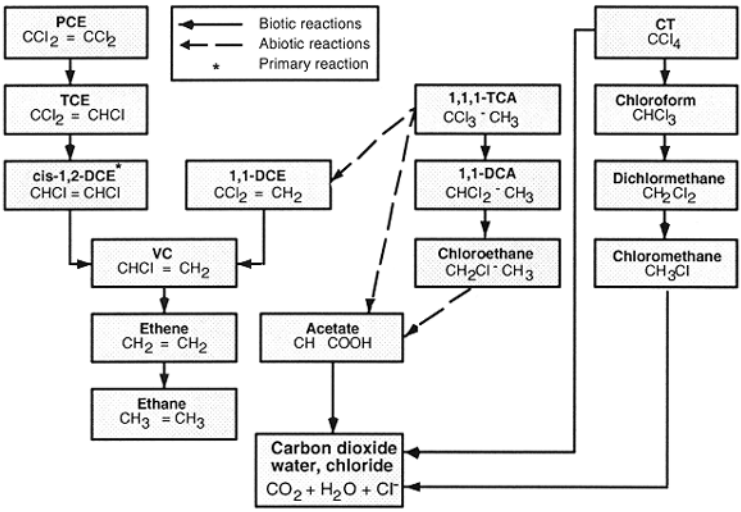

Figure 23.1.4. Abiotic and biological transformation pathways for selected chlorinated solvents. (From reference 1 after references 29, 53). [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

recently have researchers demonstrated the existence of halorespiration.[49] Prior to this research, reductive dechlorination was thought to be strictly a cometabolic process. During halorespiration, hydrogen is used directly as an electron donor. The generalized reaction is given by:

$$H_2 + C\text{-}Cl \rightarrow C\text{-}H + H^+ + Cl^- \qquad [23.1.15]$$

where C-Cl represents a carbon-chloride bond in a chlorinated solvent. In this reaction, H_2 is the electron donor which is oxidized and the chlorinated solvent is the electron acceptor which is reduced. Although a few other electron donors (also fermentation products) besides hydrogen have been identified, hydrogen appears to be the most important electron donor for halorespiration. Only in the last four years have researchers begun to fully recognize the role of hydrogen as the electron donor in the reductive dechlorination of PCE and TCE.[48,50-52]

The hydrogen is produced in the subsurface by the fermentation of a wide variety of organic compounds including petroleum hydrocarbons and natural organic carbon. Because of its importance in the microbial metabolism of the halorespirators, the relative supply of hydrogen precursors compared to the amount of chlorinated solvent that must be degraded is an important consideration when evaluating natural attenuation. In general, reductive dechlorination of the ethenes occurs by sequential dechlorination from PCE to TCE to DCE to VC and finally to ethene. A summary of key biotic and abiotic reactions for the chlorinated ethenes, ethanes, and methanes first developed by Vogel[29] is shown in Figure 23.1.4.

For halorespiration to occur, Wiedemeier et al.[1] conclude that the following conditions must exist: "1) the subsurface environmental must be anaerobic and have a low oxidation-reduction potential (based on thermodynamic considerations, reductive dechlorination reactions will occur only after both oxygen and nitrate have been depleted from the aquifer);

2) chlorinated solvents amenable to halorespiration must be present; and 3) there must be an adequate supply of fermentation substrates for production of dissolved hydrogen."

Fermentation, the process that generates hydrogen, is a balanced oxidation-reduction reaction, in which different portions of a single substrate are oxidized and reduced, yielding energy. Fermentation yields substantially less energy per unit of substrate compared to oxidation reactions which utilize an external electron acceptor; thus, fermentation generally occurs when these external electron acceptors are not available. Bacterial fermentation which can be important in anaerobic aquifers includes primary and secondary fermentation.

Primary fermentation refers to the fermentation of primary substrates such as sugars, amino acids, and lipids yields acetate, formate, CO_2 and H_2, but also yields ethanol, lactate, succinate, propionate, and butyrate. Secondary fermentation, on the other hand, refers to the fermentation of primary fermentation products such as ethanol, lactate, succinate, propionate, and butyrate yielding acetate, formate, H_2, and CO_2. Bacteria which carry out these reactions are called obligate proton reducers because the reactions must produce hydrogen in order to balance the oxidation of the carbon substrates. These secondary fermentation reactions are energetically favorable only if hydrogen concentrations are very low (10^{-2} to 10^{-4} atm or 8,000 nM to 80 nM dissolved hydrogen, depending on the fermentation substrate). Thus, these fermentation reactions occur only when the produced hydrogen is utilized by other bacteria, such as methanogens which convert H_2 and CO_2 into CH_4 and H_2O.

In the absence of external electron acceptors, the hydrogen produced by fermentation will be utilized by methanogens (methane producing bacteria). In this case, the ultimate end products of anaerobic metabolism of carbon substrates will be CH_4 (the most reduced form of carbon) and CO_2 (the most oxidized form of carbon). Methanogens will carry out the last step in this metabolism, the conversion of H_2 and CO_2 into CH_4. However, in the presence of external electron acceptors (halogenated organics, nitrate, sulfate, etc.), other products will be formed.[1]

There are a number of compounds besides the ones listed above that can be fermented to produce hydrogen. Sewell and Gibson[54] noted that petroleum hydrocarbons support reductive dechlorination. In this case, the reductive dechlorination is driven by the fermentation of biodegradable compounds such as the BTEX compounds in fuels. Metabolism of BTEX compounds to produce hydrogen likely requires the involvement of several strains of bacteria. Although the BTEX compounds are common fermentation substrates at chlorinated solvent sites, there are many other hydrocarbon substrates which are naturally fermented at sites and result in the generation of hydrogen such as acetone, sugars, and fatty acids from landfill leachate.

As hydrogen is produced by fermentative organisms, it is rapidly consumed by other bacteria. The utilization of H_2 by non-fermentors is known as interspecies hydrogen transfer and is required for fermentation reactions to proceed. Although H_2 is a waste product of fermentation, it is a highly reduced molecule which makes it an excellent, high-energy electron donor. Both organisms involved in interspecies hydrogen transfer benefit from the process. The hydrogen-utilizing bacteria gain a high energy electron donor, and, for the fermentors, the removal of hydrogen allows additional fermentation to remain energetically favorable.

A wide variety of bacteria can utilize hydrogen as an electron donor: denitrifiers, iron reducers, sulfate reducers, methanogens, and halorespirators. Thus, the production of hydrogen through fermentation does not, by itself, guarantee that hydrogen will be available for halorespiration. For dechlorination to occur, halorespirators must successfully compete

against the other hydrogen utilizers for the available hydrogen. Smatlak et al.[51] suggest that the competition for hydrogen is controlled primarily by the Monod half-saturation constant $K_s(H_2)$, the concentration at which a specific strain of bacteria can utilize hydrogen at half the maximum utilization rate. Ballapragada et al.,[52] however, provide a more detailed discussion of halorespiration kinetics and point out that competition for hydrogen also depends on additional factors including the bacterial growth rate and maximum hydrogen utilization rate.

Smatlak et al.[51] have suggested that the steady-state concentration of hydrogen will be controlled by the rate of hydrogen production from fermentation. Both laboratory results and field observations have suggested, however, that the steady-state concentration of hydrogen is controlled by the type of bacteria utilizing the hydrogen and is almost completely independent of the rate of hydrogen production.[52,55-57] Under nitrate reducing conditions, steady-state H_2 concentrations were <0.05 nM; under iron reducing conditions, they were 0.2 to 0.8 nM; under sulfate reducing conditions, they were 1-4 nM, and under methanogenic conditions, they were 5-14 nM.[56,58,59] Finally, Carr and Hughes[57] show that dechlorination in a laboratory column is not impacted by competition for electron donor at high hydrogen concentrations. Thus, it is clear that an increased rate of hydrogen production will result in increased halorespiration without affecting the competition between bacteria for the available hydrogen.

23.1.3.1.1 Stoichiometry of reductive dechlorination

Under anaerobic conditions, Gossett and Zinder[48] showed that the reductive dehalogenation of the chlorinated ethenes occurs as a series of consecutive irreversible reactions mediated by the addition of 1 mole of hydrogen gas for every mole of chloride removed. Thus, the theoretical minimum hydrogen requirement for dechlorination can be calculated on a mass basis as shown below:[1]

1 mg H_2 will dechlorinate 21 mg of PCE to ethene
1 mg H_2 will dechlorinate 22 mg of TCE to ethene
1 mg H_2 will dechlorinate 24 mg of DCE to ethene
1 mg H_2 will dechlorinate 31 mg of VC to ethene

Complete fermentation of BTEX compounds is expected to yield 0.25 to 0.4 mg H_2 per mg BTEX. Therefore, for each mg of BTEX consumed, 4.5 to 7 mg of chloride could be released during reductive dechlorination. However, the utilization of hydrogen for dechlorination will never be completely efficient because of the competition for hydrogen in the subsurface discussed previously. One rule of thumb that has been proposed is the following: for reductive dechlorination to completely degrade a plume of dissolved chlorinated solvents, organic substrate concentrations greater than 25 to 100+ times that of the chlorinated solvent are required.[60]

23.1.3.1.2 Chlorinated solvents that are amenable to halorespiration

As shown in Table 23.1.4, all of the chlorinated ethenes (PCE, TCE, DCE, VC) and some of the chlorinated ethanes (TCA, 1,2-DCA) can be degraded via halorespiration; however, dichloromethane has not yet been shown to be degraded by this process. The oxidation state of a chlorinated solvent affects both the energy released by halorespiration and the rate at which the reaction occurs. In general, the more oxidized a compound is (more chlorine atoms on the organic molecule) the more amenable it is for reduction by halorespiration.

As with the ethenes, chlorinated ethanes will also undergo halorespiration. Dechlorination of 1,1,1-TCA has been described by Vogel and McCarty[38] and Cox et al.,[61] but understanding this pathway is complicated by the rapid hydrolysis reactions (e.g., half-life is 0.5-2.5 yrs) that can affect TCA.[30] Finally, halorespiration has been observed with highly chlorinated benzenes such as hexachlorobenzene, pentachlorobenzene, tetrachlorobenzene, and trichlorobenzene.[62-64] As discussed by Suflita and Townsend,[64] halorespiration of aromatic compounds has been observed in a variety of anaerobic habitats, including aquifer materials, marine and freshwater sediments, sewage sludges, and soil samples. However, isolation of specific microbes capable of these reactions has been difficult.

23.1.3.2 Oxidation of chlorinated solvents

In contrast to halorespiration, direct oxidation of some chlorinated solvents can occur biologically in groundwater systems. In this case, the chlorinated compound serves as the electron donor, and oxygen, sulfate, ferric iron or other compounds serve as the electron acceptor.

23.1.3.2.1 Direct aerobic oxidation of chlorinated compounds

Under direct aerobic oxidation conditions, the facilitating microorganism uses oxygen as an electron acceptor and obtains energy and organic carbon from the degradation of the chlorinated solvent. In general, the more-chlorinated aliphatic chlorinated solvents (e.g., PCE, TCE, and TCA) have not been shown to be susceptible to aerobic oxidation, while many of the progeny products (e.g., vinyl chloride, 1,2-DCA, and perhaps the isomers of DCE) are degraded via direct aerobic oxidation.

Hartmans et al.[65] and Hartmans and de Bont[66] show that vinyl chloride can be used as a primary substrate under aerobic conditions, with vinyl chloride being directly mineralized to carbon dioxide and water. Direct vinyl chloride oxidation has also been reported by Davis and Carpenter,[67] McCarty and Semprini,[53] and Bradley and Chapelle.[68] Aerobic oxidation is rapid relative to reductive dechlorination of dichloroethene and vinyl chloride. Although direct DCE oxidation has not been verified, a recent study has suggested that DCE isomers may be used as primary substrates.[68] Of the chlorinated ethanes, only 1,2-dichloroethane has been shown to be aerobically oxidized. Stucki et al.[69] and Janssen et al.[70] show that 1,2-DCA can be used as a primary substrate under aerobic conditions. In this case, the bacteria transform 1,2-DCA to chloroethanol, which is then mineralized to carbon dioxide. McCarty and Semprini[53] describe investigations in which 1,2-dichloroethane (DCA) was shown to serve as primary substrates under aerobic conditions.

Chlorobenzene and polychlorinated benzenes (up to and including tetrachlorobenzene) have been shown to biodegrade under aerobic conditions. Several studies have shown that bacteria are able to utilize chlorobenzene,[71] 1,4-DCB,[71-73] 1,3-DCB,[74] 1,2-DCB,[75] 1,2,4-TCB,[76,77] and 1,2,4,5-TeCB,[77] as primary growth substrates in aerobic systems. Nishino et al.[78] note that aerobic bacteria able to grow on chlorobenzene have been detected at a variety of chlorobenzene-contaminated sites but not at uncontaminated sites. Spain[79] suggests that this provides strong evidence that the bacteria are selected for their ability to derive carbon and energy from chlorobenzene degradation in situ. The pathways for all of these reactions are similar, bearing resemblance to benzene degradation pathways.[79,80]

23.1.3.2.2 Aerobic cometabolism of chlorinated compounds

It has been reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic oxidation.[30,53,81,82] Vogel[30] further elaborates that the oxidation rate increases as the degree of chlorination decreases. Aerobic cometabolism of ethenes may be characterized by a loss of contaminant mass, the presence of intermediate degradation products (e.g., chlorinated oxides, aldehydes, ethanols, and epoxides), and the presence of other products such as chloride, carbon dioxide, carbon monoxide, and a variety of organic acids.[53,83] Cometabolism requires the presence of a suitable primary substrate such as toluene, phenol, or methane. For cometabolism to be effective, the primary substrate must be present at higher concentrations than the chlorinated compound, and the system must be aerobic. Because the introduction of high concentrations of oxidizable organic matter into an aquifer quickly drives the groundwater anaerobic, aerobic cometabolism typically must be engineered.

23.1.3.2.3 Anaerobic oxidation of chlorinated compounds

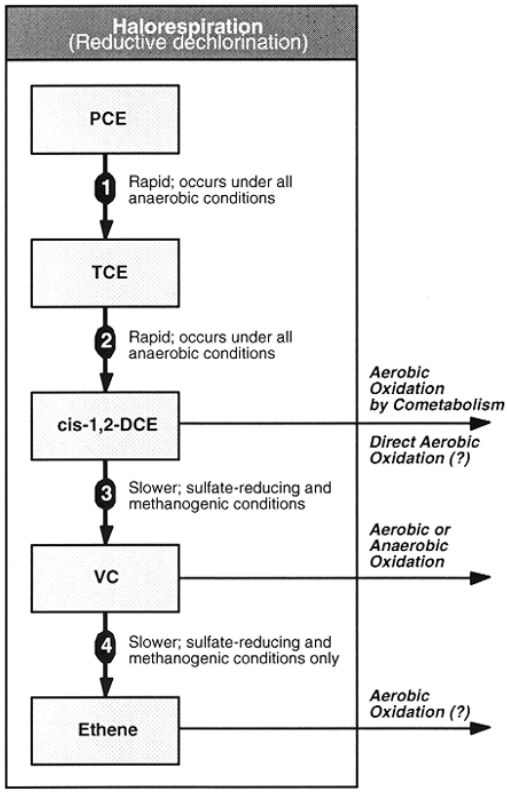

Figure 23.1.5. Reaction sequence and relative rates for halorespiration of chlorinated ethenes, with other reactions shown. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, reaction rates description from reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

Anaerobic oxidation occurs when anaerobic bacteria use the chlorinated solvent as an electron donor by utilizing an available electron acceptor such as ferric iron (Fe(III)). Bradley and Chapelle[84] show that vinyl chloride can be oxidized to carbon dioxide and water via Fe(III) reduction. In microcosms amended with Fe(III)-EDTA, reduction of vinyl chloride concentrations closely matched the production of carbon dioxide. Slight mineralization was also noted in unamended microcosms. The rate of this reaction apparently depends on the bioavailability of Fe(III). In a subsequent paper, Bradley and Chapelle[85] reported "significant" anaerobic mineralization of both DCE and VC in microcosms containing creek bed sediments. The sediments were taken from a stream where groundwater containing chlorinated ethenes continually discharges. Anaerobic mineralization was observed in both methanogenic and Fe(III) reducing conditions.

