PART II: PHYSICAL AND CHEMICAL PROCESSES IN THE SUBSURFACE

Chapter 10

Physicochemical Processes: Organic Contaminants

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10.1 Overview of Physicochemical Processes

The characterization of hazardous waste sites to design remediation strategies requires a broad range of background information. As discussed in Chapter 9, good sampling methods and strategies are required to determine the contamination level and the extent to which contaminants have moved within the subsurface. Understanding of the physical processes discussed in Chapters 4 and 5 allows determination of the rate and direction in which contaminated ground water is flowing. This information also can be used to determine whether the contaminants will be captured and removed by extraction [illegible]s. However, this information by itself is not sufficient for optimal choice of remediation schemes. Critical questions such as how much water must pass through a section of an aquifer to remove the contaminants or how much time is required for contaminants to diffuse out of low-permeability zones also must be answered. The answers to these questions depends on the physicochemical processes occurring within the subsurface.

The next three chapters address the physicochemical processes that occur within the subsurface, the parameters required for their characterization, and the implications of these processes for remediation design. In this chapter, the discussion is limited to processes occurring below the water table that affect the concentration, transport, and hence removal of organic contaminants. Chapter 11 addresses the transport of volatile organic compounds through the unsaturated zone, and Chapter 12 discusses inorganic contaminants.

The design of optimal remediation schemes often requires some "prediction" of the distribution of contaminants within the subsurface over time. These predictions then can be used to evaluate different remediation scenarios. The basis for making such predictions is generally the application of the concepts of mass balance. A common method for applying mass balance concepts to dissolved chemical constituents in ground-water systems is the advection-dispersion equation, [illegible]ch is written in its one-dimensional form as:

$$D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \pm RXN \qquad [10\text{-}1]$$

where v is the ground-water velocity (L/T), D is the dispersion coefficient (L^2/T), C is the concentration of the dissolved constituent (M/L^3), t is time, and RXN represents a general chemical reaction term. The first term in eq. 10-1 describes the net advective flux of the contaminant in and out of a volume of the aquifer (Figure 10-1). The second term describes the net dispersive flux of the contaminant. The first term on the right-hand side of the equation describes the change in concentration of the contaminant in the water contained within the volume of aquifer. The second term on the right-hand side represents the amount of contaminant that may be added or lost to the ground water by some chemical or biological reaction. If there is no reaction term, then the equation describes the transport of a conservative, nonreacting tracer such as chloride or bromide. More detailed information about the development and derivation of eq. 10-1 is found in Palmer and Johnson (1989), Gillham and Cherry (1982), Freeze and Cherry (1979), or Bear (1979, 1969).

Some understanding of this mass balance equation is useful even to the individual who is not directly responsible for making mathematical representations of the distribution of contaminants within the subsurface. The equation is an example of the current understanding of the processes controlling the fate and transport of contaminants in the subsurface. The equation lists the parameters that should be quantified either by performing appropriate field or laboratory measurements or by using the best known values. The results of the application of this modeling are unlikely to ever exactly "predict" how the contaminants behave at a particular field site but they can provide a general set of expectations that are useful in the design of a remedial system. These results also can be used to compare aquifer remediation performance.

According to eq. 10-1, two parameters that must be determined are the ground-water velocity, v, and the dispersion coefficient, D. These parameters are described in Chapters 4 and 5 as well as in other sources (e.g., Palmer and Johnson, 1989 a,b). Chemical processes that can affect the fate and transport of organic contaminants below the water table include (1) abiotic degradation, (2) biotic degradation, (3) dissolution nonaqueous phase liquids (NAPLs), (4) sorption reactions, and (5) ionization. Both abiotic and biotic

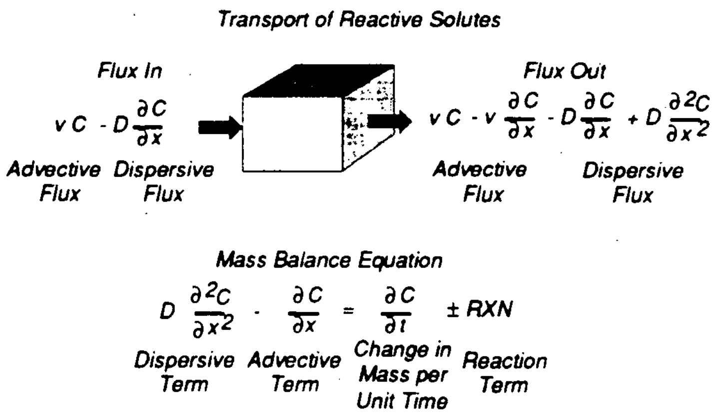

Figure 10-1. Mass balance equation for the transport of reactive solutes through porous media.

degradation are discussed in Chapter 13. The discussion in this chapter is limited to the three latter processes.

10.2 Dissolution of Nonaqueous Phase Liquids

Many of the organic chemicals of environmental concern enter the subsurface in the nonaqueous phase. How these solvents move through the soil depends on the grain size of the aquifer material, the degree of water saturation in the pore space, and the density and viscosity of the solvent relative to water (Palmer and Johnson, 1989c; Schwille, 1988). For example, if there is a spill of nonaqueous phase liquid that has a density greater than water (DNAPL), as it flows through the unsaturated zone, because the water is in the wetting phase, it will pass through the center of the pores. If there is residual water within the unsaturated zone then the combination of higher density and lower viscosity of the DNAPL relative to water results in unstable flow or significant fingering of the DNAPL as it moves through the porous media. If the spill is large enough so that the DNAPL can penetrate the capillary fringe and move below the water table, this fingering continues to occur. The transport of the DNAPLs is also very sensitive to small changes in permeability. Therefore, the DNAPL tends to spread laterally as it encounters lenses of finer grained material in the subsurface. This combination of viscous fingering and lateral flow results in a series of fingers and pools of DNAPL. The DNAPL in the fingers tends to drain to some residual saturation while the pools contain DNAPL above the residual saturation.

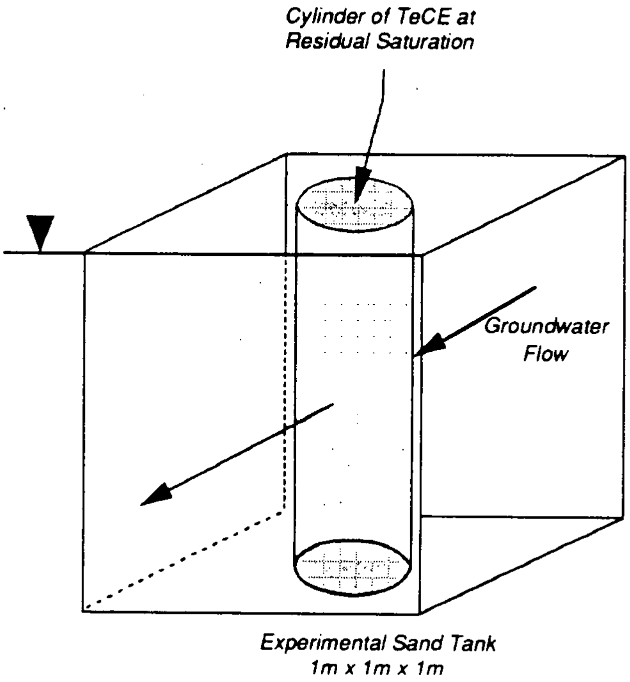

Figure 10-2. Cylindrical source of tetrachloroethylene (TeCE) used in the experiments by Anderson (1988).

