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CHAPTER 8

MODELING BIODEGRADATION AND NATURAL ATTENUATION

8.1 KINETICS AND RATES OF BIODEGRADATION

Chapter 7 focused on contaminant fate processes including sorption, volatilization, abiotic and biotic transformations. A detailed discussion of microbiologically mediated transformations was presented along with the most common pathways for biodegradation of fuel hydrocarbons and chlorinated solvents and other contaminants. These fate processes greatly affect contaminant transport and remediation; however, they are somewhat difficult to quantify at the field scale, especially biodegradation processes. A better understanding of fate processes at

the field scale can be achieved using fate and transport models that simulate these processes and their impacts on contaminant concentrations in the subsurface. This chapter, in particular, focuses on integrating the biodegradation mechanisms into the transport equations discussed in Chapter 6. Since biodegradation has been demonstrated to be a key mechanism for reducing contaminant concentrations and contaminant mass in aquifers, it is beneficial to develop models that allow an assessment of the efficacy of these processes at the field scale.

Modeling biodegradation involves selecting an applicable kinetic model as well as determining the appropriate biodegradation rates for use in the selected model. This chapter will focus on the various kinetic expressions that have been used to date for fuel hydrocarbons and chlorinated solvents and will present biodegradation rate data for these compounds. The chapter will also focus on current biodegradation models and will present a set of new tools that have recently emerged for simulating natural attenuation processes (described in more detail in Chapter 12).

8.1.1 Biodegradation Kinetics

The main expressions that have been utilized for modeling biodegradation include:

1. Monod kinetics
2. First-order decay kinetics
3. Instantaneous reaction kinetics

Monod kinetics have been described in Chapter 7. It is important to note that the main difficulty with using Monod kinetics is the lack of data for the various chemicals under different electron acceptor conditions. Suarez and Rifai (1999) reported Monod kinetic data from 18 studies for BTEX (mostly aerobic). Their research presented a range between 0.01 – 20.3 mg/L for the half-saturation constant for BTEX and a range between 4×10^{-5} and 19.0 day⁻¹ for μ_{max} . They found virtually no Monod kinetic data for chlorinated solvents.

The first-order decay model, one of the most commonly used expressions for representing the biodegradation of an organic compound, involves the use of an exponential decay relationship:

$$C = C_0 \cdot e^{-kt} \quad (8.1)$$

where C is the biodegraded concentration of the chemical, C_0 is the starting concentration, and k is the rate of decrease of the chemical in units of time⁻¹. First-order rate constants are often expressed in terms of a half-life for the chemical:

$$t_{1/2} = \frac{0.693}{k} \quad (8.2)$$

The first-order decay model shown in Eq. (8.1) assumes that the solute degradation rate is proportional to the solute concentration. The higher the concentration, the higher the degradation rate. This method is usually used to simulate biodegradation in dissolved hydrocarbon plumes. Modelers using the first-order decay model typically use the first-order decay coefficient as a calibration parameter, and adjust the decay coefficient until the model results match field data. With this approach, uncertainties in a number of parameters (e.g., dispersion, sorption, biodegradation) are lumped together in a single calibration parameter.

The electron-acceptor limited model, commonly referred to as the instantaneous reaction model, was first proposed by Borden and Bedient (1986) for simulating the aerobic biodegradation of fuel hydrocarbons. Borden and Bedient (1998) observed that microbial biodegradation kinetics are fast in comparison with the transport of oxygen, and that the growth of microorganisms and utilization of oxygen and organics in the subsurface can be simulated as an instantaneous reaction between the organic contaminant and oxygen.

From a practical standpoint, the instantaneous reaction model assumes that the rate of utilization of the contaminant and oxygen by the microorganisms is very high, and that the time required to biodegrade the contaminant is very small, or almost instantaneous. Using oxygen as an electron acceptor, for example, biodegradation is calculated using the expression:

$$\Delta C_R = -\frac{O}{F} \quad (8.3)$$

where ΔC_R is the change in contaminant concentration due to biodegradation, O is the concentration of oxygen, and F is the utilization factor, or the ratio of oxygen to contaminant consumed. The variable, F , is obtained from the redox reaction involving the organic and the electron acceptor (see Chapter 12). The instantaneous reaction model has the advantage of not requiring kinetic data. The model, however, is limited to situations where the microbial biodegradation kinetics are fast relative to the rate of ground water flow.

Example 8.1 BIODEGRADATION EXPRESSIONS

The purpose of this example is to illustrate the differences between the three expressions that can be used to simulate biodegradation: first-order decay, Monod kinetics and an instantaneous reaction. Assume that the dissolved benzene concentration at a down-gradient location in a given aquifer is 12.0 mg/L. Also assume that aerobic biodegradation is occurring in the aquifer and that 8.0 mg/L of oxygen are available for utilization by the microorganisms over a period of 10 days. A simple calculation can be made using each of the three biodegradation expressions to estimate the anticipated reduction in benzene concentrations due to the presence of the 8.0 mg/L of oxygen:

Instantaneous reaction expression. Assuming that 3.0 mg/L of oxygen are required to biodegrade 1.0 mg/L of contaminant:

$$\text{Benzene reduction} = 8.0/3.0 = 2.67 \text{ mg/L}$$

$$\text{Resulting benzene concentration} = 12.0 - 2.67 = 9.33 \text{ mg/L}$$

Monod kinetic expression. Assuming an oxygen half saturation constant of 0.1 mg/L (Borden et al., 1986), a benzene half-saturation constant of 22.16 mg/L, a maximum utilization rate of 9.3 days⁻¹ (Tabak et al., 1990) and a microorganisms population of 0.05 mg/L:

$$\text{Benzene reduction} = 9.3 \times \frac{12}{12 + 22.16} \times \frac{8}{8 + 0.1} \times 10 \times 0.05 = 1.59 \text{ mg/L}$$

$$\text{Resulting benzene concentration} = 12 - 1.59 \text{ mg/L} = 10.4 \text{ mg/L}$$

First-order decay expression. Assuming a half-life of benzene of 5 days (Howard et al., 1991):

$$\text{First-order decay rate (from 8.2)} = \frac{0.693}{t_{1/2}} = 0.1386 \text{ day}^{-1}$$

$$\text{Resulting benzene concentration} = 12 \times e^{-0.1386 \times 10} = 3.0 \text{ mg/L}$$

The above calculations show that the Monod kinetic model is the most conservative model in predicting the amount of biodegradation that occurs. Only 1.59 mg/L of benzene concentration reduction is attributed to biodegradation. The BIOPLUME II model assumes total utilization of the oxygen available during the 10-day period thus resulting in a predicted reduction in benzene concentration of 2.67 mg/L. Finally, the first-order decay expression predicts an unrealistic resulting concentration of benzene of 3.0 mg/L after 10 days. The 3.0 mg/L concentration is unrealistic because there is not enough oxygen in the aquifer to reduce the benzene concentration to the predicted level. Therefore, it is important to recognize that the first-order expression does not incorporate the electron acceptor limitation and thus care should be taken when using this expression.

8.1.1 Rates of Biodegradation

Much research has been undertaken to determine biodegradation rates for organics in the subsurface. Field biodegradation rates generally refer to the rate of mass loss or concentration declines of contaminants as a function of time. Laboratory biodegradation rates similarly refer to the rate of removal of contaminants during the controlled experiment. Overall, laboratory rates are easily determined; however, their usefulness may be limited because of the limitations of microcosm studies. Additionally, laboratory degradation rates are very dependent on the soil and ground water used in the experiment, and may vary from one location to another in the same site. A methodology has not yet been established that would allow the

transfer of laboratory determined biodegradation rates to field situations with any degree of confidence.

The main difficulty in determining field rates of biodegradation is due to the complicating transport processes such as advection, dispersion, and sorption. Additionally, biodegradation under many field situations is limited by the transport of the required nutrients into the plume. Outside of conducting controlled field experiments where the total initial mass of contaminants is known and extensive monitoring allows calculating contaminant mass at any time during the experiment, it is somewhat difficult to accurately determine the field rates of biodegradation. Often, as will be seen in the next section, researchers and practitioners indirectly verify the occurrence of biodegradation at the field scale and calculate an "apparent" rate of biodegradation based on the changes in total mass or concentration in the plume as a function of time. Such a rate may incorporate the effects of the other physical and chemical processes occurring at the site.

In recent years, there has been more interest in estimating biodegradation rates from field data using a first-order degradation rate. A number of researchers have developed methods for estimating decay rates using simplified approaches. Wiedemeier et al. (1996), for example, described the use of a normalized field data set to compute a decay rate. To determine approximate biodegradation rate constants with this method, measured concentrations of dissolved BTEX are corrected for the effects of dispersion, dilution from recharge, volatilization, and sorption using a tracer.

One tracer that has proved useful in some, but not all, ground water environments is trimethylbenzene (TMB). The three isomers of this compound (1,2,3-TMB, 1,2,4-TMB, and 1,3,5-TMB) have Henry's Law constants and soil sorption coefficients similar to (although somewhat higher than) those of the BTEX compounds. Also, the TMB isomers are generally present in sufficient quantities in fuel mixtures to be readily detectable in ground water in contact with a fuel spill. Finally, they often are recalcitrant to biodegradation in the anaerobic portion of a plume. Other compounds of potential use as conservative tracers are the tetramethylbenzene isomers, provided they are detectable throughout most of the plume.

Buscheck and Alcantar (1995) derive a relationship that allows calculation of approximate biodegradation rate constants assuming a steady-state plume. This method involves coupling the regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) to an analytical solution for one-dimensional, steady-state, contaminant transport that includes advection, dispersion, sorption, and biodegradation. The effects of volatilization are assumed to be negligible. For a steady-state plume, the first-order decay rate is approximated by (Buscheck and Alcantar, 1995):

$$\lambda = \frac{v_c}{4\alpha_r} \left(\left[1 + 2\alpha_r \left(\frac{k}{v_r} \right) \right]^2 - 1 \right) \quad (8.4)$$

where

- λ = first-order biological decay rate
 v_c = retarded contaminant velocity in the x -direction
 α_x = dispersivity
 k/v_x = slope of line formed by making a log-linear plot of contaminant concentration versus distance downgradient along flow path

When used with accurate estimates of dispersivity and ground-water flow and solute transport velocity, this method gives reasonable first-order biodegradation rates. Examples of how to apply this method are given in Buscheck and Alcantar (1995) and Wiedemeier et al. (1996). This method can also be used to estimate biodegradation rates for chlorinated solvents dissolved in ground water.

For sites where sufficient historical data have been collected (a minimum of three sampling events), a biodegradation rate constant can be calculated by estimating the change in dissolved mass within the plume as a function of time. One of the methods for calculating the dissolved mass (DM) at time t includes the use of an average plume concentration $C_{avg,t}$:

$$DM_t = C_{avg,t} \times b \times n \times L \times W \quad (8.5)$$

where

- b = aquifer thickness
 n = porosity
 L = plume length
 W = plume width

This method was used by Rifai et al. (1988) and Chiang et al. (1989) at two sites in Michigan. Their studies estimated a rate constant of approximately 0.01 day^{-1} for BTEX at these sites.

Another method (graphically based) was presented by the RTDF (1997). The method is based on having good isoconcentration maps for the site in question. The RTDF (1997) method draws several lines perpendicular to the flow and at various distances away from the source on the site isoconcentration map, and use the thickness of the aquifer and the ground water velocity to estimate the mass of ground water per year that passes through each line.

8.1.2 First-Order Biodegradation Rates for Fuel Hydrocarbons

Suarez and Rifai (1999) have compiled a database for first-order degradation rates for fuel hydrocarbons. Their data indicate a range from 0 to 6 day^{-1} for aerobic and anaerobic biodegradation rates for BTEX (using both field and laboratory data). Table 8.1 lists the minimum, maximum, mean, and median rates for BTEX sorted by electron acceptor. Suarez and Rifai (1999) developed a number of conclusions from this database:

TABLE 8.1 Summary of BTEX first-order decay rates (day^{-1}) sorted by electron acceptor

	All Studies	Redox Process					
		Aerobic Respiration	Nitrate Reduction	Iron Reduction	Sulfate Reduction	Methanogenesis	Mixed
BENZENE							
Number of rates	149	26	41	20	16	15	25
Minimum	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mean	0.0654	0.3350	0.0083	0.0085	0.0077	0.0100	0.0092
Median	0.003	0.198	0	0.00495	0.0026	0	0.004
Maximum	2.5	2.5	0.089	0.034	0.049	0.077	0.087
TOLUENE							
Number of rates	135	16	49	13	14	24	17
Minimum	0.0000	0.0160	0.0000	0.0000	0.0001	0.0000	0.0000
Mean	0.2498	0.2618	0.4589	0.0116	0.0621	0.0371	0.3018
Median	0.04	0.1665	0.09	0.0099	0.035	0.02065	0.004
Maximum	4.8	1.63	4.32	0.045	0.21	0.186	4.8
ETHYLBENZENE							
Number of rates	82		37	7	8	12	17
Minimum	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000
Mean	0.1258		0.2699	0.0034	0.0021	0.0103	0.0096
Median	0.00257		0.0158	0.0015	0.00055	0.00105	0.002
Maximum	6.048		6.048	0.017	0.0072	0.054	0.078
m-XYLENE							
Number of rates	90	4	41	8	7	12	16
Minimum	0.0000	0.0080	0.0000	0.0012	0.0040	0.0000	0.0000
Mean	0.0582	0.1630	0.0887	0.0100	0.0808	0.0194	0.0042
Median	0.0045	0.107	0.017	0.002452055	0.056	0.001	0.002
Maximum	0.49	0.43	0.49	0.037	0.32	0.104	0.025
o-XYLENE							
Number of rates	92	10	38	8	6	12	16
Minimum	0.0000	0.0080	0.0000	0.0000	0.0000	0.0000	0.0000
Mean	0.0212	0.0860	0.0117	0.0031	0.0268	0.0262	0.0087
Median	0.004	0.035	0.0045	0.001803425	0.0105	0.00105	0.003
Maximum	0.38	0.38	0.068	0.016	0.084	0.214	0.057
p-XYLENE							
Number of rates	65	3	21	8	4	10	18
Minimum	0.0000	0.0080	0.0000	0.0008	0.0023	0.0000	0.0000
Mean	0.0378	0.2070	0.0678	0.0098	0.0108	0.0180	0.0063
Median	0.00353		0.008	0.001835616	0.009	0.0025	0.002
Maximum	0.44	0.43	0.44	0.037	0.022	0.081	0.031

Source: Suarez and Rifai (1999)

- Maximum first-order biodegradation rates reported in literature for BTEX compounds were 4.8 day^{-1} and 6.05 day^{-1} under aerobic and anaerobic conditions, respectively.
- Anaerobic rates for BTEX were approximately one order of magnitude smaller than aerobic rates (average median value for aerobic BTEX biodegradation was 0.08 day^{-1} while average median value for anaerobic BTEX biodegradation was 0.009 day^{-1}).