23.1.4 BIODEGRADATION RATES FOR CHLORINATED SOLVENTS

Overall, dechlorination is more rapid for highly chlorinated compounds than for compounds that are less chlorinated.[38,86,87] Figure 23.1.5 qualitatively shows the reaction rate and required conditions for halorespiration of PCE to ethene. PCE (four chlorines) degrades the fastest under all anaerobic environments, while VC (a single chlorine) will degrade only under sulfate-reducing and methanogenic conditions, with a relatively slow reaction rate.

At many chlorinated ethene sites, concentrations of cis-1,2-DCE are often higher than any of the parent chlorinated ethene compounds. The reason for the accumulation of 1,2-DCE may be due to either slower rates of DCE halorespiration, or the prevalence of organisms that reduce PCE as far as cis-1,2-DCE over ones that can reduce PCE all the way to ethene.[48] Although many researchers have commented that reductive dechlorination will result in the accumulation of VC (e.g., see 84, 89), at many field sites VC accumulation is much lower than cis-1,2-DCE. This may occur because the vinyl chloride in many chlorinated solvent plumes can migrate to zones that can support direct oxidation of VC oxidation, either aerobically and/or anaerobically.

Suarez and Rifai[90] analyzed data from 138 studies (field and laboratory) to estimate biodegradation coefficients for chlorinated compounds. Suarez and Rifai[90] found a total of thirteen studies that reported Michaelis-Menten kinetics, 28 studies that reported zero-order rates, and 97 studies that reported first-order constants.

23.1.4.1 Michaelis-Menten rates

The data in Table 23.1.5 present the Michaelis Menten kinetic data from Suarez and Rifai.[90] Half-saturation constants varied from 0.6 mg/L to 29.5 mg/L for TCE and from 0.17 mg/L to 28 mg/L for DCE. Maximum specific degradation rates were within the ranges 0.038-478.59 $mg_{compound}/mg_{protein}$-day for TCE, and 0-11,115 $mg_{compound}/mg_{protein}$-day for DCE.

Table 23.1.5. Michaelis-Menten parameters for chlorinated solvents

Compound	Type of study	Redox environment	Culture	μ_{max}, day^{-1}	Half-saturation, K_s, mg/L	Yield, Y, mg/mg	Max. spec. degradation rate, μ_{max}/Y, mg/mg-day	Initial concentration, S_o, mg/L	Ref
1,1,1-TCA	Continuous reactor	Aerobic	Methylosinus trichosporium OB3b		28.46		4.60	>93.10	92
1,1-DCE	Growth reactor	Aerobic-Cometabolism (methane)	Mixed methanotrophic culture	1.37	0.43		0-11115	0.01	93
	Continuous reactor	Aerobic	Methylosinus trichosporium OB3b		0.48		0.84	1.94-2.91	92
1,2-DCA	Continuous reactor	Aerobic	Methylosinus trichosporium OB3b		7.62		9.26	4.95-6.93	92

Compound	Type of study	Redox environment	Culture	μ_{max}, day^{-1}	Half-saturation, K_s, mg/L	Yield, Y, mg/mg	Max. spec. degradation rate, μ_{max}/Y, mg/mg-day	Initial concentration, S_0, mg/L	Ref
cis-1,2-DCE	Growth reactor	Aerobic-Cometabolism (phenol)	Filamentous phenol-oxidizers				0.27-1.50		94
	Continuous reactor	Aerobic	Methylosinus trichosporium OB3b		2.91		25.40	12.60-25.20	92
	Methanogenic fluidized bed reactor	Anaerobic			28.00				52
trans-1,2-DCE	Continuous reactor	Aerobic	Methylosinus trichosporium OB3b		14.34		46.19	8.72-14.74	92
	Growth reactor	Aerobic-Cometabolism (methane)	Mixed methanotrophic culture	0.68	0.17		0.00-0.44	4.70	93
PCE	Methanogenic fluidized bed reactor	Anaerobic			12.00				52
	Biofilm reactor						0.00	0.99	95
	Fed-batch reactor	Anaerobic	Methanogenic consortium	0.47					96
TCE	Growth reactor	Aerobic			0.37		0.53	14.70	97
	Growth reactor	Aerobic-Cometabolism (formate)			8.20		7.60	10.10	97
	Growth reactor	Aerobic-Cometabolism (methane)	Mixed methanotrophic culture	1.07	0.13		0.00-1.13	1.00	93
	Methanogenic fluidized bed reactor	Anaerobic			19.00				52
	Growth reactor	Aerobic-Cometabolism (phenol)	Filamentous phenol-oxidizers				0.10-0.25		94

Compound	Type of study	Redox environment	Culture	μ_{max}, day^{-1}	Half-saturation, K_s, mg/L	Yield, Y, mg/mg	Max. spec. degradation rate, μ_{max}/Y, mg/mg-day	Initial concentration, S_o, mg/L	Ref
TCE	Microcosm	Aerobic-Cometabolism (toluene)		0.77-1.65		0.52	1.50	0.66	98
	Microcosm	Aerobic-Cometabolism (phenol)		0.88-1.43		0.40	3.00	0.66	98
	Growth reactor	Aerobic-Cometabolism (propane)	Propane-oxidizing culture		0.60		0.04	3.00	99
	Batch	Aerobic	Methylomonas methanica 68-1		29.48	0.10	438.59		100
	Batch		Methylosinus trichosporium OB3b		16.51	0.08	187.70		100
	Continuous reactor	Aerobic	Methylosinus trichosporium OB3b		19.00		54.71	9.17-13.10	92
	Continuous reactor	Aerobic-Cometabolism (methane)	Mixed methanotrophic culture			0.01			101
Vinyl chloride	Methanogenic fluidized bed reactor	Anaerobic			23.00				52
	Small-Column Microcosm	Aerobic-Cometabolism (methane)				1.00-3.50		1.00-17.00	102

[From M.P. Suarez and H.S. Rifai, *Bioremediation Journal,* **3**, 337-362. Copyright © 1999 *Battelle Memorial Institute*. Reprinted with permission.]

23.1.4.2 Zero-order rates

A summary of more than 40 studies reporting zero-order rates is included in Table 23.1.6. The reported zero-order rates ranged from 0 to 19.8 mg/L/day with mean values for anaerobic rates of 0.04, 2.14, 1.80, 1.74, and 0.11 mg/L/day for carbon tetrachloride, DCE, PCE, TCE, and vinyl chloride, respectively. TCE appeared to be reductively dechlorinated at the fastest rate coefficient, with a median equal to 0.76 mg/L/day. In contrast, vinyl chloride exhibited the slowest rate coefficient of reductive dechlorination with a median value of 0.01 mg/L/day.

Table 23.1.6 Summary of zero-order decay rates for reductive dechlorination obtained from laboratory studies (mg/L-day).

	CCl_4	cis -12-DCE	DCE (all other isomers)	PCE	TCE	Vinyl chloride
Number of rates[a]	8	18	8	29	7	9
minimum	0.022	0.013	0.009	0.013	0.314	0.002
25th percentile	0.024	0.183	0.023	0.288	0.511	0.006
median	0.029	0.511	0.250	0.577	0.760	0.011
75th percentile	0.042	1.318	1.385	1.040	1.297	0.075
90th percentile	0.049	3.348	2.021	2.801	3.798	0.379
maximum	0.054	16.958	3.470	19.800	7.490	0.495
mean	0.034	1.854	0.850	1.863	1.740	0.107
standard deviation	0.012	3.939	1.213	4.162	2.567	0.184
geometric mean[b]	0.000	15.513	1.471	17.323	6.590	0.034

[a]All the zero-order rates provided were calculated by the authors of the respective studies. [b]To calculate the geometric mean, values equal to zero were included as 10^{-10}. [From M.P. Suarez and H.S. Rifai, *Bioremediation Journal,* **3**, 337-362. Copyright © 1999 *Battelle Memorial Institute*. Reprinted with permission]

23.1.4.3 First-order rate constants

Table 23.1.7 summarizes the first order decay coefficients from both field and laboratory studies. As can be seen in Table 23.1.7, first-order rate constants for chlorinated solvents varied from 0 to 1.03 day^{-1} in the 90% of the cases, with mean values equal to 0.11, 0.02, 0.14, 0.05, 0.26, 0.17, and 0.23 day^{-1} for carbon tetrachloride, DCA, DCE, PCE, TCA, TCE, and vinyl chloride, respectively. The range minimum-90th percentile for aerobic rates was 0-1.35 day^{-1} while for anaerobic rates it was 0-1.11 day^{-1}. Field rates from aerobic/anaerobic studies ranged from 0 to 1.96 day^{-1}. The compound that showed the highest mean value under aerobic conditions was vinyl chloride (1.73 day^{-1}), while TCA exhibited the highest mean anaerobic rate coefficient (0.35 day^{-1}).

Table 23.1.7. Summary of first-order decay rates for chlorinated solvents (day^{-1}).

	Number of rates	Number of reported rates	Number of calculated rates[b]	mean	standard deviation	90th percentile	geometric mean[c]	range reported rates
Carbon tetrachloride								
All studies	13	0	13	0.108	0.134	0.216	0.054	0.0037-0.49
Aerobic oxidation								
In situ & laboratory	1	0	1					
In situ studies[a]	1	0	1					
Laboratory								

	Number of rates	Number of reported rates	Number of calculated rates[b]	mean	standard deviation	90th percentile	geometric mean[c]	range reported rates
Aerobic cometabolism								
Field & laboratory	1	0	1					
In situ studies[a]	1	0	1					
Laboratory								
Overall aerobic	2	0	2	0.019				0.016-0.022
Aerobic/anaerobic (field studies)								
Reductive dechlorination								
Field & laboratory	11	0	11	0.124	0.140	0.230	0.065	0.004-0.490
Field/in situ studies[a]	7	0	7	0.141	0.174	0.334	0.060	0.004-0.490
Laboratory	4	0	4	0.093			0.075	0.023-0.160
Anaerobic oxidation								
Field & laboratory								
Field/in situ studies[a]								
Laboratory								
DCA (all isomers)								
All studies	25	16	9	0.017	0.036	0.046	0.001	0-0.131
Aerobic oxidation								
In situ & laboratory	2	2	0				0.000	
In situ studies[a]								
Laboratory	2	2	0				0.000	
Aerobic cometabolism								
Field & laboratory	5	0	5	0.067	0.056	0.128	0.046	0.014-0.131
In situ studies[a]								
Laboratory	5	0	5	0.067	0.056	0.128	0.046	0.014-0.131
Overall aerobic	7	2	5	0.048	0.056	0.126	0.000	0-0.131
Aerobic/anaerobic (field studies)								
Reductive dechlorination								
Field & laboratory	18	14	4	0.005	0.012	0.016	0.001	0-0.044
Field/in situ studies[a]	16	14	2	0.002	0.003	0.004	0.001	0-0.011
Laboratory	2	0	2	0.036			0.035	0.028-0.044
Anaerobic oxidation								
Field & laboratory								
Field/in situ studies[a]								
Laboratory								
***cis*-1,2-DCE**								
All studies	34	24	10	0.004	0.395	0.257	0.004	0-1.960

	Number of rates	Number of reported rates	Number of calculated rates[b]	mean	standard deviation	90th percentile	geometric mean[c]	range reported rates
Aerobic oxidation								
In situ & laboratory								
In situ studies[a]								
Laboratory								
Aerobic cometabolism								
Field & laboratory	5	2	3	0.476	0.787	1.680	0.476	0.081-1.96
In situ studies[a]	3	2	1	0.885	0.843	1.820	0.885	0.281-1.96
Laboratory	2	0	2	0.187	0.250	0.399	0.187	0.081-0.434
Overall aerobic								
Aerobic/anaerobic (field studies)	4	4	0	0.000	0.003	0.006	0.000	0-0.008
Reductive dechlorination								
Field & laboratory	25	18	7	0.004	0.048	0.069	0.004	0-0.200
Field/in situ studies[a]	17	13	4	0.002	0.031	0.013	0.002	0-0.130
Laboratory	8	5	3	0.014	0.069	0.117	0.014	0.001-0.200
Anaerobic oxidation								
Field & laboratory								
Field/in situ studies[a]								
Laboratory								
DCE (all other isomers)								
All studies	27	14	13	0.149	0.302	0.666	0.003	0-1.150
Aerobic oxidation								
In situ & laboratory								
In situ studies[a]								
Laboratory								
Aerobic cometabolism								
Field & laboratory	8	2	6	0.458	0.416	0.845	0.002	0-1.150
In situ studies[a]	4	0	4	0.720	0.316	1.012	0.670	0.390-1.150
Laboratory	4	2	2	0.196	0.347	0.521	0.000	0-0.714
Overall aerobic								
Aerobic/anaerobic (field studies)								
Reductive dechlorination								
Field & laboratory	19	12	7	0.019	0.061	0.012	0.004	0.001-0.270
Field/in situ studies[a]	16	12	4	0.003	0.001	0.005	0.003	0.001-0.006
Laboratory	3	0	3	0.101	0.147	0.220	0.039	0.010-0.270

	Number of rates	Number of reported rates	Number of calculated rates[b]	mean	standard deviation	90th percentile	geometric mean[c]	range reported rates
Anaerobic oxidation Field & laboratory Field/in situ studies[a] Laboratory								
PCE								
All studies	50	31	19	0.051	0.084	0.153	0.000	0-0.410
Aerobic oxidation In situ & laboratory In situ studies[a] Laboratory	 10 3 7	 5 3 2	 5 0 5	 0.001 0.000 0.001	 0.001 0.002	 0.003 0.003	 0.000 0.000	 0-0.004 0.000 0-0.004
Aerobic cometabolism Field & laboratory In situ studies[a] Laboratory	 3 3	 1 1	 2 2	 0.025 0.025			 0.000 0.000	 0-0.054 0-0.054
Overall aerobic	13	6	7	0.006	0.015	0.017	0.000	0-0.054
Aerobic/anaerobic (field studies)	1	1	0					
Reductive dechlorination Field & laboratory Field/in situ studies[a] Laboratory	 36 13 23	 23 9 14	 13 4 9	 0.068 0.010 0.101	 0.093 0.022 0.101	 0.185 0.022 0.212	 0.002 0.000 0.024	 0-0.410 0-0.080 0-0.410
Anaerobic oxidation Field & laboratory Field/in situ studies[a] Laboratory								
TCA								
All studies	47	27	20	0.261	0.502	1.026	0.000	0-2.330
Aerobic oxidation In situ & laboratory In situ studies[a] Laboratory	 11 2 9	 7 2 5	 4 0 4	 0.002 0.003	 0.007 0.007	 0.009 0.005	 0.000 0.000	 0-0.022 0-0.022
Aerobic cometabolism Field & laboratory In situ studies[a] Laboratory	 5 5	 1 1	 4 4	 0.247 0.247	 0.522 0.522	 0.723 0.723	 0.001 0.001	 0-1.180 0.-1.180
Overall aerobic	16	8	8	0.079	0.294	0.030	0.000	0-1.180
Aerobic/anaerobic (field studies)								

	Number of rates	Number of reported rates	Number of calculated rates[b]	mean	standard deviation	90th percentile	geometric mean[c]	range reported rates
Reductive dechlorination								
Field & laboratory	31	19	12	0.355	0.562	1.110	0.003	0-2.330
Field/in situ studies[a]	10	3	7	0.029	0.039	0.058	0.000	0-0.125
Laboratory	21	16	5	0.511	0.629	1.280	0.007	0-2.330
Anaerobic oxidation								
Field & laboratory								
Field/in situ studies[a]								
Laboratory								
TCE								
All studies	86	52	34	0.173	0.475	0.636	0.001	0-3.130
Aerobic oxidation								
In situ & laboratory	12	6	6	0.005	0.010	0.025	0.000	0-0.028
In situ studies[a]	2	2	0					
Laboratory	10	0	10	0.006	0.011	0.026	0.000	0-0.028
Aerobic cometabolism								
Field & laboratory	17	7	10	0.586	0.566	1.418	0.309	0.024-1.650
In situ studies[a]	3	2	1	0.948			0.582	0.105-1.410
Laboratory	14	5	9	0.509	0.524	1.265	0.269	0.024-1.650
Overall aerobic	29	13	16	0.346	0.517	1.354	0.001	0-1.650
Aerobic/anaerobic (field studies)	1	1	0					
Reductive dechlorination								
Field & laboratory	56	38	18	0.086	0.434	0.022	0.001	0-3.130
Field/in situ studies[a]	32	26	6	0.003	0.005	0.006	0.000	0-0.023
Laboratory	24	12	12	0.196	0.654	0.337	0.012	0-3.130
Anaerobic oxidation								
Field & laboratory								
Field/in situ studies[a]								
Laboratory								
Vinyl chloride								
All studies	26	8	18	0.229	0.476	0.946	0.023	0-1.960
Aerobic oxidation								
In situ & laboratory	4	0	4	0.087			0.080	0.043-0.125
In situ studies[a]								
Laboratory	4	0	4	0.087			0.080	0.043-0.125
Aerobic cometabolism								
Field & laboratory	4	0	4	1.023			0.552	0.055-1.960
In situ studies[a]	2	0	2	1.730			1.715	1.500-1.960
Laboratory	2	0	2	0.316			0.178	0.055-0.576

	Number of rates	Number of reported rates	Number of calculated rates[b]	mean	standard deviation	90th percentile	geometric mean[c]	range reported rates
Overall aerobic	8	0	8	0.555	0.756	0.107	0.211	0.043-0.120
Aerobic/anaerobic (field studies)	3	2	1	0.004			0.002	0.001-0.009
Reductive dechlorination								
Field & laboratory	8	5	3	0.153	0.228	0.499	0.007	0-0.520
Field/in situ studies[a]	4	4	0	0.003			0.001	0-0.007
Laboratory	4	1	3	0.303			0.036	0-0.520
Anaerobic oxidation								
Field & laboratory	7	1	6	0.042	0.048	0.104	0.018	0.001-0.120
Field/in situ studies[a]	1	1	0					
Laboratory	6	0	6	0.049	0.048	0.107	0.028	0.008-0.120

[a]In situ studies include in situ microcosms and in situ columns
[b]When enough information was provided by the authors of a study, the authors of this paper calculated the rate coefficient assuming first-order kinetics
[c]To calculate the geometric mean, values equal to zero were included as 10^{-10}
[From M.P. Suarez and H.S. Rifai, *Bioremediation Journal,* **3**, 337-362. Copyright © 1999 *Battelle Memorial Institute*. Reprinted with permission.]