As ground water flows through the fingers, the DNAPL is dissolved by the passing ground water. Laboratory experiments (Anderson, 1988; Anderson et al., 1987) using a 15-cm-diameter cylindrical finger of tetrachloroethylene (TeCE) (Figure 10-2) demonstrate that the ground water passing through the fingers can quickly reach saturation with the TeCE. This was found to be true for ground-water velocities ranging from 10 to 100 cm/day (Figure 10-3). However, these results do not imply that where a DNAPL spill has occurred the sampled ground water is saturated with the solvent. Indeed, sampling results usually indicate that most waters are highly undersaturated with respect to the DNAPLs. Although the water that passes through the fingers or very close to the pools of DNAPL within the subsurface is saturated with the DNAPL, mass transfer of the dissolved DNAPL to the areas further from these fingers and pools is predominantly by molecular diffusion. As a result, many areas within the aquifer that lie between the pools and fingers contain little or no dissolved solvent. While the distance between such fingers and pools is generally unknown, it is probably at least as great as the mean distance between the small-scale beds within the aquifer. For the Borden aquifer in Ontario, Sudicky (1986) found this distance to be about 10 cm in the vertical direction. A typical monitoring well would have an intake length of at least 2 m. Thus, the water saturated with the solvent is mixed

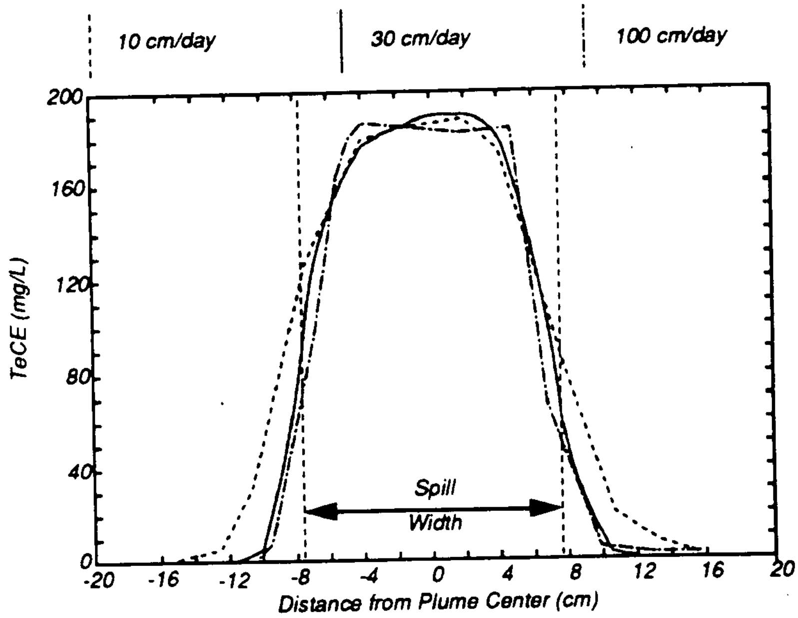

Figure 10-3. Concentration of TeCE across the flow field at the end tank in the sand box experiments conducted by Anderson (1988).

with the uncontaminated ground water resulting in measured concentrations that are substantially below saturation.

Estimating the time required to remove the nonaqueous phase liquid from the subsurface is difficult. Estimates require knowledge of the amount that was spilled and the distribution [illegible] solvent within the aquifer. While the former piece of information is often difficult to obtain, the latter is virtually impossible. If the solvent is assumed to be uniformly distributed (a residual saturation, S_r) within the aquifer, and the ground water flowing through the aquifer instantaneously equilibrates with the solvent, then the time required to remove the solvent by dissolution, t_r, is

$$t_r = S_r \theta L/(C_{eq} q) \qquad [10\text{-}2]$$

where q is the porosity of the aquifer, L is the length of the aquifer containing the solvent through which the ground water flows, C_{eq} is the equilibrium concentration of the contaminant in the ground water, and q is the ground-water flux. Estimates of removal times based on eq. 10-2, however, underestimate the actual removal time because the equation does not account for the role of soil heterogeneity, the differential times the ground water takes to flow along different flowlines, or the limitations in mass transfer of pools of NAPL that are above residual saturation. If a pump-and-treat remediation scheme is already in place, remediation time can be roughly estimated by dividing the total mass of solvent in the aquifer by the mass being removed per unit time by extraction wells.

10.3 Sorption Phenomena

10.3.1 Adsorption Isotherms

Once an organic compound has been dissolved into the ground water, it will be transported away from the source area by ground-water flow. The contaminants do not travel at the same velocity as the ground water but can be slowed by their interaction with the soil matrix. This interaction with the soil is often described graphically as an adsorption isotherm. An adsorption isotherm is simply a plot of the concentration of the contaminant on the soil versus the concentration of the contaminant in solution. Isotherms are so named because they are conducted at constant temperature. Different types of adsorption isotherms are defined according to their general shape and mathematical representation. For a Langmuir isotherm, the concentrations on the soil increase with increasing ground-water concentrations until a maximum concentration on the soil is reached (Figure 10-4). The isotherm can be represented by the equation:

$$S = S_{max}KC/(1 + KC) \qquad [10\text{-}3]$$

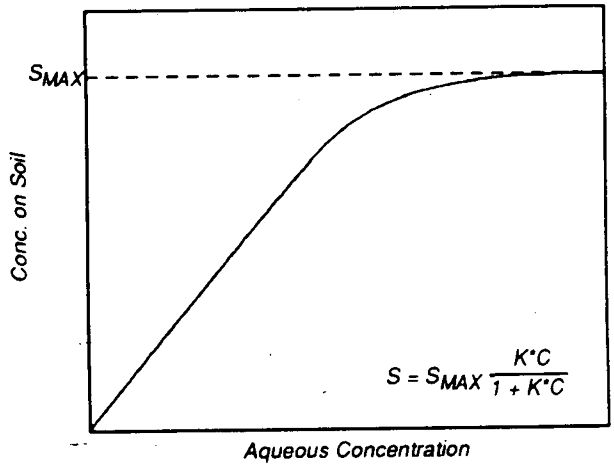

Figure 10-4. Landmuir adsorption isotherm.