- Among BTEX compounds, the most readily biodegradable substrate under aerobic conditions was benzene, whereas for anaerobic biodegradation, it was toluene.
- The median reported degradation rates for benzene, ethylbenzene and xylene were very similar with an average median value of 0.0035 or 0.35% per day for the three compounds. Toluene, the only exception, significantly exceeded this value (0.9% per day).

8.1.3 First-Order Biodegradation Rates for Chlorinated Solvents

Suarez and Rifai (1999) also compiled a similar database for chlorinated organics. Their study indicates a biodegradation rate ranging from 0 to 8 day⁻¹ for these compounds (Table 8.2). Their conclusions from the database indicate that:

- Maximum first-order biodegradation rates reported in literature for chlorinated solvents were 1.96 day⁻¹ and 3.13 day⁻¹ under aerobic and anaerobic conditions, respectively.
- The higher-chlorinated solvents biodegrade anaerobically with an average median rate of 0.033 day⁻¹ while the less-chlorinated solvents biodegrade aerobically with an average median rate of 0.16 day⁻¹.

2 MODELING BIODEGRADATION

The problem of quantifying biodegradation in the subsurface can be addressed by using models that combine physical, chemical and biological processes. Developing such models is not simple, however, due to the complex nature of microbial kinetics, the limitations of computer resources, the lack of field data on biodegradation, and the need for robust numerical schemes that can simulate the physical, chemical, and biological processes accurately.

The reduction of contaminant concentrations using Monod kinetics, for example, can be expressed as

$$\Delta C = M_t \mu_{\max} \left(\frac{C}{K_c + C} \right) \Delta t \quad (8.6)$$

where C is contaminant concentration, M_t is the total microbial concentration, μ_{\max} is maximum contaminant utilization rate per unit mass microorganisms, K_c is contaminant half saturation constant, and Δt is the time interval being considered.

Incorporating Eq. (8.6) into the 1-D transport equation, for example, results in:

TABLE 8.2 Summary of chlorinated solvent first-order decay rates sorted by redox conditions. Source: Suarez and Rifai, 1999

	All Studies	Aerobic Oxidation	Cometabolism	Reductive dechlorination					Anaerobic Oxidation Iron reducing
				Nitrate reducing	Iron reducing	Sulfate reducing	Methanogenesis	Mixed	
CARBON TETRACHLORIDE									
Number of rates	13	1	1	6	2		2		
Minimum	0.0037			0.0207					
Mean	0.1077			0.0776	0.1169		0.32		
Median	0.049			0.0645					
Maximum	0.49			0.16					
DCA (all isomers)									
Number of rates	25	2	5			13	3		
Minimum	0		0.014			0.00006			
Mean	0.0172	0.000	0.0668			0.0026	0.0061		
Median	0.0007		0.047			0.0004			
Maximum	0.131		0.131			0.028			
DCE (all isomers)									
Number of rates	61		13		8	3	8	2	
Minimum	0		0		0.00082		0.0023		
Mean	0.1406		0.5908		0.0020	0.0453	0.0470	0.0007	
Median	0.004		0.434		0.0015		0.016		
Maximum	1.96		1.96		0.0052		0.2		
PCE									
Number of rates	50	10	3	3	2	1	22	1	
Minimum	0	0					0		
Mean	0.0506	0.001	0.0247	0.000	0.0040		0.1003		
Median	0.0087	0.000					0.0795		
Maximum	0.41	0.004					0.41		
TCA									
Number of rates	47	11	5	4	1	2	17	1	
Minimum	0	0	0	0			0.0026		
Mean	0.2610	0.0021	0.2467	0.0000		0.0099	0.4976		
Median	0.0102	0	0.013	0.000			0.125		
Maximum	2.33	0.022	1.18	0.000			2.33		
TCE									
Number of rates	85	11	17	1	11	7	10	2	
Minimum	0	0	0.024		0	0.0017	0		
Mean	0.1746	0.0055	0.5862		0.0034	0.0111	0.0145	0.0014	
Median	0.0046	0	0.26		0.0016	0.0078	0.0038		
Maximum	3.13	0.0278	1.65		0.011	0.023	0.109		
VINYL CHLORIDE									
Number of rates	27	4	5		2		3	7	
Minimum	0.000034	0.043	0.055					0.0013	
Mean	0.5180	0.0873	2.4222		0.2604		0.2300	0.0421	
Median	0.051	0.091	1.5					0.012	
Maximum	8.02	0.125	8.02					0.12	

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - M_t \mu_{\max} \left(\frac{C}{K_c + C} \right) \quad (8.7)$$

where v is the seepage velocity, and D_x is the dispersion coefficient.

For aerobic biodegradation, and assuming that oxygen and the contaminant are the only substrates required for growth, the change in contaminant and oxygen concentrations due to biodegradation is given by:

$$\Delta C = M_t \mu_{\max} \left(\frac{C}{K_c + C} \right) \left(\frac{O}{K_o + O} \right) \Delta t \quad (8.8)$$

$$\Delta O = M_t \mu_{\max} F \left(\frac{C}{K_c + C} \right) \left(\frac{O}{K_o + O} \right) \Delta t \quad (8.9)$$

where O is oxygen concentration, K_o is oxygen half saturation constant, and F is ratio of oxygen to contaminant consumed.

Incorporating Eqs. (8.8) and (8.9) into the transport equation results in a system of partial differential equations as follows (Borden and Bedient, 1986):

$$\frac{\partial C}{\partial t} = \frac{1}{R_c} \nabla \cdot (D \nabla C - vC) - M_t \frac{\mu_{\max}}{R_c} \left(\frac{C}{K_c + C} \right) \left(\frac{O}{K_o + O} \right) \quad (8.10)$$

$$\frac{\partial O}{\partial t} = \nabla \cdot (D \nabla O - vO) - M_t \mu_{\max} F \left(\frac{C}{K_c + C} \right) \left(\frac{O}{K_o + O} \right) \quad (8.11)$$

$$\frac{\partial M_s}{\partial t} = \frac{1}{R_m} \nabla \cdot (D \nabla M_s - vM_s) + M_s \mu_{\max} Y \left(\frac{C}{K_c + C} \right) \left(\frac{O}{K_o + O} \right) + \frac{k_c Y(OC)}{R_m} - bM_s \quad (8.12)$$

where C is the contaminant concentration, O is the oxygen concentration, D is a dispersion tensor, v is the ground water velocity, R_c is the retardation coefficient for the contaminant, M_s and M_t are the concentration of microbes in solution and the total microbial concentration, respectively ($M_t = R_m \cdot M_s$, where R_m is the microbial retardation factor), μ_{\max} is the maximum contaminant utilization rate per unit mass of microorganisms, Y is the microbial yield coefficient, K_c is the half saturation constant for the contaminant, K_o is the half saturation constant for oxygen, OC is the natural organic carbon concentration, F is the ratio of oxygen to hydrocarbon consumed, and b is the microbial decay rate.

BIODEGRADATION MODELS

8.3.1 Developed Biodegradation Models

Many biodegradation models have been developed in recent years, most of which utilize some form of the three expressions presented earlier. Table 8.3 lists many of the biodegradation models. This section will focus on some of the more popular models and on their application to field biodegradation and bioremediation analyses.

TABLE 8.3 Biodegradation models.

Name	Dimension	Description	Author
X	1	aerobic, microcolony, Monod	Molz, et al. (1986)
BIOPLUME	1	aerobic, Monod	Borden, et al. (1986)
X	1	analytical first-order	Domenico (1987)
BIOID	1	aerobic and anaerobic, Monod	Srinivasan and Mercer (1988)
X	1	cometabolic, Monod	Semprini and McCarty (1991)
X	1	aerobic, anaerobic, nutrient limitations, microcolony, Monod	Widdowson, et al. (1988)
X	1	aerobic, cometabolic, multiple substrates, fermentative, Monod	Celia, et al. (1989)
BIOSCREEN	1	analytical first-order, instantaneous	Newell, et al. (1996)
BIOCHLOR	1	analytical	Aziz, et al. (1999)
BIOPLUME II	2	aerobic, instantaneous	Rifai, et al. (1988)
X	2	Monod	MacQuarrie, et al. (1990)
X	2	denitrification	Kinzelbach, et al. (1991)
X	2	Monod, biofilm	Odencrantz, et al. (1990)
BIOPLUME III	2	aerobic and anaerobic	Rifai, et al. (1997)
RT3D	3	aerobic and anaerobic	Clement (1998)

8.3.2 The Biofilm Model

McCarty et al. (1984) believe that the nature of the ground water environment (low substrate concentration and high specific surface area) dictates that the predominant type of bacterial activity will be bacteria attached to solid surfaces in the form of biofilm. The attached bacteria remain generally fixed in one place and obtain energy and nutrients from the ground water that flow.

Figure 8.1 is an illustration of an idealized biofilm having a uniform cell density of X_f [ML^{-3}] and a locally uniform thickness of L_f . An idealized biofilm is a homogeneous matrix of bacteria and their extracellular polymers that bind them together and to the inert surface (McCarty et al., 1981). Ground water flows past the biofilm in the x direction, while substrates are transported from the water to the biofilm in the z direction. The distance L represents the thickness of a mass-transport diffusion layer through which substrate must pass in order to go from the bulk liquid into the biofilm, where utilization occurs.

Within the biofilm, two processes occur simultaneously: namely, utilization of the substrate by the bacteria, assumed to follow a Monod-type relation, and diffusion of the substrate through the biofilm according to Fick's Law. Figure 8.2 shows the interaction of these processes—substrate utilization, molecular diffusion within the biofilm and mass transport across the diffusion layer. For a thick biofilm (Case A), the substrate concentration approaches zero and the biofilm is called deep. If the biofilm is very thin (Case C), almost no

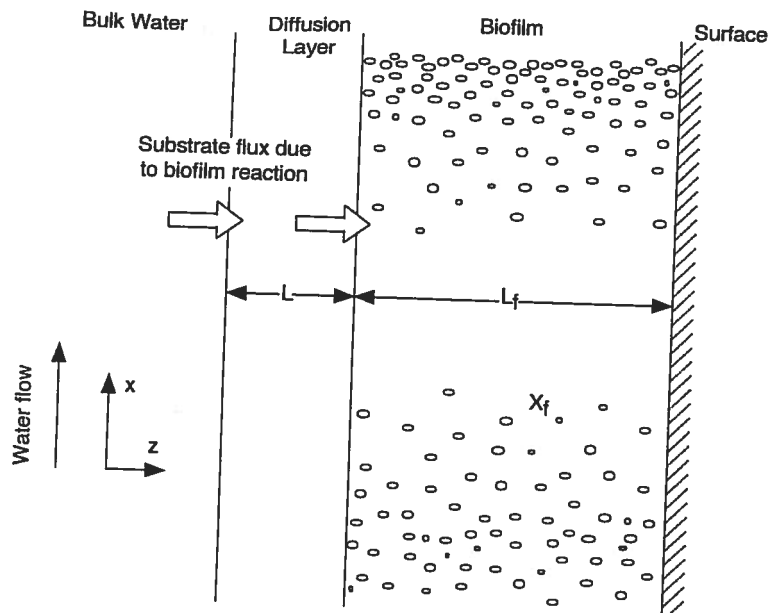


Figure 8.1 Idealized biofilm illustrating uniform cell density (X_f), thickness (L_f), water flow, and substrate flux into biofilm. Source: McCarty et al., 1984.

substrate utilization occurs and the biofilm is essentially fully penetrated at the surface concentration S_s . The remaining cases are termed shallow (Case B).

8.3.3 Microcolony Models

Molz et al. (1986) and Widdowson et al. (1987) developed 1-D and 2-D models for aerobic biodegradation of organic contaminants in ground water coupled with advective and dispersive transport. A microcolony approach was utilized in the modeling, microcolonies of bacteria were represented as disks of uniform radius and thickness attached to aquifer sediments. A boundary layer of a given thickness was associated with each colony across which substrate and oxygen are transported by diffusion to the colonies.

Their results indicate that biodegradation would be expected to have a major effect on contaminant transport when proper conditions for growth exist. Simulations of 2-D transport suggested that under aerobic conditions microbial degradation reduces the substrate concentration profile along longitudinal sections of the plume and retards the lateral spread of the plume. Anaerobic conditions developed in the plume center due to microbial consumption and limited oxygen diffusion into the plume interior.