The biodegradability under different electron acceptors for each one of the chlorinated solvents was also analyzed by Suarez and Rifai.[90] As summarized in Table 23.1.8, DCA presented very high potential for biodegradation via aerobic cometabolism and reductive dechlorination with none of the studies reporting recalcitrance. Median half-lives for this compound were 1,260 days and 15 days for reductive dechlorination and cometabolism, respectively. DCE exhibited high potential for aerobic cometabolism with 11% of the studies showing recalcitrance and a very short median half-life (1 day). None of the 44 studies on reductive dechlorination of DCE reported recalcitrance, which leads to the conclusion that DCE may undergo this process though with a relatively slow rate (median half-life equal to 234 days).

Table 23.1.8. Biodegradability of chlorinated solvents

	All Studies	Process			
		Aerobic oxidation	Cometabolism	Reductive dechlorination	Anaerobic oxidation
Carbon tetrachloride					
# rates	13	1	1	11	
# rates-recalcitrant	0	0	0	0	
half-life (days)[a]	14	NC	NC	9	
% rates recalcitrant	0%	0%	0%	0%	
potential for biodegradation[b]	almost always	NA	NA	almost always	

	All Studies	Process			
		Aerobic oxidation	Cometabolism	Reductive dechlorination	Anaerobic oxidation
DCA (all isomers)					
# rates	25	2	5	18	
# rates-recalcitrant	2	2	0	0	
half-life (days)[a]	990	NC	15	1260	
% rates recalcitrant	8%	100%	0%	0%	
potential for biodegradation[b]	almost always	NA	almost always	almost always	
DCE (all isomers)					
# rates	61		13	44	
# rates-recalcitrant	3		2	0	
half-life (days)[a]	173		2	234	
% rates recalcitrant	5%		15%	0%	
potential for biodegradation[b]	almost always		frequently	almost always	
PCE					
# rates	50	10	3	36	
# rates-recalcitrant	14	6	1	5	
half-life (days)[a]	80	NC	35	32	
% rates recalcitrant	28%	60%	35%	14%	
potential for biodegradation[b]	sometimes	barely	NA	frequently	
TCA					
# rates	47	11	5	31	
# rates-recalcitrant	14	8	1	5	
half-life (days)[a]	68	NC	53	24	
% rates recalcitrant	30%	73%	20%	16%	
potential for biodegradation[b]	sometimes	barely	frequently	frequently	
TCE					
# rates	85	11	17	56	
# rates-recalcitrant	12	6	0	5	
half-life (days)[a]	151	NC	3	201	
% rates recalcitrant	14%	55%	0%	9%	
potential for biodegradation[b]	frequently	barely	almost always	almost always	
Vinyl chloride					
# rates	27	4	5	15	7
# rates-recalcitrant	0	0	0	0	0
half-life (days)[a]	14	8	0.462	80	58
% rates recalcitrant	0	0%	0%	0%	0%
potential for biodegradation[b]	almost always	almost always	almost always	almost always	almost always

[a]Median value from the reported studies; [b]Quantitative estimation based on % occurrence of recalcitrance; NA Insufficient information; NC Not calculable (λ=0); Scale % recalcitrance - biodegradability: < 10% - Almost always, 10%-25% - Frequently, 25%-50% - Sometimes, 50%-75% - Barely, >75% - Almost never. [From M.P. Suarez and H.S. Rifai, *Bioremediation Journal,* **3**, 337-362. Copyright © 1999 Battelle Memorial Institute. Reprinted with permission.]

The process that exhibited the highest potential for biodegradation of PCE and TCA was reductive dechlorination with 86% and 84% of the analyzed studies showing

biotransformation. Median half-lives for reductive dechlorination of PCE and TCA were 34 days and 24 days, respectively. With respect of TCE, none of the 17 studies reporting aerobic cometabolism (most of them laboratory studies) showed recalcitrance and the median half-life was very short (3 days). Reductive dechlorination also appeared to be a very good alternative for biotransformation of TCE with only 9% of 56 studies reporting recalcitrance and median half-life equal to 201 days. Finally, vinyl chloride exhibited very high potential for biodegradation under aerobic conditions with no studies showing recalcitrance and median half-lives of 8 days and 0.462 days for oxidation and cometabolism, respectively.

In addition to the data reported above by Suarez and Rifai,[90] a groundwater anaerobic biodegradation literature review was performed by Aronson and Howard.[102] Based on their review, Aronson and Howard[102] developed a range of "recommended values" for the anaerobic biodegradation first order decay rate coefficients. For many of the chlorinated solvents, the authors defined the low-end rate coefficient based on the lowest measured field value, and defined the high-end value as the mean rate coefficient for all the field/in-situ microcosm studies. Table 23.1.9 shows the resulting recommended ranges for first order anaerobic biodegradation rate coefficients for several chlorinated solvents along with the mean value of the field/in-situ microcosm studies (note that some minor discrepancies exist between the reported high-end rates and the mean value for the field/in-situ microcosm studies).

Table 23.1.9. Mean and recommended first-order rate coefficients for selected chlorinated solvents presented by Aronson and Howard[102]

Compound	Mean of field/in-situ studies			Recommended 1st order rate coefficients				Comments
	1st order rate		number studies used for mean	low-end 1st order rate		high-end 1st order rate		
	coefficients, day^{-1}	half-lives, day		coefficients, day^{-1}	half-lives day	coefficients, day^{-1}	half-lives day	
PCE	0.0029	239	16	0.00019	3,647	0.0033	210	Lower limit was reported for a field study under nitrate-reducing conditions
TCE	0.0025	277	47	0.00014	4,950	0.0025	277	Lower limit was reported for a field study under unknown redox conditions
Vinyl chloride	0.0079	88	19	0.00033	2,100	0.0072	96	Lower limit was reported for a field study under methanogenic/sulfate-reducing conditions
1,1,1-TCA	0.016	43	15	0.0013	533	0.01	69	Range not appropriate for nitrate-reducing conditions. Expect lower limit to be much less
1,2-DCA	0.0076	91	2	0.0042	165	0.011	63	Range reported from a single field study under methanogenic conditions

Compound	Mean of field/in-situ studies			Recommended 1st order rate coefficients				Comments
	1st order rate		number studies used for mean	low-end 1st order rate		high-end 1st order rate		
	coefficients, day^{-1}	half-lives, day		coefficients, day^{-1}	half-lives day	coefficients, day^{-1}	half-lives day	
Carbon tetrachloride	0.37	1.9	9	0.0037	187	0.13	5	Range not appropriate for nitrate-reducing conditions. Expect lower limits to be much less
Chloroform	0.030	23	1	0.0004	1,733	0.03	23	Only one field study available. Biodegradation under nitrate-reducing conditions expected
Dichloromethane	0.0064	108	1	0.0064	108	-	-	Rate constant reported from a single field study under methanogenic conditions
Trichlorofluoromethane	-	-	-	0.00016	4,331	0.0016	433	All studies with very low concentrations of this compound
2, 4-Dichlorophenol	0.014	50	2	0.00055	1,260	0.027	26	Range may not be appropriate for nitrate reducing conditions

[From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**. Copyright © 1999 *John Wiley & Sons, Inc.* Reprinted by permission of John Wiley & Sons, Inc.]

23.1.5 GEOCHEMICAL EVIDENCE OF NATURAL BIOREMEDIATION AT CHLORINATED SOLVENT SITES

23.1.5.1 Assessing reductive dechlorination at field sites

Assessing biological activity at a field site based on monitoring data can be difficult. However, there are a number of monitoring parameters that can be indicative of halorespiration. First, the presence of methane in the groundwater indicates that fermentation is occurring and that the potential for halorespiration exists. Second, the transformation of PCE and TCE has been studied intensely and many researchers report that of the three possible DCE isomers, 1,1-DCE is the least significant intermediate and that cis-1,2-DCE predominates over trans-1,2-DCE.[103-105] Third, because chlorinated ethenes are 55 to 85% chlorine by mass, the degradation of these compounds releases a large mass of chloride. Therefore, elevated chloride concentrations also indicate reductive dechlorination.

23.1.5.2 Plume classification schemes

Wiedemeier et a1.[106] proposed a classification system for chlorinated solvent plumes based on the amount and origin of fermentation substrates that produce the hydrogen that drives halorespiration. Three types of groundwater environments and associated plume behavior, Type 1, Type 2, and Type 3, are described below. While the classification system can be used to represent entire plumes, it can also be used to define different zones within a chlorinated solvent plume.

23.1.5.2.1 Type 1

For highly chlorinated solvents to biodegrade, anaerobic conditions must prevail within the contaminant plume. Anaerobic conditions are typical at sites contaminated with fuel hydro-

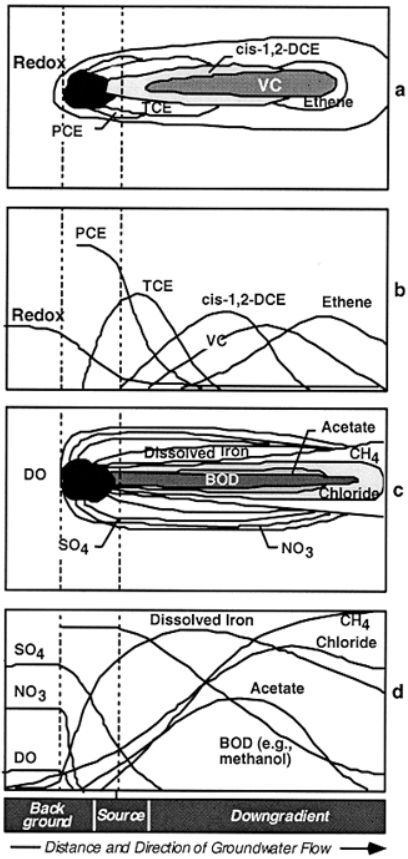

Figure 23.1.6. Conceptual model of Type 1 environment for chlorinated solvent plumes. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc.* Reprinted by permission of John Wiley & Sons, Inc.]

carbons, landfill leachate, or other anthropogenic carbon because these organics exert a tremendous electron-acceptor demand on the system. This condition is referred to as a Type 1 environment. In a Type 1 environment, anthropogenic carbon is fermented to produce hydrogen which drives halorespiration.

The geochemistry of groundwater in a Type 1 environment is typified by strongly reducing conditions. This environment is characterized by very low concentrations of dissolved oxygen, nitrate, and sulfate and elevated concentrations of Fe(II) and methane in the source zone (Figure 23.1.6). The presence of methane is almost always observed and confirms that fermentation has been occurring at the site, generating hydrogen. If measured, hydrogen concentrations are typically greater than 1 nanomolar. Importantly, a Type 1 environment results in the rapid and extensive degradation of the more highlychlorinated solvents such as PCE, TCE, and DCE: PCE $\rightarrow$ TCE $\rightarrow$ DCE $\rightarrow$ VC $\rightarrow$ Ethene $\rightarrow$ Ethane

In this type of plume, cis-1,2-DCE and VC degrade more slowly than TCE; thus, they tend to accumulate and form longer plumes (Figure 23.1.6a). In Figure 23.1.6b, the PCE declines to zero and is replaced, in sequence, by a peak in TCE concentrations, followed by a peak in cis-1,2-DCE, VC, and ethene. Fermentation constituents (BOD and acetate) and inorganics are shown in Figure 23.1.6c and 23.1.6d. Figure 23.1.6d illustrates how the fermentation substrate (represented by BOD) extends beyond the source before being consumed. Both panels show long chloride and methane plumes extending far downgradient from the plume area, because chloride is conservative and methane cannot be biodegraded in an anaerobic environment. The acetate curve indicates where active primary fermentation is occurring; declining acetate concentrations are due to consumption by methanogens in the plume area.

23.1.5.2.2 Type 2

The classification system of Wiedemeier et a1.[107] recognized that anaerobic conditions may also result from the fermentation of naturally-occurring organic material in the groundwater that flows through chlorinated solvent source zones. This Type 2 environment occurs in hydrogeologic settings that have inherently high organic carbon concentrations, such as coastal or stream/river deposits with high concentrations of organics, shallow aquifers with

recharge zones in organic-rich environments (such as swamps), or zones impacted by natural oil seeps. A Type 2 environment generally results in slower biodegradation of the highly chlorinated solvents compared to a Type 1 environment. However, given sufficient organic loading, this environment can also result in rapid degradation of these compounds. A Type 2 environment typically will not occur in crystalline igneous and metamorphic rock (see discussion of likely hydrogeologic settings for Type 3 environments).

23.1.5.2.3 Type 3

A Type 3 environment is characterized by a well-oxygenated groundwater system with little or no organic matter. Concentrations of dissolved oxygen typically are greater than 1.0 mg/L. In such an environment, halorespiration will not occur and chlorinated solvents such as PCE, TCE, TCA, and CT will not biodegrade. In this environment, very long dissolved-phase plumes are likely to form. The most significant natural attenuation mechanisms for PCE and TCE will be advection, dispersion, and sorption. However, VC (and possibly DCE) can be rapidly oxidized under these conditions. A Type 3 environment is often found in crystalline igneous and metamorphic rock (fractured or unfractured) such as basalt, granite, schist, phyllite, glacial outwash deposits, eolian deposits, thick deposits of well-sorted, clean, beach sand with no associated peat or other organic carbon deposits, or any other type of deposit with inherently low organic carbon content if no anthropogenic carbon has been released.

Two conceptual models are provided for environments in which Type 3 behavior occurs. For sources with PCE and TCE, the major natural attenuation processes are dilution and dispersion alone (no biodegradation). As shown in 23.1.7, the PCE and TCE plumes extend from the source zone and concentrations are slowly reduced by abiotic processes. Chloride concentrations and oxidation-reduction potential will not change as groundwater passes through the source zone and forms the chlorinated ethene plume. If TCA is the solvent of interest, significant abiotic hydrolysis may occur, resulting in a more rapid decrease in TCA concentrations and an increase in chloride concentrations.