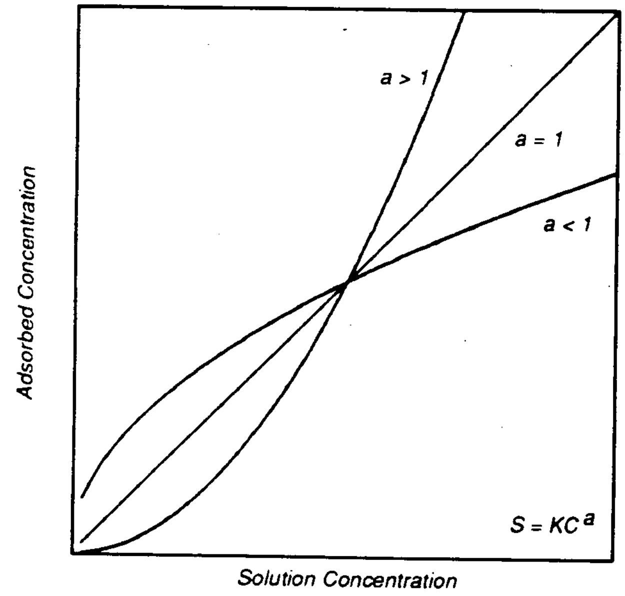

Figure 10-5. Freundlich adsorption isotherm.

where S (M/M) is the concentration on the soil, S_{max} (M/M) is the maximum concentration on the soil, K (L^3/M) is the Langmuir adsorption constant, and C (M/L^3) is the concentration in the ground water. A Freundlich (or Küster) isotherm is given by the equation:

$$S = KC^a \qquad [10\text{-}4]$$

where K is the Freundlich adsorption constant and *a* is a positive parameter. The shape of a Freundlich isotherm depends on the value of *a*. If *a* is greater than 1.0, the isotherm becomes steeper with increasing concentrations in the ground water. If *a* is less than 1.0, the isotherm becomes steeper at lower concentrations (Figure 10-5).

A linear isotherm is a special case of the Freundlich isotherm where the parameter a is equal to unity. Linear isotherms are of particular interest because (1) many nonpolar, hydrophobic organic compounds tend to follow linear isotherms (Figure 10-6) over a wide range of conditions; and (2) the application of a linear isotherm simplifies the mathematical model used to simulate the rate of contaminant movement in the subsurface and reduces the number of parameters that need to be obtained during characterization.

Another way of representing the partitioning between the soil and the ground water is by a "partition coefficient," K_p. The partition coefficient is the ratio of the change in concentration of the contaminant on the soil to the change in concentration of the contaminant in the ground water or more simply, the slope of the isotherm. When the isotherm for a particular soil is linear, the partition coefficient is constant.

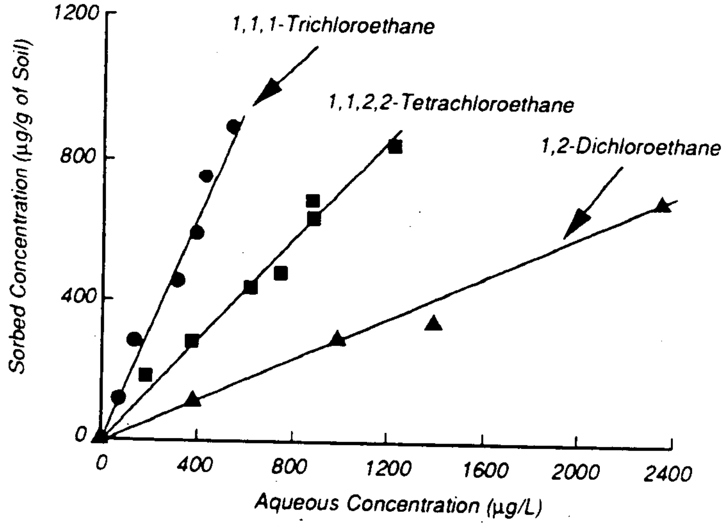

Figure 10-6. Linear sorption isotherms obtained for several priority pollutants (after Chiou et al., 1979).

The partition coefficient of an organic chemical is not constant for every soil. In general, K_p increases as the fraction of organic carbon, f_{oc}, increases in the soil (Karickhoff, 1981). In other words, the sorption of nonpolar, hydrophobic organic compounds in soils is primarily an equilibrium partitioning process into soil organic matter. K_p can be represented by

$$K_p = f_{oc}K_{oc} \tag{10-5}$$

where K_{oc} is the slope of the experimentally determined K_p versus f_{oc} curves like those in Figure 10-7. Alternatively, K_{oc} can be considered to be the partition coefficient for the organic compound into an hypothetical pure organic carbon phase.

If sorption is the primary reaction occurring in the subsurface, the right-hand side of eq. 10-1 represents the change in the total mass of contaminant within a volume of the aquifer. The total change in mass in the volume of the aquifer is equal to the change in mass in the ground water plus the change in mass on the solid phase. The reaction term in eq. 10-1 is then written as $(\rho_b/\theta)\, \partial S/\partial t$ where ρ_b and θ are the dry bulk density and volumetric water content of the soil, respectively. Substituting

$$\frac{\partial S}{\partial t} = \frac{\partial S}{\partial C}\frac{\partial C}{\partial t} \tag{10-6}$$

into this reaction term and recognizing that $\partial S/\partial C$ is equal to K_p for a linear adsorption isotherm, eq. 10-1 can now be written as

$$\frac{D}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v}{R}\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{10-7}$$

where the constant

$$R = 1 + K_p\rho/\theta \tag{10-8}$$

is known as the "retardation factor." The general form of the equation only changes by the constant R. All of the mathematical solutions that are used to solve the transport of nonreacting tracers can be used to solve for the transport of nonpolar hydrophobic organic compounds if the ground-water velocity and dispersion coefficient are divided by R.

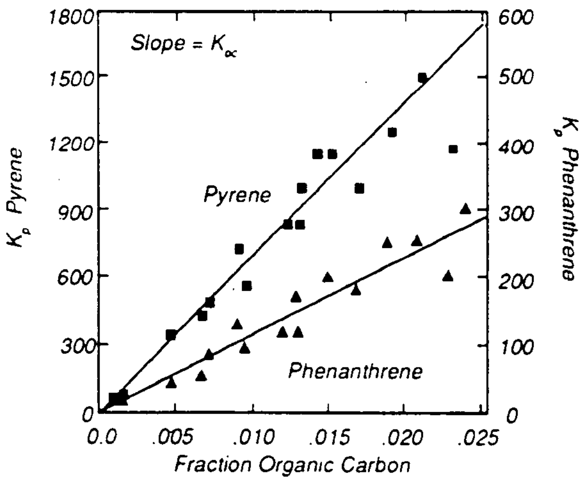

Figure 10-7. **Partition coefficients for pyrene and phenanthrene versus the fraction of organic carbon in the soil (after Karickhoff, 1981).**

The retardation factor can be interpreted in slightly different but equally valid ways. It is the ratio of the ground-water velocity, v, to the solute velocity, v_s (i.e., $R = v/v_s$). It is also the ratio of the time for the solute to travel from a source to an observation point divided by the time for the ground water to travel that same path. The retardation factor also can be thought to represent the number of pore volumes that must be flushed through a soil to remove the contaminant. All of these definitions assume that the only process occurring is linear sorption.