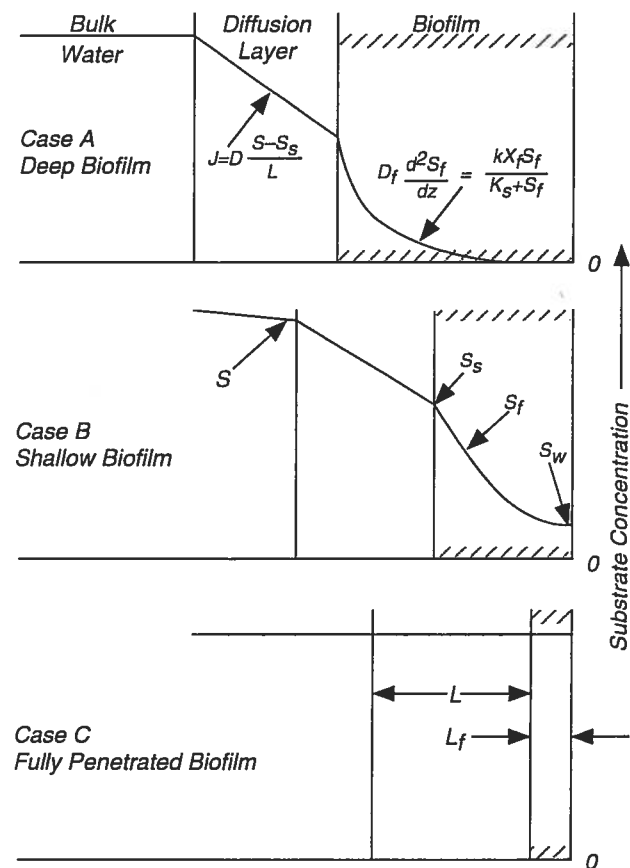


Figure 8.2 Interactions of substrate utilization, molecular diffusion within biofilm and mass transport across diffusion layer. Source: McCarty et al., 1984.

Widdowson et al. (1988) extended their 1986 and 1987 studies to simulate oxygen- and/or nitrate based respiration. Basic assumptions incorporated into the model included a simulated particle-bound microbial population comprised of heterotrophic, facultative bacteria in which metabolism is controlled by lack of either an organic carbon-electron donor source (substrate), electron acceptor (O_2 and/or NO_3), or mineral nutrient (NH_4^+), or all three simultaneously. Transport of substrate and oxygen in the porous medium is assumed to be governed by advection-dispersion equations with surface adsorption. Microbial degradation

enters the two basic transport equations as sink terms. Based on the assumptions, five coupled, nonlinear equations govern microbial growth dynamics in porous media.

8.3.4 BIO1D Model

Srinivasan and Mercer (1988) presented a 1-D, finite difference model for simulating biodegradation and sorption processes in saturated porous media. The model formulation allowed for accommodating a variety of boundary conditions and process theories. Aerobic biodegradation was modeled using a modified Monod function; anaerobic biodegradation was modeled using Michaelis-Menten kinetics. In addition, first-order degradation is allowed for both substances. Sorption can be incorporated using linear, Freundlich, or Langmuir equilibrium isotherms for either substance.

The Srinivasan and Mercer (1988) model is an extension of that presented by Borden and Bedient (1986). The governing equations are:

$$f = D \frac{\partial^2 S}{\partial x^2} - V \frac{\partial S}{\partial x} - B(S, O) - [1 + A(S)] \frac{\partial S}{\partial t} = 0 \quad (8.13)$$

$$g = D \frac{\partial^2 O}{\partial x^2} - V \frac{\partial O}{\partial x} - F \cdot B(S, O) - [1 + A(O)] \frac{\partial O}{\partial t} = 0 \quad (8.14)$$

For Aerobic Conditions:

$$B(S, O) = Mk \frac{S}{k_s + S} \cdot \frac{O}{k_o + O} \cdot \frac{S - S_{\min}}{S} \quad (8.15)$$

for

$$S \geq S_{\min}$$

and

$$O \geq O_{\min}$$

otherwise

$$B(S, O) = 0$$

For Anaerobic Conditions: $B(S, O)$ reduces to $B(S)$ and only one equation is solved for S .

$$B(S) = M_n k_n \frac{S}{k_{m_n} + S} \quad (8.16)$$

where S is the substrate concentration in the pore fluid [ML^{-3}], O is the oxygen concentration in the pore fluid [ML^{-3}], D is the longitudinal hydrodynamic dispersion coefficient [L^2T^{-1}], x is the distance, V is the interstitial fluid velocity [LT^{-1}], $B(S, O)$ is a biodegradation term expressed as a function of the dependent variables S and O [$\text{ML}^{-3}\text{T}^{-1}$], $A(S)$ is the

adsorption term expressed as a function of S (the term $[1 + A(S)]$ is the retardation factor), t is the time, M is the microbial mass, k is the maximum substrate utilization rate per unit mass of microorganisms, k_s is the substrate half-saturation constant, k_o is the oxygen half-saturation constant, S_{\min} is the minimum substrate concentration that permits growth and decay, O_{\min} is the minimum oxygen concentration that permits growth and decay, and F is the ratio of oxygen to substrate consumed. Note that M_n , k_n , and k_{m_n} are counterparts of M , k , and k_s under anaerobic conditions.

8.3.5 The BIOPLUME II Model

The BIOPLUME II model was developed by modifying an existing 2-D transport model developed by the USGS and known as the Method of Characteristics (MOC) model (Konikow and Bredehoeft, 1978; see Chapter 10). Two governing equations are solved in MOC: the ground water flow equation and the transport equation. The numerical approximation to the flow equation is a finite difference expression that is solved using an alternating-direction implicit procedure. The method of characteristics is utilized to solve the transport equation (Rifai et al., 1988).

The basic concept applied to modify the USGS MOC model and to develop the BIOPLUME II model includes the use of a dual-particle mover procedure to simulate the transport of oxygen and contaminants in the subsurface. The transport equation is solved twice at every time step to calculate the oxygen and contaminant distributions:

$$\frac{\partial(Cb)}{\partial t} = \frac{1}{R_c} \left(\frac{\partial}{\partial x_i} \left(bD_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (bCV_i) \right) - \frac{C'W}{n} \quad (8.17)$$

$$\frac{\partial(Ob)}{\partial t} = \left(\frac{\partial}{\partial x_i} \left(bD_{ij} \frac{\partial O}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (bOV_i) \right) - \frac{O'W}{n} \quad (8.18)$$

where C and O are concentrations of contaminant and oxygen respectively, C' and O' are concentrations of contaminant and oxygen in a source or sink fluid, n is effective porosity, b is saturated thickness, t is time, x_i and x_j are cartesian coordinates, W is volume flux per unit area, V_i is seepage velocity in the direction of x_i , and D_{ij} is coefficient of hydrodynamic dispersion.

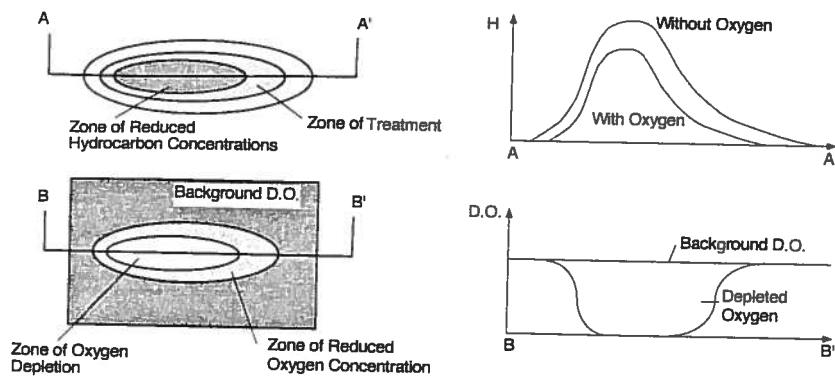


Figure 8.3 Principle of superposition for organics and oxygen in BIOPLUME II model. Source: Rifai et al., 1988.

The two plumes are combined using the principle of superposition to simulate the instantaneous reaction between oxygen and the contaminants, and the decrease in contaminant and oxygen concentrations is calculated from:

$$\Delta C_{RC} = O/F; O = 0 \text{ where } C > O/F \quad (8.19)$$

$$\Delta C_{RO} = C \cdot F; C = 0 \text{ where } O > C \cdot F \quad (8.20)$$

where ΔC_{RC} , ΔC_{RO} are the calculated changes in concentrations of contaminant and oxygen, respectively, due to biodegradation.

Figure 8.3 is a conceptual schematic of the BIOPLUME II model. On the left of the figure, a plan view of the contaminant and oxygen plumes with and without biodegradation are shown. After the two plumes are superimposed, the contaminant plume is reduced in size and concentrations. The dissolved oxygen is depleted in zones of high contaminant concentrations and reduced in zones of relatively moderate contaminant concentrations. The right schematics in Figure 8.3 present transects down the plume centerline and help to illustrate the distributions of contaminant and oxygen concentration with and without biodegradation. It is noted that field data have verified the correlation between oxygen and contaminant concentrations at sites.

There are two methods that can be used to simulate biodegradation in the BIOPLUME II model: first-order decay and instantaneous reaction. For the first-order decay model, the reaction rate, k , is required as input. The model input parameters required for the instantaneous reaction include the amount of dissolved oxygen in the aquifer prior to contamination,

and the oxygen demand of the contaminant determined from a stoichiometric relationship. Modeling the biodegradation of several components such as benzene, toluene, and xylenes (BTX) at a site requires that an average stoichiometric coefficient for the three components be calculated.

Two additional sources of oxygen can be specified in BIOPLUME II. Injection of oxygen in a bioremediation project can be simulated by using injection wells or infiltration galleries. Reaeration from the unsaturated zone can be simulated in an indirect way by specifying a first-order decay rate for the contaminants at the site. Holder et al. (1999) address reaeration using advanced methods and models.

The output from the MOC/BIOPLUME II model consists generally of a head map and a chemical concentration map for each node in the grid. Immediately following the head and concentration maps is a listing of the hydraulic and transport errors. If observation wells had been specified, a concentration history for those wells would be included in the output.

The sensitivity of aerobic biodegradation to some of the model parameters has been analyzed in detail by Rifai et al. (1988). Their analyses indicate that biodegradation is mostly sensitive to the hydraulic conductivity (Figure 8.4). This result verifies some field observations about the applicability of bioremediation for systems with relatively large hydraulic conductivities. Biodegradation was not sensitive to the retardation factor or disper-

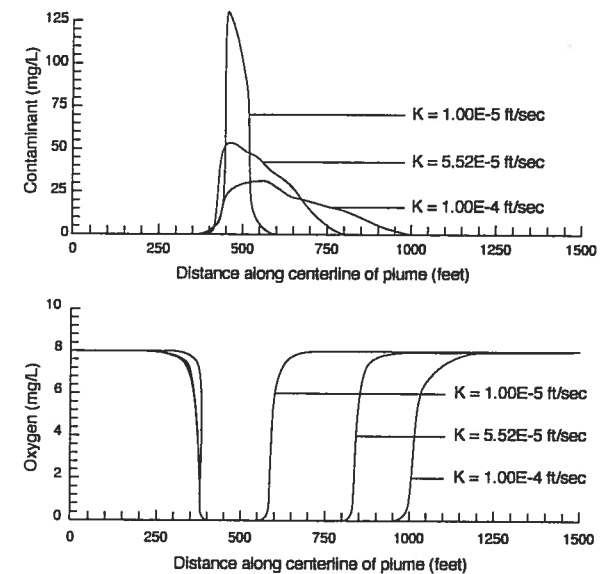


Figure 8.4 Variation of contaminant and oxygen concentrations with hydraulic conductivity. Source: Rifai et al., 1988.

sion. BIOPLUME II is one of the most widely used models for the simulation of aerobic biodegradation at field sites. A new version of the model, BIOPLUME III, is described in Section 8.5.

Example 8.2. MODELING BIOREMEDIATION USING BIOPLUME II

A modeling analysis using BIOPLUME II is presented to demonstrate how the model might be used for designing bioremediation systems. Bioremediation involves the injection of oxygen and other limiting nutrients to enhance biodegradation and accelerate the remediation of contaminated sites (see Chapter 13).

TABLE 8.4 Model parameters used in example 8.2.

Grid Size	20 x 20
Cell Size	50 ft x 50 ft
Transmissivity	0.002 sq. ft/s
Aquifer thickness	10 ft
Hydraulic Gradient	0.001 ft/ft
Longitudinal Dispersivity	10 ft
Transverse Dispersivity	3 ft
Effective Porosity	30%

A hypothetical aquifer with the parameters shown in Table 8.4 is being bioremediated for two years using three injection wells and three pumping wells. Each of the wells is pumping/injecting at rate of 1 gpm. The initial plume and well locations are shown in Figure 8.5. Three different scenarios were modeled: first, no oxygen was injected and biodegradation was due only to a background oxygen concentration of 3 mg/L. Then, 20 mg/L of oxygen were injected throughout the pumping period. Finally, in a different simulation, 40 mg/L were injected into the wells. The latter two concentrations were selected because they are values that can be obtained by the injection of liquid oxygen.

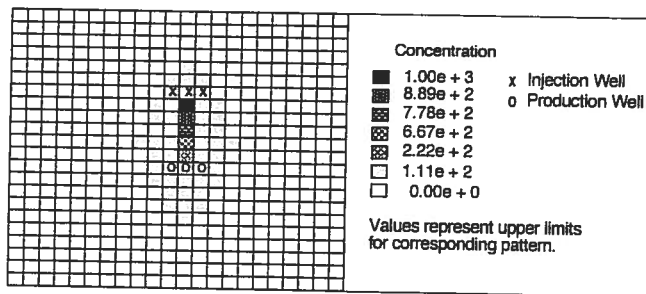


Figure 8.5 Initial contaminant plume for Example 8.2.

