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## CHAPTER 7

### Contaminant-Soil Interactions

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#### Introduction

The manner in which contaminants interact with soil is central to understanding their fate, transport, and bioavailability. Most contaminants of environmental concern interact with the organic or the inorganic portions of soil, a process called "sorption." The term "sorption" may be defined as the transfer of a chemical from one phase, such as water, to another phase, such as soil organic matter. It implies a general process of association with a stationary phase, where the precise physicochemical mechanism of interaction (e.g., adsorption, absorption, ion exchange, precipitation) either is not specified or is not known. The stationary phase can be either mineral, organic matter, or some nonaqueous-phase liquid (NAPL). Bioavailability and toxicity are generally associated with aqueous dissolved species, although there have been reports of direct uptake from the solid phase.

Studies show that the total concentration of contaminants in soil is not a good predictor of long-term bioavailability or toxicity. Chemical and biological test results provide valuable information on existing conditions in the soil, but only on a limited temporal scale. Chemical measurements usually determine chemical concentrations and availability at the time of sample procurement, while bioassays integrate chemical exposure over the duration of the toxicity test or the life span of the organism. These tests need to be coupled with models that can predict longer-term interactions between chemicals and soil components, providing methods for estimating the potential for chemical bioavailability to soil biota over extended periods of time (e.g., years).

Abiotic interactions of neutral organic compounds and inorganic ions with soils are described by sorption-desorption and precipitation-ion exchange models. Within the scope of this body of work, the goal of using these models is to help provide an estimate of the concentrations of these chemicals in the soil water that enable a risk assessment to be conducted to determine cleanup standards. As a better understanding of the mechanisms involved in the sorption or desorption process is achieved, the estimate of risk provided by current knowledge, models, etc., will come closer to the actual risk.

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Until recently, models to predict the sorption and desorption of organic and inorganic compounds involved standard kinetic and equilibrium solubility and transport relationships. These models adequately predict the interactions of the bulk of the contamination, often greater than 80%. However, it is the last 15% to 20% of the residual contamination that will have the greatest impact on risk assessment and therefore on the development of cleanup levels required. While this phenomenon is known to exist, there is neither a mechanistic rate nor an equilibrium model currently available for use in predicting the long-term release of this fraction into the soil water. This is due to the limited understanding and inability to identify the mechanisms that influence the release of this fraction under the variety of conditions present in contaminated soils.

While there is currently no model that can predict the rate or extent of release of this residual fraction, the knowledge that it exists has greatly expanded our understanding and evaluation of desorption effects. Standard practice has been to use a linear sorption isotherm to determine desorption, thereby overestimating the concentrations that could be released to the soil water. Models are needed that can provide a mechanistic interpretation of these processes and predict the long-term concentrations of components in the soil water and in the soil particle or soil organic matter.

Sorption and desorption have been modeled using a single linear isotherm, and numerous methods have been developed to estimate the numerical values of the linear partition coefficient constants (Lyman et al. 1990). Several researchers have reported a sorption-desorption hysteresis effect for both neutral organic and inorganic contaminants, wherein the desorption path is different from that of the sorption path, apparently regardless of equilibration time (Vaccari and Kaouris 1988; Fu et al. 1994; Kan et al. 1994, 1997, 1998; Yin et al. 1996; Huang and Weber 1997; Yin, Allen, Huang, Sanders 1997; Yin, Allen, Huang, Sparks, Sanders 1997; Chen et al. 1999). Hysteretic sorption and desorption has also been observed with nonsoil systems (Zawadzki et al. 1987; Hunter et al. 1995, 1996; Hunter 1996). In the past few years, it has been recognized that this hysteresis, or resistant residual, is probably not a simple complication of the linear model, but is "different" and is a consequence of some other interaction mechanism (Everett and Whitton 1952; Adamson 1990; Hunter et al. 1996; Linz and Nakles 1997; Chiou and Kile 1998; Graber and Borisover 1998; Schlebaum et al. 1998).

It is surprising that the existence of such a desorption-resistant residual phase, as a separate process, had not been recognized earlier. The failure to do so probably lies with both laboratory and field testing and their respective interpretations. In the laboratory, numerous researchers have reproduced similar linear sorption isotherms of organic chemicals to soil, and when these isotherms are normalized for organic C content of the soil, the partition coefficients are typically constant,

within expected experimental error (Hamaker and Thompson 1972; Schwarzenbach et al. 1993). Therefore, there were few reasons to suspect any other phenomena, such as the existence of additional sorption mechanisms. Also, laboratory experiments were typically conducted by spiking a soil sample with a compound, measuring the amount that sorbed, and then extracting the solid to recover the contaminant for mass balance. First, these spiking experiments were generally done within a day or 2, and it is now recognized that this is too short of a time to simulate field exposures and "develop" the resistant fraction. Secondly, few desorption experiments were performed; instead, it was tacitly assumed that sorption and desorption were reversible, that is, opposite of each other. Finally, failure of pump-and-treat and field modeling was generally ascribed to various uncertainties associated with soil heterogeneities, variations in flow, and biodegradation, to mention a few. In hindsight, there were numerous pieces of evidence that might have been interpreted as implying the existence of additional sorption and desorption mechanisms.

The practical importance of understanding the mechanism of physicochemical sorption and desorption to and from soils cannot be overstated. Once the fundamental processes responsible for resistant desorption are understood, it should be possible to use results from 1 or 2 simple tests, or assays, to predict contaminant release and bioavailability. A research goal should be to elucidate the mechanisms responsible for resistant sorption and desorption in terms of physicochemical or molecular parameters of the soil and of the contaminants.

## Soil Properties

### The universe of soils

For the purposes of this chapter, soils include any unconsolidated surface material, substantially of natural mineral origin, other than aquatic sediments. The exclusion of aquatic sediments is only for focus in this chapter and is not meant to imply that the scientific information presented does not apply to sediments; to a large extent it does. We specifically mean to include wetland (hydric) soils even though they may spend a substantial portion of the year submerged under water.

Assessments of contaminated soils, and related assessments of contaminant uptake or release, biological effects, and risks, will commonly involve soils that are not virgin, undisturbed topsoils. What will often be involved is a mixture of topsoils, deeper soils (from borrow pits or mines), and anthropogenic materials that have been commingled in conjunction with some purposeful activity such as urban or

industrial development, waste disposal and/or reuse, and agriculture. Specific examples of such "soils" would include

- native topsoils (undisturbed or disturbed),
- agricultural soils (with or without soil amendments; likely having pesticide residues),
- residential fill (i.e., fill or topsoil imported for use at a residential plot),
- urban fill (present in essentially all cities for developed land),
- industrial fill (used at most manufacturing and industrial sites),
- dredged aquatic sediments (which may have spent years in an upland disposal area or a near-shore confined disposal area, but then were selected for beneficial reuse as fill or cover material),
- mine tailings, and
- "manufactured" soils (i.e., blends of natural and anthropogenic materials specifically designed for use as topsoils or agricultural soils).

"Fill" can encompass a variety of materials from both virgin and secondary sites. The virgin sites would include "borrow" areas such as sand and gravel pits. The secondary sites might include any of the above listed soils except the native soils, as well as soils from sites undergoing demolition, abandonment, or redevelopment. In the latter case (i.e., secondary sites), there is a significant chance that waste materials and/or chemical contaminants have been purposefully or otherwise added to the soils. As would be expected, the fill material is commonly chosen on the basis of its cost, geotechnical properties (e.g., weight-bearing capacity), and/or drainage properties, not necessarily its cleanliness. Even when cleanliness is a concern, measures to protect against use of contaminated soils in fill operations may have been inadequate.

"Soil amendments," such as might be used for agricultural soils or manufactured soils, might include a variety of materials including manure, composted sewage sludge, composted or ground vegetation, peat moss, vermiculite, and chemicals intended to adjust the soil properties to enhance plant growth or stabilize contaminants (e.g., lime).

#### Soil constituents or phases

A native soil will consist of the following basic constituents or phases:

- inorganic minerals (in a wide variety of grain sizes),
- organic material (ranging from fresh plant and animal remains to highly weathered humic material),
- living plants and animals (including microbes),
- water (with dissolved minerals and organic C), and
- air.

However, the soils for which contaminant bioavailability assessments can be of interest may commonly include a variety of other materials and phases such as

- construction debris (wood, brick, cement, metal, and glass fragments),
- asphalt,
- coal,
- ash and soot,
- mine tailings,
- NAPLs, and
- tars.

Much of this foreign material may be present as very small particles, in addition to large fragments. Each of these anthropogenic materials may inherently contain, or act as sorbents for, chemical contaminants. Examples of NAPL materials commonly encountered are petroleum fuels (gasoline, diesel, heating oil, jet fuel), industrial oils and lubricants, transformer oils (including some with polychlorinated biphenyls [PCBPs]), and chlorinated solvents (e.g., trichloroethylene and perchloroethylene (Zawadzki et al. 1987). Highly weathered NAPL materials may exist as a thin film on the soil particles, evident only as a dark stain (with or without odor) on the soils. This NAPL material is generally considered to take up and release organic contaminants via the processes of dissolution, that is, a liquid-liquid partitioning (assuming water is present in the soil) rather than a solid-liquid partitioning.

It is important when conducting soil sorption and desorption studies for selected contaminants to have a good understanding of the different materials and phases present in the soil. Most of the characterization that is needed often can be accomplished by an experienced geologist during the excavation of test pits or soil borings at the site. Identification is made visually based on color and texture (and odor for some NAPLs). More definitive identifications may require specialized chemical or microscopic analyses of the soil. In unusual cases, electron microscopes (microprobes) can be used to chemically characterize (via elemental analysis) the different phases.