Application of the new expression (eq. 10-7) requires knowledge of the additional parameter R. This parameter can be obtained by several methods including (1) calculation from eq. 10-8, where K_p is obtained from correlation techniques; (2) calculation from eq. 10-8, with K_p obtained from batch sorption tests; (3) measurement from column tests; and (4) estimation from field data. The other parameters in eq. 10-8 (porosity and dry bulk density) are physical parameters that can be obtained using common techniques (see Chapter 4 and Palmer and Johnson, 1989c).

10.3.2 Determining Retardation Factors Using f_{oc} and K_{oc}

The relationship between the K_{oc} value and other known properties of organic contaminants has been examined by numerous researchers (Kenaga and Goring, 1980; Karickhoff, 1981, Schwartzbach and Westall, 1981; Chiou et al., 1982 and 1983). For example, some research has revealed linear relationships between the log of the solubility of the contaminant and the log (K_{oc}) (Figure 10-8). Similarly, Karickhoff suggested that the partitioning of organic contaminants into soil organic matter must be analogous to the partitioning of those contaminants into other organic compounds such as octanol. He found a linear relationship (Figure 10-9) between log (K_{oc}) and log (K_{ow}), where K_{ow} is the octanol-water partition coefficient. Several regression equations relating the properties of organic compounds to the K_{oc} have been derived (Table 10-1). Thus, by knowing the name of the compound of interest, these properties can be found in tables of chemical properties (Mabey et al., 1982) and the regression equations used to approximate K_{oc}. The goal, however, is to determine the partition coefficient and ultimately the retardation factor. To do this, eq. 10-5 must be applied and a measurement of the fraction of organic carbon must be obtained.

The many methods of measuring the amount of organic carbon in the soil can be broadly classified as either wet combustion or dry combustion techniques. Wet combustion techniques involve the addition of a strong oxidizing agent

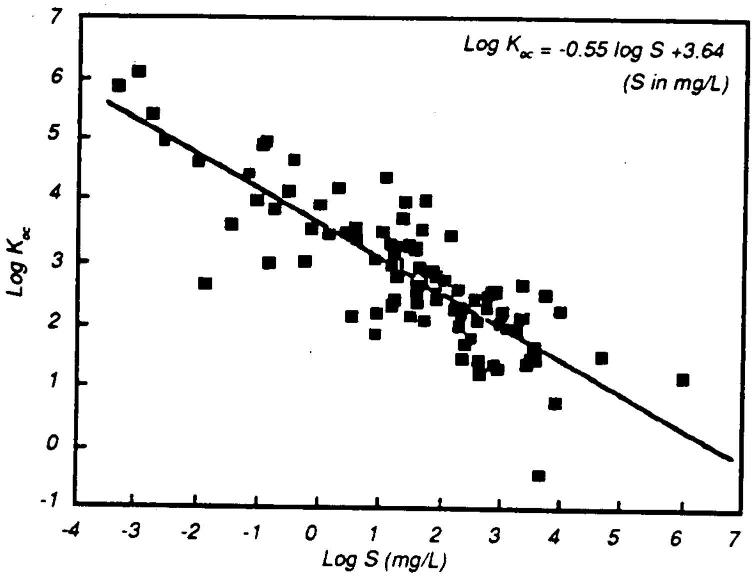

Figure 10-8. Log K_{oc} versus logarithm of the solubility of the compound in water (after Kenaga and Goring, 1980).

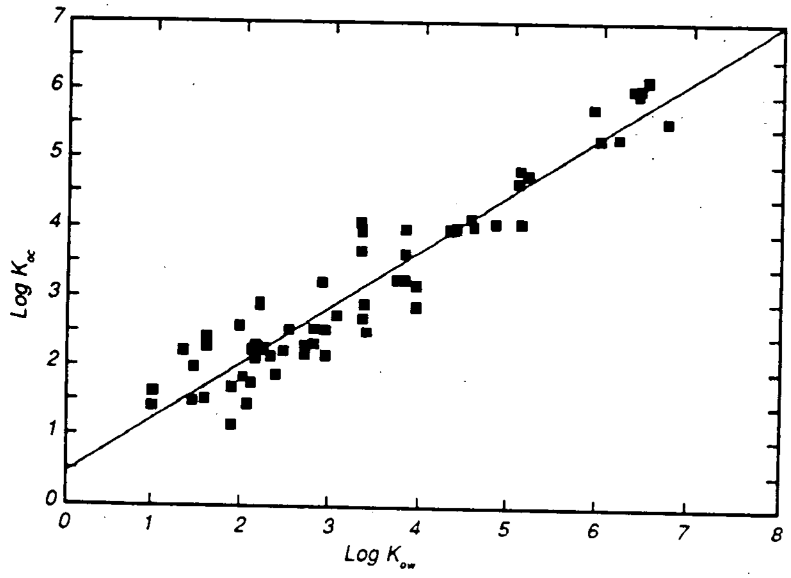

Figure 10-9. Log K_{oc} versus the octanol-water partition coefficient. Data from Karickhoff (1981).

such as dichromate to the soil. There are several such wet combustion techniques including the Walkley-Black method and the modified Mebius procedure; these procedures are discussed in detail by Nelson and Sommers (1982). In spite of some limitations, these methods can provide a relatively rapid and inexpensive method for obtaining estimates of f_{oc}.

Dry combustion methods generally involve heating the soil sample in the presence of oxygen. The oxygen reacts with the soil carbon to form carbon dioxide that can be detected by a variety of techniques.

To estimate the linear retardation factor, the K_{oc} obtained from one (or more) of the regression equations given in Table 10-1 is multiplied by the fraction of organic carbon to yield the partition coefficient (eq. 10-1). The retardation factor is obtained from the K_p, ρ_b, and θ by eq. 10-8.