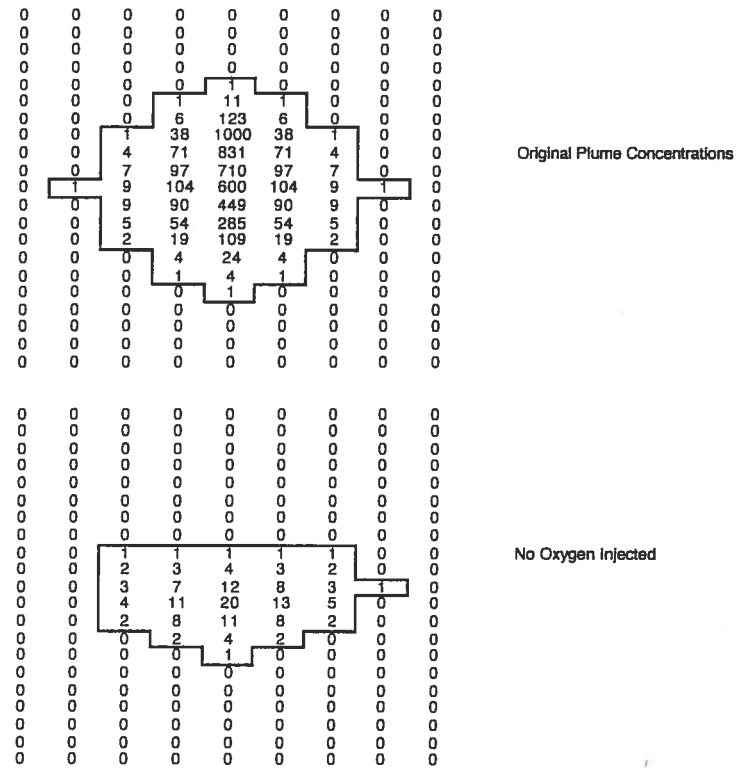


Figure 8.6 Plume concentrations with no oxygen amendment for Example 8.2.

Figure 8.6 shows the extent of the contaminant plume when pumping has occurred without enhanced biodegradation. The highest contaminant concentration after two years of pumping is 20 mg/L, down from the original maximum of 1000 mg/L. Figure 8.7 is the output for the plume after 20 mg/L of oxygen were injected. The maximum concentration in this case is 15 mg/L. Fewer cells have concentrations greater than 5 mg/L, and the resulting plume is smaller in size.

When 40 mg/L of oxygen are injected, the resulting plume shown in Figure 8.8 is not much different than that in Figure 8.7. The maximum concentration, however, is now 9 mg/L instead of 15 mg/L. This indicates marginal benefits from doubling the oxygen concentration. The main reason for this observation is the fact that oxygen is not

getting transported to the contamination areas, where it can be most useful. One way around this is to move the injection wells closer to the contaminated zones. The other alternative is to inject oxygen concentrations in gradual increments (This would save on costs because less oxygen is required).

In conclusion, there is an optimal level of oxygen that will be of benefit in cleanup operations. The overall extent of biodegradation for this hypothetical scenario can be summed up in Figure 8.9, which shows contaminant concentrations across the center-

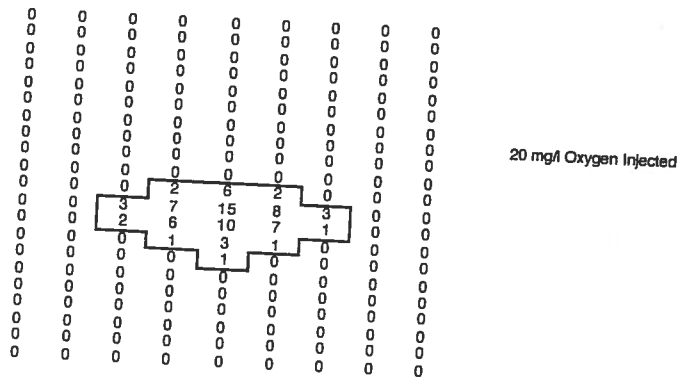


Figure 8.7 Plume concentrations with 20 mg/L oxygen injected in Example 8.2.

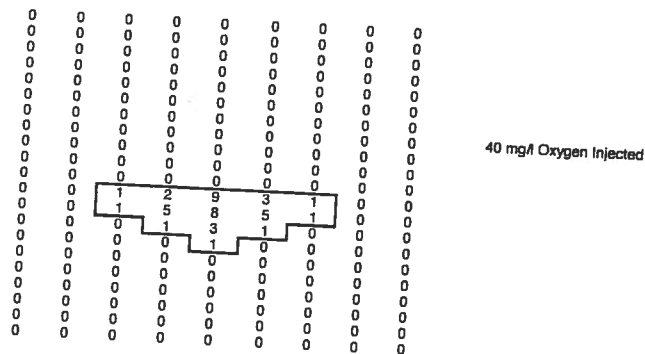


Figure 8.8 Plume concentrations with 40 mg/L oxygen injected in Example 8.2.

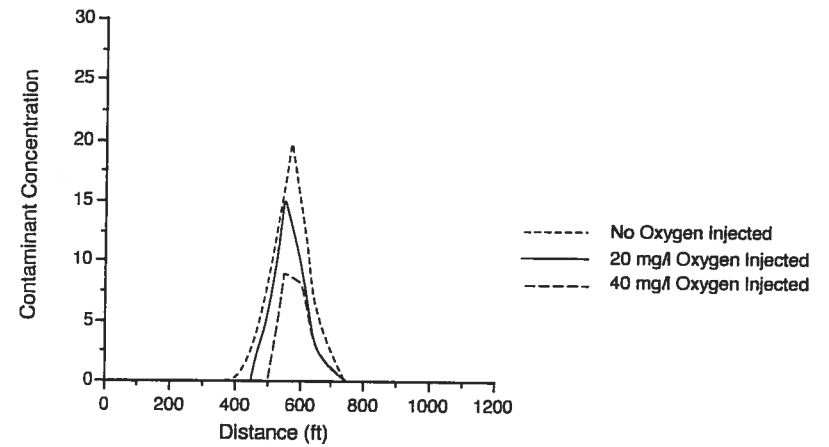


Figure 8.9 Contaminant concentration along plume centerline for Example 8.2.

line (from top to bottom) of the resultant plumes. It is obvious that biodegradation can be of immense benefit when conditions for its use prevail. Several homework problems for Chapter 8 lead the student through the above example in more detail.

8.3.6 Other Models

Other models have been presented by Kissel et al. (1984), Baek et al. (1989), McQuarrie et al. (1990) and MacQuarrie and Sudicky (1990). Kissel et al. (1984) developed differential equations describing mass balances on solutes and mass fractions in a mixed culture biological film within a completely mixed reactor. The models incorporated external mass transport effects, Monod kinetics with internal determination of limiting electron donor or acceptor, competitive and sequential reactions, and multiple active and inert biological fractions which vary spatially.

The model presented by Baek et al. (1989) simulates the mitigation of contaminants by microbial activity in unsaturated soil systems. Their model, BIOSOIL, incorporated the influence of microorganisms on soil water flow and chemical removal rates. From the modeling study, the authors concluded that the depth of the unsaturated zone seems to be less crucial in bioremediation scenarios than it would be in land disposal scenarios.

MacQuarrie et al. (1990) and MacQuarrie and Sudicky (1990) used a similar approach to those of Borden et al. (1986) and Rifai et al. (1988) to develop their model. The advection-dispersion equation was coupled with a dual-Monod relationship. The system of equations was solved using an iterative principal direction finite element technique. The authors applied

their model to laboratory columns as well as plume behavior in uniform and random flow fields.

More recently and since the early 1990s, researchers have focused their efforts on developing models in support of natural attenuation of fuel hydrocarbons and chlorinated solvents. A number of analytical and numerical models have been developed to simulate aerobic and anaerobic biodegradation of these compounds along with the other natural attenuation processes of advection, dispersion, and sorption. The following section will focus on presenting a number of these models, including BIOSCREEN, BIOCHLOR, BIOPLUME III, and the RT3D model (See Table 8.3).

8.4 ANALYTICAL NATURAL ATTENUATION MODELS

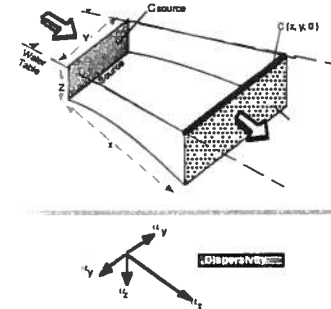
8.4.1 The BIOSCREEN Decision Support System

The BIOSCREEN Natural Attenuation Decision Support System is a public domain, spreadsheet-based, screening tool for simulating the natural attenuation of dissolved hydrocarbons at petroleum fuel release sites (Newell et al., 1996; Newell et al., 1997). The model is based on the Domenico (1987) analytical solute transport model (Figure 8.10) that simulates ground water flow and a fully-penetrating vertical plane oriented perpendicular to ground water flow. The model incorporates a linear isotherm sorption and 3-D dispersion. The model extends the Domenico solution by incorporating a decaying source concentration and a simple electron-acceptor limited "instantaneous" reaction assumption. BIOSCREEN was developed by the Air Force Center for Environmental Excellence (AFCEE) and is currently being distributed by the EPA through their website at (<http://www.epa.gov/ada/bioscreen.html>).

BIOSCREEN attempts to answer both fundamental natural attenuation questions: (1) how far will the plume migrate, and (2) how long will the plume persist? The conceptual model assumes that ground water upgradient of the source contains electron acceptor and that as the upgradient water moves through the source zone, non-aqueous phase liquids (NAPLs) and contaminated soil release dissolvable BTEX into ground water. Biological reactions occur until the available electron acceptors in ground water (biodegradation capacity, see Chapter 12) are consumed.

BIOSCREEN has the limitation that as an analytical model, it assumes simple ground water flow conditions and should not be applied where pumping systems create a complicated flow field. In addition, the model should not be applied where vertical flow gradients affect contaminant transport. Also, the model only approximates more complicated processes that occur in the field and should not be applied where extremely detailed, accurate results that closely match site conditions are required. More comprehensive numerical models such as BIOPLUME III or RT3D (described in the following section) should be applied in these cases.

Domenico Model with First Order Decay Algorithm



$$C(x, y, z, t) = C_0 \exp[-k_s(t - x/v)]$$

$$\frac{1}{8} \exp\left[-\frac{x}{\alpha_x} \left(1 - (1 + 4\lambda\alpha_x/v)^{1/2}\right)\right]$$

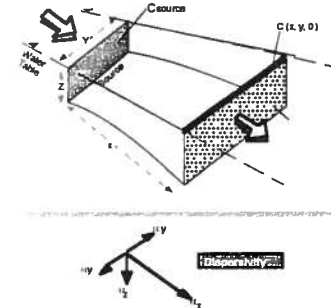
$$\operatorname{erfc}\left[\frac{x - vt(1 + 4\lambda\alpha_x/v)^{1/2}}{2(\alpha_x vt)^{1/2}}\right]$$

$$\left\{ \operatorname{erf}\left[\frac{(y + Y/2)}{2(\alpha_y x)^{1/2}}\right] - \operatorname{erf}\left[\frac{(y - Y/2)}{2(\alpha_y x)^{1/2}}\right] \right\}$$

$$\left\{ \operatorname{erf}\left[\frac{(Z)}{2(\alpha_z x)^{1/2}}\right] - \operatorname{erf}\left[\frac{(-Z)}{2(\alpha_z x)^{1/2}}\right] \right\}$$

where: $v = \frac{K \cdot i}{\theta_e R}$

Domenico Model with Instantaneous Reaction Superposition Algorithm



$$C(x, y, z, t) = (C_0 \exp[-k_s(t - x/v)] + BC)$$

$$\frac{1}{8} \operatorname{erfc}\left[\frac{(x - vt)}{2(\alpha_x vt)^{1/2}}\right]$$

$$\left\{ \operatorname{erf}\left[\frac{(y + Y/2)}{2(\alpha_y x)^{1/2}}\right] - \operatorname{erf}\left[\frac{(y - Y/2)}{2(\alpha_y x)^{1/2}}\right] \right\}$$

$$\left\{ \operatorname{erf}\left[\frac{(Z)}{2(\alpha_z x)^{1/2}}\right] - \operatorname{erf}\left[\frac{(-Z)}{2(\alpha_z x)^{1/2}}\right] \right\} - BC$$

where: $v = \frac{K \cdot i}{\theta_e R}$ $BC = \sum \frac{C(ea)_n}{UF_n}$

Definitions

BC	Biodegradation capacity (mg/L)	UF_n	Utilization factor for electron acceptor n (i.e., mass ratio of electron acceptor:product to hydrocarbon consumed in biodegradation reaction)
$C(x, y, z, t)$	Concentration at distance x downstream of source and distance y off centerline of plume at time t (mg/L)	α_x	Longitudinal groundwater dispersivity (ft)
C_0	Concentration in Source Zone (mg/L)	α_y	Transverse groundwater dispersivity (ft)
C_0	Concentration in Source Zone at $t=0$ (mg/L)	α_z	Vertical groundwater dispersivity (ft)
x	Distance downgradient of source (ft)	λ	First-order decay coefficient for dissolved contaminants
y	Distance from centerline of source (ft)	θ_e	Effective soil porosity
z	Vertical Distance from groundwater surface to measurement point (assumed to be 0; concentration is always assumed to be at top of water table)	v	Contaminant velocity in groundwater (ft/yr)
$C(ea)_n$	Concentration of electron acceptor (or by-product equivalent) n in groundwater (mg/L)	K	Hydraulic conductivity (ft/yr)
		R	Constituent retardation factor
		I	Hydraulic gradient (ft/ft)
		Y	Source width (ft)
		Z	Source depth (ft)
		t	Time (yr)
		k_s	First-order decay term for source concentration (yr ⁻¹)

Source: Newell et al. (1996)

Figure 8.10 The Domenico Analytical Model Used in BIOSCREEN.

BIOSCREEN output includes: (1) plume centerline graphs, (2) 3-D color plots of plume concentrations, and (3) mass balance data showing the contaminant mass removal by each electron acceptor (instantaneous reaction option). Other features of the original model (v. 1.3) included a concentration versus time animation module and a water balance showing the volume of water in the plume and the flux of water moving through the plume. In a later release (BIOSCREEN v. 1.4), a mass flux calculator was added, which shows the mass flux of contaminants at any point in the plume. With the mass flux calculator, dilution calculations can be performed for plumes that are discharging to streams.

The original Domenico (1987) model assumes the source is infinite (i.e., the source concentrations are constant). In BIOSCREEN, however, an approximation for a declining source concentration was added, and is based on the following assumptions:

- There is a finite mass of organics in the source zone present as a free-phase or residual NAPL. The NAPL in the source zone dissolves slowly as fresh ground water passes through.
- The change in source zone concentration can be approximated as a first-order decay process.
- The mass flux of contaminant leaving the source can be approximated by multiplying the source times a representative source concentration for the first order decay model (thereby assuming no biodegradation in the source zone) or by multiplying the source times the sum of the source concentration and biodegradation capacity (thereby assuming there is biodegradation in the source zone).