In Figure 23.1.7, a source releases VC and 1,2-DCA into the groundwater at a Type 3 site (an unlikely occurrence as more highly chlorinated solvents are typically released at sites). Because the VC and 1,2-DCA can be degraded aerobically, these constituents decline in concentration at a significant rate. Chloride is produced, and a depression in dissolved oxygen concentration similar to that occurring at fuel sites, is observed.

23.1.5.2.4 Mixed environments

As mentioned above, a single chlorinated solvent plume can exhibit different types of behavior in different portions of the plume. This can be beneficial for natural biodegradation of chlorinated solvent plumes. For natural attenuation, this may be the best scenario. PCE, TCE, and DCE are reductively dechlorinated with accumulation of VC near the source area (Type 1); then, VC is oxidized (Type 3) to carbon dioxide, either aerobically or via Fe(III) reduction further downgradient and does not accumulate. Vinyl chloride is removed from the system much faster under these conditions than under reducing conditions.

A less ideal variation of the mixed Type 1 and Type 3 environments is shown in the conceptual model in Figure 23.1.8. An extended TCE and 1,2-DCE plume results because insufficient fermentable carbon results in an anaerobic zone which is too short for complete biodegradation. Therefore, TCE extends well into the aerobic zone where no biodegradation occurs. A long DCE plume also extends into the aerobic zone, indicating in-

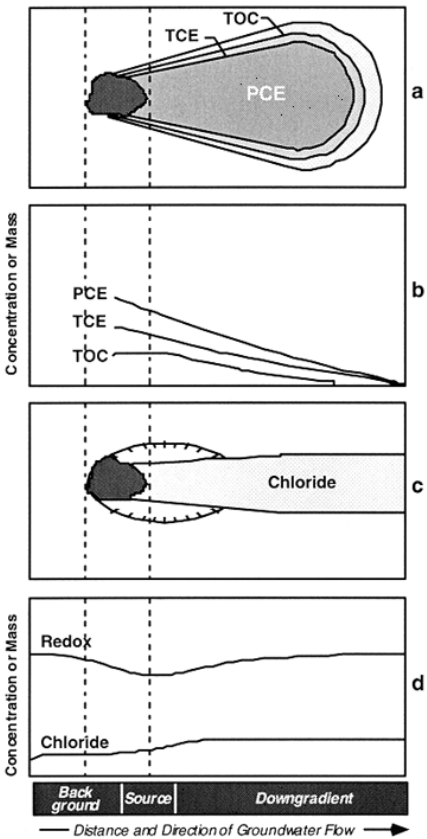

Figure 23.1.7. Conceptual model of Type 3 environment for chlorinated solvent plumes. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

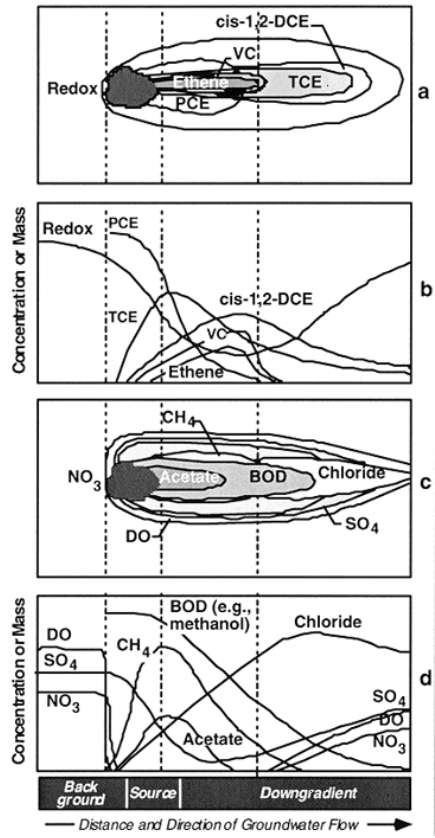

Figure 23.1.8. Conceptual model of mixed environments with Type 1 environment in source zone and Type 3 environment downgradient of source. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

significant direct aerobic biodegradation was assumed. While a long chloride plume will be observed, the short anaerobic zone means much less methane is produced, allowing dilution/dispersion to limit the extent of the methane plume.

23.1.6 CHLORINATED SOLVENT PLUMES - CASE STUDIES OF NATURAL ATTENUATION

23.1.6.1 Plume databases

Two different databases provided chlorinated solvent site data. The first database, the Hydrogeologic Database (HGDB),[2] provided information on plume length, plume width, plume thickness, and highest solvent concentration for 109 chlorinated solvent sites. The second database[1] condensed extensive site characterization data from 17 Air Force chlorinated solvent sites, with information on parent compounds vs. progeny products concentrations, competing electron acceptors, hydrogen, and metabolic by-products.

The data in the HGDB were broken into two groups: the chlorinated ethenes, where one or more of the chlorinated ethenes (PCE, TCE, DCE, or VC) was reported to be the major contaminant, and other chlorinated solvent sites, where all other chlorinated solvents besides the ethenes (e.g., TCA, DCA, chlorobenzene) were lumped together. As shown in Table 23.1.10, the median length of the 75 chlorinated ethene plumes was 1000 ft, with one site reporting a plume length of 13,200 ft. These median lengths are longer than those reported for fuel hydrocarbon plumes and this may be attributed to the competition for hydrogen during halorespiration.

Table 23.1.10. Characteristics of chlorinated solvent plumes from HGDB database

	Plume length, ft	Plume width, ft	Vertical penetration, ft	Highest concentration, mg/L
Chlorinated ethenes (e.g., PCE, TCE, etc.)				
Maximum	13,200	4,950	500	28,000
75th percentile	2,500	1,000	100	72
Median	1,000	500	40	8.467
25th percentile	600	200	25	0.897
Minimum	50	15	5	0.001
n	75	75	78	81
Other chlorinated solvents (e.g., TCA, DCA)				
Maximum	18,000	7,500	150	2,500
75th percentile	2,725	1,000	51	13.250
Median	575	350	35	3.100
25th percentile	290	188	24	0.449
Minimum	100	100	8	0.016
n	24	24	24	28

Note: Highest concentration for chlorinated ethenes (28,000 mg/L) was for TCE, which is above the solubility limit. The highest concentration for "other chlorinated solvents" (2500 mg/L) was for chloromethane and toluene. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

The other category, "other chlorinated solvent sites," had shorter plumes, with a median plume length of 575 ft compared to 1000 ft for the chlorinated ethene sites. Twelve of the 24 plumes were comprised of TCA, which is degraded biologically via halorespiration and other mechanisms and abiotically by hydrolysis (half life of 0.5 to 2.5 years). Despite the degradability of TCA, the TCA plumes had a median length of 925 ft. The shorter plumes in this database of 24 sites were reported to be comprised of either a general indicator, such as Total Organic Halogens, or individual compounds such as 1,1-dichloroethane, dichloromethane, or chlorobenzene. The median highest concentration at these "other chlorinated solvent sites" was 3.1 mg/L (see Table 23.1.10).

Data compiled from 17 Air Force sites using the AFCEE (Air Force Center for Environmental Excellence) natural attenuation protocol[107] showed a median plume length of 750 ft (based on 14 plumes). There were significant differences in plume length for different plume classes, with Type 1 plumes (sites with available man-made fermentation substrates such as BTEX) being shorter than Type 3 plumes (sites without available fermentation substrates). Twelve of the sites exhibiting Type 1 plumes had a median plume length of 625 ft,

while the two sites with Type 3 plumes had lengths of 1100 and 5000 ft. Four mixed plumes (Type 1 in source zone, Type 3 in the downgradient part of the plume) had a median length of 2538 ft.

Site-specific biodegradation rate information was developed using several methods, including one developed by Buscheck and Alcantar,[108] one based on the use of conservative tracers (the trimethylbenzenes), and other methods such as model calibration. Rates varied significantly, with half-lives ranging from over 300 years for a Type 3 site located in Utah to 0.2 years for a Type 1 site (see Table 23.1.11). The median first order half-life for the 14 chlorinated plumes was 2.1 years.

Table 23.1.11. Chlorinated solvent plume characteristics

No.	State	Type	Plume length, ft	Plume width, ft	Plume thickness, ft	Total chlor. solvents, mg/L	Seepage velocity, ft/yr	First-order biodegradation rate coeff. for solvents, day^{-1}	Half-life, years	Method for calculating rate coefficient
13	UT	Type 3	5000	1400	40	4.953	60	0.000006	316.4	Other
9	NY	Mixed	4200*	2050	60	774.721	139	0.001*	1.9*	Other
10	NE	Mixed	3500	1400	50	164.010	152	0.000001	1899	Other
8	MA	Type 1	1800	1200	50	4.340	106	0.0005	3.8	Other
11	FL	Mixed	1575*	400	15	1258.842	113	0.0009*	2.1*	Other
14	AK	Type 3	1100	250	25	4.899	260	0.0065	0.3	Other
1	SC	Type 1	750	550	5	328.208	1600	-	-	-
7	MA	Type 1	750	250	50	50.566	20.8	0.0095	0.2	Conserv. tracer
12	MS	Mixed	750	550	5	0.472	1500	0.01	0.2	Buscheck
4	NE	Type 1	650	450	30	47.909	6.7	0.0006	3.2	Buscheck
3	FL	Type 1	600	350	20	0.429	36	0.0007	2.7	Buscheck
5	WA	Type 1	550	300	10	3.006	32.9	0.001	1.9	Buscheck
2	MI	Type 1	375	100	10	0.397	292	-	-	-
6	OH	Type 1	100	60	10	15.736	25	-	-	-
Maximum			5,000	2,050	60	1,259	1,600	0.0095	316.4	
75^{th} percentile			1,744	1,038	48	136	233	0.00375	3.5	
Median			750.0	425.0	22.5	10.3	109.5	0.0009	2.1	
25^{th} percentile			613	263	10	3.3	34	0.00055	1.1	
Minimum			100	60	5	0.397	7	0.000006	0.2	
n			14	14	14	14	14	11	11	

*Plume discharges into stream; may not represent maximum potential plume length.
Mixed refers to Type 1 conditions in source zone, Type 3 conditions in downgradient part of plume. Median length Type 1 sites: 625 ft, mixed sites 2538 ft, Type 3: 3050 ft (two sites). [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

23.1.6.2 Modeling chlorinated solvent plumes

Very few models exist (analytical or numerical) which are specifically designed for simulating the natural attenuation of chlorinated solvents in ground water. Ideally, a model for simulating natural attenuation of chlorinated solvents would be able to track the degradation of a parent compound through its daughter products and allow the user to specify differing decay rates for each step of the process. This may be referred to as a reactive transport model, in which transport of a solute may be tracked while it reacts, its properties change due to those reactions, and the rates of the reactions change as the solute properties change. Moreover, the model would also be able to track the reaction of those other compounds that react with or are consumed by the processes affecting the solute of interest (e.g., electron donors and acceptors).

Two models: BIOCHLOR and RT3D for the natural attenuation of chlorinated solvents have been presented recently in the general literature and will be briefly discussed in this section.

23.1.6.2.1 BIOCHLOR natural attenuation model

The BIOCHLOR Natural Attenuation Model[109] simulates chlorinated solvent natural attenuation using an Excel based interface. BIOCHLOR simulates the following reductive dechlorination process:

$$PCE \xrightarrow{k_1} TCE \xrightarrow{k_2} DCE \xrightarrow{k_3} VC \xrightarrow{k_4} ETH$$

The equations describing the sequential first order biodegradation reaction rates are shown below for each of the components:

$$r_{PCE} = -k_1 C_{PCE} \quad [23.1.16]$$

$$r_{TCE} = k_1 C_{PCE} - k_2 C_{TCE} \quad [23.1.17]$$

$$r_{DCE} = k_2 C_{TCE} - k_3 C_{DCE} \quad [23.1.18]$$

$$r_{VC} = k_3 C_{DCE} - k_4 C_{VC} \quad [23.1.19]$$

$$r_{ETH} = k_4 C_{ETH} \quad [23.1.20]$$

where:

k_1, k_2, k_3, k_4	the first order rate constants
C_{PCE}, C_{TCE}, C_{DCE}, C_{VC} and C_{ETH}	the aqueous concentration of PCE, TCE, DCE, vinyl chloride, and ethene, respectively.

These equations assume no degradation of ethene.

To describe the transport and reaction of these compounds in the subsurface, one-dimensional advection, three-dimensional dispersion, linear adsorption, and sequential first order biodegradation are assumed as shown in the equations below. All equations, but the first, are coupled to another equation through the reaction term.

$$R_{PCE}\frac{dC_{PCE}}{dt} = -v\frac{dC_{PCE}}{dx} + D_x\frac{d^2C_{PCE}}{dx^2} + D_y\frac{d^2C_{PCE}}{dy^2} + D_z\frac{d^2C_{PCE}}{dz^2} - k_1C_{PCE} \quad [23.1.21]$$

$$R_{TCE}\frac{dC_{TCE}}{dt} = -v\frac{dC_{TCE}}{dx} + D_x\frac{d^2C_{TCE}}{dx^2} + D_y\frac{d^2C_{TCE}}{dy^2} + D_z\frac{d^2C_{TCE}}{dz^2} + k_1C_{PCE} - k_2C_{TCE} \quad [23.1.22]$$

$$R_{DCE}\frac{dC_{DCE}}{dt} = -v\frac{dC_{DCE}}{dx} + D_x\frac{d^2C_{DCE}}{dx^2} + D_y\frac{d^2C_{DCE}}{dy^2} + D_z\frac{d^2C_{DCE}}{dz^2} + k_2C_{TCE} - k_3C_{DCE} \quad [23.1.23]$$

$$R_{VC}\frac{dC_{VC}}{dt} = -v\frac{dC_{VC}}{dx} + D_x\frac{d^2C_{VC}}{dx^2} + D_y\frac{d^2C_{VC}}{dy^2} + D_z\frac{d^2C_{VC}}{dz^2} + k_3C_{DCE} - k_4C_{VC} \quad [23.1.24]$$

$$R_{ETH}\frac{dC_{ETH}}{dt} = -v\frac{dC_{ETH}}{dx} + D_x\frac{d^2C_{ETH}}{dx^2} + D_y\frac{d^2C_{ETH}}{dy^2} + D_z\frac{d^2C_{ETH}}{dz^2} + k_4C_{ETH} \quad [23.1.25]$$

where:

R_{PCE}, R_{TCE}, R_{DCE}, R_{VC}, R_{ETH}	retardation factors
V	seepage velocity
D_x, D_y, D_z	dispersivities in the x, y, and z directions.

BIOCHLOR uses a novel analytical solution to solve these coupled transport and reaction equations in an Excel spreadsheet. To uncouple these equations, BIOCHLOR employs transformation equations developed by Sun and Clement.[110] The uncoupled equations were solved using the Domenico model, and inverse transformations were used to generate concentration profiles. Details of the transformation are presented elsewhere.[110] Typically, source zone concentrations of cis-1,2-dichloroethythene (DCE) are high because biodegradation of PCE and TCE has been occurring since the solvent release.

BIOCHLOR also simulates different first-order decay rates in two different zones at a chlorinated solvent site. For example, BIOCHLOR is able to simulate a site with high dechlorination rates in a high-carbon area near the source that becomes a zone with low dechlorination rates downgradient when fermentation substrates have been depleted.

In addition to the model, a database of chlorinated solvent sites is currently being analyzed to develop empirical rules for predicting first-order coefficients that can be used in BIOCHLOR. For example, at sites with evidence of considerable halorespiration, the use of higher first order decay coefficients will be recommended. Indicators of high rates of halorespiration may include: i) high concentrations of fermentation substrates such as BTEX at the site, ii) high methane concentrations, which indicate high rates of fermentation, and iii) large ratios of progeny products to parent compounds, and iv) high concentrations of source zone chloride compared to background chloride concentrations.