There are several limitations to the use of the correlation techniques described above. The linear relationship between f_{oc} and K_p is not always easy to determine. In particular, the relationship is most likely to fail when (1) the f_{oc} is very low (<0.001), (2) when there are large amounts of swelling clays present, and (3) the organic compound is polar (e.g., compounds that contain amine or carboxylic acid groups) (Pankow,

Table 10-1. Some Reported Correlation Equations

Equation	*Data Base*[a]	*Reference*
$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	*aromatic hydrocarbons (8)* *carboxylic acids and esters (5)* *P containing insecticides (5)* *ureas and uacils (7)* *symmetrical triazines (6)* *miscellaneous (14)*	*Kenaga and Goring (1978)*
$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	*polycyclic aromatics (8)* *chlorinated hydrocarbons (2)*	*Karickhoff et al. (1979)*
$\log K_{oc} = -0.55 \log S_w + 3.64$ [b]	*aromatic hydrocarbons (8)* *carboxylic acids and esters (5)* *P containing insecticides (5)* *ureas and uacils (7)* *symmetrical triazines (6)* *miscellaneous (14)*	*Kenaga and Goring (1978)*
$\log K_{oc} = -0.56 \log S_w + 0.93$ [b,c]	*polychlorinated biphenyls (3)* *pesticides (4)* *halogenated ethanes & propanes (6)* *tetrachloroethene* *1,2-dichlorobenzene*	*Chiou et al. (1979)*
$\log K_{oc} = -0.54 \log x_s + 0.44$ [d]	*polycyclic aromatics* *chlorinated hydrocarbons*	*Karickhoff (1979)*

[a] *Number in parentheses refer to the number of compounds in data base.*
[b] S_w *is the solubility of the compound in water in ppm.*
[c] *Derived from the original equation assuming* $K_s = 1.7 K_{om}$
[d] x_s *is the mole fraction solubility at 25°C.*

After Pankow, 1984

1984). There are also several reasons why the relationship between log (K_{oc}) and log (K_{ow}) may not always be linear (Pankow, 1984). If mechanisms other than simple partitioning into soil organic carbon are contributing to the adsorption of the organic contaminant, then the K_{oc} value, computed as the ratio K_p/f_{oc}, will be in error. Also, if the molecule is large it may not fit into the soil organic matter to the same extent as it would in octanol (steric limitations). Finally, if the adsorption is strong, a contaminant may take a substantial period of time to equilibrate with the soil organic carbon.

10.3.3 Determining Retardation Factors Using Batch Tests

Retardation factors also can be measured with batch tests. These tests are, in principle, easy to perform, and the method is outlined in Figure 10-10. A known volume of solution, V_w, containing an initial concentration, C_0, of a contaminant is placed into a container. A known mass of soil, M_s, is then added and the mixture is shaken and allowed to equilibrate. The soil then is separated from the solution by centrifuging, and an aliquot of the supernatant is sampled. The concentration of the contaminant in this aliquot, C, is measured and the concentration on the soil, S, is calculated by

$$S = V_w(C_0 - C)/M_s \qquad [10\text{-}9]$$

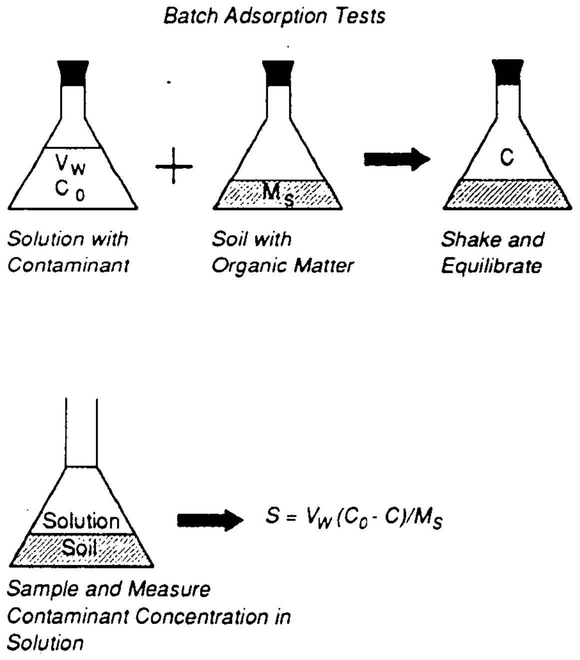

Figure 10-10. Batch adsorption tests.

This test can be run several times with different initial concentrations or different masses of soil. The result is a series of contaminant concentrations with corresponding aqueous phase concentrations that yield an isotherm when they are plotted. If the isotherm is linear, the slope, or partition coefficient, can be easily determined. The retardation factor then can be calculated from K_p, ρ_b, and θ using eq. 10-8.

Prior to conducting such batch adsorption tests, the soil is prepared by drying and then sieving through a 2-mm sieve. The sieving is to ensure that aggregated soil particles are relatively small, thus reducing the time for the contaminant to diffuse into the particles and equilibrate with the soil. Another important preparatory step is to estimate the K_p using, for example, the correlation methods described in Section 10.3.2. This is important in choosing the proper amount of soil to use in the tests. If K_p is large and too much soil is added to the reaction vessel, then most of the contaminant is partitioned to the soil and the concentration in solution cannot be accurately determined. Similarly, if K_p is small and too little soil is added to the reaction vessel, then the measured contaminant concentration falls within the analytical error of the initial concentration and an accurate estimate of the contaminant concentration of the soil cannot be obtained. Both of these cases lead to poor measures of the partition coefficient.

There are some problems that complicate the use of batch tests for determining K_p. For example, batch tests assume that equilibrium is established between the soil and the solution, but some contaminants may take a very long period of time to equilibrate. Experiments on the desorption of hexachlorobenzene from soils (Karickhoff and Morris, 1985) indicated that even after 35 days equilibrium was not obtained (Figure 10-11).

Another problem involves nonsettling particles. The separation of the soil and the water is assumed to be complete before sampling of the supernatant; however, very fine, colloidal-size particles may remain in suspension. The contaminants attached to these particles are stripped during the analysis of the water, which causes overestimation of the aqueous phase concentration. This results in underestimation of the partition coefficient (e.g., Gschwend and Wu, 1984). The magnitude of the effect depends on the concentration of nonsettling particles (NSPs) and the true partition coefficient onto those particles (Figure 10-12). If the partition coefficient is small, then most of the mass of the contaminant is in solution and the error caused by the NSPs is negligible. If the partition coefficient is large, then a significant mass of the contaminant is really partitioned onto the soil particles causing significant errors in the aqueous phase concentration and hence C_p.

A third problem arises from the loss of contaminant by volatilization during equilibration, sampling, and analysis. This problem can be minimized by eliminating head-space and using properly sealed reaction vessels.

Uncontaminated background soils are recommended for batch adsorption tests. If the soils contain any NAPLs, the contaminant being investigated will partition into the NAPL, yielding a potentially large and incorrect partition coefficient. Once K_p is determined in the batch test, the retardation factor, R, can be estimated by using eq. 10-8.