#### Important physicochemical properties of soils

There are a number of physicochemical properties of soils that are known to be important in understanding—and modeling—the nature and extent of chemical sorption and desorption to or from the soil. Table 7-1 provides a list of these parameters, segregating those dealing with the sorption of organic and inorganic chemicals. Each list is further subdivided into "primary importance" and "secondary importance" groups. These are the parameters that may need to be measured in soils from the site of interest in order to carry out general assessments of the extent of sorption and/or the desorption modeling described later in this chapter.

**Table 7-1** Soil properties important for understanding contaminant-soil interactions

Parameter	Importance
<b>Organic chemicals</b>	
<i>Primary importance</i>	
Organic carbon content ( $f_{oc}$ )	Controls the extent of sorption (especially if $f_{oc} \geq 0.1\%$ by weight)
Clay content or surface area	May control the extent of sorption (especially if $f_{oc} < 0.1\%$ )
Temperature	Affects rate and extent of sorption and desorption
Moisture content	Controls mechanism and extent of vapor sorption
<i>Secondary importance</i>	
Characteristics of organic C	Characteristics include aromatic or aliphatic character, polarity, content of natural carbon black or soot (from forest fires), will affect extent of sorption
Aqueous phase cosolutes, dissolved organic matter or nonsettling particles	Presence may diminish extent of sorption to soil
Presence of biota	May affect the extent of sorption or apparent desorption and potential reactivity
<b>Inorganic chemicals</b>	
<i>Primary importance</i>	
Soil pH	Controls many speciation and precipitation reactions
Redox potential	Controls oxidation-reduction reactions
Cation exchange capacity	Controls the extent of sorption by ion exchange
Temperature	Affects rate and extent of sorption and desorption
Presence of key soil phases: organic matter, iron oxides, and manganese oxides	Controls nature and extent of sorption
Solution chemistry (e.g., presence of complexing ligands such as carbonate, sulfide, and phosphate)	Controls extent of complexation and precipitation
<i>Secondary importance</i>	
Presence of biota	May affect the extent of sorption

### Soil heterogeneity

Given an understanding of the various origins and phases of "soils" as defined above, it should not be surprising that the concentrations of the various phases, and the concentrations of the chemical contaminants of interest, will be highly variable over both horizontal and vertical dimensions. Also, there will be significant variability in the particle size distribution, and associated soil porosity and moisture retention characteristics. Extreme variability may even be seen in samples as small as 1 gram taken adjacent to one another at a given site. Because many chemical analyses use only about 1-gram aliquots for analysis, it is clear that soil characterization must either include carefully composited or homogenized samples or a large number of samples. Geostatistics can provide guidance on selection of the appropriate sample size needed to obtain specified confidence levels on the means. The use of homogenization (e.g., grinding, sieving) that involves a change in the natural grain size of the soil particles may lead to altered results of any subsequent sorption or bioavailability tests, and thus should be undertaken with due consideration.

### Sorption and Desorption of Organic Contaminants

#### Introductory remarks

The main emphasis in this section will be on neutral organic compounds because they are the most common; however, many of the same principles apply as well to ionic and ionizable compounds. "Sorption" is defined in the broad sense as the association of contaminant molecules with nonfluid, or stationary, phases. "Fluid phase" refers to the soil solution or the soil atmosphere. "Stationary phase" refers to both solids and NAPLs adhering to or filling pores of the solids. Thus, sorption includes adsorption on surfaces, partitioning into natural organic matter, condensation (liquefaction or crystallization) in the pores of particles, and partitioning into NAPLs associated with the solid phase.

The principal factor governing contaminant bioavailability at any instant is its concentration—more accurately, its chemical potential—in the fluid phase in contact with the receptor membrane. The fluid-phase concentration is governed by thermodynamic and kinetic parameters specific to the contaminant-soil-fluid-receptor system and may or may not vary during exposure. In general, the rate of change in the fluid-phase contaminant concentration is a function of the forward and reverse rates of transport across the receptor-membrane interface (uptake and depuration) and the forward and reverse rates of transport across the particle-fluid interface (sorption and desorption). Assimilation by the receptor may be rate limited by receptor uptake from the fluid phase or by desorption from particles, and the rate-limiting step may change during the exposure. At present, the rates of sorption and desorption from soil particles are poorly predictable on the basis of



easily obtainable information, such as total contaminant concentration and typical soil properties.

#### "Available" and "sequestered" states

As is often the case, the contaminant is not rapidly equilibrated between the stationary and fluid phases on time scales appropriate to the exposure period (Pignatello and Xing 1996). Hence, with respect to a given receptor, there exist "available" and "sequestered" states of sorbed molecules (Alexander 1995). No sharp distinction exists between the 2—rather there appears to be a continuum of sorbed states, from instantaneously in equilibrium to very slowly in equilibrium with the fluid phase. Some fraction may even be considered to be completely immobilized in the stationary phase. An understanding of the factors that govern this complex distribution has evolved into a major branch of environmental science. It must be clearly understood that the sequestered fraction is highly context specific—that is, it depends on the contaminant, soil, receptor, mode of uptake, and duration of uptake. What is considered sequestered for one organism may be wholly or partially available for another. It is this specificity that results in difficulty in the development of predictive models.

In cases where the fluid-phase concentration is not altered significantly by uptake, such as when uptake is very slow, or when the receptor moves rapidly through the contaminated medium, bioavailability may be controlled mainly by the status-quo fluid-phase concentration. In all other cases, kinetics (mass transfer laws) describing the flux of contaminant through the particle, across the particle-bulk fluid interface, and across the fluid-membrane interface will be important. When the organism perturbs the fluid-phase concentration by uptake during the exposure, the concentration gradient between the particle and fluid and between the receptor and fluid are both altered. Because sorption and desorption rates from particles are governed primarily by molecular diffusion, and because diffusion depends on the concentration gradient, such biologically induced changes in concentration gradient may influence contaminant flux out of the particle. Therefore, an accurate bioavailability model will require linkage of biological uptake or depuration kinetics with sorption or desorption kinetics. Such coupled models are practically absent from the literature.

#### Mechanisms of sorption

The molecular scale mechanisms of sorption in ordinary natural soils are still incompletely understood and controversial despite decades of investigation. Characterization of sorption of typical contaminants to anthropogenic materials lags even further behind that of natural soils. It is important to note that intermolecular interactions of most organic compounds with soil components involve only physical forces (dispersion and dipolar interactions) and not chemical forces

(covalent bonding). These physical interactions are generally weak (a few kJ/mole) and practically instantaneous in the absence of steric constraints.

#### Sorption to organic materials

The dominant component of natural soils influencing the sorption of neutral organic compounds is the soil organic matter (SOM) fraction. SOM consists primarily of humic substances originating from the decomposition of plants and microorganisms (Hayes et al. 1989). The modern paradigm of SOM is a random 3-dimensional network of humic macromolecules. Sorption to SOM occurs by absorption into its matrix, analogous to the absorption of small molecules by synthetic polymers. A major driving force for absorption is hydrophobic expulsion from water—the so-called "hydrophobic effect" (Schwarzenbach et al. 1993). However, direct functional group interactions with SOM macromolecules obviously take place in some cases (e.g., hydrogen bonding, charge-transfer interactions) and may contribute to the overall driving force for absorption.

Recent studies (Pignatello 1998; Xing and Pignatello 1998) indicate that humic substances are composed of rubberylike phases that have an expanded, flexible, highly solvated structure, and glassylike phases that have a condensed, rigid, and less solvated structure. More than likely there is a continuum between these 2 extremes. Sorption has been interpreted in terms of a polymer model based on this rubbery-glassy concept. Interaction with the rubbery phase occurs by solid-phase dissolution, analogous to liquid-phase dissolution. Interaction with the glassy phase occurs by a dual mode mechanism, in which both solid-phase dissolution and "hole-filling" processes occur. The holes are postulated to be closed nm-size pores in which the guest molecules undergo an adsorption-like interaction with the pore walls.

Organocations, typically quaternary ammonium ions, sorb by ion exchange at charged sites both on mineral surfaces and within the SOM phase. Sorption may be facilitated by the hydrophobic effect of the apolar (nonpolar or weakly polar) parts of the molecule. Organoanions, typically carboxylates and phenolates, sorb primarily to SOM. Sorption of an organoanion is considerably weaker than its neutral (protonated) form due to greater solvation in water and charge repulsion with the negatively charged groups on SOM.

Soils may contain other forms of C not usually classified as SOM. These include ancient carbonaceous materials like coal, kerogen, and shale, as well as "soot" carbon, which refers to incompletely combusted organic material from natural or anthropogenic sources. Such materials have a high affinity for organic compounds and may be widely distributed in the environment (McGroddy et al. 1996; Gustafsson et al. 1997). Sorption to these carbonaceous materials may occur by adsorption or by condensation in fixed micropores, whose surfaces are hydrophobic.

### Sorption to inorganic materials

Unlike SOM, minerals are impenetrable by organic molecules or ions. Sorption therefore occurs at the solid–fluid interface. At high relative humidity, the sorption of apolar compounds to mineral oxide and external clay surfaces is small on a mass basis compared to sorption to SOM or carbonaceous materials (Mader et al. 1997). This is because mineral surfaces, being polar, are coated with strongly bound water molecules. Thus, sorption of apolar compounds to polar minerals is important only at low moisture levels, or, under wet conditions, only in very low C materials such as aquifer sediments.