The BIOCHLOR model was used to reproduce the movement of the Cape Canaveral plume from 1965 to 1998. The Cape Canaveral site (Figure 23.1.9) is located in Florida and exhibits a TCE plume which is approximately 1,200 ft long and 450 ft wide. TCE concentrations as high as 15.8 mg/L have been measured recently at the site. The site characteristics used in the BIOCHLOR model are listed in Table 23.1.12. The hydraulic conductivity assumed in the model was 1.8×10^{-2} cm/sec and the hydraulic gradient was 0.0012. A porosity of 0.2 was assumed as well as the Xu and Eckstein model for longitudinal dispersivity.[8] The lateral dispersivity was assumed to be 10% of the longitudinal dispersivity and vertical dispersion was neglected.

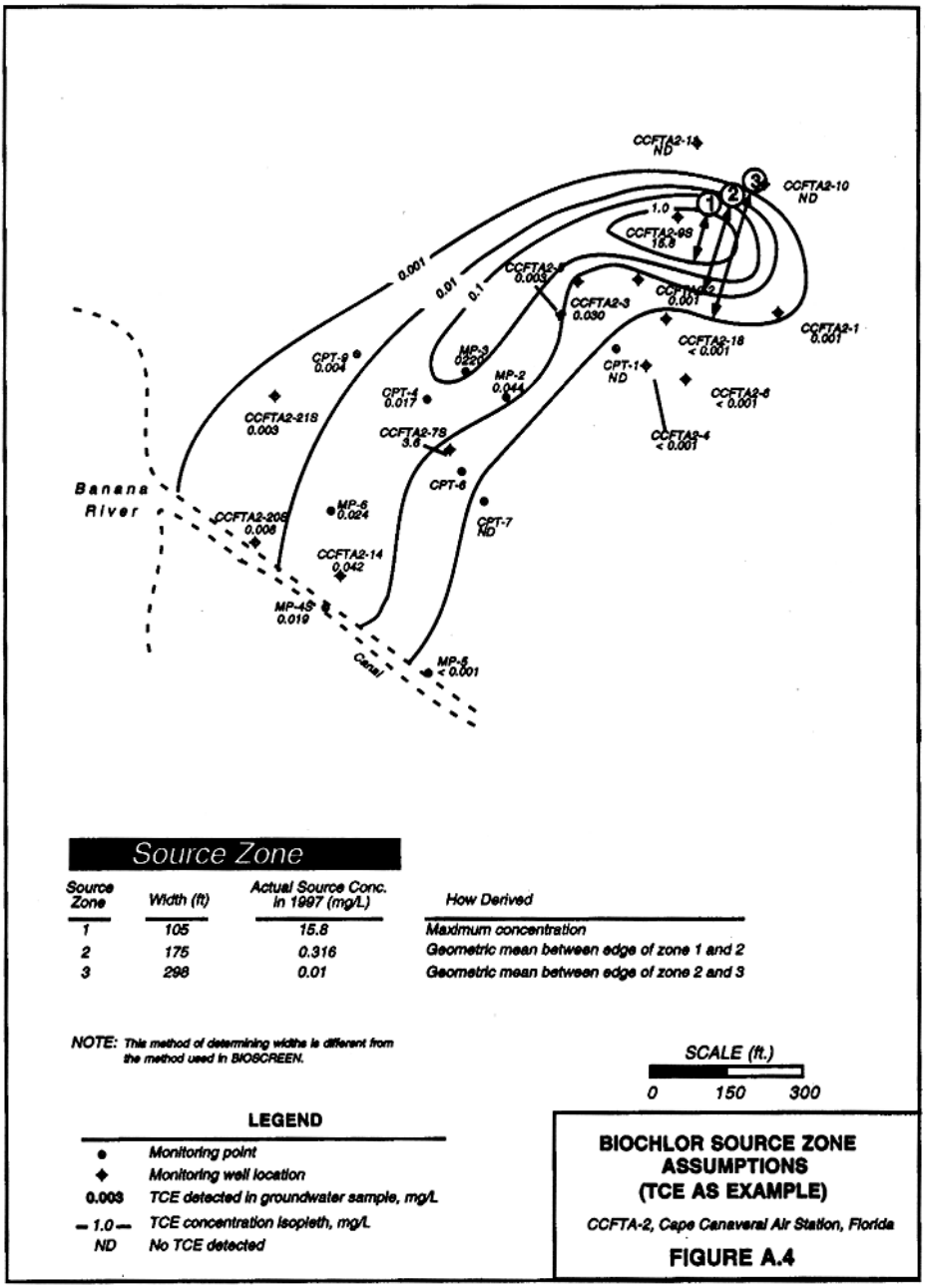

Figure 23.1.9. BIOCHLOR source zone assumptions (TCE as example), CCFTA-2, cape Canaveral Air Station, Florida [From reference 109].

Table 23.1.12. BIOCHLOR example, Cape Canaveral Air Station, Florida. [From reference 109]

Data type	Parameter	Value	Source
Hydrogeology	Hydraulic conductivity: Hydraulic gradient: Porosity:	1.8×10^{-2} cm/s 0.0012 ft/ft 0.2	Slug-tests results Static water level measurement Estimated
Dispersion	Original Longitudinal dispersivity: Transverse dispersivity: Vertical dispersivity:	 varies with x varies with x 0 ft	Based on estimated plume length of 1450 ft. Note: No calibration was necessary to match observed plume length
Adsorption	Individual retardation factors: Common retardation factor: Soil bulk density ρ_b: f_{oc}: K_{oc}: (L/kg)	PCE: 6.7 TCE: 2.8 c-DCE:2.8 VC: 5.6 ETH: 5.3 5.3 1.6 kg/L 0.184% PCE: 398 TCE: 126 c-DCE: 126 VC: 316 ETH: 302	Calculated Median value Estimated Lab analysis Literature correlation using solubilities at 20°C
Biodegradation	Biodegradation rate coefficients (1/year): PCE → TCE TCE → c-DCE c-DCE → VC C → ETH	 2.0 0.9 0.6 0.4	Based on calibration to field data using a simulation time of 32 yr. Started with literature values and then adjusted model to fit field
General	Modeled area length Modeled area width Simulation time	1085 ft 700 ft 33 yrs	Based on area of affected groundwater plume from 1965 (first release) to 1998 (present)
Source data	Source thickness Source widths, ft Source concentrations, mg/L PCE TCE c-DCE VC ETH	56 ft *Zone 1* *Zone 2* *Zone 3* 105 175 298 *Zone 1* *Zone 2* *Zone 3* 0.056 0.007 0.001 15.8 0.318 0.01 98.5 1.0 0.01 3.080 0.089 0.009 0.030 0.013 0.003	Based on geologic logs and monitoring data. Source concentrations are aqueous concentrations
Actual data	Distance from source, ft PCE concentration, mg/L TCE, mg/L c-DCE, mg/L VC, mg/L ETH, mg/L	*560* *650* *930* *1085* <0.001 ND <0.001 <0.001 0.22 0.0165 0.0243 0.019 3.48 0.776 1.200 0.556 3.080 0.797 2.520 5.024 0.188 ND 0.107 0.150	Based on observed concentration at site near centerline of plume
Output	Centerline concentration	see Figure 23.1.10	

A median value for the retardation factor was used (R=5.3) since BIOCHLOR accepts only one value for this parameter. The site was modeled using one anaerobic zone with one set of rate coefficients as shown in Table 23.1.12. This is justified because the dissolved ox-

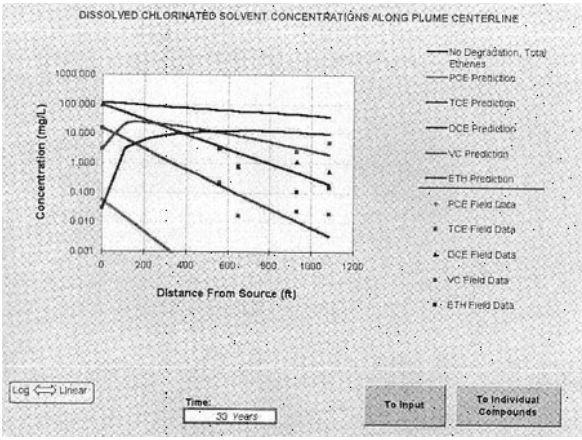

Figure 23.1.10. Centerline output. Cape Canaveral Air Force Base, Florida. [From references 109].

ygen readings at the site were less than 0.7 mg/L at all monitoring points. The rate coefficients were calculated by calibrating the model to the 1997 field data. The source zone was simulated as a spatially-variable source and the source concentrations ranged from 0.001 to 98.5 mg/L for the various compounds as shown in Table 23.1.12. The source thickness was estimated by using the deepest point in the aquifer where chlorinated solvents were detected.

Centerline concentrations for all five species (PCE, TCE, c-DCE, VC and ETH) predicted by the model are shown in Figure 23.1.10. Figure 23.1.10 shows the centerline predictions for each chlorinated solvent and a no degradation curve for all of the chlorinated solvents as well as field data. The data in Figure 23.1.10 indicate that TCE concentrations discharging into the ocean will be less than 0.001 mg/L.

23.1.6.3 RT3D numerical model

RT3D (Reactive Transport in 3 Dimensions)[111] is a FORTRAN 90-based model for simulating 3D multi-species, reactive transport in groundwater. This model is based on the 1997 version of MT3D (DOD Version 1.5), but has several extended reaction capabilities. RT3D can accommodate multiple sorbed and aqueous phase species with any reaction framework that the user needs to define. RT3D can simulate different scenarios, since a variety of pre-programmed reaction packages are already provided and the user has the ability to specify their own reaction kinetic expressions. This allows, for example, natural attenuation processes or an active remediation to be evaluated. Simulations can be applied to modeling contaminants such as heavy metals, explosives, petroleum hydrocarbons, and/or chlorinated solvents.

RT3D's pre-programmed reaction packages include:

1 Two species instantaneous reaction (hydrocarbon and oxygen).
2 Instantaneous hydrocarbon biodegradation using multiple electron acceptors (O_2, NO_3^-, Fe^{2+}, SO_4^{2-}, CH_4).
3 Kinetically limited hydrocarbon biodegradation using multiple electron acceptors (O_2, NO_3^-, Fe^{2+}, SO_4^{2-}, CH_4).
4 Kinetically limited reaction with bacterial transport (hydrocarbon, oxygen, and bacteria).
5 Non-equilibrium sorption/desorption. Can also be used for non-aqueous phase liquid dissolution).
6 Reductive, anaerobic biodegradation of PCE, TCE, DCE, and VC.
7 Reductive, anaerobic biodegradation of PCE, TCE, DCE, and VC combined with aerobic biodegradation of DCE and VC.
8 Combination of #3 and #7.

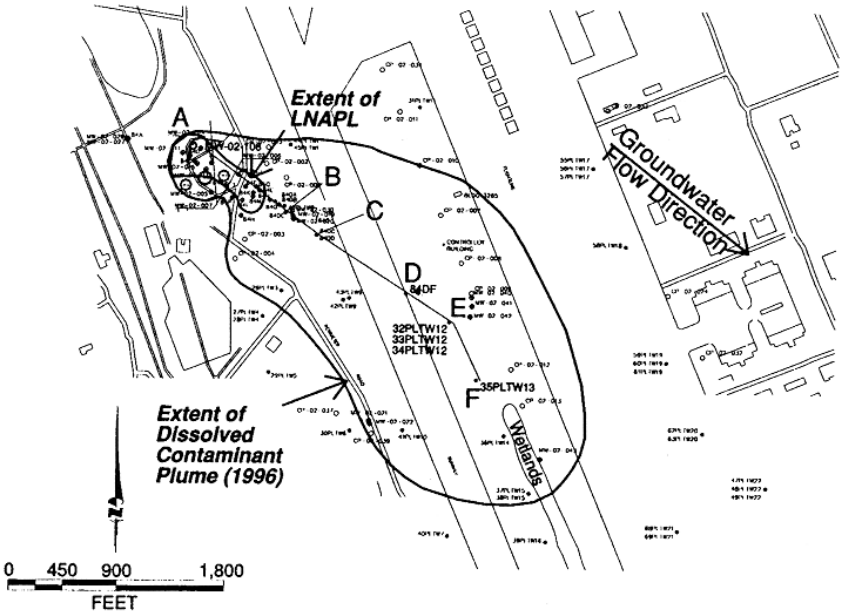

Figure 23.1.11. Site layout, Plattsburg Air Force Base, New York. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

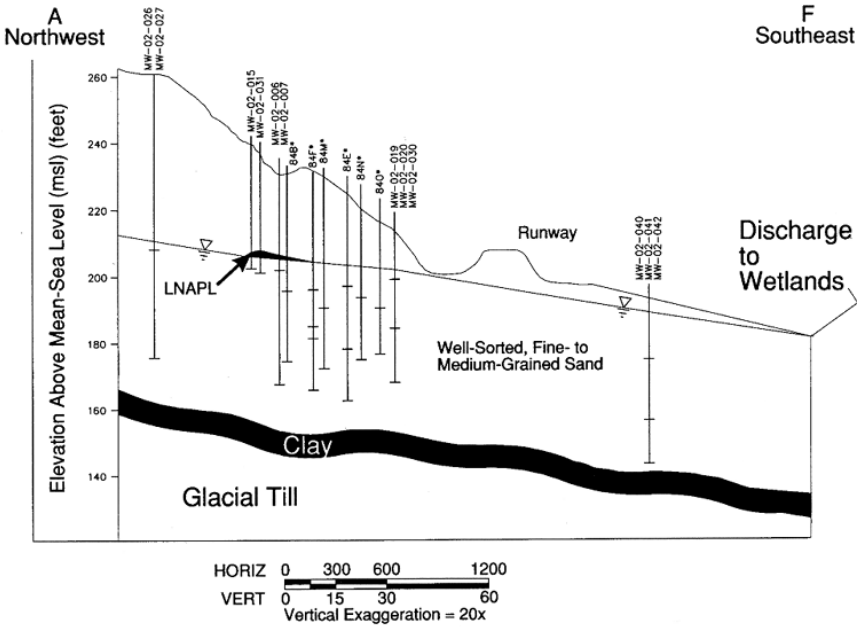

Figure 23.1.12. Hydrogeologic section, Plattsburg Air Force Base, New York. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

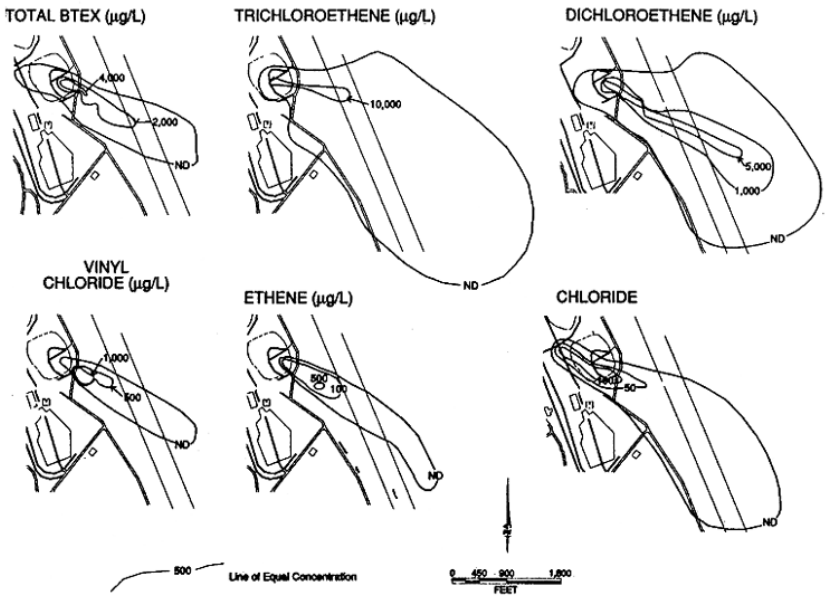

Figure 23.1.13. Chlorinated solvents and by-products, 1995, Plattsburg Air Force Base, New York. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

RT3D represents a remarkable breakthrough in the development and solving of optimization models of bioremediation design. It is a modular, three-dimensional simulator capable of predicting mufti-species (solutes and microbes), bio-reactive transport while understanding natural attenuation and active bioremediation processes.

