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## CHAPTER 6

### Transport of Contaminants in Soil

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#### Introduction

This chapter will review major mechanisms by which organic compounds and metals move from the location of their initial deposit in the soil, and how resistant desorption and sorption processes may influence contaminant transport. Approaches for incorporating realistic partitioning, including slow desorption, into transport models are reviewed. Discussion of how the extent and rate of release of contaminants enters into transport calculations and equations is presented.

The primary focus of the chapter is on presentation of a framework for representing the relationship between the mass transport and the source term that is used in risk assessments. Mass transport from the contaminated soil source region decreases the source term mass, and the other processes occurring in the source region determine the mass that is available for transport from the source. Thus, the behavior of mass transport and the source term are coupled. One objective of this chapter is to present a simple, physicochemical characteristic-based source term model that includes sequestration of contaminant mass and slow desorption of mass from soil. The transport mechanisms that are included in the source term model are leaching, volatilization, and erosion or soil resuspension. The fate mechanisms include sequestration, biphasic desorption, various transformations, and bioaccumulation of contaminant mass within the soil biotic community.

This discussion assumes that a mobile nonaqueous-phase liquid (NAPL) phase is not present. If present, a mobile NAPL phase can dominate the release and transport of organic chemicals. These sites are typically managed on a case-by-case basis. The present discussion relates to the release of chemical from a soil-waste matrix, which can then be available for further transformation and/or migration. The presence of an immobile, residually trapped NAPL phase is included in this chapter.

The source term represented in this chapter provides the contaminant mass source term for release to environmental pathways for risk assessment. In addition, because many remediation methods involve the passage of fluids through the

contaminated soil mass, this representation provides the framework for estimating efficacy of remediation efforts.

This chapter is based on 3 significant findings and conclusions:

- 1) The slow release mechanisms that operate in soil and subsurface environments have the greatest effect directly within the source itself. Although resistant sorption and desorption processes may occur in the downgradient zone, they are relatively less important to environmental transport and risk compared to the release from the source. As such, it is assumed that conventional transport methods outside of the source are adequate, and this chapter will focus exclusively on interactions of chemicals in the source.
- 2) The presence of residually trapped NAPL in the soil-waste significantly affects the release of chemicals and should be considered in risk and site management determinations.
- 3) While the detailed mechanisms for chemical interactions in the soil-waste matrix are not well understood, computational and experimental methods can be applied today that provide improved estimates of release from field soils and that are environmentally protective and useful in a site risk management context.

### Context of Contaminant Transport in Risk Characterization

The transport of contaminants through soil depends on physicochemical characteristics of the contaminants and on site-specific characteristics such as soil type, soil heterogeneity, geochemical environment, and moisture. Within the analysis of risk characterization, transport analysis provides the link between contaminant source and potential exposure. From the subsurface environment, common transport pathways include volatilization (diffusion through soil air), leaching (advection, diffusion, dispersion in soil water), and for some contaminant releases, transport through NAPL flow. Transport pathways that are not commonly considered include facilitated transport (e.g., colloidal or particulate transport) and transport through the food chain.

Discussions of contaminant transport in soil are intimately tied to those of contaminant fate. At the contaminant source, the mechanisms that determine the availability of contaminants for transport also may be important in determining contaminant bioavailability to organisms, and these may be the same mechanisms involved in contaminant fate. Uncertainty in quantifying contaminant fate (release) mechanisms adds directly to uncertainty in quantifying contaminant transport and ultimately to uncertainty in quantifying potential exposure. These uncertainties are compounded by limitations on predicting transport through heterogeneous media and by transport through preferential flow paths. Furthermore, there also is

considerable uncertainty in identifying significant transport pathways. For example, contaminants can move out of the soils and into the food chain in a variety of ways. Metals tend to move into a portion of the soil invertebrate food web and are subsequently taken up into the aboveground system by insectivorous wildlife species. Other contaminants accumulate in plants that, in turn, are ingested by herbivores.

### Conventional Risk Assessment Models

The assessment of risks from contaminated sites relies on 3 pieces of information, as shown in Figure 6-1. First, one must know certain characteristics of the contaminant source zone. These include the chemicals that are present, along with their concentrations within the various phases (water, air, soil, NAPL, biomass), and the significant mass transport mechanisms, along with estimates of important parameters that characterize the environment. The second piece of information that is required concerns the potential transport pathways from the point of contaminant release to the point of exposure. For ecological risks, the point of exposure may coincide with the location of the release, and environmental transport is not involved. However, for other potential human or ecological exposures, contaminant migration through environmental pathways is necessary. The mechanisms for transport through environmental pathways include volatilization, leaching, and suspension or erosion of surface soil particles. The third requirement for assessing risks is to estimate the uptake and dose at the point of exposure. One of the primary objectives of transport modeling in risk assessment is to relate the contaminant concentration at the source to the exposure concentration (Charbeneau 2000).

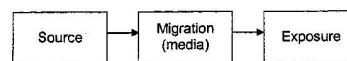


Figure 6-1 Assessment of risks from contamination

There are 3 basic mechanisms by which miscible and immiscible contaminants are transported in the subsurface environment: advection, diffusion, and mechanical dispersion. For transport within the vadose zone, the primary mechanisms are leaching, which involves advective and dispersive transport in the aqueous phase, and volatilization, which involves diffusive transport through the soil air.

"Leaching" refers to the soluble species being carried along with the flow of subsurface water. In representing the groundwater source term from contaminated soil, it is usually assumed that the leachate release rate is equal to the product of

the net infiltration rate and the average porewater concentration. This assumes that water moves uniformly through the contaminated soil and that the soil water concentration is uniform. Neither of these assumptions is true. Because of soil heterogeneities and the presence of preferential flow paths, contaminant transport occurs only through a fraction of the soil mass. This is especially true in well structured soils. In addition, the contaminant mass is not evenly distributed.

Volatilization is the mass transfer of chemical substances from soil to the atmosphere. Contaminants may leave the soil by vaporizing into the soil air and then exiting to the atmosphere by diffusion in soil air to the ground surface or by being carried in soil air as it is forced from the soil by vacuum extraction in wells. The rate of volatilization is affected by many factors, such as soil properties, chemical properties, and environmental conditions. It is ultimately limited by the chemical vapor concentration that is maintained at the soil surface and by the rate at which this vapor is carried away from the soil surface to the atmosphere. The factors that control the rate of volatilization have been studied mostly for pesticides, but there is little that distinguishes pesticides from other organic chemicals in this context.

Mass transport models may be used to relate contaminant concentrations at the source to exposure concentrations at a receptor. Groundwater pathway models usually include the processes of advection, transverse and vertical dispersion, retardation, and decay. It is also usually assumed that the source is infinite and that steady-state conditions exist. Under these assumptions, the results of the transport model may be expressed using dilution-attenuation factors (DAFs), or the ratio of the porewater concentration at the source to the groundwater concentration at the receptor. Generic default DAF values have been suggested by the U.S. Environmental Protection Agency (USEPA 1994) and site-specific DAF values have been calculated for transient conditions with a finite source and residual NAPL in contaminated soil (Johnson et al. 1998).

Similar models have been developed for atmospheric transport and indoor air. Atmospheric dispersion models are used for air pathways, and screening models are available that relate the pore air concentration at the source to the air concentration at the receptor (ASTM 1998).

### Incorporation of Abiotic and Biotic Processes in Transport Models

Chemical processes (e.g., adsorption, precipitation, complexation, hydrolysis, oxidation, or reduction) and bacterial processes (e.g., bacterial degradation) that occur in the soil system and alter the solubility of the contaminant in the soil system need to be considered as input variables in mass transfer processes. Additionally, loss mechanisms (e.g., plant uptake, animal ingestion of soil) need to be

accounted for in mass transfer processes. Discussion of these topics and their importance can be found in Chapter 5.