10.3.4 Determining Retardation Factors from Column Tests

A third method for estimating linear retardation factors is with column tests. In these tests, a column of soil is prepared,

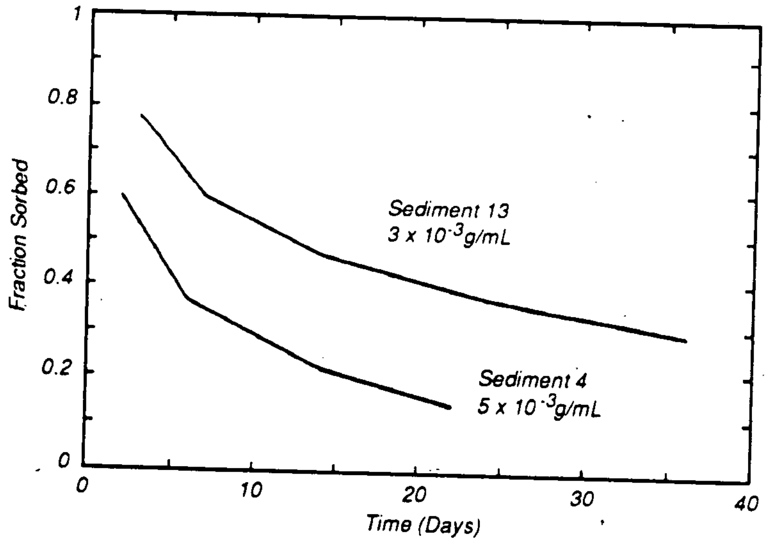

Figure 10-11. The fraction of hexachlorobenzene sorbed to two soils versus time during desorption tests (after Karickhoff and Morris, 1985).

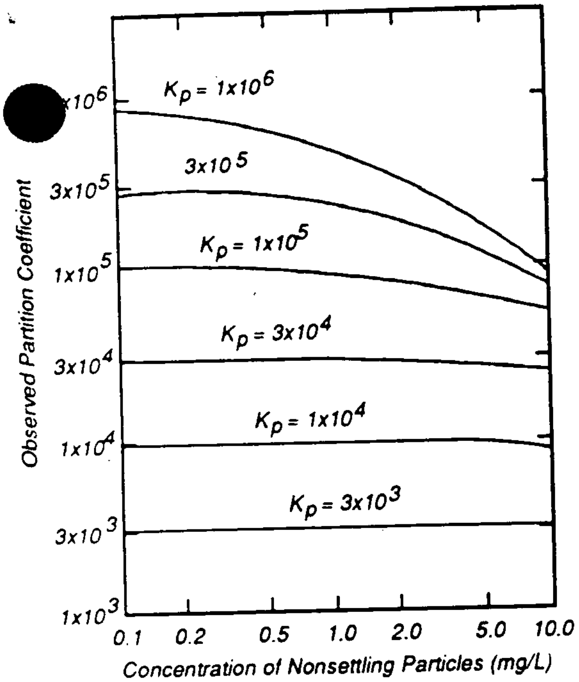

Figure 10-12. **The effects of nonsettling particles on the observed partition coefficient (after Pankow, 1984).**

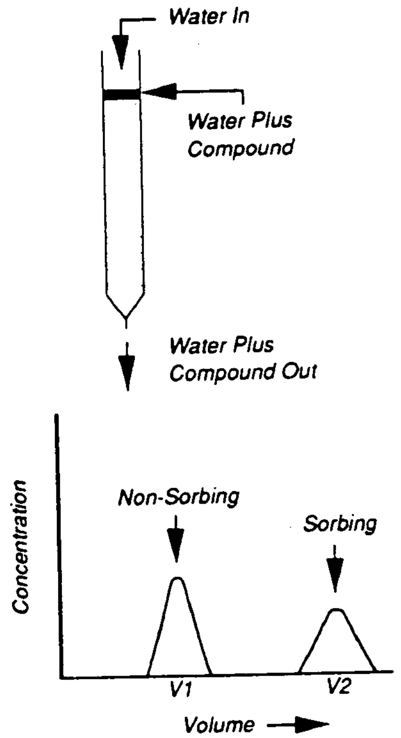

Figure 10-13. **Column tests for determination of retardation factors.**

and a solution containing a nonadsorbing tracer and the conta[illegible]nt of interest is run through the column (Figure 10-13). T[illegible]oncentrations of the tracer and contaminant can be measured in the water that has passed through the column. The retardation factor is then the ratio of the time (or volume) for the center of mass of the contaminant to break through the column to the time (or volume) for the center of mass of the nonreactive tracer to break through the column. This technique provides a direct measure of R; however, it is only well suited for those contaminants that have a relatively small (< 10) retardation factor. Contaminants with retardation factors much greater than 10 require too much time to measure to be practical. Other disadvantages of using column tests include the slow flow rates in fine-grained material, the destruction of soil structure by soil repacking, and the difficulty in distinguishing kinetic behavior from the heterogeneous packing within the column.

10.3.5 Determining Retardation Factors from Field Data

Site-specific field information obtained during the Remedial Investigation/Feasibility Study (RI/FS) can, in some cases, be used to estimate contaminant retardation. While in principle retardation factors can be back-calculated from breakthrough curves obtained at monitoring wells or through the spatial distribution of the contaminants in the subsurface, in practice, only the latter is likely to be obtained. The retardation factors can be estimated by dividing the velocity of [illegible]nd water by the velocity of the contaminant. The ground-[illegible]r velocity can be estimated from Darcy's Law and the porosity, or alternatively by the distance some nonadsorbing solute travels after the release. The solute velocity can be estimated by dividing the mean distance the contaminant has traveled by the time since its release into the subsurface. One of the potential disadvantages of this method is that other processes that are not included in the data analysis are occurring within the aquifer. Ignoring these processes can result in poor estimates of the retardation factor.

10.3.6 Comparison of Methods for Estimation of Retardation

Each of the methods for estimating the retardation factor has advantages and disadvantages. One of the key questions, however, is how do these different methods for estimating retardation compare. The best technique for comparison is to look to large-scale field tracer experiments where very accurate field values have been obtained. This has been done for the Stanford-Waterloo tracer experiment that was conducted in the sandy aquifer on Canadian Forces Base Borden in Ontario, Canada. Details of the experiment and analysis of the results can be found in Mackay et al. (1986); Roberts et al. (1986); Curtis et al. (1986); Freyburg (1986); and Sudicky (1986).