Sorption to mineral surfaces from solution is proportional to surface area and is solvent motivated—that is, it is driven mainly by the hydrophobic effect (Schwarzenbach et al. 1993). The nature of the association is best described as a concentration enhancement in near-surface (vicinal) water layers, rather than a direct interaction with the surface atoms. Sorption may be greater for compounds that are capable of hydrogen bonding with surface oxygens or coordinated water molecules and inner sphere coordination with surface metal ions (e.g., carboxylates). In addition, sorption of both apolar and polar compounds may be greater in clay interlayers than on exposed surfaces. At low relative humidity (approximately 50%), 2 additional mechanisms become increasingly important: direct interaction with the bare mineral surface and condensation to a liquidlike or crystalline state in small pores not completely filled with water.

### Sorption to nonaqueous-phase liquids

The partitioning of contaminants between fluid phases and tars, petroleum oils, and other NAPLs may be assumed to occur by a simple liquid-phase dissolution process, analogous to that which occurs between water and organic solvents like hexane or octanol. Partitioning in such systems is therefore governed by Raoult's Law (water–NAPL) or Henry's Law (vapor–NAPL); that is, the fluid-phase concentration is proportional to the mole fraction of contaminant in the NAPL times the solubility (or vapor pressure) of a pure reference state (Schwarzenbach et al. 1993).

### Molecular modeling

Recent attempts to understand sorption have employed molecular modeling, and no doubt this will become more common in the future. Lasaga (1990) has used theoretical molecular methods to characterize the energetics of the silica surface in contact with water and then to better understand the mechanisms of weathering. Similar ideas might be applied to sorption of metals. Shulten (1995) has used molecular modeling to study the interactions of pollutant molecules with hypothetical humic acid macromolecules in the presence and absence of silica minerals. Several commercial software products are available to do these calculations. At present, these molecular calculations are limited by the speed and size of computers, but these limitations are decreasing rapidly.

### Thermodynamic relationships

A number of isotherms have been used to describe solid-solution sorption, including Freundlich and Langmuir isotherms and modifications thereof (Carter et al. 1995). Historically, the most commonly used isotherm is the Freundlich equation

$$q = K_d C^n \quad (7-1)$$

where  $q$  is the sorbed concentration [moles/kg],  $C$  the aqueous concentration (moles/L),  $K_d$  the sorption distribution coefficient [(moles/kg)(moles/L)<sup>-n</sup>], and  $n$  an exponent. The Freundlich model is often simplified to the linear form ( $n = 1$ ) on the assumption that SOM is the predominant sorbent and that sorption to SOM is dominated by solid-phase dissolution, which, in theory, should be linear. The  $K_d$  is commonly normalized to the fraction organic C ( $K_{oc} = K_d/f_{oc}$ ). The thermodynamic relationships governing vapor–particle sorption are complex because they involve other processes including pore condensation, adsorption on nonhydrated surfaces, dissolution in liquid water films, and adsorption on water film surfaces. Hence, they will not be discussed here.

The linear isotherm model has been used to develop the proposed Equilibrium Partition Model that is under consideration by the U.S. Environmental Protection Agency (USEPA) for setting sediment-quality criteria for aquatic sediments (Di Toro et al. 1991). The assumption of this model is that bioavailability, and eventually biological effects, can be predicted from the equivalent porewater concentration. The porewater concentration is calculated from the total concentration present in the solids (after exhaustive extraction) using experimentally determined  $K_{oc}$  values or  $K_{oc}$  values estimated from established linear free-energy relationships (LFERs), such as those with octanol–water partition coefficients ( $K_{ow}$ ) or solubility (Schwarzenbach et al. 1993). Although there is an extensive database of  $K_{oc}$  values and LFERs, most of these data are based on isotherms constructed over short equilibration times (<48 h). Therefore, their relevance to highly aged contaminated systems is questionable. In a number of cases, the apparent  $K_{oc}$  for historically contaminated soils and sediments has been as much as 2 orders of magnitude greater than laboratory-determined values with clean soils that are freshly spiked with the contaminant (Pignatello and Xing 1996). In addition, the Equilibrium Partition Model is inapplicable when nonequilibrium conditions prevail during exposure.

### Dual-mode model

Sorption isotherms in soils are frequently observed to be nonlinear. Moreover, competitive effects occur between contaminants in multicomponent systems (e.g., chlorinated hydrocarbons, polycyclic aromatic hydrocarbons [PAHs]) and between contaminants and naturally occurring compounds (e.g., aromatic acids). Cosolute

competitive effects have been shown to increase the bioavailability of the principal solute (White, Hunter, Nam et al. 1999).

The dual-mode model (Equation 7-2) places nonlinearity and competition in a mechanistic framework for SOM. The model relates total sorption to the sum of solid-phase dissolution, a linear term, and hole filling, described by a summation of Langmuir terms representing each unique type of site:

$$q = K_D C + \sum_i \frac{b_{H,i} Q_{H,i} C}{1 + b_{H,i} C} \quad (7-2)$$

where  $K_D$  is the dissolution domain coefficient, and where  $Q_{H,i}$  and  $b_{H,i}$  are the maximum sorbed capacity and affinity constant, respectively, for the  $i$ th hole of the hole-filling domain. The value of  $K_D$  can be obtained from the competitive effect, which blocks the holes and thereby eliminates the Langmuir term (Pignatello 1998). Individual  $Q_{H,i}$  and  $b_{H,i}$  cannot be determined because we do not know the number of unique sites. However, Langmuir parameters for a hypothetical composite site may be obtained, once  $K_D$  is known, by fitting the experimental isotherm using 2-parameter nonlinear regression.

### Hysteresis

A fundamental motivation for reexamining the question of "environmentally acceptable endpoints" is the observation that desorption is not simply the opposite of sorption, as has been previously thought. It is often observed that a fraction of the sorbed compound is not removable, as would be expected based upon sorption isotherms such as Equation 7-1. The fraction of sorbed compound that is not readily removed is observed to increase with aging times, from days to weeks and longer. When equilibrium desorption is vastly different from sorption, the process is termed "hysteresis." Hysteresis implies the existence of a time-independent process, that is, the desorption points do not approach the sorption isotherm curve even after long equilibration times, yet the original compound can be recovered quantitatively. A necessary thermodynamic requirement for sorption hysteresis is that there must be a rearrangement after sorption, or simply that desorption takes place from a different molecular environment than sorption.

To explain hysteresis, Kan et al. (1997) have proposed that sorption includes an irreversible fraction. The term "irreversible" does not imply permanent immobilization, but only that molecules come off a site by a different microscopic pathway than they go on. They interpret the sorption and desorption as 2-step processes. They propose that the bulk of sorption takes place via normal hydrophobic linear mechanisms (Equation 7-1, with  $n = 1$ ). Then, in a second step, the SOM rearranges and entraps a portion of the sorbed compound. This rearrangement may be

triggered by the very process of hydrophobic sorption, as occurs with various enzymes. Such rearrangement is supported by molecular modeling studies of the interaction of pollutant molecules with hypothetical humic acid macromolecules (Schulten 1995) and by direct membrane studies with atrazine (Devitt and Wiesner 1998). Desorption takes place from both the first and the second fractions. Desorption from the first fraction is described by linear partition coefficients (Equation 7-3). For the second fraction, it has been found empirically that for each soil-contaminant combination there is a fixed maximum capacity,  $q_{\max}^{\text{irr}}$  (mg/kg); the value of  $q_{\max}^{\text{irr}}$  is generally found to be about 1 to 10 mg/kg. The maximum soil capacity,  $q_{\max}^{\text{irr}}$ , can be filled in one or multiple steps; the fraction of  $q_{\max}^{\text{irr}}$  filled is termed " $f$ ." Generally, about one-half to one-third of the total amount of contaminant sorbed is entrapped in this second fraction until it is filled (i.e.,  $f = 1$ ). In models, the value of  $f$  is generally set to 1. Desorption from this second fraction is characterized by a single organic C-normalized partition constant for most hydrophobic organic compounds studied to date ( $K_{\text{oc}}^{\text{irr}} = 10^{5.5 \pm 0.5} \text{ L/kg}$ ), which might be expected if the sorption were related to an entrapped material, but much more work is needed to test the general applicability of these ideas. These ideas can be represented with the following isotherm (Fu et al. 1994; Kan et al. 1994, 1998):

$$q(\text{mg/kg}) = K_{\text{oc}} \text{OC} \times C(\text{mg/L}) + \frac{K_{\text{oc}}^{\text{irr}} q_{\max}^{\text{irr}} f \times \text{OC} \times C}{q_{\max}^{\text{irr}} f + K_{\text{oc}}^{\text{irr}} \text{OC} \times C} \quad (7-3)$$

Only preliminary work has been done on the desorption kinetics from the irreversible compartment.

### Sorption and desorption kinetics in relation to bioavailability

Desorption of the fraction of the contaminant that is not instantaneously available to the receptor is subject to mass-transfer rate laws. The factors responsible for retardation of desorption are not completely understood. Because only physical forces are involved in the interaction of most compounds with soil materials, the underlying cause of retardation is not breakage of bonds, but mass transport (molecular diffusion) within the particle. Diffusion is the random movement of molecules under the influence of the gradient in its chemical potential. Stated another way, a molecule migrates from "site" to "site" in the interior of the particle like a drunken sailor until it reaches the surface-bulk-fluid interface where it undergoes a final desorptive step to escape into bulk solution. Thus, diffusion is exquisitely sensitive to the nature and geometry of the diffusive medium. Obviously, natural particles are highly heterogeneous in composition and geometry.