From the perspective of contaminant transport, these processes can be considered as simple linear constants or as mathematical expressions requiring independent solutions. Bioaccumulation (of metals) in plants can present an additional storage reservoir for contaminant mass and, if plants are growing and are harvested, additional loss terms. Both representations can be incorporated in the sequestered source model.

### Representing Sorption and Desorption and Nonaqueous-Phase Liquids in Transport Models

The conventional approach for modeling solute partitioning in multimedia environments has been through application of a linear partition model that states that the concentration in one phase (water, air, soil, or NAPL) is proportional to the concentration in another phase. For risk characterization, the solute concentration in soil water is significant for estimating sources to environmental transport pathways. For soil-water interactions, air-water interactions, and NAPL-water interactions, respectively, the linear partition models are

$$q = K_d C_w \quad (6-1)$$

$$C_a = K_H C_w \quad (6-2)$$

$$C_o = K_o C_w \quad (6-3)$$

where  $q$  is the sorbed concentration (mg/kg), the parameter  $K_d$  is called the "soil-to-water distribution coefficient" (L/kg),  $C_w$  is the soil porewater concentration (mg/L),  $C_a$  is the soil-pore-air concentration (mg/L),  $K_H$  is the dimensionless Henry's Law constant,  $C_o$  is the solute concentration (mg/L) within the NAPL phase (oil, organic immiscible liquid), and  $K_o$  is the dimensionless NAPL-to-water partition coefficient. If a contaminated soil sample is taken and the entire chemical mass is extracted, then the total concentration,  $C_T$ , is measured, which is the total contaminant mass per total (bulk) volume. The total concentration is related to the concentration within the various phases through

$$C_T = \phi (S_w C_w + S_a C_a + S_o C_o) + \rho_b q \quad (6-4)$$

where  $\phi$  is the soil porosity,  $S_w$  is the water saturation,  $S_a$  is the air saturation,  $S_o$  is the NAPL saturation, and  $\rho_b$  is the bulk density of the soil (kg/L). When combined with Equations 6-1 through 6-3, Equation 6-4 may be written as

$$C_T = [\phi (S_w + S_a K_H + S_o K_o) + \rho_b K_d] C_w \equiv B_w C_w \quad (6-5)$$

Equation 6-5 defines the bulk water partition coefficient,  $B_w$ , which is dimensionless. Equivalent coefficients may be defined for each phase in a multiphase system (Charbeneau 2000). Equation 6-5 shows that the relationship between the porewater concentration for a solute and its bulk (or total) concentration in soil is dependent on soil porosity and bulk density, saturation of the 3 phases that might be present, and linear partition coefficients for the solute between the phases and water. The equation assumes that the solute concentrations within the various phases are in equilibrium with one another. In the application of Equation 6-5, it is assumed that the same distribution coefficient ( $K_d$ ) applies for both the sorption and desorption processes. However, this assumption must be used with caution, because the distribution coefficient for desorption may be quite different from the distribution coefficient for sorption (Chapter 7). If the total soil concentration is analytically determined for a soil sample, and if the other parameters are estimated, then the corresponding aqueous concentration is calculated from

$$C_w = \frac{C_T}{B_w} \quad (6-6)$$

In risk assessments, Equation 6-5 may be used to back-calculate the allowable concentration that may be left in soil. If  $C_{wE}$  is the allowable screening level concentration in water at a potential receptor or exposure location, and (DAF) is the dilution attenuation factor that accounts for environmental transport between the contaminant source and the exposure location, then the allowable porewater concentration at the source is  $C_w = (\text{DAF}) \times C_{wE}$ . The allowable concentration that may be left in soil is then calculated from

$$C_T = B_w (\text{DAF}) C_{wE} \quad (6-7)$$

If the presence of NAPL is not accounted for so that the  $S_o K_o$  term is neglected in  $B_w$ , then application of Equation 6-7 is overly restrictive because the  $B_w$  value would be underestimated.

Recent research suggests that application of Equation 6-1 can lead to overestimation of aqueous solute concentrations when applied to a source region where the contaminant has been present for sufficient time to become sequestered (aged contaminants in soils). If only a fraction,  $F$ , of the sorbed mass was readily available for desorption, then the corresponding porewater concentration would be

$$C_w = \frac{F q}{K_d} \quad (6-8)$$

Neglecting the sequestered mass results in overestimation of the source porewater concentration and subsequently the resulting potential exposures in risk assessments and remediation performance using techniques such as pump-and-treat, soil vapor extraction, and soil flushing. Sequestered chemicals are not readily released to soil water, and the kinetics of desorption should be considered for source term models.

Empirical evidence suggests that sorption sites may be classified into 2 types: those that are readily available for desorption (or allow rapid though kinetically controlled desorption) and those that only allow desorption at a slow rate. Relatively simple models may be developed to produce the observed behavior, and there are cases where use of such models may be important in risk assessment, just as consideration of the presence of residual NAPLs may be important. The following subsections describe such models and their applications and limitations.

#### Development of multiprocess sequestered source models

Development of new, contaminant source zone models that include sequestered contaminant mass may be significant for risk calculations and for assessing the significance of some soil remediation efforts. In the following subsections, a multiprocess source zone model is presented that specifically includes sorbed mass that is sequestered and slowly released and NAPLs that may be present at residual saturation. Assessment of mobile NAPL source zones is not considered because these require more detailed assessments of NAPL migration. A schematic view of the resulting model is shown in Figure 6-2. The figure shows a region of contaminated soil with water, air, soil, and NAPL phases depicted. Within the soil phase, contaminant mass is shown in 3 different locations that are designated by accessibility to interact with soil pore water. Part of the soil mass is readily available to interact with pore water, and this mass is assumed to be in equilibrium with the porewater concentration. This corresponds to a fraction  $F$  of the sorbed mass. Another part of the sorbed mass is designated as "sequestered." This mass is available for desorption, but its desorption rate is kinetically limited, and it is released at a slower rate. Finally, some of the soil mass is designated as "immobile." This designation applies to mass that cannot be released to the soil solution. It does not imply that the soil particle cannot be transported through suspension or erosion or through ingestion by mobile soil invertebrates.



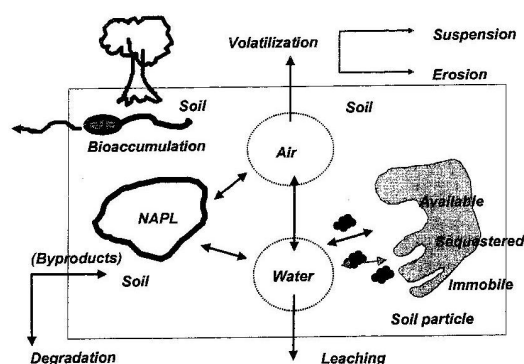


Figure 6-2 Schematic view of the sequestered source model

Figure 6-2 also shows 3 different mass transport mechanisms. Contaminant mass may be leached from the source zone by water moving through the soil. Contaminant mass may partition into soil air and diffuse to the soil surface and volatilize into the atmosphere. Mass that is sorbed to soil particles may be transported in bulk if the particles are moved through suspension or soil erosion.

Three general fate mechanisms are also shown in Figure 6-2. For organic contaminants, the contaminant may biodegrade, resulting in a loss of mass. However, degradation of a parent compound may generate products also considered to be soil contaminants, so the degradation fate of one constituent may result in a source term for byproduct of organic chemical degradation. The soil contaminants may also bioaccumulate, which may result in a loss term as far as migration potential is concerned. Finally, through biotic or abiotic processes, the soil contaminant may be immobilized.