Example 8.3 BIOSCREEN MODELING OF THE HILL AFB UST SITE 870

The Hill Air Force Base (AFB) is located in north central Utah. Site 870 at the base is on a plateau-like bench formed by sediment deposits of the ancient Weber River. Surface topography slopes to the southwest. The site has a base fuel tank farm including the former location of a 1,000-gallon tank and a plume of contaminated ground water extending to the southwest of the tank site (Figure 8.11). The shallow aquifer at the site, composed of medium to coarse grained sands, ranges from 3ft to 22 ft in thickness at a depth varying from 4 to 15 ft. Slug tests performed in five monitoring wells at the site indicate an average hydraulic conductivity of 8.05×10^{-3} cm/sec. Ground water flow is to the southwest with an approximate gradient of 0.048 ft/ft with almost no seasonal variation (Montgomery Watson, 1994). More details about this site are provided in example 8.5.

The BIOSCREEN model was used to reproduce plume movement at Site 870. The site characteristics are listed in Table 8.5. An infinite source in the high concentration zone of the plume area (near MW-1, Figure 8.11) was assumed for the site because no esti-

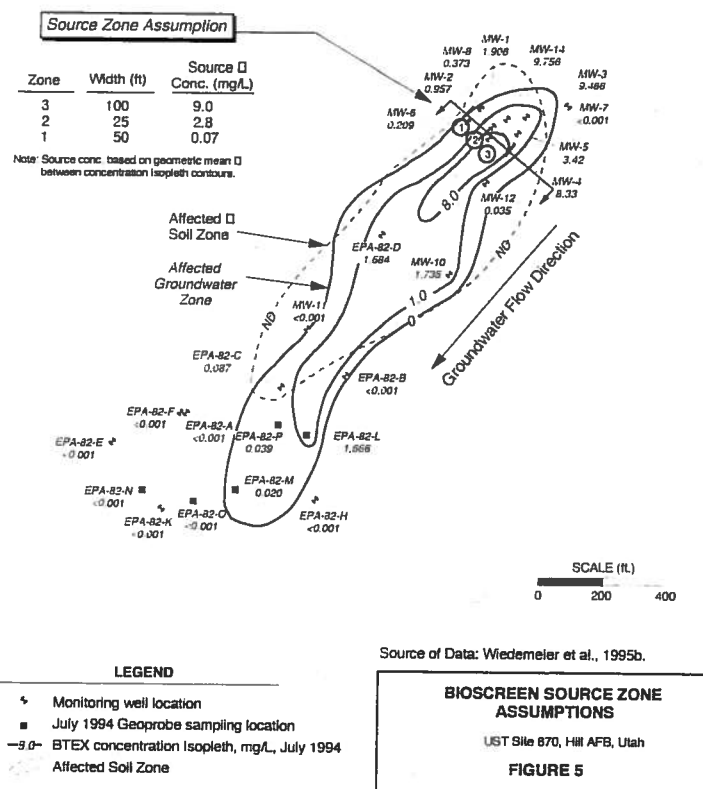


Figure 8.11 BIOSCREEN Source Zone assumptions, UST Site 870, Hill AFB, Utah. Source: Newell et al., 1996

mates for source mass were available from soil sampling data. Instantaneous reaction kinetics were assumed. Model results indicate a reasonable match between the modeled plume and the measured concentrations, as can be seen in Figure 8.12. Using the BIOSCREEN model without biodegradation, in comparison, generated a plume over 8,000 ft long in contrast with the 1,450 ft plume that was delineated at the site. Plume mass calculations using the "no biodegradation" scenario and the calibration scenario indicated a greater than 99% reduction in dissolved mass during the five-year simulation run.

TABLE 8.5 Example 8.3, Hill Air Force Base, UST Site 870, Utah

DATA TYPE	PARAMETER	VALUE	SOURCE
Hydrogeology	Hydraulic Conductivity:	8.05 x 10 ⁻² (cm/sec)	Slug-tests results
	Hydraulic Gradient:	0.048 (ft/ft)	Static water level measurements
	Porosity:	0.25	Estimated
Dispersion	Original		Based on estimated plume length of 1450 ft. Note: No calibration was necessary to match observed plume length
	Longitudinal Dispersivity:	28.5 ft	
	Transverse Dispersivity:	2.85 ft	
	Vertical Dispersivity:	0 ft	
Adsorption	Retardation Factor:	1.3	Calculated Estimated Lab Analysis Literature - use Koc =38
	Soil Bulk Density pb:	1.7 (kg/L)	
	foc:	0.08%	
	Koc:	B: 38 T: 135 E: 95 X: 240	
Biodegradation	Electron Acceptor:	O ₂ NO ₃ SO ₄	Based on July 1994 ground water sampling program conducted by Parsons Engineering Science, Inc.
	Background Conc. (mg/L)	6 17 100	
	Minimum Conc. (mg/L)	-0.22 0 0	
	Change in Conc. (mg/L)	5.78 17 100	
	Electron Acceptor:	Fe CH ₄	
	Max. Conc. (mg/L) Avg. Conc. (mg/L)	50.5 2.04 11.3 0.414	
General	Modeled Area Length	1450 (ft)	Based on area of affected ground water plume Steady-state flow
	Modeled Area Width	320 (ft)	
	Simulation Time	5 (yrs)	
Source Data	Source Thickness	10 (ft)	Based on geologic logs and lumped BTEX monitoring data
	Source Concentration	see Figure 8.11	
Actual Data	Distance from Source (ft)	340 1080 1350 1420	Based on observed concentration contour at site (see Figure 8.11)
	BTEX Concentration (mg/L)	8.0 1.0 0.02 0.005	
OUTPUT	Centerline Concentration	see Figure 8.12	

Source: BIOSCREEN Manual

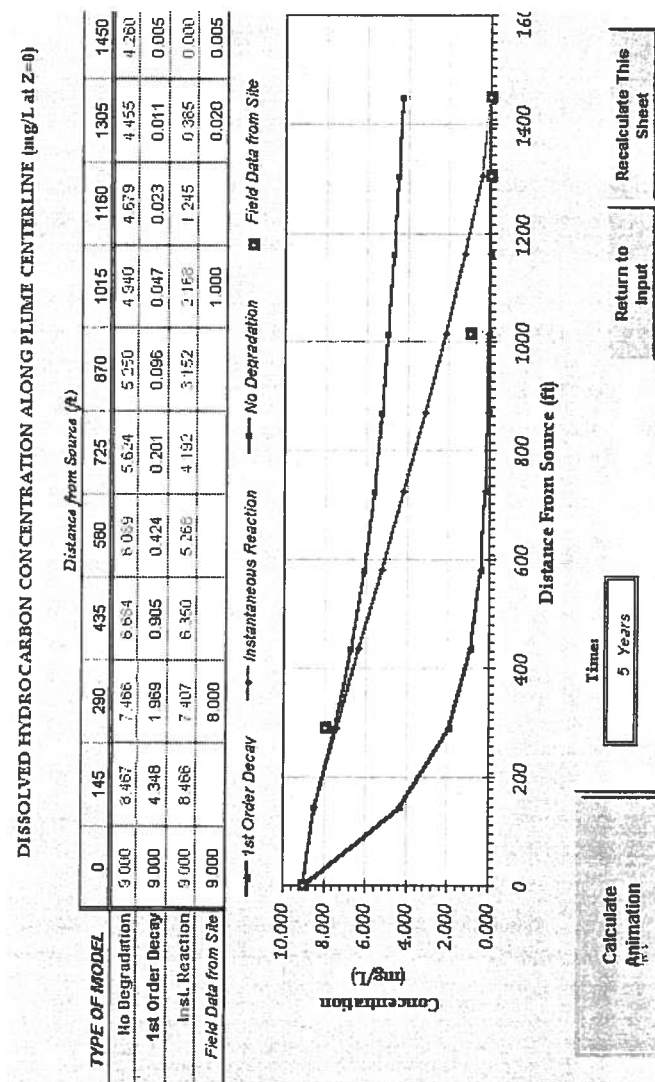
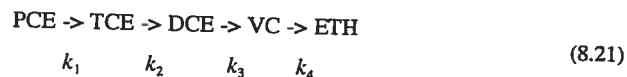


Figure 8.12 Centerline output. Hill AFB, Utah. Source Newell et al. 1996

8.4.2 The BIOCHLOR Decision Support System

The BIOCHLOR Natural Attenuation Model (Aziz et al., 1999) simulates chlorinated solvent natural attenuation using an interface similar to BIOSCREEN. BIOCHLOR simulates chlorinated solvent biodegradation, where the reaction kinetics may be much slower. This process involves sequential reactions, where the parent compound biodegrades into a daughter product and that daughter product biodegrades into another daughter product, and so on. For the chlorinated ethenes, the reaction sequence is shown below for the degradation of PCE through ethene (ETH):



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

$$r_{PCE} = -k_1 C_{PCE} \quad (8.22)$$

$$r_{TCE} = k_1 C_{PCE} - k_2 C_{TCE} \quad (8.23)$$

$$r_{DCE} = k_2 C_{TCE} - k_3 C_{DCE} \quad (8.24)$$

$$r_{VC} = k_3 C_{DCE} - k_4 C_{VC} \quad (8.25)$$

$$r_{ETH} = k_4 C_{VC} \quad (8.26)$$

where k_1, k_2, k_3, k_4 are the first order rate constants and $C_{PCE}, C_{TCE}, C_{DCE}, C_{VC}$ and C_{ETH} are the aqueous concentrations 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, 1-D advection, 3-D 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.

$$R_{PCE} \frac{dC_{PCE}}{dt} = -v \frac{dC_{PCE}}{dx} + D_x \frac{d^2 C_{PCE}}{dx^2} + D_y \frac{d^2 C_{PCE}}{dy^2} + D_z \frac{d^2 C_{PCE}}{dz^2} - k_1 C_{PCE} \quad (8.27)$$

$$R_{TCE} \frac{dC_{TCE}}{dt} = -v \frac{dC_{TCE}}{dx} + D_x \frac{d^2 C_{TCE}}{dx^2} + D_y \frac{d^2 C_{TCE}}{dy^2} + D_z \frac{d^2 C_{TCE}}{dz^2} + k_1 C_{PCE} - k_2 C_{TCE} \quad (8.28)$$

$$R_{DCE} \frac{dC_{DCE}}{dt} = -v \frac{dC_{DCE}}{dx} + D_x \frac{d^2 C_{DCE}}{dx^2} + D_y \frac{d^2 C_{DCE}}{dy^2} + D_z \frac{d^2 C_{DCE}}{dz^2} + k_2 C_{TCE} - k_3 C_{DCE} \quad (8.29)$$

$$R_{VC} \frac{dC_{VC}}{dt} = -v \frac{dC_{VC}}{dx} + D_x \frac{d^2 C_{VC}}{dx^2} + D_y \frac{d^2 C_{VC}}{dy^2} + D_z \frac{d^2 C_{VC}}{dz^2} + k_3 C_{DCE} - k_4 C_{VC} \quad (8.30)$$

$$R_{ETH} \frac{dC_{ETH}}{dt} = -v \frac{dC_{ETH}}{dx} + D_x \frac{d^2 C_{ETH}}{dx^2} + D_y \frac{d^2 C_{ETH}}{dy^2} + D_z \frac{d^2 C_{ETH}}{dz^2} + k_4 C_{VC} \quad (8.31)$$

where $R_{PCE}, R_{TCE}, R_{DCE}, R_{VC},$ and R_{ETH} are the retardation factors, v is the seepage velocity, and $D_x, D_y,$ and D_z are the 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 Clement et al., (1998). The uncoupled equations were solved using the Domenico model, and inverse transformations were used to generate concentration profiles. Details of the transformation are presented in Clement et al., 1998. Example concentration profiles for biodegradation of PCE through ethene are shown in Figure 8.13. Typically, source zone concentrations of *cis*-1,2-dichloroethylene (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.

Example 8.4 BIOCHLOR MODELING AT CAPE CANAVERAL

The BIOCHLOR model was used to reproduce the movement of the Cape Canaveral plume from 1965 to 1998. The Cape Canaveral site (Figure 8.14) in Florida exhibits a TCE plume 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 8.6. 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. The lateral dispersivity was assumed to be 10% of the longitudinal dispersivity, and vertical dispersion was neglected.

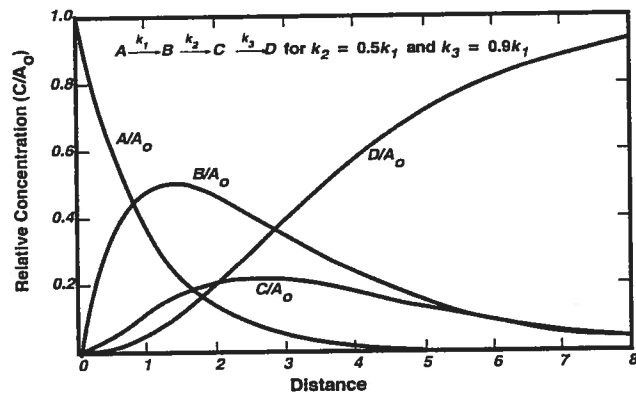


Figure 8.13 Concentration profiles simulated in BIOCHLOR. Source: Wiedemeier et al. 1999.

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, shown in Table 8.6. This is justified because the dissolved oxygen 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, shown in Table 8.6. 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 Figures 8.15 and 8.16. Figure 8.15 shows the centerline predictions for each chlorinated solvent and a no-degradation curve for all of the chlorinated solvents as well as field data. Figure 8.16 shows the centerline concentrations for TCE, with and without biodegradation. The data in Figure 8.16 indicate that TCE concentrations discharging into the ocean will be less than 0.001 mg/L .