A summary of the retardation factors obtained for five different compounds using a correlation method, batch tests, and temporal and spatial data from the field experiment is given in Table 10-2. The batch tests agree closely with the field data. The correlation technique tends to consistently underestimate the retardation factors. The underestimation of the retardation factors may be the result of poor estimates of the fraction of organic carbon (e.g., Powell et al., 1989) or errors in the assumptions in eq. 10-5, or they may be the result

Table 10.2 ***Comparison of Methods for Retardation Factors***

Solute	Office Estimated	Lab Batch	Field Values Temporal	Field Values Spatial
CTET	1.3	1.9	2.7	2.1
BROMO	1.2	2.0	1.7	2.2
TeTE	1.3	3.6	3.3	4.3
DCB	2.3	6.9	2.7	6.2
HCB	2.3	5.4	4.0	6.5

After Curtis et al. (1986)

of the inherent error in the regression equations. Recall that the regression equations are based on the logarithms of the values; therefore, the best estimates of the K_{oc} and hence the retardation factor may be a factor of 2 or 3 from the "true" value. Nonetheless, the correlation techniques do provide the correct order of magnitude estimate of the retardation factor at very little expense. Such values would be appropriate for the preliminary design of the remedial strategies. If more accurate estimates are required, then the more expensive batch or column tests should be used. Enough samples should be tested, however, to estimate the uncertainty of the retardation factor for each of the important geologic units.

10.3.7 Applicability and Limitations of Linear Partitioning and Retardation

Most of the emphasis in this section has been on the linear partitioning and retardation model for the adsorption of neutral, hydrophobic organic compounds in the environment. While this model is adequate for many situations, it is important to recognize the limitations in the assumptions so that it is not applied to situations where it is inappropriate.

Retardation only describes the process of the partitioning of the contaminant between the ground water and soil organic matter. If the nonaqueous solvent phase is dissolving or the organic compounds are degrading, then these additional processes also must be taken into account. However, for describing the partitioning process, the linear retardation model is reasonable for many compounds if the concentration of the contaminant is less than 10^{-5} molar or less than half the solubility, whichever is lower (Karickhoff et al., 1979; Karickhoff, 1984). At high or low concentrations the linear isotherm may deviate. Some data on the adsorption of TCE to glacial till suggest that the partition coefficient is not constant but may vary by as much as 50-fold over range in groundwater concentrations from 10 to 10,000 parts per billion (ppb) (Figure 10-14). This variation occurs even though the partition coefficient is approximately constant over the range from 100 to several thousand ppb.

The linear retardation model assumes that equilibrium is achieved quickly. In some circumstances, the rate of adsorption and desorption can be an important factor. As mentioned in Section 10.3.3, Karickhoff and Morris (1985) found that during the desorption of hexachlorobenzene, equilibrium was not achieved even after 35 days of reaction time (Figure 10-11).

10.4 Ionization and Cosolvation

Another important reaction that can affect sorption and hence the rate of removal of organic contaminants from the subsurface is ionization. Acidic compounds such as phenols, catechols, quinoline, and organic acids can lose or gain protons (H^+) depending upon the pH. The resultant ions are much more soluble and less hydrophobic than the uncharged forms. Therefore, the ionized forms have much lower K_{oc} values than the uncharged forms. The pH at which this reduction in K_{oc} becomes substantial can be predicted based on the acidity of the compound. This acidity is often represented as the pK_a of the compound, which is the pH at which 50 percent of the molecules are ionized.

Table 10-3 lists pK_a's for a number of environmentally significant ionizing compounds. For example, trichlorophenol ionizes to a phenolate (Figure 10-15). The trichlorophenol has a relatively large K_{oc} value (2330) and readily partitions into the soil organic matter. The ionized form is not as hydrophobic and its K_{oc} value is substantially smaller than the K_{oc} of the trichlorophenol. As the pH increases, the fraction of the phenol that is ionized increases and the K_{oc} decreases (Figure 10-16). Therefore, the K_{oc} value based on the total concentration of the phenolic compound is dependent on the degree of ionization of the compound. While the phenolate compound may be retarded mainly by anion adsorption to oxide surfaces in low carbon soils, there is evidence that the phenolate also partitions into the soil organic carbon Schellenberg et al., 1984).

Studies with other compounds also have indicated the relative importance of ionization of organic compounds. Studies of quinoline in low carbon soils suggest that the main mechanism for sorption is primarily by ion adsorption (Zachara et al., 1986; Ainsworth et al., 1987).

It often is assumed that water at hazardous waste sites has about the same chemical properties as pure water and that the solubilities of hydrophobic organic contaminants are relatively constant within a very narrow range. However, many of the chemical properties of mixtures of solvents, such as water and methanol, can change as the fraction of the cosolvent in the mixture changes. The thermodynamic basis for some of these cosolvation effects is described by Rao et al. (1985) and Woodburn et al. (1986). Of particular interest is that the solubility of many organic compounds can be increased by orders of magnitude within mixtures of water and other miscible solvents (Nkedi-Kizza et al., 1985; Fu and Luthy, 1986a and 1986b; Zachara et al., 1988). For example, the partition coefficient of anthracene decreases more than an order of magnitude as the fraction of methanol (the cosolvent) is increased from 0 to 50 percent (Figure 10-17).

Such cosolvation effects may be either advantageous or disadvantageous depending on the specific problem. If these miscible liquid cosolvents have been codisposed with priority pollutants on site and the main concern is compliance monitoring, then the lower partition coefficient results in higher transport rates to the compliance boundary. If the focus, however, is on remediation, then the cosolvation effect may allow a technology such as pump-and-treat to be considered a

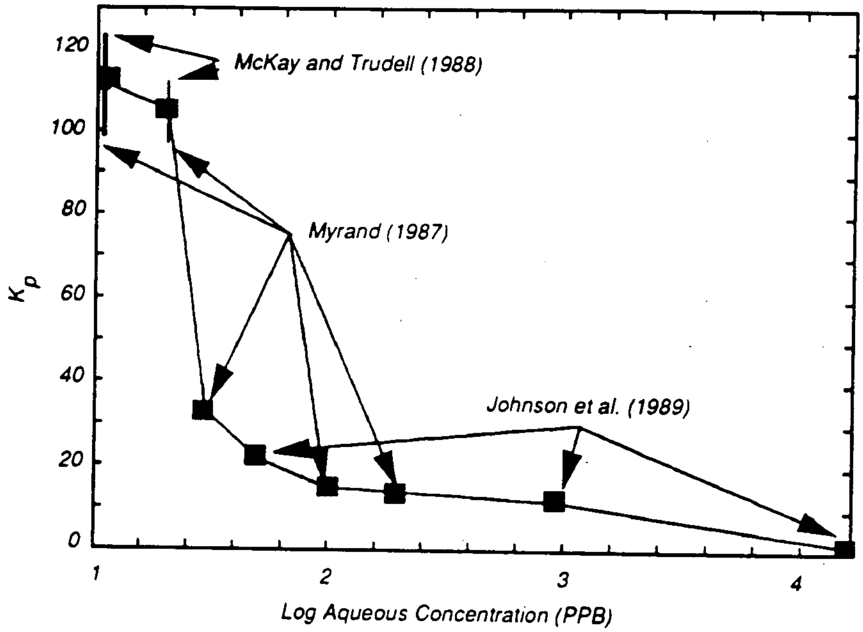

Figure 10-14. Partition coefficients for TCE on glacial till.