The following discussion outlines how these transport and fate processes may be represented in a sequestered source model (SSM).

### Methods for representing sorption and desorption in transport models

In this section, a simple 2-site partitioning model will be presented that will describe the release of contaminant from the soil in the presence of other processes that occur in the source zone. As described previously we will limit our discussion to characterizing the processes that are important to transport in the source zone, since it is in the source region where physicochemical unavailability will impact transport to receptors relative to the case when the contaminant is entirely available.

Treating the source zone as a well mixed cell in a region of the vadose zone, a mass balance accounting for both equilibrium- and mass transfer-limited release from soil with simultaneous losses due to volatilization, degradation, and uptake into organisms can be written as

$$AL \frac{dC_T}{dt} = -\Lambda C_w AL \quad (6-9)$$

In Equation 6-9,  $A$  is the cross-sectional area of the source zone ( $m^2$ ),  $L$  is the vertical thickness of the source zone ( $m$ ),  $C_T$  is the total or bulk constituent concentration ( $mg/L$ ). On the right side of Equation 6-9,  $\Lambda$  is the first-order loss rate coefficient that includes losses due to leaching, degradation, volatilization, and biological uptake ( $day^{-1}$ ), and  $C_w$  is the aqueous concentration ( $mg/L$ ). Equation 6-9 is a mass conservation equation that states that the rate of change of constituent mass within the source zone volume ( $AL$ ) is equal to the constituent loss rate due to leaching, degradation, volatilization, and biological uptake (loss). However, because the source zone volume is constant in size (as assumed by this model), Equation 6-9 may be written in the simpler form

$$\frac{dC_T}{dt} = -\Lambda C_w \quad (6-10)$$

Equation 6-10 is the conventional first-order decay (loss) equation, except that it relates the total mass loss to the concentration within an individual phase of a multiphase system.

### Mass storage capacity of the source zone

In Equation 6-10,  $C_T$  is the total concentration of the constituent within the source zone and includes both the available sorbed mass and the sequestered or slowly released mass. It may be expressed

$$C_T = \rho_b (q_1 + q_2) + \phi (S_w C_w + S_a C_a + S_o C_o) + \rho_B q_B \quad (6-11)$$

where  $q_1$  is the available mass in soil (mg/kg soil),  $q_2$  is the slowly released amount in soil (mg/kg soil),  $\rho_b$  is the biological mass per unit volume of soil within which the constituent may accumulate, including plants, soil invertebrates, etc. (kg/L soil), and  $q_b$  is the constituent concentration in the biological matter (e.g., plants; mg/kg biomass).

The readily available concentration,  $q_1$ , will be assumed to be in equilibrium with the porewater concentration and will be characterized by a linear equilibrium partitioning coefficient:

$$q_1 = K_d F C_w \quad (6-12)$$

The less available contaminant concentration,  $q_2$ , will be characterized by a linear driving force, mass transfer rate-limited process as follows:

$$\frac{dq_2}{dt} = k_2 [K_d (1-F) C_w - q_2] \quad (6-13)$$

where  $k_2$  is the rate constant for slow release ( $\text{day}^{-1}$ ).

The relationship between the mass of constituent per unit plant biomass and the soil concentration is defined through the plant-to-soil concentration ratio (Peterson 1983)

$$q_b = K_B q_1 \quad (6-14)$$

In the definition of the plant-to-soil concentration ratio,  $K_B$  (dimensionless), given in Equation 6-14 is assumed, though there are some questions of whether it is consistent with reported data. The mass of the soil is usually expressed on a dry weight basis but results based on both dry and wet (fresh) weights for crops have been reported. Further, the soil constituent mass likely includes both the aqueous and sorbed concentrations in the soil sample.

With these results, Equation 6-11 may be written

$$C_T = \rho_b q_2 + [(\rho_b + \rho_B K_B) F K_d + \phi (S_w + S_a K_H + S_o K_o)] C_w \quad (6-15)$$

where Equation 6-13 is used to model the changing concentration of the slowly released constituent.

### Mass loss rate from the source zone

The right side of Equations 6-9 and 6-10 represents the mass loss rate from the source zone from leaching, volatilization, degradation, and biological uptake. These are written in the form of first-order rate expressions. Explicitly, the right side of Equation 6-9 is written

$$- \Lambda C_w A L = -(\lambda_L + \lambda_V + \lambda_D + \lambda_B) C_w A L \quad (6-16)$$

Each of the loss rate coefficients is based on a physicochemical description of the loss process.

The leachate loss-rate coefficient is defined by

$$\lambda_L = \frac{u}{L} \quad (6-17)$$

where  $u$  is the water volumetric flux (Darcy velocity) through the source zone (m/d). With this formulation, the advection flux from the source zone is written as follows:

$$\lambda_L C_w A L = u C_w A \quad (6-18)$$

The volatilization first-order constant can be expressed in terms of the effective vapor diffusivity as follows:

$$\lambda_V = \frac{D_e K_H}{L L_v} \quad (6-19)$$

where  $D_e$  is the effective vapor diffusivity through soil ( $\text{m}^2/\text{day}$ ), and  $L_v$  is the diffusion length for vapor diffusion (m). With this formulation,

$$\lambda_V C_w A L = \frac{D_e C_a}{L_v} A \quad (6-20)$$

which is Fick's first law for vapor diffusion through soil with effective diffusion coefficient  $D_e$ , source vapor concentration  $C_a$ , concentration zero at the ground surface, and effective diffusion length  $L_v$ . The length for vapor diffusion will be time dependent. However, for our development here, we will assume an average constant value of  $L_v$ .

The first-order decay coefficient  $\lambda_D$  is related to the constituent degradation half-life  $T_{1/2}$  through

$$\lambda_D = \frac{\ln(2)}{T_{1/2}} \quad (6-21)$$

Finally, the biomass uptake loss rate coefficient is

$$\lambda_B = \frac{\dot{m} K_B K_d F}{L} \quad (6-22)$$

where  $\dot{m}$  is the biomass harvest rate (kg biomass per  $m^2$  per day). With this formulation, the biomass loss rate is expressed by the following

$$\lambda_B C_w A L = \dot{m} A q_B \quad (6-23)$$

#### Sequestered soil model

Equations 6-10 and 6-15 may be combined to give

$$\rho_b \frac{dq_2}{dt} + [(\rho_b + \rho_B K_B) F K_d + \phi (S_w + S_a K_H + S_o K_o)] \frac{dC_w}{dt} = -\Lambda C_w \quad (6-24)$$

Equations 6-24 and 6-13 can be solved simultaneously, and the concentrations in the soil phase can be related to the concentrations in the pore water for any time  $t$ . The solution to these equations for the soil and porewater concentrations as a function of time for the various parameters that appear in these equations is presented in the appendix to this chapter (p 248).

Figure 6-3 shows how the slow release of a fraction of the sorbed contaminant can impact the porewater concentrations. The equations from the appendix to this chapter were used to calculate the curve for  $k_2 = 0.1 \text{ yr}^{-1}$ . For Figure 6-3, it was assumed that the fraction of contaminant available was originally 50% of the total sorbed amount. It was assumed that the contaminant, naphthalene for this example, was in contact with the soil (aged) for a sufficient amount of time so that the slowly released fraction is in equilibrium with the pore water. As weathering of the contaminant in the soil begins to occur through volatilization, degradation, leaching, and other processes, the concentrations in the soil and pore water will decrease with time. As the soil concentrations decrease, the corresponding porewater concentrations will be affected by the slow release of the contaminant from the sequestered fraction as shown by the 3 curves in Figure 6-3.