Diffusion in soil particles may be retarded by the following mechanisms:

- chromatographic retention in fixed pores,
- hindered diffusion within SOM owing to its viscous nature, and
- temporary holdup at specific sorption sites within the particle.

Soil particles are porous by nature. Diffusion through the fixed intraparticle pore system is an important retardation process. The void spaces within individual grains (e.g., clays) and between grains that make up particle aggregates include macropores (>50 nm wide), mesopores (2 to 50 nm), and micropores (<2 nm). Pores smaller than about 1 nm have been referred to as "ultramicropores," "submicropores," or "nanopores." Pore size distributions of soil materials, especially in the micropore and nanopore region, are not readily obtainable at present, although progress is being made through innovative techniques using gas adsorption coupled with molecular models. It should be noted that even the smallest cells are larger than approximately 200 nm in diameter, excluding them from most of intraparticle pore system where the majority of the surface area exists.

From studies in mesoporous and microporous fixed-pore reference materials (e.g., zeolites, silica gel, and carbons) (Karger and Ruthven 1992), we know that diffusion may occur in the aqueous fluids filling the pore or along pore surfaces. Diffusion is retarded by 1) tortuosity, which takes into account deviation of pore paths from linearity and dead end pores; 2) sorption to the pore walls, which is most significant when the pore wall is hydrophobic; and 3) steric hindrance by pore walls, which is important only in pores smaller than a few times the molecular diameter (practically speaking, micropores and smaller mesopores).

Diffusion through SOM is another important retardation mechanism. SOM may be regarded as a highly viscous liquid phase. Diffusion of small gas and organic molecules through rubbery and glassy polymers has been well studied (Rogers 1965; Berens 1989). Diffusion through glassy polymers can be many orders of magnitude slower than through rubbery polymers, owing to their more condensed and rigid nature. The existence of nanopores within the glassy phase has important implications for the physical and biological availability of contaminants. Because such pores are of molecular dimensions, it is possible that the entrance and exit of some pores may be sterically hindered but not completely impenetrable by a given molecule. Steric constraints may assume greater importance as molecular size increases. The humic rearrangement hypothesis discussed in relation to hysteresis phenomena represents the extreme case of steric hindrance because, if it were true, a major reorganization of the humic backbone would be required to permit release. It should be appreciated that release from a sterically hindered site is not necessarily directly into solution but instead may be into the surrounding organic matrix where it is then subject to encountering another sterically hindered site.

### Rate models

Mechanistic, semiempirical, and stochastic models all have been used to describe sorption and desorption rates. The literature is limited primarily to experiments on samples that have been newly spiked rather than on historically contaminated samples. Common assumptions are that the particles are uniform and spherical, the diffusion coefficient is single-valued, and the contaminant is uniformly distributed at equilibrium. Diffusion models for glassy organic polymers are available (Horas and Nieto 1994). These models require parameters for both the dissolution and hole-filling domains and become exceedingly complex when the holes are energetically inhomogeneous. A combined pore diffusion-organic matter diffusion model has been derived (Yiacoumi and Rao 1996). Additional complexities in the application of classical diffusion models include 1) the possibility that the diffusion coefficient is concentration dependent; 2) the wide particle size distribution ordinarily found in soils; 3) the inhomogeneities of contaminant concentration within the particle; 4) the sorption nonlinearity; 5) the likelihood that local sorption partition coefficients are distributed over a range of values; and 6) the likelihood of nonequilibrium condition at the start of the experiment. It is even unclear what the relevant diffusion length scale is in natural particles; in some cases, it appears to be the nominal particle radius, while in others it is considerably smaller, perhaps on the order of mm or less (Pignatello and Xing 1996).

The most widely used models in the soils literature are the multisite models that assume discrete sites governed by first-order sorption and desorption rate laws. The popular 2-site model includes an instantaneously reversible site and a kinetic site. In recognition of soil heterogeneity, some researchers have employed stochastic models that assume an array of parameters that are distributed according to probability density function (Connaughton et al. 1993; Pedit and Miller 1995). For example, Pedit and Miller (1995) modeled the months-long uptake of the herbicide diuron with a model that treated  $K_d$  and desorption rate constant as continuously distributed variables ranging over certain limits. While stochastic models are successful for a given contaminant-soil system, it remains to be seen whether the parameters can translate to other systems.

### Correlations of rate with molecular structure, soil properties, and conditions

Two-site model desorption rate constants have been found to depend inversely on the  $K_d$ ,  $K_{ow}$ , or molecular connectivity index, a measure of topological size and degree of chain branching in the molecule (Piatt and Brusseau 1998). Thus, for a given class of compounds, large molecules desorb more slowly than small and branch more slowly than linear. Polar compounds appear to desorb more slowly than apolar compounds having the same  $K_{ow}$ , as expected due to the additional drag of functional group interactions (e.g., hydrogen bonding) occurring at each molecular jump through the matrix. It should be noted that these relationships

have been developed from sorption experiments occurring over only minutes to hours; although the relative relationships are likely to hold over longer times, it is still not possible to predict desorption rates in aged systems with any certainty.

The rate of desorption depends on the quality of SOM. For example, White, Hunter, Pignatello, Alexander 1999 showed that aged phenanthrene desorbed faster from a peat soil than from the humin fraction of the peat soil, that is, the organic matter left after base extraction of humic acids. This is consistent with the dual-mode model, since the humin fraction is believed to be enriched in glassy SOM. Weber and Huang (1996) and Xing and Pignatello (1996) have observed decreasing isotherm linearity with time and interpreted this result to mean that sorption occurs faster to the "amorphous" (rubbery) SOM than to the "condensed" (glassy) SOM. The rate of desorption is quite sensitive to temperature. For example, highly resistant fractions of 1,2-dibromoethane in an aged field sample gave a desorption activation energy of approximately 60 kJ/mole (Steinberg et al. 1987). Desorption of aged phenanthrene in a sandy loam was accelerated in the presence of a competitive cosolute (pyrene) (White, Hunter, Nam et al. 1999; White, Hunter, Pignatello, Alexander 1999).

#### Speciation of organics in aqueous solution in relation to bioavailability

Most nonionic organic compounds exist as a single chemical entity; however, in soil solution, the compound may be freely dissolved or be associated with nonsettling particles (NSPs). Ubiquitous in soil systems, NSPs are colloidal size particles made up of humic substances often associated with inorganic materials. Because it is the humic fraction that usually dominates sorption, NSPs are often referred to simply as "dissolved organic matter" (DOM). Sorption of contaminants to NSPs presumably takes place by the same mechanisms as the bulk soil. The fraction of total solution-phase concentration associated with NSPs depends on the hydrophobicity of the compound and becomes important as its  $K_{ow}$  exceeds approximately  $10^4$ . Sorption to NSPs may affect the apparent sorption distribution coefficient by giving an artificially high aqueous-phase concentration. Corrections for NSP sorption can be made through, for example, solubility enhancement experiments, which give some measure of the affinity.

The bioavailability of molecules associated with NSPs is unknown. Solutes partitioned into surfactant micelles are less available than freely dissolved, but appear to be somewhat more available than crystalline or sorbed-phase molecules. Due to their small size, rates to or from NSPs might be expected to be faster than the bulk soil particles. However, recent studies suggest that some molecules associated with DOM may become sequestered. For example, desorption of pentachlorobenzene from "dissolved" humic acid gave a fast and a slowly desorbing fraction (Schlebaum et al. 1998). This issue warrants additional study.

#### Sorption in biologically influenced microenvironments

The presence of an organism may accelerate the flux of contaminant from soil particles in a variety of ways: 1) by increasing the concentration gradient across the particle-fluid interface as a result of depletion of contaminant in the fluid, thereby accelerating particle-to-fluid flux; 2) through organism-caused changes in the composition of the fluid phase that affect the chemical potential of the solute and, as a result, its sorption coefficient; and 3) through organism-caused alteration of properties via changes in fluid-phase composition.

Single-cell organisms may attach to soil surfaces by molecular forces or via extracellular exudates. It is inconclusive whether or not attached cells are capable of abstracting sorbed organic molecules directly from the surface. However, bioavailability is probably not enhanced by this mechanism for 3 reasons: 1) most sorbed organic molecules exist within the interstices of SOM and, therefore, are inaccessible to cells at any given instant; 2) molecules adsorbed to surfaces are similarly unavailable because the preponderance of soil surface area is located in mesopores and micropores, which are inaccessible to even the smallest cells; and 3) because of the external surface and the solution are in rapid equilibrium at the microscale, surface abstraction, even if possible, can only enhance bioavailability if the rate of abstraction from the surface is significantly greater than the rate of uptake from the solution, which seems doubtful.