23.1.6.4 CS case study - The Plattsburgh Air Force Base

The Plattsburgh Air Force Base (AFB) in New York is a former fire training facility (site FT002). Activities at FT-002 (Figure 23.1.11) have caused contamination of shallow soils and groundwater with a mixture of chlorinated solvents and fuel hydrocarbons. Groundwater contaminants include TCE, cis-1,2-DCE, VC and BTEX. The site is underlain with 4 distinct stratigraphic units: sand, clay, till and carbonate bedrock. The depth to groundwater in the sand aquifer ranges from 45 ft below ground surface (BGS) on the west side of the site to zero on the east side of the runway (Figure 23.1.12). Groundwater flow is to the southeast and the average gradient is about 0.01 ft/ft.[1] Hydraulic conductivity values for the unconfined sand aquifer range from 0.059 to 90.7 ft/day. Wiedemeier et al.[1] estimated an average velocity of 142 ft/yr for the sand aquifer.

The extent of Light Non-Aqueous Phase (LNAPL) contamination at Plattsburgh is shown in Figure 23.1.13. The LNAPL is a mixture of jet fuel and waste solvents from which BTEX and TCE dissolve into the ground water (DCE and VC are not present in the waste mixture). The dissolved BTEX plume (Figure 23.1.13) extends approximately 2000 ft downgradient from the site and has a maximum width of about 500 ft. BTEX concentrations as high as 17 mg/L were measured in the source area. Historical data from FT-002 indicate that the dissolved BTEX plume has reached a quasi-steady state and is no longer expanding.

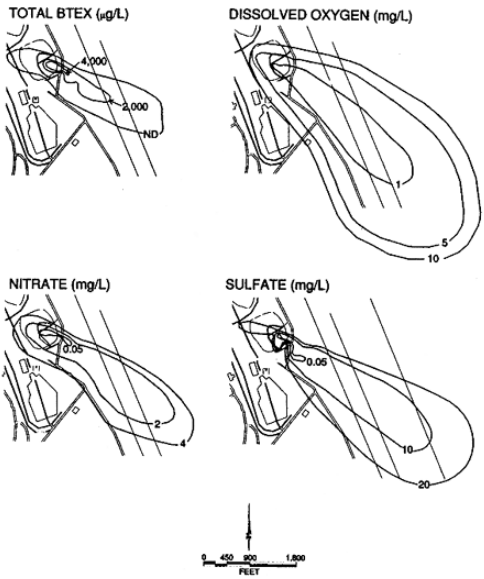

Figure 23.1.14. BTEX and electron acceptors, 1995, Plattsburg Air Force Base, New York. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

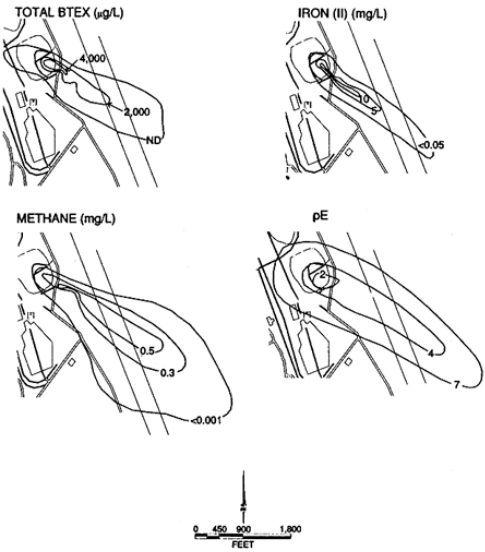

Figure 23.1.15. BTEX and metabolic by-products, 1995, Plattsburg Air Force Base, New York. [From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

The chlorinated solvent plumes (Figure 23.1.13) in groundwater extend about 4000 ft downgradient from FT-002. Concentrations of TCE, DCE and VC as high as 25, 51, and 1.5 mg/L, respectively, have been observed recently. Since DCE and VC were not measured in LNAPL samples from the source area, the presence of DCE and VC at the site can be attributed to dechlorination. The data in Figure 23.1.14 show the distribution of electron acceptor concentrations observed at the site including dissolved oxygen, nitrate and sulfate. Background concentrations for these compounds are 10, 10 and 25 mg/L, respectively and their absence within the contaminated zones is an indication of biodegradation of BTEX and chlorinated solvents at the site.

Figure 23.1.15, on the other hand, shows the distribution of metabolic by-products of the biodegradation reactions including ferrous iron and methane. The presence of these by-products is further evidence of biological activity in the aquifer. Elevated chloride and ethene concentrations as shown in Figure 23.1.13 suggest that TCE, DCE and VC are being biodegraded. Wiedemeier et al.[1] calculated apparent biodegradation constants for FT-002 using trimethylbenzene as a conservative tracer. Their results are shown in Table 23.1.13. The data in Table 23.1.13 indicate biodegradation rates of the chlorinated solvents at the site ranging between 0 and 1.27 per yr.

Table 23.1.13. Approximate first-order biodegradation rate constants

Compound	Correction method	A-B 0-970 ft, year^{-1}	B-C 970-1240 ft, year^{-1}	C-E 1240-2560 ft, year^{-1}
TCE	Chloride	1.27	0.23	-0.30
	TMB	1.20	0.52	NA
	Average	1.24	0.38	-0.30
DCE	Chloride	0.06	0.60	0.07
	TMB	0.00	0.90	NA
	Average	0.03	0.75	0.07
VC	Chloride	0.00	0.14	0.47
	TMB	0.00	0.43	NA
	Average	0.00	0.29	0.47
BTEX	Chloride	0.13	0.30	0.39
	TMB	0.06	0.60	NA
	Average	0.10	0.45	0.39

[a]NA, not analyzed

[From T.H. Wiedemeier, H. S. Rifai, C. J. Newell and J.T. Wilson, **Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface**, after reference 88. Copyright © 1999 *John Wiley & Sons, Inc*. Reprinted by permission of John Wiley & Sons, Inc.]

Available geochemical data were analyzed by Wiedemeier et al.[1] and they concluded that the geochemistry of the ground water near the source area and for about 1500 ft downgradient is significantly different from the groundwater further downgradient from the source (between 1500 and 4000 ft downgradient). This led the authors to conclude that Plattsburgh exhibits Type 1 behavior near the source and Type 3 behavior within the leading edge of the plume (see Section 23.1.5.2).

In the area extending to 1500 ft downgradient from the source, BTEX and TCE are comingled in the ground water. This area is characterized by anaerobic conditions that are strongly reducing. BTEX is being used as a primary substrate and TCE is being reductively dechlorinated to cis-1,2-DCE and VC. Between 1500 and 2000 ft downgradient from the source, however, the majority of the BTEX has been biodegraded and the system exhibits Type 3 behavior. These conditions are not optimal for reductive dechlorination, and it is likely that VC is being oxidized via ferric reduction or aerobic respiration.

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23.2 REMEDIATION TECHNOLOGIES AND APPROACHES FOR MANAGING SITES IMPACTED BY HYDROCARBONS

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23.2.1 INTRODUCTION

Subsurface contamination of soils and aquifers by chlorinated hydrocarbons (CHC) and non-chlorinated hydrocarbons (HC) is likely the largest environmental issue in industrialized nations worldwide. Decades without controlled disposal practices, inadequate storage and distribution systems, and accidental releases have resulted in a large number of contaminated drinking water and aquifer systems. In addition, an untold number of ecosystems are subject to future contamination by impinging hydrocarbon plumes. The extent of potential contributors ranges from neighborhood facilities, such as laundries or gas stations, to major fuel refineries, industrial operations and chemical manufacturing facilities.

While characterization, control, and cleanup of these impacted areas may seem daunting, it is clear that not every impacted or potentially impacted area requires extensive remedial efforts. In fact, many impacts do not represent a significant risk to human health or the environment. In other areas, natural attenuation processes are effective in controlling the migration of the dissolved-phase plume (see Chapter 23.1). If, however, the presence of HCs elicits undesirable effects, then a number of strategies and developing remedial technologies can be used. This chapter will discuss these technologies and strategies and present a number of case studies documenting their effective implementation.

23.2.1.1 Understanding HC and CHC in the environment

As summarized by Mueller et al.,[1] hydrocarbons have been produced in the environment throughout geological time. Likewise CHCs are ubiquitous and are also of ancient ancestry.[2] It follows, therefore, that microorganisms have developed mechanisms for utilizing these compounds as growth substrates. Depending on the inherent recalcitrance of the HC, biodegradation mechanisms may be associated with various abiotic degradation processes. While catabolic interactions are often complex and not fully elucidated, a more thorough understanding of integrated processes allows today's scientists and engineers to design and implement more effective systems to mitigate situations where the concentration of HC in a given environment exceeds a desirable value.

23.2.1.2 Sources of HC in the environment

Hydrocarbons found in the environment are of diverse structure and are widely distributed in the biosphere, predominantly as surface waxes of leaves, plant oils, cuticles of insects, and the lipids of microorganisms.[3] Straight-chain HC, or alkanes, with carbon number maxima in the range of C17 to C21 are typically produced by aquatic algae. Conversely terrestrial plants typically produce alkanes with C25 to C33 maxima.[4] Plants also synthesize aromatic HC such as carotenoids, lignin, alkenoids, terpenes, and flavenoids.[5] Polycyclic

aromatic hydrocarbons (PAH) are also of biogeochemical origin, formed whenever organic substances are exposed to high temperature via a process called pyrolysis. Here, the compounds formed are generally more stable than their precursors, usually alkylated benzene rings.[6] The alkyl groups can be of sufficient length to allow cyclization and then, with time, these cyclic moieties become aromatized. The temperature at which this process occurs determines the degree of alkyl substitution.

It follows, therefore, that fossil fuels such as coal and oil provide the largest source of mononuclear and polynuclear aromatic HC. Contemporary anthropogenic sources of HC in the environment thus originate from two primary sources: i) point source releases such as spills at industrial facilities which utilize large volume of fossil fuels, or ii) chronic lower-level inputs such as from atmospheric deposition.

23.2.1.3 Sources of CHC in the environment

Chlorinated hydrocarbons are also abundant in nature.[2] For example, it is estimated that 5×10^9 Kg of chloromethane are produced annually, mainly by soil fungi.[7] However, CHCs of industrial origin perhaps represent an even greater contribution of CHC to the environment. These compounds include a variety of alkanes, alkenes, and aromatic compounds used principally as solvents and synthetic catalysts or intermediates. Reisch[8] estimated that approximately 18 billion pounds of 1,2-dichloromethane are produced in the United States annually. More information on the production and distribution of CHCs can be found herein (see Chapter 3).

While a majority of the CHC is used in a safe and conscientious manner, some material results in environmental contamination. This is often a result of accidental release, although improper disposal is also a common problem. Unfortunately, as a group, CHCs represent the most problematic of the environmental contaminants. This classification is based on their toxicity and environmental persistence. Thus effective means of remediating environments potentially impacted by CHCs is often necessary.

23.2.2 *IN SITU* BIOTREATMENT

When the degree of impact or nature of contamination exceeds safe or acceptable conditions then environmental remediation may be proposed. When the contamination is confined and physically accessible then relatively quick and simple remedial efforts can be implemented. For example, impacted soils can be excavated and disposed in a safe manner. Other related remedial efforts have been reviewed and discussed previously.[9-10]

However, many CHC impacts are not easy to remediate because the point of impact, volume of release, and/or the magnitude of the problem are often not known. Moreover, the physical nature of CHC is such that they often concentrate in areas as non-aqueous phases. In these situations, a variety of *in situ* remediation and source management strategies have been developed. The potential benefits of these *in situ* approaches are many, with the more important features being that they are: non-invasive, applicable to large areas of impact, and usually represent the most cost-efficient remedial alternative.

Various remedial approaches are presented below along with case studies summarizing their effective implementation.

23.2.2.1 Microbial-enhanced natural attenuation/bioremediation

Remediation by monitored natural attenuation has been thoroughly reviewed in Chapter 23.1. In the environment, HCs are susceptible to a variety of physical, chemical, and microbiological transformation processes. Specifically, they can undergo biotransformation reac-

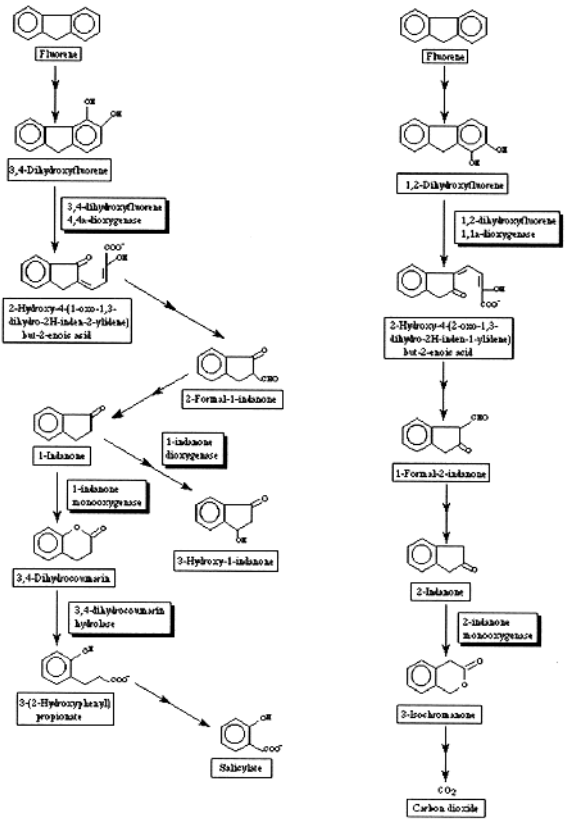

Figure 23.2.1. Aerobic degradation of fluorene. A typical aerobic biodegradation processes, using fluorene as the example where the compound is completely mineralized. Here, fluorene is utilized as a sole source of carbon and energy for microbial growth. Two pathways for fluorene degradation by *Arthrobacter sp.* Strain 101 as suggested by Casellas et al. [M. Casellas, M. Grifoll, J.M. Bayona, and A.M. Solanas, *Appl Environ Microbiol*, **63**(3), 819 (1997)].

tions under aerobic (presence of oxygen), hypoxic (low oxygen), and anaerobic (absence of oxygen) conditions. Examples of recognized biogeochemical reaction sequences are summarized in Figures 23.2.1 and 23.2.2. Some of these biological reactions are co-metabolic meaning that the microbes that catalyze them do not gain carbon or energy for growth and must therefore have a primary carbon source available to drive the processes.

Our ability to understand and capitalize on biological processes, such as biotransformation, in *in situ* and *ex situ* strategies, often result in a low cost, simple alternative to conventional treatment strategies. Several methods to better understand these processes, including direct measure of microbial activity,[11] transformation of tracer compounds into CO_2 or metabolic intermediates,[12] and microbial utilization of specific carbon sources through stable isotopes measurements[13] have been developed and applied to a number of hydrocarbon-impacted sites. Other indirect measurements used in the 1970's and 1980's such as plate counts have led investigators to believe that biodegradation was occurring, where direct measurements of biodegradation were not conducted to support those conclusions. Furthermore, the use of plate counts grossly underestimates the population of catabolically relevant biomass.[1] Biodegradation likely occurs in most systems, however the level of biodegradation may be insufficient to expect reasonable cleanup to target levels in the desired time frames.