Table 10-3. Acid Dissociation Constants for Several Priority Pollutants

Compound	pK_a
phenol	9.89
2-chlorophenol	8.85
2,4-dichlorophenol	7.85
2,4,6-trichlorophenol	5.99
pentachlorophenol	4.74
2-nitrophenol	8.28
4-nitrophenol	7.15
2,4-nitrophenol	3.96
2,4-dimethylphenol	10.6
4,6-dinitrocresol	4.35
benzidine	4.66, 3.57

Source: Mabey et al., 1982.

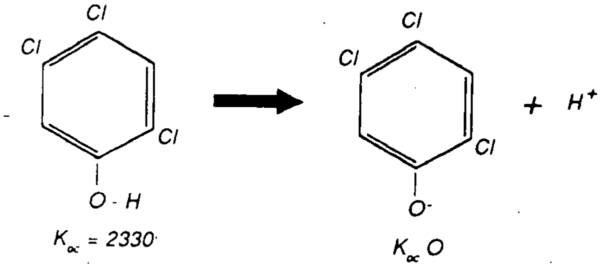

Figure 10-15. Ionization of trichlorophenol to trichlorphenolate.

viable option. Alternatively, the addition of cosolvents to the subsurface for the express purpose of enhancing the removal of these organic contaminants in a timely and cost-effective manner may be a possibility; however, such technology has yet to be demonstrated in the field.

10.5 Expressions for Other Chemical Processes

The emphasis in the discussion above centered mostly on the dissolution of the NAPL phases and equilibrium adsorption with linear partitioning. These processes are emphasized because under many conditions they are the more important processes controlling the rate of transport and removal of organic contaminants from the subsurface. However, other chemical processes may be taking place within the subsurface and equilibrium may not always be a reasonable assumption. These other equilibrium and nonequilibrium processes also can be represented in the general expression given by eq. 10-1. A few of the expressions for different chemical processes are given in Table 10-4. If one of these other expressions is required to describe the reactions that are occurring within the subsurface, then other parameters must be measured or estimated. For example, if adsorption/desorption for a particular compound is rate-controlled rather than equilibrium-controlled, then the rates of adsorption and desorption should be determined. These rates can be inferred from batch or column tests similar to those described above, but they require measurements over time and a more sophisticated level of interpretation and analysis. Such models should be called upon if required for understanding the processes at a particular site.

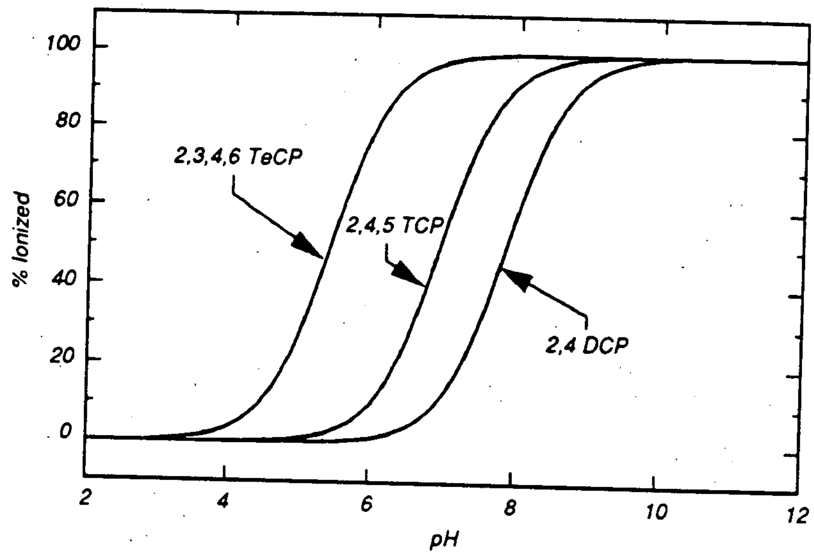

Figure 10-16. Percent of ionization of three different chlorophenolic compounds versus pH. Based on data from Schellenberg et al. (1984).

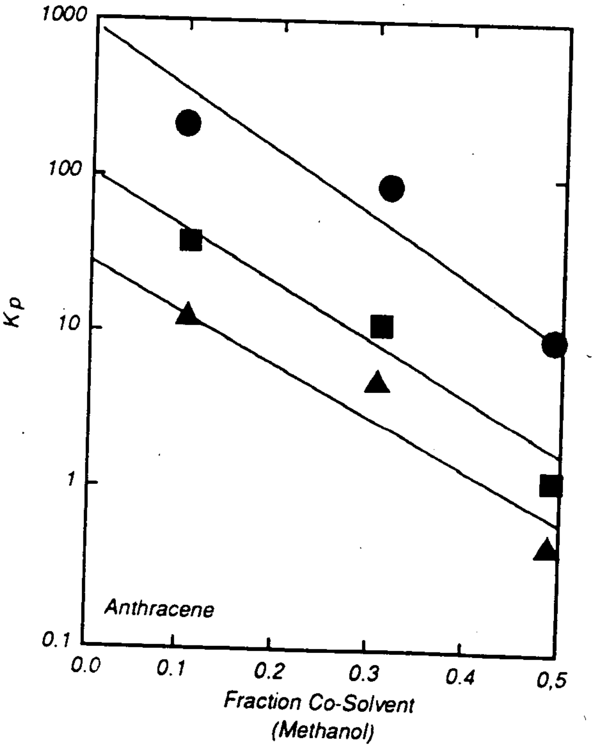

Figure 10-17. Partition coefficient of anthracene on three different soils versus fraction of methanol present as a cosolvent (adapted from Nkedi-Kizza et al., 1985).

Table 10-4. ***Reaction Terms for Various Chemical Processes***

Process	Reaction Term in Mass Balance Equation
Zero Order Production	K
First Order Decay	$-KC$
nth Order Decay	$-KC^{n}$
Langmuir Adsorption	$(\rho_b/\theta_s)S_{max}K/(1+KC)^2$
Freundlich Isotherm	$(\rho_b/\theta_s)\,aKC^{a-1}$
First Order Kinetics	$(k_r/\theta_s)S - (k_f/\theta_s)C$
Langmuir Kinetics	$(k_r/\theta_s)S - (k_f/\theta_s)C(S-S_{max})$
Nonlinear Kinectics	$(k_r/\theta_s)S - (k_f/\theta_s)C^{n}$

10.6 References

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