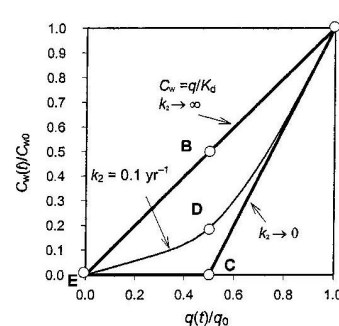


Figure 6-3 Effect of slow release on the porewater concentrations as a naphthalene-contaminated soil is weathered. The initial soil and porewater concentrations are  $q_0 = 12.3 \text{ mg/kg}$  and  $C_{w0} = 1.9 \text{ mg/L}$ , respectively, and  $K_d = 6.5 \text{ L/kg}$ . Equations and parameters for determining curve A-D-E are given in the appendix (p 248).

If the release rate of the slow fraction is fast relative to the weathering processes within the source, then the porewater concentrations will always be related to the soil concentrations by a constant value of  $K_d$  and will follow the path A-B-E shown in Figure 6-3. When the release rate for the sequestered fraction is slow, however, the porewater concentrations will be less for a given soil level as the weathering processes proceed. If the slow release rate constant is zero (i.e., the desorption process is irreversible), then for a soil that originally had 50% of the naphthalene sequestered, the porewater concentration would follow a path given by A-C in Figure 6-3. At point C, the porewater concentrations would be 0. In other words, the effective  $K_d$  for the sorbed amount remaining at point C would be infinite.

For many soils, the release rate constant will be finite. The effect of a finite release rate on porewater concentrations for a given soil concentration will be dependent upon how this rate of release compares with the rate of loss of contaminant from weathering. For a slow rate constant that is small relative to the weathering processes, the relationship between the porewater and soil concentrations will follow a path like that given by A-D-E in Figure 6-3. Curve A-D-E was determined using the equations presented in the appendix (p 248) for porewater and soil concentrations. Calculations were carried out with a rate constant  $0.1 \text{ yr}^{-1}$ . (Values for the

various parameters for these equations that would be expected to characterize typical rates of volatilization, degradation, and leaching for naphthalene are also presented in the appendix. A comparison of Points B and D shows the effect that a slow desorption rate constant of  $0.1 \text{ yr}^{-1}$  would have on porewater concentrations when the majority of the available contaminant has been removed from the soil, and all that remains is the slowly released fraction.

From Figure 6-3, it should also be clear that contaminated soil would have values of  $F$  that can range from 0 to 1. The actual value of  $F$  will depend upon how much weathering has occurred and how much of the contaminant was originally sequestered in the soil.

It is instructive to decouple the slow and fast release processes because a very simple equation (simpler than those presented in the appendix to this chapter) describes the relationship between soil and porewater concentrations for slow release. The point on the curve will be described when the release from the soil becomes rate limiting, that is, the readily available fraction has been removed.

We can describe the porewater concentration by neglecting the rate of change in the aqueous concentration (see Equation 6-24). The following relationship between the concentration in the soil and the porewater concentration is obtained:

$$\frac{q_2}{C_w} = K_d(1-F) \left[ 1 + \frac{\lambda_L + \lambda_D + \lambda_V + \lambda_B}{K_d(1-F)\rho_b k_2} \right] \quad (6-25)$$

Alternatively, the porewater concentration can be measured for a given soil concentration by rearranging Equation 6-25 as follows:

$$C_w = \frac{q_2}{K_d(1-F) \left[ 1 + \frac{\lambda_L + \lambda_D + \lambda_V + \lambda_B}{K_d(1-F)\rho_b k_2} \right]} \quad (6-26)$$

Equation 6-26 shows more simply the relationship between porewater and soil concentrations for a given value of the slow rate constant  $k_2$ . If the rate of release is slow (characterized by a long half-life for the sequestered fraction) relative to other processes such as leaching, degradation, volatilization, or other processes that might occur in the source region (e.g., plant or invertebrate uptake), then the second term (in the brackets) becomes large relative to the first and enhances the "apparent" distribution coefficient between soil and pore water. Note that if the rate constant is large (short half-life) relative to the corresponding constants for leaching, degradation, etc., then the partition coefficient approaches the normal equilibrium partition coefficient that characterizes the partitioning of the available contaminant.

Equation 6-26 can be used to estimate the range of slow release constants that will be significant with respect to the exposure of a chemical to various environmental receptors.

To illustrate when  $k_2$  becomes important, consider the release of some representative compounds that reflect reasonable ranges of volatility and sorption potential.

### Slow release relative to leaching and volatilization

Assume the following values for source region parameters:

$$\begin{aligned} L &= 1 \text{ m} \\ u &= 0.2 \text{ m/y (sandy loam)} \\ S_w &= 0.40 \\ \phi &= 0.35 \\ L_v &= 0.3 \text{ m} \end{aligned}$$

Some physicochemical properties of selected organic compounds are given in Table 6-1.

Table 6-1 Physicochemical properties of selected organic compounds\*

| Compound         | $K_{oc}$<br>L/kg | $D_{air}$<br>cm <sup>2</sup> /s | $D_{water}$<br>cm <sup>2</sup> /s | $K_u$ dimensionless |
|------------------|------------------|---------------------------------|-----------------------------------|---------------------|
| <i>o</i> -Xylene | 3.63E+02         | 8.70E-02                        | 1.00E-05                          | 2.13E-01            |
| Naphthalene      | 2.00E+03         | 5.90E-02                        | 7.50E-06                          | 1.98E-02            |
| Anthracene       | 2.95E+04         | 3.24E-02                        | 7.74E-06                          | 2.67E-03            |
| Benzo[a]pyrene   | 1.02E+06         | 4.30E-02                        | 9.00E-06                          | 4.63E-05            |

\*Attachment C, USEPA soil screening-level guidance (1996).

### Slow release relative to leaching, volatilization, and degradation

Using the values presented above and in Table 6-1, one can estimate when slow release is important relative to the various loss processes that occur in the source zone. In Table 6-2, half-lives for slow releases correspond to losses for leaching, volatilization, and degradation. These were determined by equating the second term in the brackets in Equation 6-26 to 1 and translating the rate constant,  $k_2$ , to a half-life ( $T_{1/2} = \ln(2)/k_2$ ).

**Table 6-2** Half-lives (years) necessary for slow release to be important relative to various loss processes in the vadose zone

| Compound         | Leaching              | Volatilization      | Degradation |
|------------------|-----------------------|---------------------|-------------|
| <i>o</i> -Xylene | 5                     | 0.1                 | 2.5         |
| Naphthalene      | 3(10)                 | 10                  | 1.5         |
| Anthracene       | 4(10 <sup>3</sup> )   | 2(10 <sup>3</sup> ) | 6           |
| Benzo[a]pyrene   | 1.5(10 <sup>6</sup> ) | 3(10 <sup>6</sup> ) | 16          |

Table 6-2 shows that slow release of contaminants from soils will impact the porewater concentrations calculated by the conventional  $K_d$  approach when the rate is slow enough relative to those loss processes. For example, if the only loss process occurring in the vadose zone was loss from leaching due to infiltration, then the half-life for slow release for a compound with  $K_d$  values similar to xylene would have to be of the order of 5 to 10 years to have an impact on porewater concentrations. For more strongly partitioning compounds, required half-lives would be longer in proportion to the partition coefficient of the compound. However, when degradation and/or volatilization losses are considered, there will be cases when smaller half-lives (larger values of  $k_2$ ) for the slow release of contaminants from soil yield lower porewater concentrations for a given soil concentration. To put these values in perspective, half-lives for slow release reported in the literature range from days to several months (Ball and Roberts 1991; Brusseau et al. 1991; Grathwohl and Reinhard 1993; Farrell and Reinhard 1994; Kan and Tomson 1994; Pignatello and Xing 1995; Williamson et al. 1998; Rixey et al. 1999). It should be made clear, however, that the lowest values of the rate constants reported in the literature have been limited by the duration of laboratory experiments. Note that, for the calculations given in Table 6-2, it was assumed that the source of contamination is close to the surface, and for contamination further down in the vadose zone, the losses due to volatilization will be considerably reduced relative to those represented in Table 6-2.