8.5 NUMERICAL NATURAL ATTENUATION MODELS

Numerical models provide approximate (relative to analytical methods) and, in some cases, non unique solutions to the governing advection-dispersion equation. As with analytical

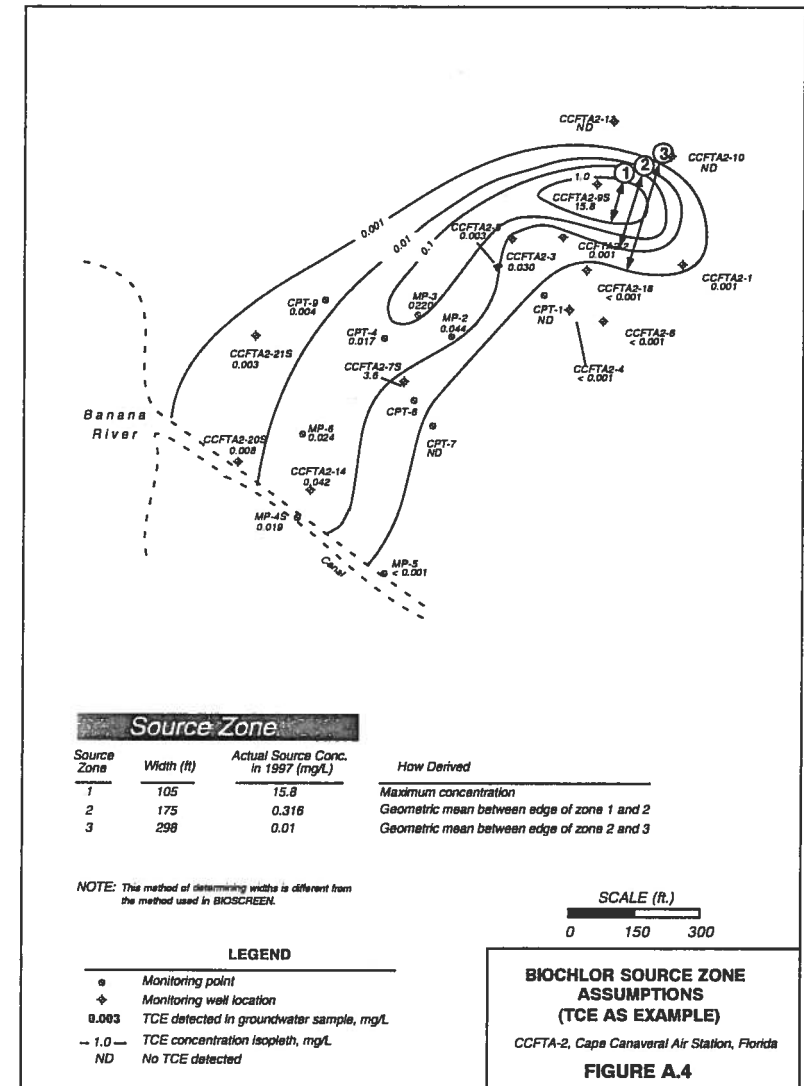


Figure 8.14 BIOCHLOR source zone assumptions (TCE as example), CCFTA-2, Cape Canaveral Air Station, Florida. Source: Aziz et al. 1999.

TABLE 8.6 BIOCHLOR Example, Cape Canaveral Air Station, Florida

DATA TYPE	PARAMETER	VALUE	SOURCE
Hydrogeology	Hydraulic Conductivity: Hydraulic Gradient: Porosity:	1.8 x 10 ⁻⁴ (cm/sec) 0.0012 (ft/ft) 0.2	Slug-tests results Static water level measurements 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 pb: foc: Koc: (L/kg)	PCE: 6.7 c-DCE: 2.8 ETH: 5.3 5.3 1.6 (kg/L) 0.184% PCE: 398 c-DCE: 126 ETH: 302 TCE: 2.8 VC: 5.6 TCE: 126 VC: 316	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 VC → ETH	 2.0 0.9 0.6 0.4	Based on calibration to field data using a simulation time of 32 years. Started with literature values and then adjusted model to fit field data.
General	Modeled Area Length Modeled Area Width Simulation Time	1085 (ft) 700 (ft) 33 (yrs)	Based on area of affected ground water plume from 1985 (first release) to 1998 (present)
Source Data	Source Thickness Source Widths (ft) Source Concentrations (mg/L)	56 (ft) Zone 1 Zone 2 Zone 3 105 175 298 Zone 1 Zone 2 Zone 3 PCE 0.056 0.007 0.001 TCE 15.8 0.316 0.01 c-DCE 98.5 1.0 0.01 VC 3.080 0.089 0.009 ETH 0.030 0.013 0.003	Based on geologic logs and monitoring data (see Figure 8.14) 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 0.0185 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 concentrations at site near centerline of plume
OUTPUT	Centerline Concentration	see Figures 8.15, 8.16	

Source: BIOCHLOR Manual

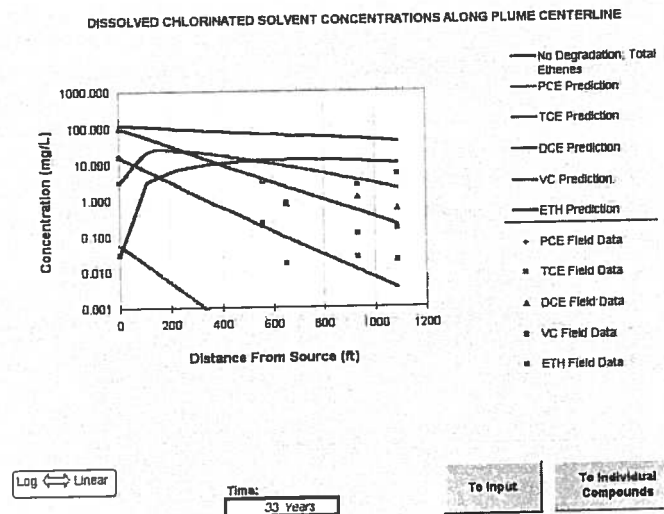


Figure 8.15 Centerline output. Cape Canaveral Air Force Base, Florida.
Source: Aziz et al. 1999.

models, the use of numerical models requires the user to make some simplifying assumptions about the solute transport system. However, numerical models can simulate more complex systems. Numerical models can be used to simulate contaminant transport affected by multiple reactions for which rates or properties may vary spatially. More details on numerical modeling are provided in Chapter 10.

8.5.1 The BIOPLUME III Model

The BIOPLUME III model (Rifai et al., 1997) is a recent and major upgrade to the BIOPLUME II model presented by Rifai et al. in 1988. The main enhancement to the model was the incorporation of anaerobic biodegradation processes explicitly rather than lumping them together using a first-order decay model as was the case in BIOPLUME II. The model simulates biodegradation using a number of aerobic and anaerobic electron acceptors: oxygen, nitrate, iron (III), sulfate, and carbon dioxide. BIOPLUME III is still based on the U. S. Geologic Survey (USGS) Method of Characteristics model dated July 1989 (Konikow and Bredehoeft, 1978). The model can be downloaded from EPA's website (<http://www.epa.gov/ada/csmos>).

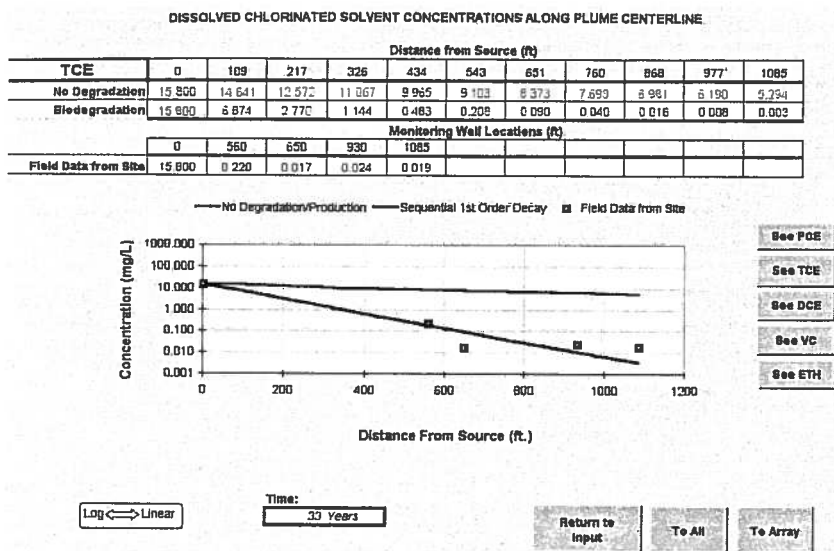


Figure 8.16 Individual centerline output for TCE, Cape Canaveral Air Station, Florida. Source: Aziz et al. 1999.

The BIOPLUME III code was developed primarily to model the natural attenuation of organic contaminants in ground water. The model solves the transport equation six times to determine the fate and transport of the hydrocarbons and the electron acceptors/reaction by-products. For the case where iron (III) is used as an electron acceptor, the model simulates the production and transport of iron (II) or ferrous iron. Three different kinetic expressions can be used to simulate the aerobic and anaerobic biodegradation reactions. These include: first-order decay, instantaneous reaction, and Monod kinetics. The principle of superposition is used to combine the hydrocarbon plume with the electron acceptor plume(s).

Major differences between BIOPLUME II and BIOPLUME III include:

- BIOPLUME III runs in a Windows95 environment, whereas BIOPLUME II was mainly developed in a DOS environment.
- BIOPLUME III model was integrated with a sophisticated ground water modeling platform known as Environmental Impact System from ZEi/MicroEngineering, Inc., of Annandale, Virginia.

The conceptual model used in BIOPLUME III to simulate these biodegradation processes tracks six plumes simultaneously: hydrocarbon, oxygen, nitrate, iron (II), sulfate, and carbon dioxide. Iron (III) is input as a concentration matrix of ferric iron in the formation. Once ferric iron is used for biodegradation, BIOPLUME III simulates the production and transport of ferrous iron.

Biodegradation occurs sequentially in the following order:

Oxygen → Nitrate → Iron (III) → Sulfate → Carbon Dioxide

The biodegradation of hydrocarbon in a given location using nitrate, for example, can occur only if oxygen has been depleted to its threshold concentration at that location.

BIOPLUME III is generally used to answer a number of questions regarding natural attenuation:

1. How long will the plume extend if no engineered/source controls are implemented?
2. How long will the plume persist until natural attenuation processes completely dissipate the contaminants?
3. How long will the plume extend or persist if some engineered controls or source reduction measures are undertaken (for example, free phase removal or residual soil contamination removal)?

The model can also be used to simulate bioremediation of hydrocarbons in ground water by injecting electron acceptors (except for iron(III)) and can also be used to simulate air sparging for low injection air flow rates. Finally, the model can be used to simulate advection, dispersion, and sorption without including biodegradation.

As with any model, there are limitations to the use of BIOPLUME III. The assumptions used in the USGS MOC code include:

1. Darcy's law is valid and hydraulic-head gradients are the only driving mechanism for flow.
2. The porosity and hydraulic conductivity of the aquifer are constant with time, and porosity is uniform in space.
3. Gradients of fluid density, viscosity, and temperature do not affect the velocity distribution.
4. No chemical reactions occur which affect the fluid properties or the aquifer properties.
5. Ionic and molecular diffusion are negligible contributors to the total dispersive flux.
6. Vertical variations in head and concentration are negligible.

7. The aquifer is homogeneous and isotropic with respect to the coefficients of longitudinal and transverse dispersivity.

The limitations imposed by the biodegradation expressions incorporated in BIOPLUME III include:

1. The model does not account for selective or competitive biodegradation of the hydrocarbons. This means that hydrocarbons are generally simulated as a lumped organic, which represents the sum of benzene, toluene, ethyl benzene or xylene. If a single component is to be simulated, the user would have to determine how much electron acceptor would be available for the component in question.
2. The conceptual model for biodegradation used in BIOPLUME III is a simplification of the complex biologically mediated redox reactions that occur in the subsurface.

Much like the approach used in developing BIOPLUME II, the 1989 version of the MOC model was modified to become a six-component particle mover model to simulate the transport of hydrocarbon, oxygen, nitrate, iron(II), sulfate, and carbon dioxide. Since the biodegradation of hydrocarbon uses iron (III) as an electron acceptor, iron (III) concentrations are simulated as an initial concentration of ferric iron that is available in each cell. Once the iron (III) is consumed, hydrocarbon concentrations are reduced and ferrous iron is produced. The resulting ferrous iron is then transported in the aquifer. The BIOPLUME III equations are very similar to those presented earlier for BIOPLUME II. Three additional equations similar to Eqs. 8.17 and 8.18 are written for nitrate, sulfate, and carbon dioxide.

The biodegradation of hydrocarbon using the aerobic and anaerobic electron acceptors is simulated using the principle of superposition and the following equations:

$$H(t+1) = H(t) - R_{HO} - R_{HN} - R_{HFe} - R_{HS} - R_{HC} \quad (8.32)$$

$$O(t+1) = O(t) - R_{OH} \quad (8.33)$$

$$N(t+1) = N(t) - R_{NH} \quad (8.34)$$

$$Fe(t+1) = Fe(t) - R_{FeH} \quad (8.35)$$

$$F(t+1) = R_{FeH} \quad (8.36)$$

$$S(t+1) = S(t) - R_{SH} \quad (8.37)$$

$$C(t+1) = C(t) - R_{CH} \quad (8.38)$$

where R_{HO} , R_{HN} , R_{HFe} , R_{HS} , R_{HC} are the hydrocarbon concentration losses due to biodegradation using oxygen, nitrate, ferric iron, sulfate and carbon dioxide as electron acceptors, respectively. The terms R_{OH} , R_{NH} , R_{FeH} , R_{SH} , R_{CH} are the corresponding concentration losses in the electron acceptors. These reaction terms are computed using one of the three biodegradation expressions: first-order, instantaneous, or Monod, which were discussed previously in the chapter. The reader is referred to Rifai et al. (1997) for additional information on equation formulation, and solution methods. A detailed example is described in Example 8.5.