Multicellular organisms probably are less capable of abstracting organic contaminants directly from the sorbed state than single-cell organisms, but they may affect sorption in other ways. Little work has been done in this area, however. Dermal contact may involve transfer of skin or hair oils to the particle surface, which may facilitate uptake of hydrophobic contaminants. Ingestion of soil particles exposes organisms suddenly to an aqueous environment that may include acids, biosurfactants, and enzymes. Weston and Mayer (1998) have shown enhanced bioavailability of pesticides in stomach fluid experiments. Acids and enzymes may affect soil structure, and surfactants can affect both soil structure and, through micelle formation, the apparent aqueous solubility of the contaminant. The solution pH affects soil mineralogy, as well as the structure of SOM. Acidification of a soil to below pH approximately 2 was shown to release sequestered fractions of halogenated hydrocarbons (Pignatello 1990), possibly by dissolving Fe or Al oxide cements binding particle aggregates or organic macromolecules together. Soils ingested by animals may be subject to pulverization in the gizzard, thus facilitating desorption by increasing diffusion path lengths. Grinding in a ball mill was shown to release sequestered fractions of halogenated compounds in soil (Steinberg et al. 1987; Pignatello 1990) and aquifer materials (Ball and Roberts 1991). The effect of biological fluids in the lung on desorption of inhaled particles is an open question. Animals may facilitate uptake by altering the rhizo-microenvironment. Plant exudates could potentially facilitate desorption by a surfactant effect or by a competi-

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tive sorption effect. For example, it has been shown that naturally occurring aromatic acids, which are released from living and decomposing plants, facilitate desorption of chlorinated aromatic hydrocarbons, chlorinated phenols, and PAHs by a competitive displacement mechanism (Xing and Pignatello 1998).

#### Potential release mechanisms for sequestered fractions

An important question for setting soil-quality criteria and establishing environmentally safe remediation endpoints is the potential for release of sequestered fractions through sudden change in environmental conditions at some unanticipated time in the future. The desorption of sequestered fractions is accelerated by abrasion, application of heat, or introduction of solvents and oils. It is possible that competing cosolutes (either natural or anthropogenic) introduced to the soil could displace sequestered fractions, but this has not been clearly established. Natural microbial decomposition of SOM could, in principle, lead to the release of fractions sequestered therein, but it is hard to envision such a process occurring suddenly and without being replaced by newer SOM. However, the younger SOM is likely to have a more rubbery structure.

#### Soil heterogeneity considerations

Contaminated sites are spatially inhomogeneous with respect to many properties, including contaminant concentration, mineralogy, fraction of organic C, and moisture. Chemical concentrations may vary up to a 1000-fold over a site (Keith 1996). Thermodynamic coefficients and rate parameters may vary correspondingly with these disperse properties and conditions. For example, sorption coefficients and diffusion coefficients are concentration dependent. Diffusion coefficients are highly dependent on soil geometry and other properties. It is quite possible that the "bioavailability factor" of a given compound varies spatially over a site from near zero to near unity. Research is needed to establish the site-scale heterogeneity of thermodynamic and kinetic parameters of desorption if we are to have any real confidence in predicting bioavailability.

#### Prescription for bioavailability protocols

Sorption and desorption thermodynamic and kinetic models are presently inadequate for predicting bioavailable fractions using only the total contaminant concentration and soil properties typically available. As discussed above, the literature  $K_{oc}$  values generally overestimate risk because short-term sorption studies underestimate  $K_{oc}$  values of aged contaminants. Therefore, measurements are required on a site-specific basis in order to obtain the minimal thermodynamic and kinetic information necessary to make bioavailability predictions. What is more, the variability in these data within a site is expected to be considerable. It is

felt that some simple measurements can be made to help assess bioavailability.

These measurements can tell us the following:

- the prevalent porewater concentration, and
- the desorption rate profile for the contaminants that will give the maximum desorbable contaminant mass over a given period.

#### The prevalent porewater concentration

In cases where NAPLs are known to be present, it may be possible to estimate the prevalent porewater concentration by the Raoult's Law or Henry's Law relationships between the NAPL and water (or air) phases, as discussed above. The reader should be warned that the validity of this method of estimation in the field has not been rigorously tested. In many cases, the prevalent porewater concentration may be measured directly. For reasons mentioned above, the relationship between measured porewater concentration and total solids-based concentration is not likely to be highly predictable based on short-term  $K_{oc}$  values. The relationship between biological effect and porewater concentration is still controversial. Provided there is enough moisture in the soil, the pore water can be separated by centrifugation through a filter and the contaminant concentration determined by established methods. Potential pitfalls using this technique include losses by volatilization, adsorption to the apparatus, or sorption to NSPs in the pore water. Techniques for direct measurement of porewater concentration without separation have not been established.

#### A desorption rate profile

A desorption rate profile can be obtained by suspending the contaminated soil in water and stripping the contaminant from solution as it desorbs. Stripping can be accomplished in the case of volatile compounds by air sparging, or by *in situ* adsorption with a third-phase polymeric trap, such as Tenax. The amount of polymer must be at least 10-fold excess over the amount of organic C to ensure efficient removal. At all but very short times (tens of minutes), desorption into solution, and not removal from the aqueous phase, is rate limiting. This type of experiment will give a desorption profile over any given time period, and thus will yield the maximum desorbable fraction of contaminant at any point along the time curve. The information gained using this approach should be used cautiously because the soil is placed under conditions where the rate of contaminant desorption is maximized due to the steep concentration gradient created by its removal.

#### Heavy metals

Metal problems are frequently found at contaminated sites. Forstner (1995) reported that of the 952 National Priority List (Superfund) sites in the U.S. in 1986, 389, or 41%, reported metal problems. Of the sites reporting metals, 71% reported the presence of multiple metal contaminants. The most frequently reported metal

contaminant was Pb, followed by Cr, As, Cd, Cu, Zn, Hg, and Ni. Other metals were reported at 10 or fewer of the sites. Of the 8 metals found at more than 10 sites each, all but C and As are predominantly found in the +II oxidation state. C can be present in 2 oxidation states, as Cr(+III) and as the chromate (+VI) oxyanion. As is most commonly present as the (+III) arsenite and (+V) arsenate oxyanions. This section will focus on those metals present in the +II oxidation state, with additional reference to interactions of soils with the arsenite, arsenate, chromate oxyanions, and Cr(+III).

Interaction of heavy metals with soils reduces the toxicity of the metals. Addition of metal salts to soils results in greater bioavailability of the metal than for metal that has been allowed to age in the soil, or for metal that is added together with components with which it can react, such as sewage sludge. Metals added to natural or artificial soils have been used to ascertain dose-response relationships. When the concentrations of chemicals in field samples are compared to these, the level of biological effect is overestimated. If metal concentrations are determined on the basis of aqua regia digests rather than on milder procedures, this effect is exacerbated. The importance of considering bioavailability in setting soil-quality standards has been discussed by Peijnenburg et al. (1997).

### Chemical equilibrium

Equilibrium calculations can help estimate the limits of metal-water-soil interactions. In order for these calculations to be useful for most metals of environmental concern, numerous solution-phase, solid-phase, and interface processes must be considered.

### Lattice metals

The chemistry of metals in soil is complicated by the fact that metals may be present both in highly inert and nonreactive pools and in pools where there is significant exchange of metal with the soil solution. The inert metal is present in the crystal lattice of the parent material of the soil. Digestion with strong acids, for example, aqua regia, and other strenuous digestion procedures liberate this metal. Aqua regia digestions of soil are employed in many countries for assessing compliance with environmental regulations (Houba et al. 1996). These concentrations of metals cannot be related to the potential for risk because they include metal that will not be accessible by normal environmental processes.

### Oxidation-reduction processes

The redox status of a soil can affect the oxidation state of a trace metal directly, and it can affect chemistry of soil components that are responsible for partitioning of trace metals. Of the trace metals of primary concern, both As and C are present in multiple oxidation states in soil systems.

The 2 predominant forms of As,  $\text{AsO}_3^{3-}$  and  $\text{AsO}_4^{3-}$ , are both anionic species that sorb to iron oxides. As(+III) can be oxidized As(+V) in soil systems at pH greater than 8. Manning and Goldberg (1997) reported that As(+V) sorbs more strongly to soil under most conditions than does As(+III). Both As(+III) and As(+V) are released into solution in anaerobic soils as a consequence of the dissolution of the manganese and iron oxides that are responsible for their sorption.

Carbon can be present in the +III and +VI forms. The toxicity of  $\text{Cr}^{3+}$ , which forms a very insoluble hydroxide, is very low. Chromate,  $\text{CrO}_4^{2-}$ , on the other hand, being quite soluble, is very toxic and can be formed by the oxidation of Cr(+III) by  $\text{MnO}_2$  in soil. SOM can reduce Cr(+VI) to Cr(+III) (Rai et al. 1989).

### Partitioning processes

It is necessary to determine the concentration of metal in the pool that is capable of interchanging with metal in the solution phase. As will be discussed in Chapter 9, there are several extraction methods that have been used for this purpose or for direct correlation with biological responses (Conder and Lanno 2000). The quantity of metal contained in this exchangeable pool constitutes the capacity, and the equilibrium concentration of the dissolved free metal ion in the solution phase constitutes the intensity.

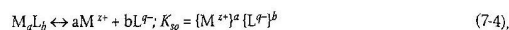
The free metal ion concentration (actually its activity or chemical potential) has been correlated to the availability of metals to organisms in aquatic systems and higher plants in soils (Morel 1983; Pagenkopf 1983; Checkai et al. 1987; Lund 1990; Playle et al. 1992, 1993a, 1993b; Bergman and Dorward-King 1997; Parker and Pedler 1997). Because the partitioning of the metal between the solid and solution phases is dependent on the strength of binding of the metal by the soil, it is likely that with appropriate considerations of changes in the local environment (e.g., gut or dermal conditions), a similar approach can be applied to the prediction of bioavailability to other classes of organisms. On the other hand, for groundwater contamination, it is the total soluble concentration of the metal, irrespective of chemical form, that is of interest.

Metals are retained by the solid phase by 3 processes: precipitation, ion exchange, and adsorption. In addition, the redox status of the system can greatly affect the partitioning of the metal. The extent of removal from the solution to the solid phase is a function of the chemical composition of both the solid and the solution phases.