#### Incorporation of residual nonaqueous-phase liquid into the source term

In general, NAPLs almost always are present in soils with organic chemical concentrations greater than 10,000 mg/kg, and often are present in soils containing room temperature organics exceeding concentrations on the order of 100 mg/kg. Feenstra et al. (1991) provide a method to estimate if NAPLs are present in soils based on equilibrium partitioning relationships, and a variety of field techniques are available to help determine if NAPLs are present in soil samples. In practice, NAPLs are probably present in contaminated soils at many or most petroleum hydrocarbon and chlorinated solvent sites.

The presence of NAPLs is important to the source term in risk assessments for several reasons:

- partitioning between the NAPL phase and the aqueous and vapor phases is controlled by different relationships than partitioning between the aqueous, sorbed, and vapor phases in soils that do not contain NAPLs;
- because of the relatively large mass associated with NAPLs, chemicals in soils containing NAPLs can have a longer half-life than chemicals in soils without NAPLs;
- many NAPLs contain relatively inert organic compounds (e.g., long-chained alkanes in gasoline) that act as a relatively large reservoir of organic carbon that will slowly release soluble contaminants from the NAPL to the aqueous phase.

#### Nonaqueous-phase liquid–water partitioning

When infiltrating water comes in contact with residual or free-phase NAPL in the soil, the aqueous-phase concentration can be estimated from the concentration in the NAPL phase with  $K_o$ , the NAPL (or "oil") partition coefficient. The partition coefficient  $K_o$  can be based on actual measurements of NAPL-containing soils, it can be approximated using  $K_{ow}$ , or it can be calculated more rigorously from the following equation (Cline et al. 1991; Lane et al. 1992):

$$K_o = \frac{C_o}{C_L} = \frac{1}{\gamma_i^o} \frac{MW_i \times 10^6}{MW_o S_i^{aq}} \quad (6-27)$$

where  $\gamma_i^o$  is the activity coefficient of the chemical in the oil phase (as in Raoult's Law; unit less; typically assumed to be  $\rho_o$  is the oil density (g/mL),  $S_i^{aq}$  is the subcooled liquid solubility of chemical compound in water (mg/L),  $MW_i$  is the molecular weight of chemical compound, and  $MW_o$  is the molecular weight of oil phase. Note that the aqueous-phase concentration ( $C_L$ ) is often approximated by multiplying the pure-phase solubility by the mole fraction of the contaminant in the NAPL.

Banerjee (1984) and Broholm and Feenstra (1995) have used experimental evidence to conclude that the effective solubility relationship produces reasonable approximations of effective solubilities for mixtures of structurally similar compounds and that the relationship works best for binary mixtures of similar compounds. In general, the method is appropriate for many environmental studies for which there are many other uncertainties (Pankow and Cherry 1996).

For complex mixtures (e.g., multiple identified and unidentified solvents, or mixed fuels and solvents), it is necessary to estimate the weight percent and an average molecular weight of the unidentified fraction of the NAPL before the calculation

can be completed. For example, a molecular weight of 90 to 100 is typically used for gasoline. Pankow and Cherry (1996) provide an example of these calculations for a mixture of chlorinated and nonchlorinated compounds.

With this partition coefficient, the total concentration of the contaminant dissolved in the leachate remains constant, even if the total concentration of the NAPL in the soil increases. Aqueous-phase concentrations will increase together with soil concentrations only while the soil contaminants are sorbed (no NAPL). With NAPL present, the leachate contaminant reaches a maximum concentration determined by the mole fraction of the contaminant in the NAPL and the aqueous solubility of the contaminant. This is shown in Figure 6-4.

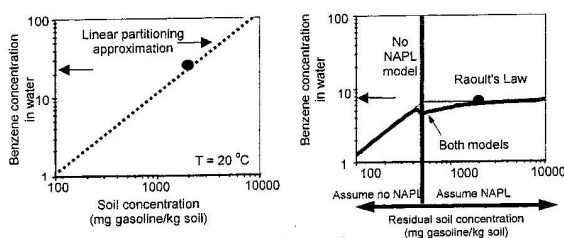


Figure 6-4 Conventional linear partitioning model compared to combined NAPL model

For example, soils with residual gasoline concentrations of 2000 mg/kg would yield a predicted aqueous-phase benzene concentration of 25 mg/L using the conventional linear partition approach, as shown in Figure 6-4. Using the NAPL partition relationship, the predicted aqueous-phase benzene concentration would be about 6 mg/L. Therefore, accounting for the presence of NAPL would result in a 4-fold reduction in the predicted aqueous-phase concentration. The error would increase for soils with higher concentration, while no error would result in use of linear partitioning alone for soils with concentrations below the level where NAPL is expected (typically total organic chemical concentrations on the order of a few hundreds of mg/kg).

Note that application of the effective solubility relationship to field sites requires the assumption of homogeneous soils and homogeneous NAPL distribution. However, at many field sites, the distribution of NAPL is heterogeneous, and some flow lines do not come into contact with NAPL, and therefore dilute the bulk leachate. Therefore, at actual field sites, the average leachate concentration reflects

the contribution of high-concentration flow lines that came into contact with NAPL and non-NAPL flow lines at much lower concentrations.

### Impact of nonaqueous-phase liquids on source mass

The impact of NAPLs on the distribution of contaminants in soils can be seen in Figure 6-5, where 100 mg of benzene in 1 L of soil has been assumed under 2 different conditions: first, a soil with no NAPL, and second, a soil with NAPL. For this calculation, the soil is also assumed to have a natural organic C fraction of 0.005 g C/g soil. Using Equation 6-5 for the bulk water coefficient that describes the relationship between the total contaminant concentration in the soil and the pore water, the distribution of benzene in the water, soil (sorbed to the organic C on the soil), and NAPL was determined. Note that the calculation assumes that the NAPL is a mixture of benzene and other chemicals, with the other compounds having an average molecular weight of 150 g/mole. The NAPL-water partition coefficient was determined from Raoult's Law using Equation 6-27 with  $\gamma_1 = 1$ .

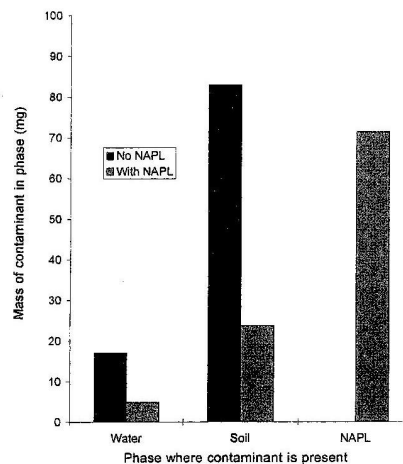


Figure 6-5 Distribution of benzene mass among various phases for soils with and without residual NAPL (Basis: Total concentration of benzene = 100 mg/L of media.)