The fact that HCs are amenable to aerobic biological treatment has been fully and convincingly established in the scientific literature (see also recent review[1]). In the absence of oxygen as an electron acceptor, microbially catalyzed reductive dehalogenation of CHC has been documented.[14-19] Recently, Yang and McCarthy[20] have demonstrated the reductive dechlorination of chlorinated ethenes at H_2 tension too low to sustain competitive growth of hydrogenotrophic methanogens. Anaerobic biotransformation of non-chlorinated HCs typ-

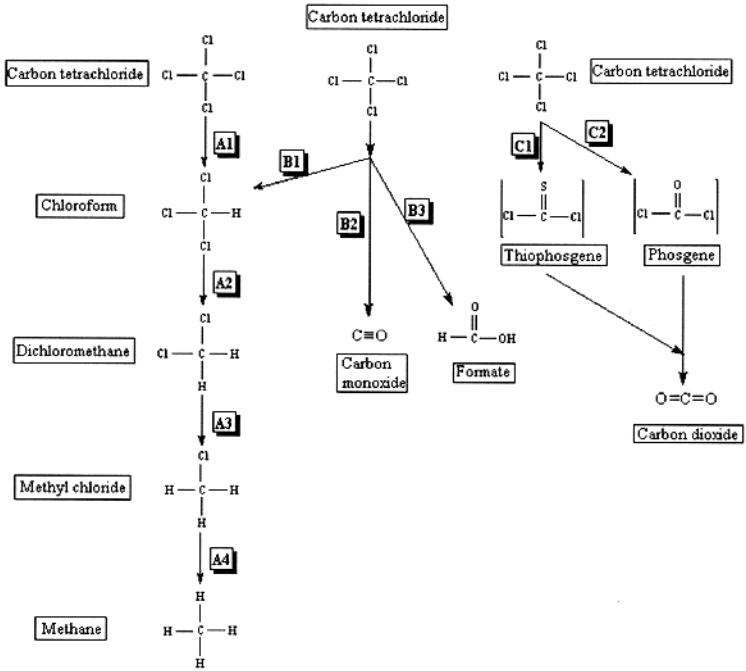

Figure 23.2.2. Anaerobic degradation of carbon tetrachloride. An example of anaerobic dehalogenation, using carbon tetrachloride as the model compound. In many cases, these reactions occur under cometabolic conditions meaning that an alternative growth substrate must be present to serve as an electron donor to drive the reduction reactions whereby carbon tetrachloride is used as the electron acceptor. Three known pathways for microbial degradation of carbon tetrachloride have been identified [U.E. Krone, R.K. Thauer, H.P. Hogenkamp, and K. Steinbach, *Biochemistry*, **30**(10), 2713 (1991); C.H. Lee, T.A. Lewis, A. Paszczynski, and R.L. Crawford, *Biochem Biophys Res Commun,* **261**(3), 562 (1999)]. These pathways are not enzymatically driven but rely on corrinoid and corrinoid-like molecules to catalyze these reactions.

ical of those prevalent in the dissolved phase, including PAH constituents, has also been demonstrated.[21-28]

It is therefore accepted that aerobic and anaerobic biodegradation of organic compounds occurs through the action of natural, indigenous microflora. As a result of these natural *in situ* microbial processes, many sites with elevated concentrations of biodegradable organics exhibit highly reducing and anaerobic conditions in areas containing elevated concentrations (i.e., suspected source areas). Moving outward laterally and down-gradient within the plume, the aquifers tend to become more oxidizing as a result of lower constituent levels, infiltration, and recharge with oxygenated water.

23.2.2.1.1 Case study - Cooper River Watershed, Charleston, SC, USA

The Cooper River Watershed empties into the Charleston Harbor on the southern Atlantic coast of the United States. In the lower reaches, the Cooper River is a highly industrialized and urbanized watershed with storm sewer and surface run-off impact. The river supports industries such as a wood pulp processing plant, a former naval shipyard, and a chromium mining/processing facility. In addition a number of fossil fuel refineries, storage facilities,

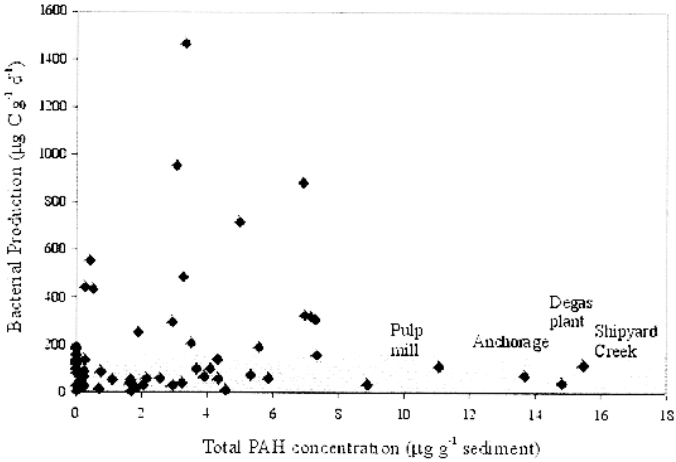

Figure 23.2.3. Bacterial productivity, a measure of bacterial activity, was compared with the level of contaminants at a number of site in the Cooper River watershed, South Carolina (USA). Where productivity is low and PAH concentration is high, the concentration of PAH or other mitigating factors suggest that the potential for PAH biodegradation may be limited in these systems compared to the other sampling points in this watershed. [Figure adapted from M. T. Montgomery, B. J. Spargo, and T.J. Boyd, Naval Research Laboratory, Washington, DC, NRL/MR/6115—98-8140, (1998)].

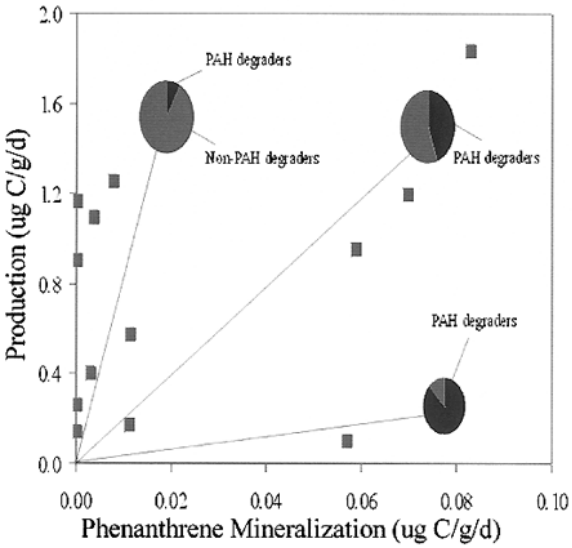

Figure 23.2.4. Microbial communities have the remarkable ability to adapt to utilize a number of carbon sources. Montgomery et al. suggest that the proportion of PAH degraders (shown as pie fraction) in a population can be reflected by their overall activity (measured by protein production) and their ability to mineralize the contaminant to CO_2. [Figure adapted from: Montgomery, M. T. , T. J. Boyd, J. K. Steele, D. M. Ward, D. C. Smith, B. J. Spargo, R. B. Coffin, J. W. Pohlman, M. Slenska, and J. G. Mueller, International Conference on Wetlands & Remediation, Salt Lake City, UT, November 16-17, 1999.]

and commercial shipping and recreational docks are scattered along the river. The physical characteristics of the Cooper River have been documented.[29]

In 1997 a study was initiated to examine the capacity of the Cooper River to "self-remediate" if source input was reduced or eliminated from the system. Specifically, pressure was placed on the Charleston Naval Shipyard to dredge the sediments in the area adjacent to the Navy property. A site study was conducted in this region and showed an elevated number of hydrocarbons, heavy metals and other regulated compounds. The study was expanded to include the larger watershed and to place the contaminant levels in the context reflective of regional inputs of contaminants. Concomitantly, the "bio-capacity" of the sediments, overlying

boundary layer, and water column of the Cooper River were examined. Figures 23.2.3-23.2.4 illustrate the overall biological activity of the ecosystem and the capacity to degrade specific HCs.

In this case, an argument can be made that the system with limited non-point source HC input will self-remediate to acceptable levels in an reasonable time frame. However, several specific sites (Pulp Mill, Anchorage, Degas Plant, Shipyard Creek), where other contributing factors impede the microbial turnover rates of HC, are candidates for dredging or other technology. It was concluded that source control coupled with long term monitoring and strategic management of this ecosystem is a cost effective alternative to disruptive dredging or high-cost high technology approaches. The impact of these remediation approaches on adjacent, less-impacted ecosystems are compelling factors for avoiding their implementation.

23.2.2.2 Phytoremediation

Phytoremediation is the use of higher plants in order to contain, sequester, reduce, or degrade soil and groundwater contaminants for the eventual closure of hazardous waste sites. This rapidly emerging technology can be applied to a diverse range of environmental conditions and contains many potential advantages over conventional remediation technologies; such as substantially lower costs, improved safety, better aesthetics, and wider public acceptance.

There are at least three areas where phytoremediation *per se* can be utilized to treat soil or groundwater impacted by HCs and related compounds or co-constituents of interest such as heavy metals: 1) *Rhizosphere-Enhanced Phytoremediation*: Plants are used to stimulate the relevant catabolic activities of indigenous, root-colonizing soil microorganisms which results in enhanced remediation of soils (and potentially groundwater) impacted by HCs; 2) *Phytoextraction*: Specially selected plants are utilized to hyperaccumulate inorganic materials such as salts, heavy metals, trace elements, radionuclides, and naturally occurring radioactive materials (NORM), and; 3) *Plant-Based Hydraulic Containment*: Entails the use of the natural water uptake and transpiration ability of highly transpiring, specially selected trees or plants for either surficial or groundwater hydraulic control.

As summarized in the schematic (Figure 23.2.5), these phytoremediation processes often occur simultaneously. Here, water uptake and evapotranspiration serves to transport CHC and other solutes through the plant as it partakes in the normal physiological mechanisms of plant life. Successful application of phytoremediation technology thus requires a thorough understanding of agronomy, plant physiology, biochemistry, and soil sciences.

23.2.2.2.1 Case study - phytoremediation for CHCs in groundwater at a chemical plant in Louisiana

URS/Radian proposed the use of phytoremediation to treat groundwater contaminated with dissolved phase CHC at a chemical plant. The State of Louisiana regulatory agency recommended standard pump & treat technology. However, Radian was able to convince the State to use a new more cost effective remedy. Hybrid Poplar trees were planted to achieve hydraulic containment and phytoextraction of the entire dissolved plume. The shallow groundwater and long growing seasons were ideal for this remedial approach. Radian was eventually able to close the site and obtain a no further action letter from the State of Louisiana.

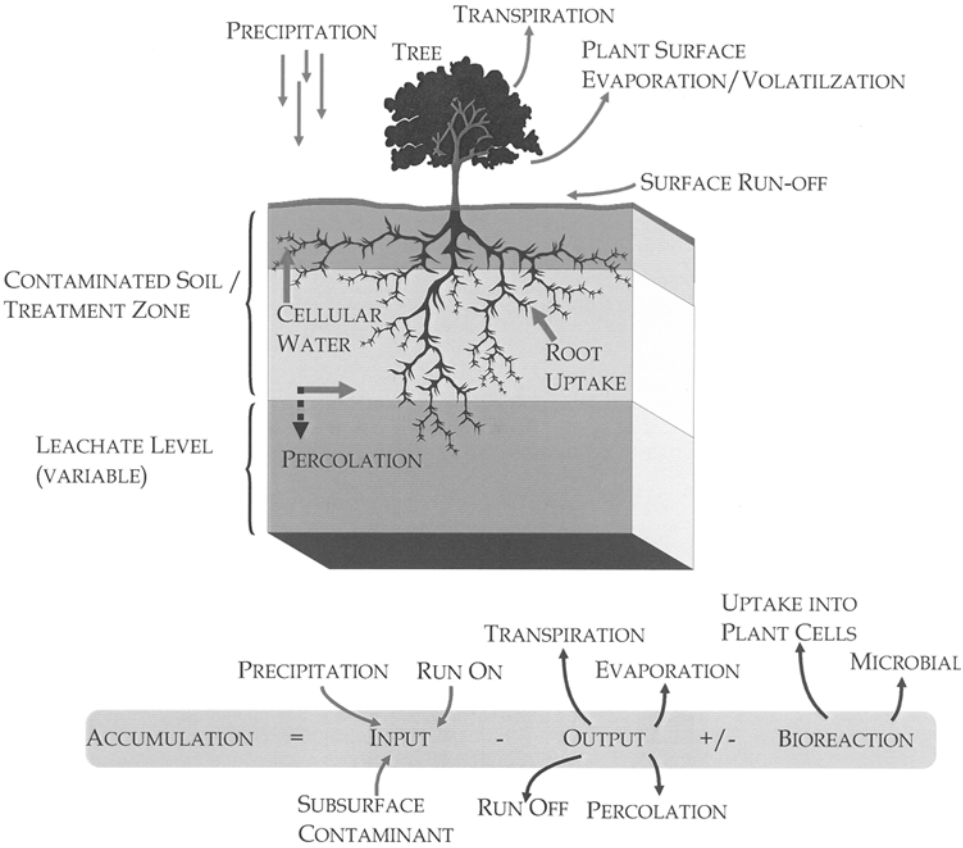

Figure 23.2.5. Phytoremediation: transport modes for HC and CHC in plant systems. Transformation of HC and CHC can be found in the root system with root-associated microbes and tissues of many plant species. HC and CHC are transported by normal plant physiological processes, such as water uptake and evaporation and transpiration. [Schematic courtesy M.A. Bucaro.]

23.2.3 *IN SITU* TREATMENT TECHNOLOGIES

23.2.3.1 Product recovery via GCW technology

Vertical groundwater circulation wells (GCW) create three-dimensional, *in situ* groundwater circulation cells to mobilize and transport dissolved phase constituents of interest from the aquifer to a central well for treatment via a number of biotic and/or abiotic processes. GCW technology relies on a positive- or negative-pressure stripping reactor in a specially adapted groundwater well. Often pressure is attained by an above-ground mounted blower and off-air treatment system, such as activated carbon. A generic GCW is shown in Figure 23.2.6. The basic principle of operation of one GCW technology depends on moving water within the well to a well screen area above the water table, where water cascades into the vadose zone surrounding the well. Water is drawn in at a screened area in the aquifer usually found below the contaminated zone creating vertical water circulation. Volatile organics are stripped from the dissolved phase by air-stripping and biodegradation is enhanced. For

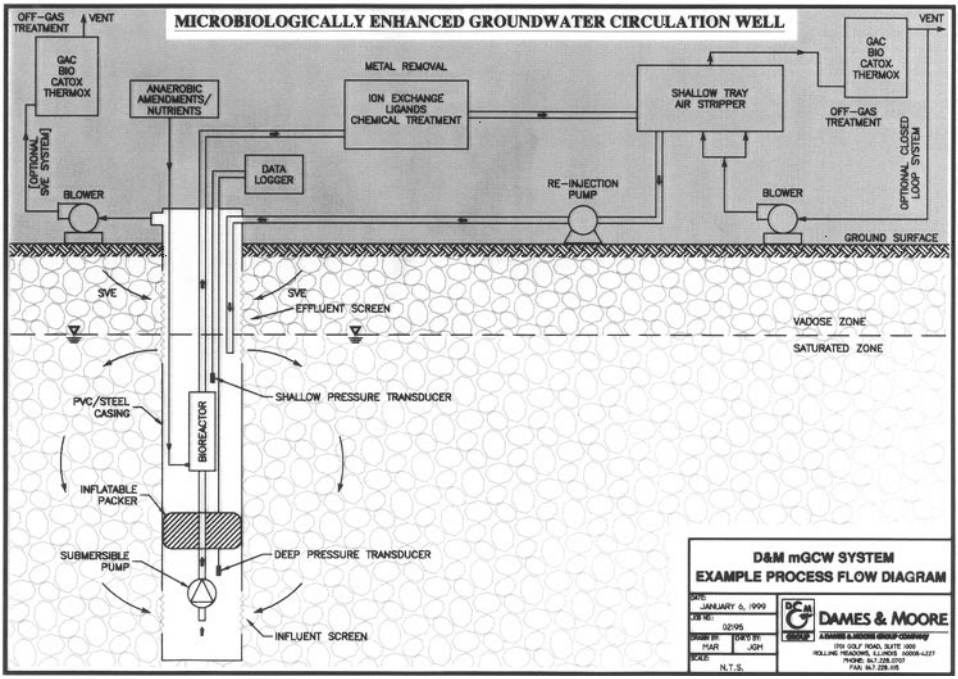

Figure 23.2.6. GCW process diagram. Effective hydrocarbon stripping in the water column is observed in these systems using a vacuum extraction. A circulation cell is created by directional flow of water in the vertical direction creating a capture zone extending several meters from the well. In addition a bioreactor (high surface area bacterial biofilm) can be used in the system to degrade low volatile contaminants [Adapted from Bernhartt et al., **U.S. Patent 5,910,245**, 1999]

more information on other GCW systems and their various modes of operation see Mueller et al.[30] and Allmon et al.[31]

Modifications of the technology have evolved as promising solutions for *in situ* remediation, source management, and/or accelerated recovery of phase-separated hydrocarbons. In each of these applications, however, success requires that the GCW zone of influence (ZOI) be validated. Accurate information on the direction and velocity of groundwater flow is equally important because it determines the rate of transport of contaminants being released or treated in the sub-surface. Toward this end, pressure transducers, conservative dye tracers, and *in situ* permeable flow sensors have been used to validate theoretical predictions of flow fields and the corresponding ZOI. The resulting information is then used to reassess the model and make operational changes to the system in order to meet clean-up goals and objectives.