### Precipitation

The concentrations of metals present at hazardous waste sites are commonly several orders of magnitude greater than in undisturbed background soils. At these sites, metals will precipitate to form secondary minerals in the soil. Metal-contaminated soils are often remediated through the addition of chemical reactants to the soil to enhance the secondary mineral formation process. For example, phos-

phate fertilizer can be added to Pb-contaminated sites to promote the formation of Pb pyromorphite, which has low solubility and bioavailability. The extent of removal of the metal through formation of the mineral,  $M_2L_b$ , is described by the solubility product,  $K_{so}$ , for the process



where the braces,  $\{\}$ , indicate chemical activity. Common precipitates are hydroxides, oxides, oxyhydroxides, carbonates, hydroxycarbonates, phosphates, and silicates. The extent of metal removal from solution by precipitation is commonly a function of the pH of the solution. For example, for a metal carbonate,  $MCO_3$ , the solubility relationship given in Equation 7-4 is valid in terms of the  $M^{2+}$  and  $CO_3^{2-}$  ions. The total concentrations of metal and carbonate species in the solution phase are functions of the solution pH and will be given by Equations 7-5 and 7-6, respectively:

$$\begin{aligned} [M]_T &= [M^{2+}] + [MOH^+] + [M(OH)_2^0] + \\ &[M(OH)_3^-] + [M(OH)_4^{2-}] + [MCO_3^0] \end{aligned} \quad (7-5)$$

$$[CO_3]_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [MCO_3^0] \quad (7-6)$$

where the brackets,  $[\ ]$ , indicate concentration.

Often, one does not find distinct mineral phases even though the existence of a solid phase, such as  $CdCO_3$ , is predicted from equilibrium considerations. Mixed solid phases, such as  $CdCO_3$  within  $CaCO_3$ , may be formed through coprecipitation.

#### **Ion exchange**

In ion exchange, metal ions in solution react with the negatively charged sites of soil particles. Permanent charge sites occur in layer silicate clays. Relatively weak outer sphere complexes in which the metal ions retain their water of hydration are formed. This exchange is termed "nonspecific adsorption," or more commonly, "ion exchange." The charge available at the constant charge sites, effective in ion exchange, depends on the clay mineralogy and can be far greater than that at the variable charge sites which are responsible for adsorption, which is discussed in the next section. Ion exchange is a particularly important mechanism for the retention of alkali and alkaline earth ions, including  $Na^+$ ,  $K^+$ ,  $Cs^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ , as well as for the retention of  $NH_4^+$ . Ion exchange is generally not an important process in controlling the solution-phase concentrations of heavy metal ions because the selectivity for exchange of the heavy metals is too low for them to successfully compete with the major ions for the exchange sites.

#### **Adsorption**

A third category of partitioning, referred to as "adsorption," occurs at sites that are variably charged, depending on pH and to a lesser degree on ionic strength. The dependency on pH results from the reaction of protons with oxide and hydroxide minerals and with certain functional groups of humic substances (Sposito 1984).

#### **Adsorption onto hydrous metal oxides**

A common surface group that reacts with protons is hydroxide. A surface hydroxide,  $S-OH^0$ , can undergo 2 protolysis reactions:



The corresponding conditional stability constants are

$$K_{cond, a1} = \frac{[\equiv S-OH^0] \{H^+\}}{[\equiv S-OH_2^+]} \quad (7-9)$$

$$K_{cond, a2} = \frac{[\equiv S-O^-] \{H^+\}}{[\equiv S-OH^0]} \quad (7-10)$$

Because adsorption is a surface phenomenon, concentrations of bound metals and of surface sites are expressed on an area basis, rather than mass basis, to enable one to relate different materials. The surface area is most commonly determined from the N adsorption isotherm at 77 °K. The Brunauer-Emmett-Teller (BET) equation enables the calculation of the area for a complete monolayer surface sorption (Hiemenz 1986).

As the surface undergoes ionization, for instance, during a titration with base, the surface becomes progressively more negatively charged and it becomes more difficult to remove subsequent protons. Thus, the conditional stability constant varies with the charge on the surface. It is necessary to incorporate a Boltzmann, or electrostatic, factor to convert this conditional constant into an intrinsic constant that does not vary with pH (Huang 1981; Stumm and Morgan 1996; Sposito 1984; Hiemenz 1986; Schindler and Stumm 1987). The intrinsic constant,  $K_{int}$ , is given by the relationship

$$K_{cond} = K_{int} \exp [-\Psi_0 F/RT] \quad (7-11)$$

where  $\Psi_0$  is the electrical potential at the surface,  $F$  is the Faraday,  $R$  is the gas constant, and  $T$  is the absolute temperature. The value of  $\Psi_0$  is also dependent on ionic strength. However, the ionic strength of the soil solution is usually low.

The surface potential is proportional to the surface charge (Hiemenz 1986; Singh and Uehara 1986; Schindler and Stumm 1987; Westall 1987):

$$\sigma_0 = \kappa \Psi_0 \quad (7-12)$$

The surface charge is directly determined from the proton or hydroxide consumption by the solid phase in an acid or base titration (Huang 1981).

One of the major difficulties is that sorption constants are expressed using different models of the solution-solid interface. This results in the use of different parameters among the models and an inability to directly compare the parameters that are common among them (Dzombak and Hayes 1992). The electrical double layer theory of Equation 7-11 can be extended to account for the adsorption of ions at planes other than at the surface. The triple layer model of surface complexation requires an additional potential at the Stern layer (James and Parks 1982). The zeta potential, which is the potential at the plane of shear, is subject to easy instrumental measurement and is a good approximation of the Stern potential (Hiemenz 1986). Experimental data fit the simpler model as well as they fit the more sophisticated models (Morel 1981; Westall and Hohl 1980). A widely used model is the diffuse double layer model for which there is a large compilation of internally consistent constants (Dzombak and Morel 1990).

It is now easy to understand the reason that metal sorption is so highly pH dependent. Protons and metal ions compete with each other for available surface binding sites. When adsorption of a divalent metal, such as Cd, onto a solid, such as goethite, is determined as a function of pH, there is little adsorption at low pH and virtually complete adsorption at high pH values. The transition between low and very high adsorption occurs over a region of approximately 2 pH units. For a divalent metal ion,  $M^{2+}$ , the adsorption can be written

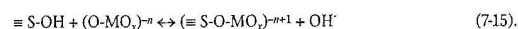


for which the conditional stability constant is

$$K_{\text{cond}} = \frac{[\equiv S-OM^+]\{H^+\}}{[\equiv S-OH^0]\{M^{2+}\}} \quad (7-14)$$

This conditional constant is related to an intrinsic constant in a similar fashion to that in Equation 7-11. An analogous reaction to Equation 7-13 can be written for the binding of the metal ion to 2 soil surface sites with the concurrent release of 2 protons, rather than 1. The binding of the hydrolyzed metal,  $MeOH^+$ , to  $S-O^-$  to give  $S-OMeOH$ , with no release of protons, is also possible. If one is to be able to predict the adsorption of a metal at any pH, it is essential to have the acid base equilibrium constants of Equations 7-7 and 7-8.

The adsorption of oxyanions, such as chromate, can be described in an analogous fashion to that of metal cations (Parfitt 1978; Mott 1981). Binding is represented by the reaction



Again, the pH dependency of the reaction is predicted and accounted for by the conditional constants

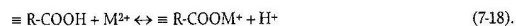
$$K_{\text{cond}} = \frac{[(\equiv S-O-MO_3)^{-n+1}]\{OH^-\}}{[\equiv S-OH]\{(O-MO_3)^{-n}\}} \quad (7-16)$$

which can be converted to an intrinsic constant by Equation 7-11.

As noted in the section on oxidation-reduction processes, reducing conditions may result in the release of trace metals to the soil pore water as a consequence of the dissolution of metal oxide phases.

#### Adsorption onto humic materials

Binding of metals by the humic materials, fulvic and humic acids, can be viewed in a similar manner as the sorption onto metal oxides. The carboxyl and phenolic functional groups give rise to the variable charge. For example, the protonation and metal complexation reaction of a metal with a carboxyl group on the humic surface can be represented by the reactions



Transition metal ions form inner sphere complexes with humic materials, which accounts for the high stability of these complexes relative to those with the more prevalent alkali and alkaline earth elements. Neither humic nor fulvic acid is a discrete chemical entity, rather they are composed of molecules that differ in properties, including functional groups. Because humic substances contain a large

number of ligands differing in concentration and stability constants, simple models that consider reactions with only 1 or 2 sites do not reproduce the measured degree of chemical interaction. Titration of humic materials with either protons or metal ions results in nearly featureless titration curves, which do not rise sharply like titration curves of distinct chemical substances. To model these titration curves, it is necessary to recognize that they represent a mixture of many substances. A number of different approaches have been taken to describe the binding of protons and metal ions by humic substances (Perdue and Lytle 1983; Ephraim and Marinsky 1986; Fish 1986; Cabaniss and Shuman 1988; Tipping 1990). These approaches include discrete site models, models with a continuum of binding sites of varying  $pK$ , and models that incorporate electrostatic interactions.

#### Sorption onto soils

A large body of literature exists on the adsorption of metals onto soils. Most studies show that adsorption onto soil shares characteristics with the adsorption of metals onto the iron and manganese oxides and humic material coatings on particles. Most adsorption isotherms are L-shaped. Adsorption is a function of the solution pH with a transition from low to high adsorption over a pH range of approximately 2 units.