As can be seen in Figure 6-5 for the "no NAPL" case, most of the benzene (a total of 82 mg) is in the soil (sorbed) phase, with only 18 mg in the water phase. When NAPL is present, however, the majority of the benzene is in the NAPL (71 mg) with lesser amounts (24 mg) in the soil phase and only a small amount in the water phase (5 mg). In other words, for a fixed amount of contamination in soil, the presence of a NAPL changes the relative distribution of the contaminant among the different phases (water, sorbed, and NAPL) so that water-phase concentrations are lower when NAPL is present.

This type of calculation was extended for 5 different contaminants (benzene, toluene, *p*-xylene, naphthalene, and phenanthrene) in Table 6-3, using the same assumptions (100 mg contaminant/L soil, fraction natural organic C on soil = 0.005). The table shows that for each of the 5 contaminants, the water-phase concentration is lower when NAPL is present, compared to the no-NAPL case. For a fixed amount of contamination in soil, the presence of NAPL will reduce the resulting concentration of contaminants in the water phase, that is, the contaminant is less available to the aqueous phase.

**Table 6-3** The effect of NAPL on water-phase concentrations (Basis: Total concentration of contaminant = 100 mg/L soil; fraction of natural organic C in soil = 0.005)

|                  | Molecular weight | $K_{ow}$ ( $L_o/L_a$ ) | Solubility (mg/L) | Concentration in water phase (mg/L) |                |
|------------------|------------------|------------------------|-------------------|-------------------------------------|----------------|
|                  |                  |                        |                   | Soil without NAPL                   | Soil with NAPL |
| Benzene          | 8.1              | 135 <sup>e</sup>       | 1780              | 38.3                                | 34.9           |
| Toluene          | 92.1             | 490 <sup>e</sup>       | 515               | 38.3                                | 9.1            |
| <i>p</i> -Xylene | 106.2            | 1413 <sup>f</sup>      | 198               | 13.8                                | 3.1            |
| Naphthalene      | 128.2            | 2290 <sup>e</sup>      | 31                | 8.6                                 | 1.5            |
| Phenanthrene     | 178.2            | 37,150 <sup>e</sup>    | 1.1               | 0.5                                 | 0.1            |

#### Impact of nonaqueous-phase liquids on contaminant release

While NAPLs in soils greatly increase the mass of contaminants in soil, they also restrict the release of these contaminants to other phases. Both the vapor-phase and aqueous-phase partitioning are based on the mole fraction of the contaminant in the NAPL, and as contaminant is reduced, the mole fraction is reduced. Therefore, the mass flux of contaminants leaving the source zone over time (either via vaporization or dissolution) will be reduced over time.

In other words, the NAPL phase acts as if the organic C content of the soil was greatly increased. If a soil with a natural organic C content of 0.001 g C/g soil (0.1%) is contaminated with NAPL so that only 5% of the pore space is filled with

NAPL (5% residual saturation), then the total organic C content of the soil is increased by 0.009 g C/g soil. The total of 0.010 g C/g soil is 10 times the original C content of the soil. Furthermore, the effective partitioning of an organic-based NAPL is larger than an equivalent amount of natural organic C, as it may be assumed that only a fraction, approximately 60%, of the natural organic C is available for sorption (Olsen and Davis [1990]) note that  $K_{oc} = 1.724 K_{om}$ , where  $K_{om}$  is the partition coefficient for organic matter).

The key partitioning relationships described above are based on the amount of organic C in the soil where many organic contaminants will be sorbed (in the case of natural organic C) or dissolved (in the case of NAPL). When NAPL invades the soil, the total mass of the contaminants is increased, but extremely rapid release rates do not occur as the NAPL-aqueous-phase partitioning moderates the release of the soluble contaminants to the aqueous phase. In summary, the presence of NAPL changes both the magnitude of the contaminated soil problem (greatly increases the mass to be managed) and the nature of contaminant release to the environment by moderating release compared to classic linear desorption.

#### Parameter Estimation

If it is assumed that there is not a mobile (or potentially mobile) NAPL phase in the contaminated source area, and that facilitated transport mechanisms are unimportant in subsurface environments, then the most significant considerations for determination of release from a source are the partitioning behavior, especially relative to desorption, and the release rate of chemical from the soil matrix. Partition coefficients are typically estimated from 1) a default or measured soil organic carbon fraction and the organic carbon-water partition coefficient for the chemical of interest or 2) a measurement based on the standard American Society for Testing and Materials (ASTM) sorption method. As discussed in the previous sections, the calculation of release from field soils based on either a calculated or measured sorption partition coefficient is likely to overpredict, perhaps significantly, chemical release from the soil-waste matrix. In addition, the chemical release process can be kinetically limited, further affecting the accuracy of prediction of release.

In this section, methods will be suggested to obtain the parameters needed for improved prediction of release from the source. These methods are based on the empirical observation that release from field soils is not instantaneous but tends to occur over long periods of time. Although the mechanisms for this behavior are complex and not well-defined, it is useful to depict the release behavior as occurring from a readily releasable compartment (releasing the readily releasable fraction  $F$  in a relatively short time) and from a slowly releasable compartment (releasing the slowly releasable fraction over a relatively long period of time at a



slow release rate  $k_2$ ). Though mechanistically simplistic and inaccurate, this depiction is useful for developing improved estimates of kinetically constrained release while still being conservative and environmentally protective. It also allows for a reliable measurement of a partition coefficient to be made based on a desorption experiment in a reasonable period of time (1 or 2 days). Specifically, methods suggested for improved partition coefficient estimates are

- measurement of field soil organic C content,
- estimation of partition coefficients for soils containing residually trapped NAPL using Raoult's Law,
- desorption method for measurement of site-specific partition coefficient,
- estimation and measurement of  $F$ , and
- estimation and measurement of  $k_2$ .

### Improved partition coefficients

The first step that can be taken to improve a partition coefficient estimate is typically to use a laboratory measurement of soil organic C. Standard laboratory methods for soil organic C are adequate.

A further refinement of the estimation is appropriate for soils containing residually trapped NAPL (total petroleum hydrocarbons or oil and grease concentrations on the order of 0.1% to 0.2%). A better  $K_d$  value is calculated by adding the  $K_{oc} \times f_{oc}$  value to the  $K_o \times f_o$  value (Rutherford et al. 1997). The  $K_o$  value is obtained by Raoult's Law knowing the subcooled liquid solubility of the chemical of interest and the average molecular weight of the NAPL phase (Equation 6-27). The molecular weight can be estimated from composition data or boiling point data or can be measured using osmometry.

A further possible refinement is to measure an experimental partition coefficient for a field sample of the source. The standard ASTM procedure for measuring a partition coefficient involves sorption of a chemical from a solution onto a soil sample. The values determined for field soils by this method may be significantly less than values measured for desorption from field soils, especially if the field soils contain sequestered and weathered residues. This leads to an overprediction of partitioning from the soil to water. Because of slow release from these soils, an unreasonably long desorption experiment may be required to derive reliable partition coefficients. If a relatively short desorption experiment of 1 or 2 days is conducted, it is possible that only a fraction of the chemical is available to be released. If this is not accounted for in the calculation of a partition coefficient, the result will be in error.

To address this situation, an alternate procedure is suggested, in which the partition coefficient for the readily available fraction is measured in a reasonable time period such as 1 or 2 days. The assumption in using this approach is that there is a readily available fraction of chemical in equilibrium with the soil that determines

the porewater concentration, and that the partition coefficient for the readily available fraction is relatively constant with concentration (linear desorption isotherm). If it can be determined what the readily available fraction is in a 1- or 2-day time period, then by a mass balance, an estimate of the partition coefficient for the sample, can be obtained. A second experiment is needed to determine the readily available fraction in order to develop a partition coefficient estimate normalized to the total soil mass.