8.5.2 The RT3D Model — Chlorinated Organics

Very few models exist (analytical or numerical) that 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).

Researchers at Battelle Pacific Northwest Laboratories have developed a numerical model referred to as RT3D. RT3D (Reactive Transport in 3 Dimensions, Sun et al., 1996) is a FORTRAN 90-based model for simulating multi-species, reactive transport in ground water. This model is based on the 1997 version of MT3D (DOD Version 1.5), but has several extended reaction capabilities. The model requires the USGS ground water flow code MODFLOW for computing ground water head distributions.

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 seven preprogrammed reaction packages are already provided and users have 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. Instantaneous Aerobic Decay of BTEX
2. Instantaneous Degradation of BTEX 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. Rate-Limited Sorption Reactions
5. Double Monod Model

6. Sequential Decay Reactions

7. Aerobic/Anaerobic Model for PCE/TCE Degradation

A more detailed example of RT3D is shown in Section 10.8.

FIELD SITE APPLICATIONS

8.6.1 Gas Plant Facility in Michigan

Soluble hydrocarbon and dissolved oxygen (DO) were characterized in a shallow aquifer beneath a gas plant facility in Michigan by Chiang et al. (1989). The distributions of benzene, toluene, and xylene (BTX) in the aquifer had been monitored in 42 wells for a period of three years. A general site plan including the locations of the wells is shown in Figure 8.17.

Results from the three-year sampling period showed a significant reduction in total benzene mass with time in ground water (Figure 8.18). The plume sampled in 1984 contained an approximate total mass of 9.83 kg, while the plume sampled in 1985 and 1986 contained 5.66 kg and 2.27 kg, respectively.

Chiang et al. (1989) determined the attenuation rates of the soluble benzene, and determined the effects of DO on the biodegradation of BTX through a combination of material balance, statistical analyses, soluble transport modeling, and laboratory microcosm experiments.

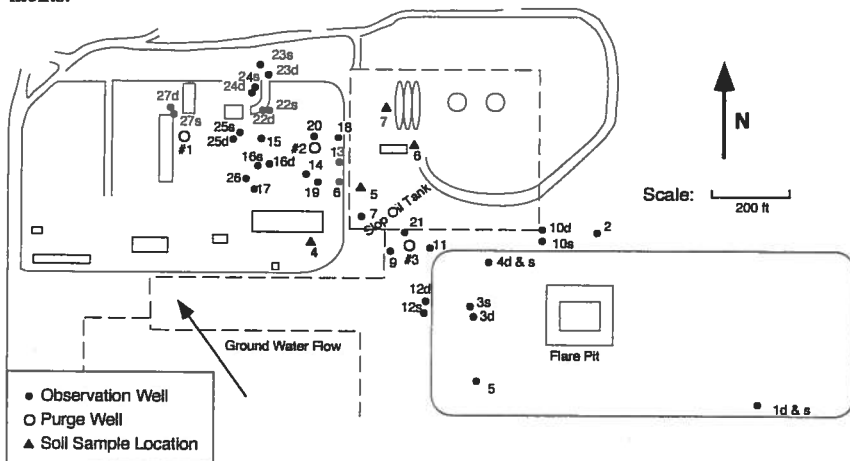


Figure 8.17 General plan of gas plant facility. Source: Chiang et al., 1989.

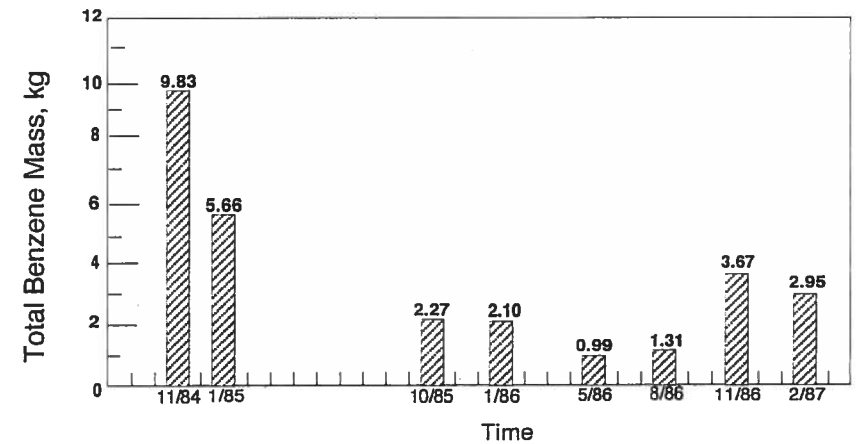


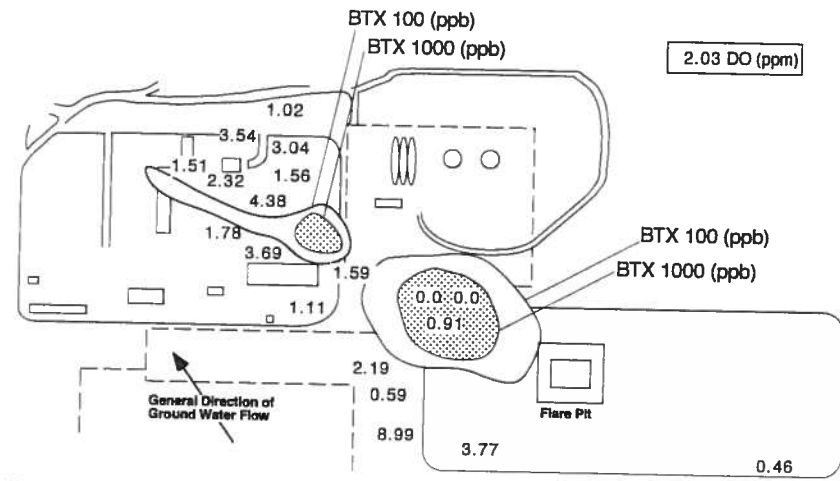
Figure 8.18 Calculated total soluble benzene mass in aquifer vs. time, November 1984 to February 1987. Source: Chiang et al., 1989

The site geology is characterized as a medium to coarse sand with interbeds of small gravel and cobbles. The general direction of ground water flow is northwesterly. The depth to water table ranges from 10 ft to 25 ft below land surface, and the slope of the water table was estimated as 0.006. Based on ground water and soil sampling data, Chiang et al. (1989) concluded that the flare pit was the major source of the hydrocarbons found in the aquifer; while the slope oil tank was a secondary source.

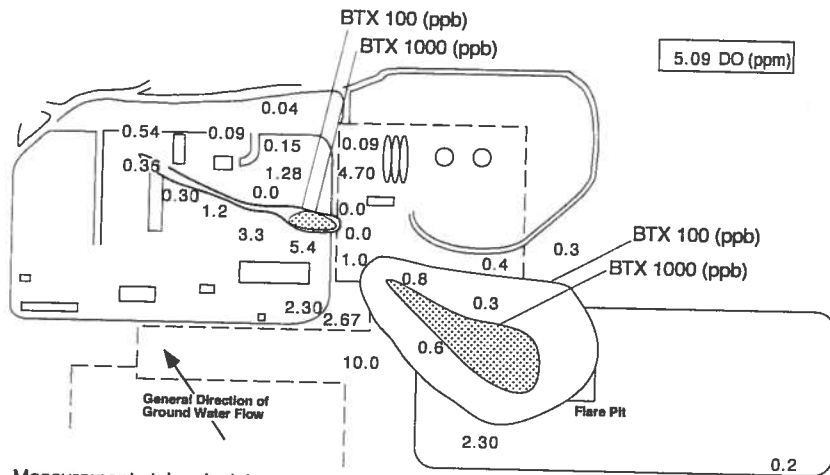
Dissolved oxygen concentrations in the ground water were measured by the Winkler titration method and with a field DO probe on two occasions (February and July 1987). Figure 8.19 shows the total BTX and DO concentration distributions of the February and July analyses, respectively. It can be seen from Figure 8.19 that the DO concentrations are high at low BTX concentrations and vice versa. The DO concentrations increase from their low values of < 1.0 ppm inside the 1,000 ppb BTX contour to higher concentrations of > 1.0 ppm outside the 100 ppb BTX contour line.

Chiang et al. (1989) also studied the decay rates of BTX in soil microcosms at an initial DO concentration of 0 to 6 ppm and concluded that a minimum DO (threshold) level may exist in ground water, which could sustain the natural biodegradation of BTX by microorganisms. Chiang et al. (1989) also conducted a detailed modeling analysis of their field data using the BIOPLUME II model as will be seen in Section 8.6.

Chiang et al. (1989) evaluated a first-order decay biodegradation approach and the BIOPLUME II model for simulating biodegradation at the gas plant facility. Using the model and assuming first-order decay, they performed several simulations to match the observed benzene concentration distribution of 1/22/85 by setting the observed concentration distribution of 11/1/84 as the initial condition. The variables involved included the distribution of



Measurements taken in February 1987



Measurements taken in July 1987

Figure 8.19 Total BTEX and dissolved oxygen concentration distributions in ground water. Source: Chiang et al., 1989

0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	158	4	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	63	0	532	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	6	82	923	5317	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	1503	3421	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	10690	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	10544	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	38	12	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	4	1387	5876	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	1573	5024	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1301	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1398	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure 8.20 Predicted (bottom number) and observed (top number) BTX by BIOPLUME II (ppb). Source: Chiang et al., 1989.

the leakage/spill rates between the flare pit and the slop oil tanks and macrodispersivities of the aquifer.

The BIOPLUME II model was used to simulate the July 1987 data by setting the observed concentration distribution of February 1987 as an initial condition. Figure 8.20 shows correlations between the measured and the simulated soluble BTX concentrations of July 1987. As can be seen from Figure 8.20, the correlations for BTX were reasonable. The correlations, however, for oxygen were not as similar. The authors attributed the differences to the fact that the BIOPLUME II model assumes a requirement of 3 ppm of oxygen for 1 ppm of benzene, whereas the actual requirement is in the range of 1 - 3 ppm.

Example 8.5 MODELING THE HILL AFB UST 870 SITE WITH BIOPLUME III

The 870 site at Hill AFB was modeled previously with BIOSCREEN in order to simulate the movement of the dissolved BTEX plume and estimate the mass loss due to biodegradation (see Example 8.3). This site was further analyzed with the BIOPLUME III model in an effort to evaluate the effectiveness of natural attenuation as a remedy for the contaminated ground water. The source and mass of contamination at UST Site 870 is uncertain as was seen in the BIOSCREEN example. The former UST may have contributed to contamination, but it is also possible that former underground pipelines contributed to the spill. Soil BTEX contamination is widespread; extending approximately 1,600 ft downgradient from the source area and exhibiting a width of 500 ft at

its thickest extent (see Figure 8.21). The highest observed soil concentration is 554 mg/kg in the heart of the contamination at soil boring EPA-82-I.

Mobile LNAPL is present at several monitoring wells, as shown in Figure 8.22. The LNAPL plume extends 750 ft downgradient from the source area with an areal extent of approximately 225,000 sq. ft. Ground water sampling during 1991-1994 provided BTEX concentrations in the shallow aquifer (Figure 8.23). BTEX was detected in 79 of the 125 samples collected with the highest dissolved BTEX measured at 26.85 mg/L in well MW-03 in August 1992. Comparison between the plume extent in 1993 and that of 1994 suggests a significant reduction in contaminant concentrations and aerial extent. Ground water samples analyzed for geochemical characteristics yielded information on the electron acceptor capacity in the shallow aquifer (Figures 8.24a through 8.24e).

A 20 x 30 model grid (85 ft wide by 110 ft long) was used in BIOPLUME III, (Figure 8.25). Tables 8.7 and 8.8 list the model parameters used for the site. Constant head boundaries were established along the northeast and southwest (top and bottom) grid perimeter to simulate the northeast to southwest ground water flow direction. A 12-yr source release scenario was used to simulate the existing plume delineated in 1994. A total of 20 injection wells were used to simulate release from the LNAPL plume into the ground water.

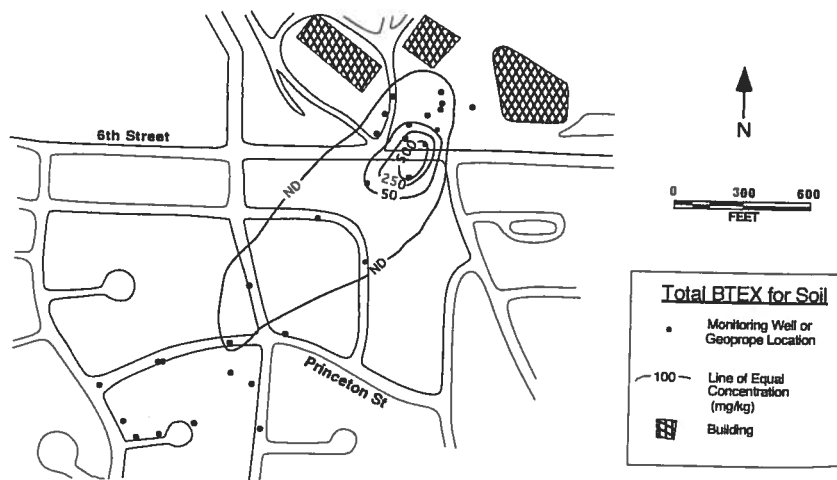


Figure 8.21 Soil Contamination contour map: Hill AFB. Source: Parsons Engineering Science, 1994.