The dominant factor controlling the partitioning of metals between the soil and solution phases is the pH. For example, Anderson and Christensen (1988) studied the sorption of Cd on 38 soils with samples being taken at several depths. For their 117 sorption measurements made at very low Cd(II) concentrations (0.7 to 12.6  $\mu\text{g/L}$ ), regression of log of the Cd(II) sorption  $K_D$  on the pH gave a slope of 0.64. The regression had a  $R^2$  value of 0.776, indicating that proton concentration is the principal factor affecting the partitioning process. The scatter of data about the line suggests that the strength of binding of Cd by the different samples was not the same. To improve the level of prediction, the concentrations of the components of the soil responsible for the metal binding and the strength of the sorption by these materials should be included.

Lexmond (1980) studied the sorption of Cu onto a Dutch, slightly loamy, gravelly sand as a function of concentration and pH. They found that the sorption of Cu could be described by an empirical pH-dependent Freundlich equation:

$$Q_S = K_S(\text{Cu}^{2+})^a / (\text{H}^+)^b \quad (7-19)$$

where  $Q_S$  is the amount of Cu bound to the soil solid phase,  $(\text{Cu}^{2+})$  and  $(\text{H}^+)$  are the activities of the Cu and hydrogen ions, respectively, and  $a$  and  $b$  are fitting parameters.

Radovanovic and Koelmans (1998) developed a model to predict metal binding to natural solids that considers sorption onto individual sorption phases as well as the

effect of pH on the sorption process. The system is modeled as a series of simultaneous equilibria. The applicability of such a model for the prediction of partitioning assumes that the metal in each of the phases considered will equilibrate between the solid and solution phases during the exposure period. This is a function of the time allowed for equilibration and the geometry of the solid phases. For example, if the surface of the particle is covered by only one of the materials, equilibration with fresh solution phase will be with that sorption material only if there is sufficient time allowed for the diffusion of the metal of interest from the deeper-lying phases to the sorption phase on the surface. One example of such a system would be for redox cycling systems that can have iron hydroxide deposited onto the surface. One would need to know if there was sufficient time for the contaminant metal to diffuse into the iron hydroxide to maintain equilibrium with the underlying solid phases. Davis (1984) suggested that most soils have a surface coating of organic matter. If this is the case, in the equilibration of a soil with water, metal is transferred between the aqueous phase and the particulate organic matter coating of the soil.

Lee et al. (1996) studied the adsorption of Cd onto 15 soils as a function of pH. They found a dependence of partitioning on pH that was nearly the same as that reported by Anderson and Christensen (1988). The variation of the data values (log  $K_D$  versus pH) about the line reported by Lee et al. (1996) was about a factor of 30. When the value of  $K_D$  was normalized to the fraction of organic matter, the variation was reduced to a factor of approximately 3, a 10-fold improvement in the correlation. These results suggest either that the surface is indeed coated by organic matter and that in the 24-hour equilibration period there was not sufficient time for penetration of the added Cd through the organic matter to reach other sorption sites on, for instance, Fe and Mn oxides, or that sorption of the Cd onto the organic matter dominated the sorption relationship.

Yin et al. (1996) studied the adsorption of Hg(II) from dilute solution onto the same 15 soils that had been studied previously by Lee et al. (1996). A much different result was found for the adsorption of Hg onto the soils as a function of pH than is found for most other metals. At the lowest pH studied, approximately 3 pH, 80% to 90% of the Hg was adsorbed. A maximum extent of adsorption, generally >90%, was attained at pH approximately 4, and the extent of adsorption then decreased with increasing pH. By pH 10, the adsorption ranged from 10% to 50%. This decrease in adsorption was found to be caused by the dissolution of particulate organic matter that could then complex the released Hg. The dissolution of organic matter is a strong function of the pH of the soil, increasing with increasing soil pH. The role of pH in sorption processes is therefore many-fold: It controls the protonation of the solid phase, it is important in the speciation of ligands in the solution phase, and it regulates the distribution of ligands, particularly humic substances, between the solid and the solution phases.



Yin, Allen, Huang, Sanders (1997) found that adsorption isotherms on the higher organic matter content soils had an S-shape. The organic matter released to the solution reacted with the Hg. The complex was more poorly adsorbed than were the inorganic forms of Hg, which predominated only after sufficient Hg had been added to complex the dissolved organic matter.

#### Modeling partitioning

There are a number of computer programs currently available to compute geochemical speciation, including MINEQL+ (Schecher and McAvoy 1992), MINTEQA2 (Allison et al. 1991) and WHAM (Tipping 1994). The most important factor in these models is the quality of the database. WHAM best handles the binding of metals by humic substances, and its database is validated by the large number of independent data sets for which it has been used. It considers humic substance to be a series of discrete ligands whose relative concentration is greatest for ligands having intermediate stability constants. The binding spectrum for reaction with protons forms the basis for its representation and for reaction of metals the binding spectrum is considered to shift in strength. Several questions are of importance. First, is there a small fraction of the ligands that have a very high stability constant? For example, in the case of Hg, which selectively and strongly binds to thiols, there could be a small concentration of ligands that have a very high affinity that is not included in the models of the humic substances. Second, to what extent are metals competitive for the same binding sites? It is assumed that all metals can react with all sites.

Usually organic C is used as a surrogate for the humic substances. If there is a large percentage of the organic matter that is not reactive with metals, an alternative approach is required. A most important input is the total concentration of metal. In general, partitioning of the metal in precipitates and adsorbed phases are the only pools of metal considered. Therefore, an extraction of that pool of metal is required to provide the necessary information.

#### Partition coefficient

Information on the metal distribution between the solid and the solution phases is typically expressed as a partition coefficient, similar to what is done with organic compounds (Schwarzenbach et al. 1993). The metal in the soil can be present in several solid phases. In the solution phase, the metal will be present in a number of different chemical forms, including association with dissolved organic matter. Inorganic ligands of importance in the speciation of the metal include hydroxide, carbonate, bicarbonate, and chloride. Stability constants for the formation of inorganic complexes are, in general, well known. The chemical species distribution among the inorganic complexes then can be easily computed using any of the computer models previously discussed. Complexation with dissolved organic matter can be included if these constants are available.

Because the partition coefficient is the ratio of the concentration of the metal in the solid and solution phases, its utility is very limited. The value will depend on the metal speciation in each of the 2 phases, and thus it is a sample-specific parameter (van der Kooij et al. 1991). The partition coefficient is solely a representation of measured values without predictive capability. This can be best understood by writing the partition coefficient,  $K_D$ , which is

$$K_D = \frac{[\text{Metal in Soil}]}{[\text{Metal in Solution}]} = \frac{[\text{M-POM}] + [\text{M-FeOx}] + [\text{M-MnOx}] + \dots}{[\text{M}^{2+}] + [\text{MOH}^+] + [\text{MCO}_3] + [\text{M-DOM}] + \dots} \quad (7-20)$$

An alternative formulation of the partitioning relationship may provide a means to predict the distribution of a metal between the solution and solid phases. The partitioning of a metal between the solution and sorption phases in the soil can be rationalized through consideration of conventional chemical equilibrium concepts. For example, the partitioning of the metal with the particulate organic matter (POM) fraction of the soil can be represented as



The equilibrium is then represented

$$K_{eq} = \frac{[\text{M-POM}]}{[\text{M}^{2+}][\text{POM}]} \quad (7-22)$$

This equation can be rewritten to provide a prediction of the concentration of metal ion in solution

$$[\text{M}^{2+}] = K_{eq} \frac{[\text{M-POM}]}{[\text{POM}]} \quad (7-23)$$

This indicates that the concentration of free metal ion can be predicted from the knowledge of the concentration of the sorbed metal and the concentration of the sorbent. As was discussed, the free metal ion concentration is believed to be directly related to bioavailability. Thus, prediction of the free metal ion concentration would provide a theoretical measure of bioavailability.

### Desorption

As for organics, hysteresis is observed in the desorption of metals from soils. For example, Yin, Allen, Huang, Sanders (1997) studied the desorption of Hg that they had adsorbed onto soils. After 4 steps of desorption, about 11% of the adsorbed Hg had been removed from a soil containing 0.12% organic matter, but less than 2% of the Hg that had been adsorbed was removed from a soil containing 5.0% organic matter. Furthermore, the ability to desorb metal decreases as time of aging increases.

Because of the lack of concurrence between adsorption and desorption results, partition results from adsorption experiments cannot be used to infer release of metal from soil. Desorption data from freshly contaminated soils cannot be used to infer the desorption of metal from aged materials. The processes and mechanisms responsible for the hysteresis must be understood to enable an adequate description of chemical equilibria.

A number of potential reasons for hysteresis have been discussed previously in this chapter in the section that deals with the sorption of organic compounds. These processes may be responsible for hysteresis observed in adsorption and desorption of metals too. In the case of metals, hysteresis could occur if adsorbents such as iron and manganese oxides were coated by organic matter. The organic matter surface would equilibrate with the solution. Metals would have to diffuse through the organic matter and then be sorbed by the metal oxide. Desorption would then need to follow a tortuous reverse path.

### Kinetics

The adsorption of metal ions to soil is relatively rapid. In typical batch equilibration experiments, the aqueous-phase concentration is rapidly depleted. Most adsorption studies are allowed to proceed for 24 hours. However, the hysteresis observed on desorption, which is discussed above, indicates that the process is more complicated than that of a simple surface adsorption and desorption process.

Gerth and Brummer (1983) and Brummer et al. (1988) showed that there is a slow diffusion of heavy metals into the goethite structure. The diffusion rates are related to the ionic diameters of the ions. They postulated that micropores or defect positions were responsible for this slow diffusion.