The following is a brief description of 2 possible approaches for which procedures need to be developed and validated. In the first approach, 2 water desorption experiments on a split sample are conducted, one with a resin sorbent to remove the chemical from the water phase. The partition coefficient normalized to the entire soil mass can be calculated from a material balance of the 2 experiments, assuming the readily available fraction of chemical in the soil is in equilibrium with the water phase.

Alternatively, the second approach uses multiple batch desorption experiments of split samples at different soil-to-water leachate ratios. A material balance of these experiments at different soil-to-water leachate ratios will allow an estimate of the equilibrium porewater concentration, which is generally the number of interest. This estimate of equilibrium porewater concentration can be obtained without knowing the starting total concentration of chemical in the soil sample. If the starting soil concentration is known, an estimate of the partition coefficient can be obtained as well.

It must be noted that these methods assume that the chemical in the sorbed and water phases is in equilibrium in the field. If a soil is highly weathered and biodegraded in the environment, then these methods may not yield the maximum possible porewater concentration. Preliminary studies show that these methods may underestimate the maximum porewater concentration slightly, but in no case by more than a factor of 2. These methods are an improvement over methods that are typically used to obtain desorption partition coefficient measurements. However, their usefulness may be limited for very low solubility chemicals because of achievable detection levels in the water phase.

### Estimation and measurement of $k_2$

The first approach involves estimation of mass diffusion through nanopores (Wu and Gschwend 1986; Carroll et al. 1994). This approach requires approximations of soil parameters such as pore size and tortuosity. It may be possible to estimate  $k_2$  within 1 or 2 orders of magnitude using this approach.

The preferred approach would be to experimentally measure the slow release rate. It must be recognized that this may require unreasonably long time periods because of the slow desorption mechanisms discussed throughout this publication. One experimental approach involves the measurement of leaching from a fixed

bed. The  $k_2$  value can be derived from the data by using the standard mathematical formulation for leaching from a porous media bed, modified to incorporate a 2-compartment mathematical model for the release term in the mass transfer balance (Garg 1998). This second approach involves the use of multiple batch aqueous and resin extractions carried out for different lengths of time. Each extraction provides a measurement of the mass released (available fraction) for the time period. A plot of this release data against time is then fit to a first-order rate expression to yield the  $k_2$ .

Both of these methods may require several months to measure slow rates as low as  $0.0001 \text{ day}^{-1}$ . It may be possible to reduce the time by using supercritical fluid extraction, co-solvents, or elevated temperatures. More work is needed to correlate these accelerated methods to actual field leaching behavior before they can be used for determining  $k_2$ .

### Practical Utility of Transport Models in Risk Characterization

#### Application of simple models

Transport models can be used in risk characterization and establishment of soil-quality limits at several levels or contexts. At the lowest level, simple equilibrium assumptions using linear partitioning are used along with conservative assumptions related to source size and location to relate source concentrations to some concentration at a receptor. An example of this is the development of risk-based screening levels (RBSLs in risk-based corrective action [RBCA] Tier 1) or soil-screening levels (USEPA Superfund SSLs) for soil. RBSLs and SSLs are developed based on a risk-based concentration limit for groundwater or air, a default partition coefficient, and a default DAF. This is essentially a trivial transport application as the concentration in the transport media (e.g., groundwater or air) is given by equilibrium partitioning from an assumed infinite source. This may be useful for site management screening purposes for many sites, but it can result in unrealistic prediction of air or groundwater concentrations, or soil-quality limits. The information in this chapter provides straightforward approaches for refining this lowest-level estimate. In this case, the improved transport information is in the form of an improved estimate or measurement of partition coefficient. It is also possible to develop improved site-specific DAF values based on simplified transport methods and nomographs (Johnson et al. 1998).

A second level of use of the information in this chapter is improved representation of the release from a source that takes into account mass transfer and other kinetic limitations in field soils. This can be done in the context of development of site-specific soil-quality criteria, or the development of a site-specific risk assess-

ment. The methods outlined in this chapter provide guidance on implementing these approaches.

#### Biphasic release

This chapter suggests a method to model release from source areas that accounts for the biphasic (or multiphasic) slow release behavior exhibited for many field soils. It is concluded that this available or unavailable fraction approach provides a more accurate and useful method to define interactions and release in source areas. It is suggested that this method be formalized and incorporated into routine site management practice.

#### Incorporation of nonaqueous-phase liquids into risk characterization

Currently some soil models and risk assessment protocols (e.g., API 1994; Connor et al. 1997; ASTM 1998) do not incorporate NAPLs in the source-leachate calculations. Instead, these approaches make the assumption that soil contaminants exist in only 3 phases (vapor, aqueous, or sorbed), with no contaminants in the fourth phase (NAPLs). In general, this assumption of instantaneous equilibrium partitioning will tend to overestimate the contaminant mass transferred from the affected soil zone to infiltrating rainwater. Connor et al. (1997) showed that use of a 3-phase rather than a 4-phase partitioning relationship resulted in a conservative overestimation of leachate concentrations by a factor of 1.3 to 4.2 times, corresponding to residual NAPL saturations of 0.1% and 1%, respectively. Because most of the models and risk assessment protocols assume either an infinite source or perform a mass balance on the source using soil concentrations, the large mass associated with the NAPL phase is either directly or indirectly incorporated into these models.

In summary, 3-phase equilibrium partitioning is a convenient and common modeling assumption that simplifies transport modeling of contaminants from soil source zones. Use of slightly more complex modeling approaches that incorporate NAPL-leachate modeling will make improvements in leachate concentration estimates on the order of 5- to 10-fold. This can be significant for many site situations that contain mixtures of contaminants, for example, petroleum hydrocarbons.

#### Steady-state source assumption

One assumption routinely used for determination of soil-quality criteria and risk assessment transport and fate boundary conditions is that of an infinite steady-state source. This assumption typically leads to a gross overprediction of transport away from the source. More realistic estimates can be made using methods that account for transients and source depletion (Johnson et al. 1998). The slow release method

suggested in this chapter provides a significantly more accurate estimate of porewater concentrations than does the conventional infinite source assumption approach. It should be noted that if time-dependent release approaches are to be useful, the exposure duration for completed pathways must be known (or assumed).

### Incorporating erosion or particulate loss terms in source transport

At some sites, mechanical surface processes that move contaminated soils may be important drivers for evaluating ecological risk. Two key processes are surface erosion and particulate emission.

Soil erosion can be estimated using empirical relationships, such as the universal soil loss equation (USLE), that correlate soil type, rainfall, and other factors to erosion rate. In practice, the erosion rate estimates reflect any soil that is eroded, and does not account for subsequent deposition processes. In other words, if the erosion rate from the USLE is extrapolated to an entire watershed, the amount of suspended solids actually reaching the stream will be greatly overpredicted. Sediment delivery ratios are empirical relationships that show the fraction of eroded material that will be transported to receiving streams for watersheds of different area (Shen and Julien 1993).

A second general approach is to use runoff data from nonpoint source studies, such as the Nationwide Urban Runoff Program (NURP) (USEPA 1983). Field studies provide estimates of suspended solids concentrations and annual solids loadings measured in runoff from small study areas (typically 1 to 100 acres). The data, expressed as either concentration or loading per acre, can be used to estimate the amount of solids that are transported from soil source zones by water-driven processes.

The same rate-limited processes discussed previously (i.e., the biphasic release methodology) control the partitioning between contaminated soils and the aqueous phase (in this case, the runoff). While contaminants in suspended soils in runoff are available for transport on a macroscale (i.e., moving in the runoff), some are unavailable for immediate cross-media transport to the aqueous phase because of the hysteretic effects of sorption. The contaminants that are unavailable for cross-media transport to the aqueous phase may or may not be bioavailable, depending on how receptors are exposed to the contaminants (i.e., ingestion of water containing the contaminated sediments versus ingestion of aqueous-phase materials only).