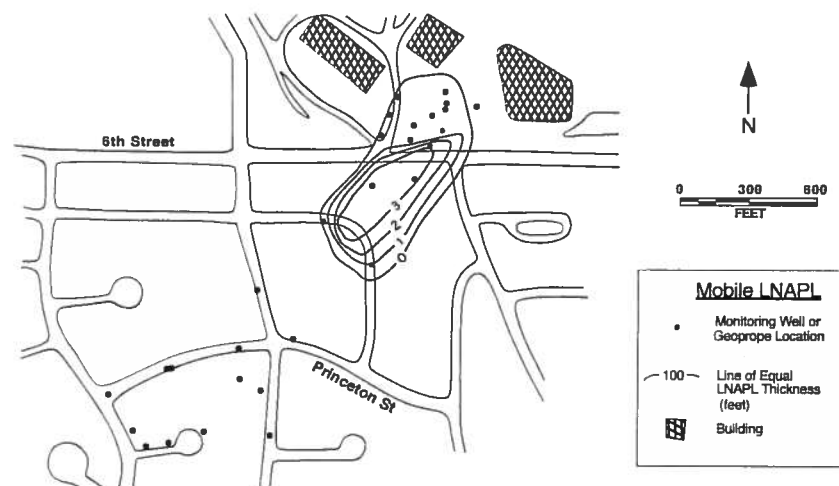


Figure 8.22 Total BTEX contour map for groundwater: Hill AFB. Source: Parsons Engineering Science, 1994.

The extent of the calibrated plume is in good agreement with the measured BTEX plume, as can be seen from Figure 8.23. The maximum modeled concentration of 13.6 mg/L is comparable to the observed 9.8 mg/L.

The calibrated model was used to analyze plume conditions 12 years into the future without source control. Plume predictions indicate that the plume reaches a quasi-steady state with the plume extent remaining approximately the same as the calibrated plume. Concentrations within the plume, however, attenuate from 13.6 mg/L to 5.4 mg/L with the heart of the plume having migrated nearer the area of greatest mobile LNAPL thickness, approximately 450 ft downgradient. The BIOPLUME III modeling results suggest that further reductions in plume size and concentrations can be achieved through source reduction.

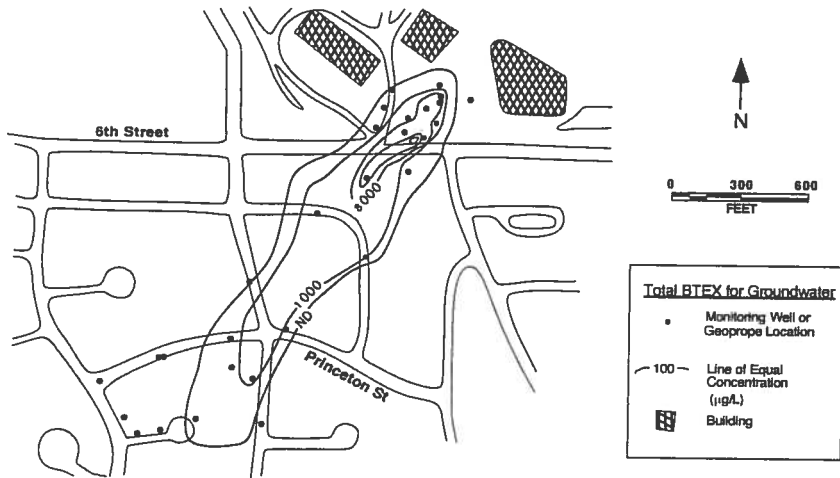


Figure 8.23 Total BTEX contour map for groundwater: Hill AFB. Source: Parsons Engineering Science, 1994.

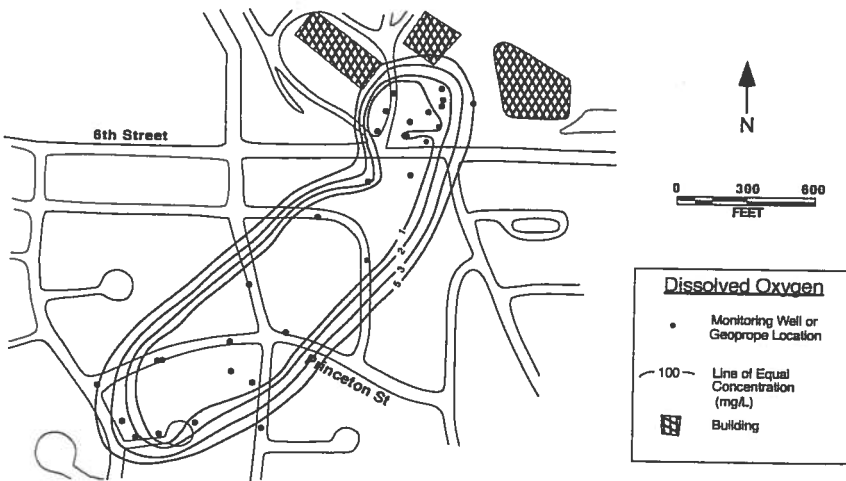


Figure 8.24a Dissolved oxygen contour map, Hill AFB; Source: Parsons Engineering Science, 1994.

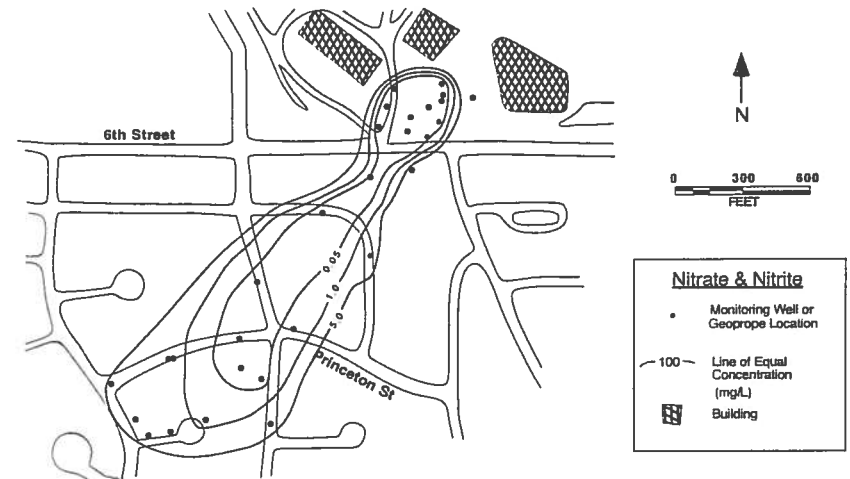


Figure 8.24b Nitrate and nitrite contour map, Hill AFB; Source: Parsons Engineering Science, 1994.

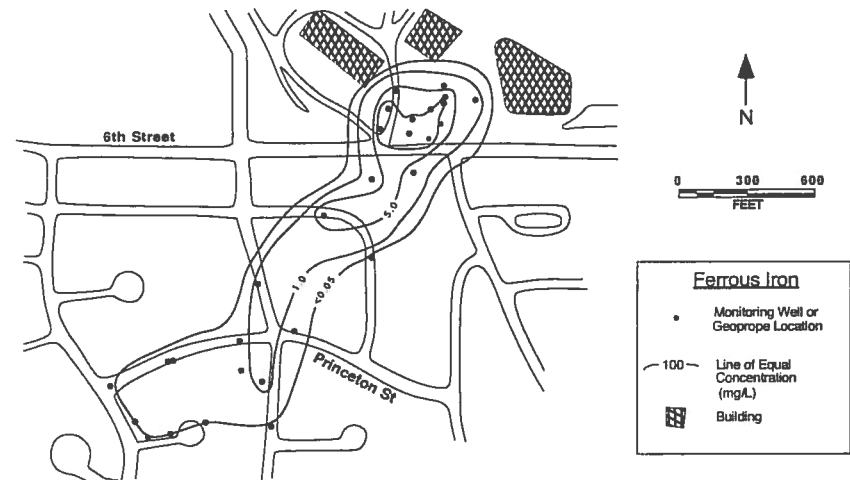


Figure 8.24c Ferrous iron contour map, Hill AFB; Source: Parsons Engineering Science, 1994.

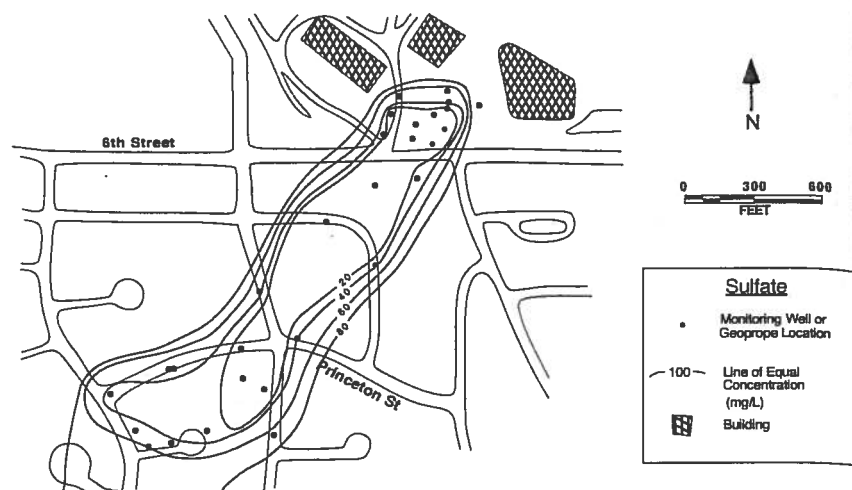


Figure 8.24d Sulfate contour map, Hill AFB; Source: Parsons Engineering Science, 1994.

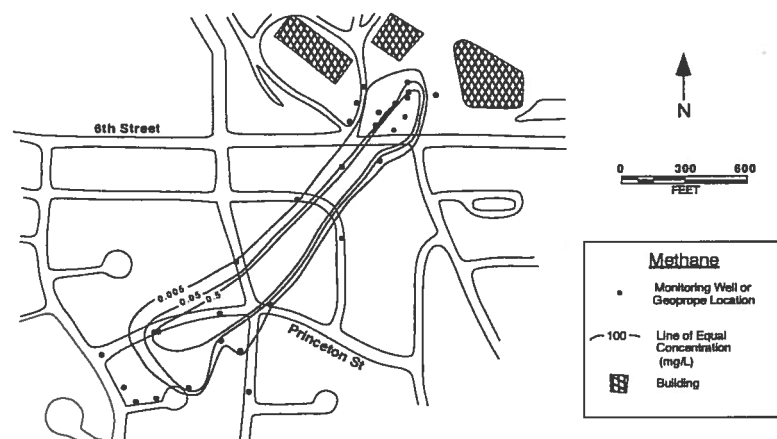


Figure 8.24e Methane contour map, Hill AFB. Source: Parsons Engineering Science, 1994.

TABLE 8.7 BIOPLUME II Model Parameters for Hill AFB

Description	Calibrated Model Setup
Time step interval for printing data	1
Number of iteration parameters	7
Max. allowable number of iterations in ADIP	200
Initial number of particles per node	9
Particle movement interval (IMOV)	0
Option for printing computed velocities	2
Option to print computed dispersion equation coefficients	2
Option to print computed changes in concentration	1
Option to punch velocity data	0
Option for biodegradation, retardation and decay	1
Convergence criteria in ADIP	0.001
Storage coefficient	0 (Steady-state)
Time increment multiplier for transient flow	
Ratio of transverse to longitudinal dispersivity	0.1
Max. cell distance per particle move	0.5
Ratio of T_{yy} to T_{xx}	1 (Isotropic)
Stoichiometric ratio of hydrocarbon to oxygen	3.1

TABLE 8.8 Electron Acceptor Input Data for Hill AFB

Description	Value
Background concentration for oxygen (mg/L)	6.0
Biodegradation kinetics specifier for oxygen	2
Stoichiometric ratio of oxygen to contaminant	3.14
Threshold concentration of oxygen (mg/L)	0
Background concentration for nitrate (mg/L)	5.0
Biodegradation kinetics specifier for nitrate	2
Stoichiometric ratio of nitrate to contaminant	4.8
Threshold concentration of nitrate (mg/L)	0
Background concentration for iron (mg/L)	5.0
Biodegradation kinetics specifier for iron	2
Stoichiometric ratio of iron to contaminant	21.5
Threshold concentration of iron (mg/L)	0
Background concentration for sulfate (mg/L)	54.0
Biodegradation kinetics specifier for sulfate	2
Stoichiometric ratio of sulfate to contaminant	4.6
Threshold concentration of sulfate (mg/L)	0
Background concentration for carbon dioxide (mg/L)	1.0
Biodegradation kinetics specifier for carbon dioxide	2
Stoichiometric ratio of carbon dioxide to contaminant	2.14
Threshold concentration of carbon dioxide (mg/L)	0

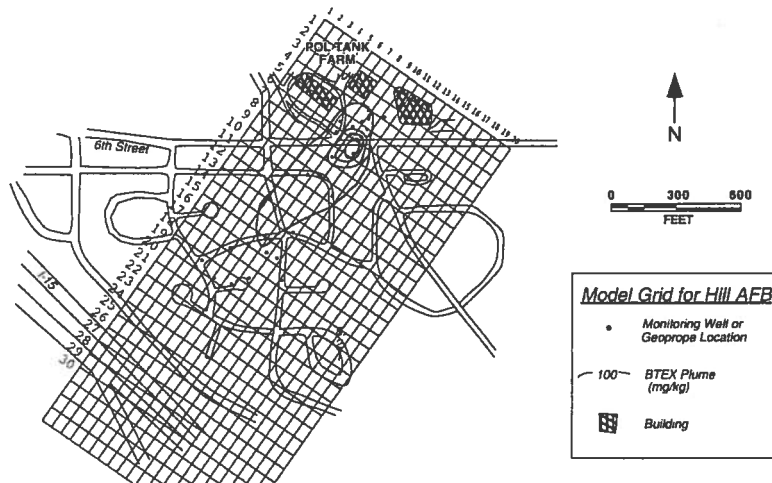


Figure 8.25 BIOPLUME III Model Grid, Hill AFB. Source: Parsons Engineering Science, 1994.

SUMMARY

Biodegradation processes attenuate contaminant concentrations in ground water. A variety of laboratory and field procedures are necessary to verify and quantify the contribution of these processes to contaminant transport in ground water aquifers. Biodegradation models can then be used to predict contaminant behavior for different conditions and scenarios. Both analytical and numerical models are available for the analysis of biodegradation processes. A number of these are reviewed in this chapter (Table 8.3). In particular BIOPLUME III and RT3D are used in a number of applications.

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