Yin, Allen, Huang, Sparks and Sanders. (1997) found that there was a fast and a slow kinetic step for both the uptake and release of Hg(II) by soil. Both uptake and release rate coefficients were related to the organic matter content of the soil. They reported that a portion of the adsorbed Hg was resistant to desorption and that the greater the organic matter content, the greater the fraction that was resistant to

desorption. They felt that diffusion of the Hg through intraparticle micropores in the organic matter was responsible for the irreversibility of sorption.

As a consequence of the slow adsorption and desorption process and/or hysteresis, metals added to soils as salts and metals added as a result of environmental contamination become less mobile and available with age. Short-term laboratory equilibration may indicate a higher risk than that present in field conditions.

### The Need for Protocols

The most critical output of contaminant-soil interaction studies in support of bioavailability assessments would be reliable information on the porewater concentration of the contaminant of interest. This can come from discrete measurements of porewater concentrations and/or from measurements of chemical-specific and soil-specific parameters that can be used in some models to predict porewater concentrations under a variety of soil and site conditions, as well as over a reasonable time frame. The desired chemical-specific parameters include partition coefficients, rate constants, and diffusion coefficients. The soil-specific parameters would include those listed in Table 7-1 (p 256). This focus on porewater concentration is not meant to detract from the likelihood that other, artificial means might provide a more direct basis for estimating bioavailability in specific circumstances. These other means might involve, for example, specialized leaching with liquids other than natural waters and/or uptake by manufactured items (e.g., plastic beads or semipermeable membrane devices) that mimic biological systems.

For either of the above approaches, direct porewater measurements of concentration or the measurement of model-related parameters, protocols are desperately needed. There are, however, some significant questions that need to be answered before we decide what protocols are needed. For direct measurements, the questions are relatively easy. They would include number of samples needed for characterization, porewater contact time, and porewater recovery technique. For model-related parameters, the initial issue is which model? Should the model accurately describe the mechanisms that are responsible for the sorption and desorption, or is it felt that empirical models, or models based on a simplistic representation of the sorption and desorption processes, will be adequate?

Both mechanistic and empirical models are needed. The ones that will accurately describe the sorption and desorption mechanisms are needed, at least in these research programs, to better understand the underlying processes. They will also allow more realistic (and sophisticated) assessments at high priority sites where such detailed assessments (and the related resource use) are warranted. However, the problems with this "mechanistic" modeling approach are that the mechanisms

are not currently understood; there is insufficient consensus among experts on which mechanisms and models are the most representative; they require too many inputs and are, consequently, not easy to use; and there is little likelihood of regulatory near-term acceptance.

Empirical models are needed in order to deal with near-term problem sites, that is, those for which management decisions will be made in the next few years. While these models may be based on strictly empirical correlations, or on simplistic (or even wrong) assumptions regarding the sorption and desorption process, they are all we have today that are relatively easy to use and generally acceptable to the regulatory agencies (at the level that most sites are given regulatory oversight). Properly applied and qualified, the use of such models should provide reasonable estimates of porewater concentrations under many conditions of concern. Perhaps what a protocol could spell out is the conditions under which the simplistic models do and do not provide a reasonably reliable basis for assessment. By conditions, we mean soil and contaminant types, spatial and temporal scales, exposure scenarios and receptors. In many cases, it may be that the uncertainty in the outputs from the simplistic and empirical models is acceptable.

#### Available protocols

There is very little in the way of standard protocols—issued by regulatory agencies or standard-setting organizations—that can be properly used to measure porewater concentrations or to measure model-related parameters for use in sorption and desorption models. The American Society for Testing and Materials (ASTM) has published a protocol for measuring organic C normalized sorption constants, that is,  $K_{oc}$  values (ASTM 1993). However, this protocol stipulates measurement via spiking of a clean soil and suggests the use of a relatively short contact time (4 to 48 hours) for the soil and the chemical in the soil slurry used. This protocol would not provide a reliable sorption constant that would apply to situations where hindered desorption was a factor.

In addition to the standard method for  $K_{oc}$  determination, ASTM provides specifications for other sorption tests including, for example, 24-hour batch sorption (D 4646-87 and D 5285-92), single batch extraction of wastes (D 5233-92), sequential batch extraction of wastes (D 4793-93), and leaching in a column apparatus (D 4874-98). Other methods that might provide roughly equivalent information include toxicity characteristic leaching procedure, synthetic precipitation leaching procedure, multiple extraction procedure, and other leaching procedures (Bricka et al. 1991; USEPA 1995). Other leaching tests are described in an USEPA guidance document for testing solidified wastes (USEPA 1989). However, protocols do not exist for measuring most of the parameters that may be required in the more mechanistic models, including rate constants and diffusion coefficients.

#### Technical issues for a protocol for measuring a desorption constant

There are a number of technical issues that would need to be addressed during protocol development for the measurement of a desorption constant. The desorption constant is a solid-to-liquid concentration ratio, presumably measured under near-equilibrium conditions, by means of contaminant desorption from a historically contaminated soil. Estimating chemical desorption from historically contaminated soils specifically avoids problems associated with traditional approaches for measuring soil sorption constants that involved either spiking a clean soil (in a soil-water slurry) with the chemical and measuring the amount of chemical remaining in the aqueous phase after a relatively short mixing time (hours to several days), or spiking a clean soil (dry or in a slurry) and allowing a long contact time (weeks to months or years) before conducting desorption studies. Many technical issues need to be addressed in the development of a protocol for determining desorption constants. These include

- **Soil sampling:** A sufficient number of soil samples should be collected from the site to sufficiently represent the range of soil types, habitats (if ecological concerns are involved), contaminant concentration range, and aerial extent and depth of contamination. Geostatistics can help in determining the number of samples required to achieve a defined confidence level in mean values. Initial (on-site) analyses of soil contaminant concentrations may be helpful in assuring sufficient coverage of the range of concentrations.
- **Sample preparation:** The protocol will need to specify when (if ever) and how to 1) prescreen the soil (to remove oversized particles), 2) composite samples, 3) homogenize samples (e.g., via grinding), and/or 4) sterilize the samples (to prevent unwanted contaminant biodegradation).
- **Leachant selection:** The protocol might allow the use of natural waters (e.g., rain water, site groundwater and/or tap water) or specify that a more aggressive aqueous solution needs to be prepared, for example, addition of acetic acid for organic contaminants and an inorganic acid for inorganic contaminants.
- **Contact mode:** The protocol could stipulate batch contact in a soil slurry or a packed column. Alternatively, contact in a flow-through column could be specified.
- **Solids-to-liquids ratio:** For slurries, the protocol will need to stipulate a solids-to-liquids ratio. This is necessary because the extent of sorption, and thus the derived sorption constant, has been found to be a function of this ratio.
- **Mixing method:** For slurries, the method of mixing will need to be specified. In most cases, a low-energy mixing method (e.g., slow rolling on a roller table) will be preferred in order to avoid excessive alteration of the particle size configuration in the sample.

- Biological inhibition: Although the initial soil may have been sterilized, the soil-water mix may have to be further treated to prevent unwanted biodegradation of the contaminant. Such treatments may involve the addition of mercuric chloride, acid, azide, or formaldehyde.
- Chemical control: If the desorption test is long, changes in the basic soil chemistry (e.g., pH and redox potential) may take place. If such changes could adversely affect the desorption process, then the protocol will need to allow for adjustment of the chemistry during the test.
- Desorption time: Because a desorption "constant" is being measured, the protocol will have to stipulate a time period for the soil-water contact that will allow a reasonable approach to an equilibrium partitioning state. The protocol may require that an initial time-series test be carried out to determine how long a time is required. Desorption times of days to months may be required.
- Solids-liquids separation: The protocol will need to stipulate what means are acceptable for the separation of the solid and liquid phases at the end of the contact period. The typical choices include fabric filtration and centrifugation. In either case, the protocol may need to require special tests to determine if the separation was adequate, that is, there was no solids carry-over into the aqueous sample. For strongly sorbed chemicals, even a small amount of solids carry-over would ruin the results.
- Analyses: The final analyses of the contaminant in the aqueous phase (i.e., the desorbed chemical) can probably be done by standard methods as long as the detection limits are adequately low. The solid phase may also have to be analyzed if a significant fraction of the chemical was desorbed from the soil by the desorption test.

As mentioned above, this material was provided only as an example. It is intended to illustrate the types of technical issues that would need to be addressed and the types of solutions that might be allowed or stipulated. Putting together a single protocol, even in a limited case, that would achieve the right balance of scientific merit, ease of use, and regulatory acceptance will require time.

## Research and Development Needs

Specific research and development needs include

- obtaining a thorough understanding of sorption hysteresis, specifically including an elucidation of the responsible mechanism (where possible, develop methods to correlate and predict data on sorption hysteresis);
- developing models, preferably mechanistic, to describe the kinetics of contaminant desorption from soils and, where appropriate, coupled sorption and desorption-bioaccumulation models;
- developing easy-to-use tools for the routine application of state-of-the-art information or models relating to soil sorption and desorption (tools must include protocols for measuring or obtaining the chemical-specific and soil-specific parameters required by the models);
- evaluating the impacts of soil heterogeneity at different scales (i.e., micro and macro) on contaminant-soil interactions. Particularly, determining the range in kinetic and thermodynamic sorption parameters expected across a site;
- assessing the significance of biofacilitated desorption, both in the environment and in vivo; and
- establishing technical protocols for measuring sorption and desorption parameters.

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### SECTION III

## MEASURING BIOAVAILABILITY