Particulate emission is a wind-driven process that is currently incorporated into some risk assessment protocols (e.g., ASTM RBCA standard; ASTM 1998). For example, the ASTM methodology prescribes a generic value of  $6.9 \times 10^{-14} \text{ g/cm}^2 \times$

sec (about  $20 \text{ mg/m}^2 \times \text{year}^{-1}$ ) for a particulate emission rate. A site-specific method is outlined in USEPA's Soil Screening Guidance (USEPA 1996).

### Special situations

It must be noted that the suggested methods may not be applicable in certain site situations such as fractured rock, mobile NAPL phases that can transport much greater levels of contamination than can be transported by solute transport, and fractured clay systems. More detail on the third situation is provided below.

Recently, a new conceptual model for free-phase organic releases to fractured clay systems has been introduced (Parker et al. 1994; Pankow and Cherry 1996). With this conceptual model, relatively rapid rates of transport from the NAPL phase to the aqueous phase are proposed for systems where NAPL first penetrates vertical fractures in clays and then is trapped in the fractures. The high aqueous-phase concentration adjacent to the trapped NAPLs and the low concentrations within the trapped water in clays cause a large driving force for diffusion of the soluble contaminants into clays. Based on examples provided by Parker et al. (1994), large masses of soluble contaminants can be transferred from NAPLs to fractured clays (typical fracture spacing on the order of feet) in relatively short time periods (a few years). While this transport mechanism is reversible, the kinetics of the diffusion out of clay are very slow, because the driving force is typically much smaller. Therefore, fractured clays that have been exposed to vertical NAPL transport will serve as long-term sources of contaminants for long time periods and may be immune to most remediation technologies.

### Model validation

Finally, it should be noted it is always prudent to provide validation or ground-truthing for model predictions. It is noted that for some site situations, a few strategic samples (e.g., porewater analyses) may provide more reliable, more useful site management decision data more quickly and cost effectively.

### Transport and bioavailability

There are a number of issues that arise in developing models to describe the transport of contaminant mass from source regions, especially when these source term models include mass sequestration. One issue concerns the question of whether contaminant availability for transport always coincides with its bioavailability. While in many cases it does, the answer in general is negative. For example, if Pb is complexed with EDTA, then it is available for transport. It may even be consumed by soil organisms, but it is not bioavailable. Because it is strongly complexed, it will pass through organisms and not be absorbed or metabolized. A second example concerns chemicals that are surface complexed on soils and are not available for transport but can be bioavailable through secretion of enzymes that result in release of the chemical. Similarly, sequestered chemicals in soil can

be consumed by soil invertebrates and partially metabolized. NAPLs present a fourth example. Long-chain residual NAPLs are not available for transport, but there is evidence that soil microbes can go directly to the interface and promote the degradation of these molecules. Thus, while chemical availability for transport and chemical bioavailability include many similar characteristics, generally they should be considered separately on a case-specific basis.

### Preferential flow

Another factor that complicates the description of transport of contaminants from source regions is preferential flow. "Preferential flow" refers to the rapid movement of solutes through fractures, root holes, worm burrows, and other heterogeneities, at rates much greater than expected from consideration of the porous medium as a whole. Dyes and other chemical tracers have been used to study contaminant movement through the vadose zone. Kung (1990) notes that funneling due to heterogeneities may result in flow occurring through less than 1% of the soil. Unstable flow and fingering occurs in layered soils and may cause lateral spreading of contaminants. Factors such as these make flow and transport difficult to predict and measure; point samples can easily miss narrow fingers of solute. Unfortunately, there are no proven predictive models for vadose zone transport with preferential flow.

### Summary

This chapter discusses the major mechanisms that control the release of organic compounds and metals from their source zone in contaminated soils. The focus has been on how resistant desorption processes may influence contaminant transport and the assessment of risks from contaminated soils. It is noted that conventional methods of characterizing chemical partitioning may result in prediction of exposure concentrations that are too large, and when these methods are used to establish soil cleanup levels, the resulting requirements may be overly conservative (and thus overly expensive).

The chapter develops and presents a multiprocess sequestered source model for contaminated soils. This model incorporates biphasic desorption and residual NAPL, in addition to the processes of volatilization, leaching, and first-order biodegradation. The behavior of the model is shown through example, and various limiting conditions are discussed. Criteria show when application of the biphasic desorption model leads to significantly different predictions of aqueous-phase concentrations (Table 6-2) than use of conventional equilibrium partitioning models. However, a more complete characterization of the significance of biphasic

desorption and residual NAPL will require coupling of the sequestered source model with a contaminant transport model to evaluate the effects on predicted exposure concentrations available for interaction with organisms. Finally, methods for estimating parameters are described, and use and limitations of the models are discussed.

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## APPENDIX TO CHAPTER 6

## Continuity Equation for Contaminated Soil

$$A L \left( B_w \frac{dC_w}{dt} + \rho_b \frac{dq_2}{dt} \right) = - \left( u A C_w + \frac{D_e A K_H C_w}{L_v} + \lambda_D A L C_w \right) \quad (6-28)$$

where  $B_w = \phi (\Sigma_w + S_a K_H + S_o K_o) + \rho_b F K_d$ . Equation 6-28 may be simplified by writing

$$B_w \frac{dC_w}{dt} + \rho_b \frac{dq_2}{dt} = -\Lambda C_w \quad (6-29)$$

where  $\Lambda = \frac{u}{L} + \frac{D_e K_H}{L L_v} + \lambda_D$ . The slow release of mass satisfies the kinetic equation

$$\frac{dq_2}{dt} = k_2 [K_d (1-F) C_w - q_2] \quad (6-30)$$

Substitution of Equation 6-30 into Equation 6-29 gives

$$B_w \frac{dC_w}{dt} = \rho_b k_2 q_2 - [\Lambda + \rho_b k_2 K_d (1-F)] C_w \quad (6-31)$$

Equations 6-30 and 6-31 provide 2 coupled ODEs to find the porewater concentration and the sequestered soil concentration. To find the initial conditions, assume that the initial total concentration is  $C_T$ . Then the initial water concentration is

$$C_w(0) = \frac{C_T}{B_w + \rho_b K_d (1-F)} \quad (6-32)$$

and the initial sequestered soil concentration is

$$q_2(0) = K_d (1-F) C_w(0) \quad (6-33)$$

To simplify notation, write Equations 6-31 and 6-30 as

$$\begin{aligned} \frac{dC}{dt} &= \alpha C - \beta C \\ \frac{dq}{dt} &= \xi C - \eta q \end{aligned} \quad (6-34)$$

The solution to Equation 6-34 is

$$C(t) = \frac{1}{2\psi} \left\{ 2\psi C_o + [(\psi - \beta + \eta) C_o + 2\alpha q_o] (e^{\psi t} - 1) \right\} e^{-0.5(\beta + \eta + \psi)t} \quad (6-35)$$

where  $\psi = \sqrt{(\beta - \eta)^2 + 4\alpha\xi}$ .

The corresponding solution for the sequestered soil concentration is

$$q(t) = \frac{1}{2\psi} \left\{ [2\xi C_o + (\beta - \eta + \psi) q_o] e^{-0.5(\beta + \eta - \psi)t} - [2\xi C_o + (\beta - \eta - \psi) q_o] e^{-0.5(\beta + \eta + \psi)t} \right\} \quad (6-36)$$

Calculations for curve A-D-E in Figure 6-1 are developed using Equations 6-35 and 6-36.