23.2.3.1.1 Case study - GCW recovery of creosote, Cabot/Kopper's Superfund Site, Gainesville, FL

This site is a former pine tar and charcoal generation facility and a active wood treatment facility. Creosote used in the wood treating operation is the primary HC. The soil is 93% sand with some silt and clay. Remedial investigation results indicated that ground water in the shallow aquifer (10 to 23 ft below ground) had been impacted. Horizontal and vertical con-

ductivities were 9×10^{-3} cm/s and 9×10^{-4} cm/s, respectively, with a horizontal gradient of 0.006. Initial total concentrations of PAHs in the soil exceeded 700 mg/kg. Total concentrations of PAHs in groundwater for all wells tested ranged from 5-50 mg/L. A single GCW well was installed at a depth of 3 to 8.5 m immediately down gradient from a lagoon area that had been identified as a source of creosote constituents. The system was started in February 1995 and continues to operate to date, having been taken over by the client in 1998. Samples taken after 18 months of operation indicated total PAH concentrations of 10-35 mg/L in up gradient wells. Concentrations in down gradient wells were measured at 0.04-2 mg/L indicating a marked reduction in HC in the aquifer as groundwater moved down gradient through the GCW circulation cell.

23.2.3.2 Surfactant enhanced product recovery

A possible remedy for CHC dense non-aqueous phase liquid (DNAPL) is to install an increased-efficiency pump-and-treat system based on introducing surfactants into the aquifer to increase the solubility of CHC and the rate at which it transfers into the water phase. In this type of system, groundwater is extracted, DNAPL is separated (if present), dissolved CHC is air-stripped or steam-stripped from the water, surfactant is added to the groundwater, and the surfactant-rich water is re-injected into the aquifer up-gradient of the suspected DNAPL deposit. As the surfactant-laden groundwater passes across the DNAPL zone it is capable of reaching a CHC saturation level that is many times the natural CHC solubility, thus removing DNAPL more efficiently.

Surfactant-aided product recovery differs significantly from surfactant flushing approaches in that the goal of the efforts is to increase the dissolution of DNAPL into the aqueous phase to expedite its removal. The goal is not to physically mobilize DNAPL through the addition of high concentrations of surface-active agents (i.e., surfactant flushing). In general, surfactant flushing *per se* is not advocated unless the geophysical properties of the aquifer are extremely well characterized, and the nature and source of CHC impact are well defined. Since these requisites are rarely met, the more aggressive use of surfactants is rarely considered.

23.2.3.2.1 Case study - Surfactant-aided chlorinated HC DNAPL recovery, Hill Air Force Base, Ogden, Utah

Hill Air Force Base at Ogden, Utah used large amounts of solvents as degreasing agents. From 1967 to 1975, unknown amounts of perchloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA), and dichloromethane (MC) were placed in shallow, unlined trenches as the means of disposal. In the mid-1980s, pools of CHC DNAPL were found at the base of the uppermost aquifer. These DNAPL pools were several feet thick in some areas and extended over 36 acres. As such, DNAPL was a significant and continuing source of off-site migration of dissolved-phase CHCs. As an interim remedial action, the Air Force designed and implemented conventional pump-and-treat technology to serve as a "Source Recovery System". In its first year of operation, the system recovered over 23,000 gallons of DNAPL. After several years of operation, DNAPL recovery decreased but thousands of gallons of product remained in the form of residual saturation (on the order of 20 percent of the pore volume). This residual material was not recoverable by normal pump-and-treat methods. In an effort to enhance the recovery of residual CHC DNAPL, URS/Dames & Moore initiated a surfactant-aided DNAPL recovery system. About 8 percent sodium dehexyl sulfosuccinate (an anionic surfactant), 4 percent isopropanol and 7,000 mg/L NaCl

were combined to create an average DNAPL solubility of 620,000 mg/L (compared with a TCE solubility of 1,100 mg/L in natural groundwater). The solution was injected over a period of time, in an amount equal to 2.4 pore volumes in the test portion of the aquifer. DNAPL removal was 99 percent (estimated) and surfactant recovery at the extraction wells was 94 percent. Based on these results, a full-scale system was designed and implemented.

23.2.3.3 Foam-enhanced product recovery

The use of foams to remove heavy immiscible fluids such as DNAPL from soil was developed by the petroleum industry for crude oil production. Subsequently, The Gas Research Institute developed the use of foams to release and mobilized DNAPL contaminants in the subsurface. Coupled with *in situ* or *ex situ* bioremediation, foam-enhanced product recovery can, potentially, transport CHC contaminants upward in the groundwater, thus reducing the potential for driving the contamination to previously non-impacted areas.

The use of foam for CHC DNAPL is currently viewed as experimental. The delivery of the foam, its sweep front, the foam stability, its ability to release CHC DNAPLs in the subsurface, and the resultant biodegradability of residuals can potentially be aided through the proper selection of foaming agents and nutrients. In theory, the technology can tailor the foam system to aerobic or anaerobic subsurface environments, depending on the selection of the carrier gas. This allows adequate biodegradation for the particular CHC in the foam-pollutant system. For example, DCE can be biodegraded aerobically, whereas PCE needs to be degraded anaerobically.

23.2.3.4 Thermal desorption - Six Phase Heating

Six-Phase Heating™ (SPH) is a polyphase electrical technology that uses *in situ* resistive heating and steam stripping to achieve subsurface remediation. The technology was developed by Battelle's Pacific Northwest Laboratories for the U.S. Department of Energy to enhance the removal of volatile contaminants from low-permeability soils. The technology is also capable of enhancing the removal of DNAPLs from saturated zones.

SPH uses conventional utility transformers to convert three-phase electricity from standard power lines into six electrical phases. These electrical phases are then delivered throughout the treatment zone by steel pipe electrodes inserted vertically using standard drilling techniques. Because the SPH electrodes are electrically out of phase with each other, electricity flows from each electrode to the adjacent out-of-phase electrodes. *In situ* heating is caused by resistance of the subsurface to this current movement. In this manner, a volume of subsurface surrounded by electrodes is saturated with electrical current moving between the electrodes and heated. By increasing subsurface temperatures to the boiling point of water, SPH speeds the removal of contaminants such as CHCs via three primary mechanisms: increased volatilization, steam stripping, and enhanced residual mobility toward extraction wells via viscosity reduction.

Once subsurface soil and groundwater reach the boiling point of water, the *in situ* production of steam begins. Through preferential heating, SPH creates steam from within silt and clay stringers and lenses. As this steam moves towards the surface, it strips contaminants such as CHCs from both groundwater and soil matrix. Released steam can act as a carrier gas, sweeping CHC out of the subsurface and to extraction wells. However, it can also cause constituent migration and CHC displacement if the steam is allowed to condense prior to extraction.

23.2.3.4.1 Case study - Six-Phase Heating removal of CHC at a manufacturing facility near Chicago, IL

SPH has been employed to remove TCE and TCA from the subsurface at a former manufacturing facility near Chicago, Illinois.[32] Since 1991 combined steam injection with both ground water and soil vapor extraction had resulted in significant mass removal, but had left behind three hot spot areas after seven years of operation. These areas, which contained DNAPL in tight heterogeneous soil, were treated in less than four months by SPH.

Site lithology consisted of heterogeneous sandy silts to 18 ft below grade (bg) and a dense silty clay till from 18-55 ft bg. A shallow groundwater table was encountered at 7 ft bg and hydraulic conductivity through the remediation zone ranges from 10^{-4} - 10^{-5} cm/sec.

A network of 107 electrodes covering two-thirds of an acre was established. To treat beneath a warehouse, 85 of those electrodes were constructed directly through the floor of the building. Electrically conductive from 11-21 ft bg, the electrodes actively heated the depth interval from 5-24 ft bg. Once subsurface temperatures reach boiling, steam laden with chlorinated solvents was collected by a network of 37 soil vapor extraction wells screened to 5 ft bg.

SPH operations began on June 4, 1998. Within 60 days, temperatures throughout the entire 24,000 cubic yard treatment volume had reached the boiling point of water. With another 70 days of heating, separate phase DNAPL had been removed and TCE/TCA groundwater concentrations reduced to below the risk based target cleanup levels. Cleanup results are shown in Table 23.2.1.

Table 23.2.1. Summary of groundwater cleanup results

Well	Compound	Jun. '98, µg/l	Oct. '98, µg/l	Reduction, %
B-3	TCE TCA	58,000 82,000	790 non detect	98.6 >99.4
Da2	TCE TCA	370,000 94,000	8,800 290	97.6 99.7
F13	TCE TCA	2,800 150,000	280 non detect	90.0 >99.9

In 100 days of heating, 23,000 cubic yards of DNAPL impacted subsurface were remediated to the site cleanup goals set by a State RBCA Tier III evaluation. Based upon these results, the site owner has elected to continue SPH to reach the lower cleanup goals to lessen long term liability. SPH preferentially heats subsurface zones with higher electrical conductivity. At this site, these zones included clay-rich soil lenses and areas with elevated chloride ion concentrations. DNAPL are typically trapped in silt and clay-rich stringers and lenses, while locations of elevated chloride ion concentrations, created from the biological dehalogenation of chlorinated solvents, also correspond to locations of elevated DNAPL concentrations. Thus, SPH targeted the specific subsurface locations of the DNAPL mass.

Calculations of costs included project permitting, preparation of work plans, installation and operations of the SPH, vapor extraction, air abatement, and condensate treatment systems, electrical use, waste disposal, and interim sampling and reporting. Final demobilization, sampling, and reporting were not in the costing calculations. As of 20 November 1998, remedial costs of SPH were estimated at $32 per cubic yard of treatment area. At this time 1,775 MW-hr of electrical energy were consumed, representing an electrical usage rate

of $14,000 per month plus $40 per MW-hr for an electrical cost of $148,000 or $6.41 per cubic yard of treatment volume (personal communication, Greg Smith, URS/Radian).

23.2.3.5 *In situ* steam enhanced extraction (Dynamic Underground Stripping)

Dynamic Underground Stripping (DUS), developed by Lawrence Livermore National Laboratory (LLNL) in Livermore, California and the College of Engineering at the University of California at Berkeley, is a combination of the following technologies: 1) Steam injection at the periphery of the contaminated area to heat permeable zone soils, vaporize volatile compounds bound to the soil, and drive the contaminants to centrally located vapor/groundwater extraction wells; 2) Electrical heating of less permeable clays and fine-grained sediments to vaporize contaminants and drive them into the steam zone; 3) Underground imaging, primarily Electrical Resistance Tomography (ERT) and temperature monitoring, to delineate the heated area and track the steam fronts to insure plume control and total cleanup; and 4) Vapor and steam extraction followed by treatment of effluent vapors, NAPL, and impacted groundwater before discharge.

DUS is potentially effective for material above and below the water table, and is also potentially suited for sites with interbedded sands and clay layers. DUS raises the temperature of the soil and groundwater leading to rapid removal of the contaminants due to the thermodynamic processes discussed above.

23.2.3.6 *In situ* permeable reactive barriers (funnel and gate)

In situ permeable reactive barriers are used to convert CHC to less toxic and biodegradable intermediates using zero-valent metals such as iron. Permeable reactive barriers, primarily developed at the University of Waterloo, Groundwater Research Center, Canada and EnviroMetals Technologies, Inc. offer a unique cleanup option which does not require transport of contaminated materials (e.g., soil or groundwater) to the surface. Groundwater in the contaminate site can be directed to a permeable barrier region (usually through the use of non-permeable barriers) which is the reactive cell composed granular zero-valent iron. The thickness of the cell is based on the retention time (resident time of water within the cell, based on horizontal flow velocities), the ratio of granular iron to sand/pea gravel, and the types of contaminants. However, in the case study described below, 100% granular iron was used as an added safety factor to ensure complete transformation of the CHCs.

Degradation of CHC occurs through a reduction of iron. This is fundamentally an iron metal corrosion event, where elemental iron is converted to ferrous iron in the presence of water and hydroxyl ions. When dissolved oxygen or the oxygen tension of the surrounding groundwater is low, reactive hydrogen is produced, resulting in reductive dehalogenation of the CHC species, as shown:

$$Fe^{o} + X\text{-}Cl + H_2O \rightarrow X\text{-}H + Cl^{-} + OH^{-}$$

Using permeable reactive barriers, investigators have shown virtually complete dechlorination of CHCs, such as TCE to ethene or ethane (for review see[33]).

23.2.3.6.1 Case study - CHC remediation using an in situ permeable reactive barrier at Naval Air Station Moffett Field, CA

In late 1995, an *in situ* permeable reactive barrier demonstration at Naval Air Station Moffett Field near Mountain View, CA was constructed by URS/Dames & Moore. The pri-

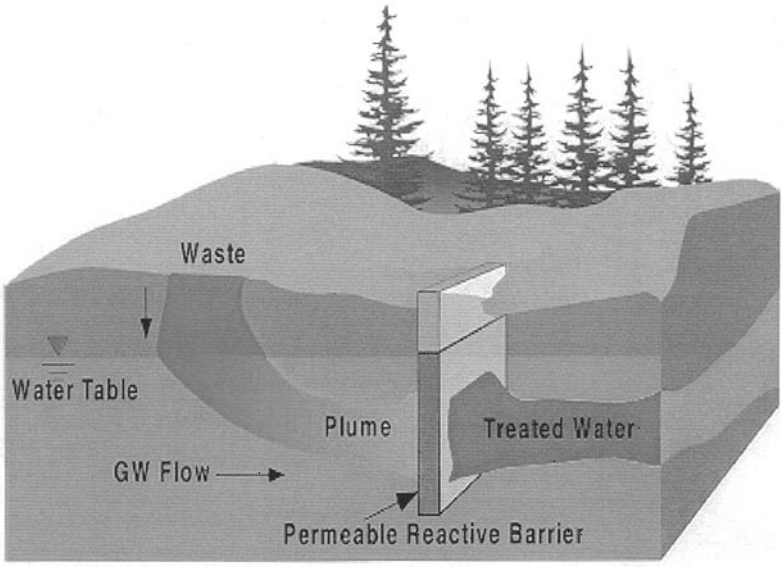

Figure 23.2.7. Schematic of a permeable reactive barrier. [From Permeable Reactive Barrier Technologies for Contaminant Remediation, EPA/600/R-98/125, 1998].

mary groundwater contaminants were TCE, PCE and *cis*-1,2-DCE (cDCE). The lithology of the site has been characterized as alluvial-fluvial clay, silt, sand and gravel, with an aquifer extending 5 to 60 ft below ground surface. The lithology is complex in this region and separates the aquifer into two zones with a discontinuous semi-confining aquitard. The mixed TCE, PCE, cDCE plume was ca. 10,000 ft by 5,000 ft extending along the direction of groundwater flow. Prior to installation of the permeable barrier system, TCE levels exceeded 5,000 µg/L, PCE 1,000 µg/L. A permeable reactive barrier was constructed with the dimensions 10 ft wide, 6 ft long, and 25 ft deep with a 2 ft pea gravel layer in front of and behind the cell. The cell was filled with granular zero-valent iron and a steel corrugate wall was constructed on each of the sides of the cell to form a funnel redirecting groundwater flow in that area through the iron cell. After nearly 4 years of operation, monitoring wells down gradient of the permeable barrier continue to shown non-detect for CHCs.

23.2.4 CONCLUSIONS

There are a number of technologies and strategies for managing hydrocarbon remediation. We have reviewed a number of the more promising, simple, and perhaps higher-technology solutions. However, a number of other demonstrated (pump and treat, air sparging) and emerging technologies do exist.[34] The basic themes of preventing migration passively, and removal of contaminant via degradation (biotic and abiotic) are seen in all the technologies. The proper use of particular technologies and strategies is very dependent on the extent and type of contamination, the site characteristics (hydrology, lithology, etc), the cleanup goals, and applicable regulations to name a few. Unfortunately, there are no hard and fast rules for the use of a particular technology; past experience suggests that the more that is known about site characteristics the greater the success of technology application.

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