FUNDAMENTAL ISSUES IN SORPTION RELATED TO PHYSICAL AND BIOLOGICAL REMEDIATION OF SOILS

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Abstract: Sorption of organic contaminants to natural particles plays a fundamental role in their biological availability. This paper considers the influence of sorption thermodynamics and kinetics on contaminant bioavailability, with emphasis on the author's prior work. Equilibrium bioavailability is evaluated by examining the effects of sorption behavior on the Biomembrane-Soil Organic Carbon Concentration Factor ($BS_{OC}CF$), defined as the ratio of biomembrane-water to soil OC-water distribution coefficients. Phosphatidylcholine liposomes are used to model the biomembrane phase. The influence of sorption kinetics is discussed for circumstances in which desorption from particles is rate limiting to bio-uptake. Factors examined include the influence of contaminant structure, contaminant concentration, the concentration of competing co-solutes, and irreversible sorption phenomena such as hysteresis and conditioning effects. The generation of a highly desorption-resistant fraction and the underlying causes of desorption resistance are discussed, especially in the context of a 'matrix collapse' outcome of irreversible sorption. A section is included on 'facilitated bioavailability,' in which cells may access sorbed molecules directly or are able to promote desorption by altering the chemical or physical properties of the soil particle or surrounding liquid.

Key words: liposomes; dual mode model; polycyclic aromatic hydrocarbon; polychlorinated biphenyl; bioremediation; glassy polymer; nonlinear sorption; competitive sorption; sequestration; pore deformation hypothesis

1.   INTRODUCTION

Sorption plays a role in all aspects of contamination of soils and sediments by organic compounds. Sorption governs the transport of contaminant molecules, regulates the fluid-phase concentration surrounding the biological membrane through which contaminant molecules must pass to exert a toxic effect, and governs the availability of contaminant residues for physical-chemical or biological removal. The study of sorption has been a major branch of environmental science for decades because of its central importance. Usually, the emphasis is on the role of sorption in contaminant transport in the environment. This paper will focus primarily on the influence of sorption on bioavailability. It will mainly review the work of our group directed toward an understanding of the thermodynamics and kinetics of sorption regarding its influence on bioavailability.

2.   THERMODYNAMIC REGULATION OF BIOAVAILABILITY

The uptake of a pollutant molecule by an organism occurs after that molecule has passed from the gas or aqueous solution phase through a biological membrane (cell membrane or higher-order membrane) and into the interior of the organism where it can accumulate, be metabolized, or exert a toxic effect. There is no convincing evidence that molecules can pass directly from the soil-sorbed state to the membrane, bypassing the fluid phase. The uptake of most anthropogenic organic pollutants is believed to be passive — that is, it occurs by diffusion through the membrane rather than by active transport processes. The flux into the cell at any instant is governed by the concentration existing at the interior interface of the biomembrane.

To evaluate the thermodynamic regulation of bioavailability by sorption for a contaminant, i, we consider the situation in which the sorbed, dissolved, and the membrane-bound states are close to equilibrium, and in which the rate-limiting step is mass transport from the membrane into the interior, or some other intracellular step (Scheme 1).
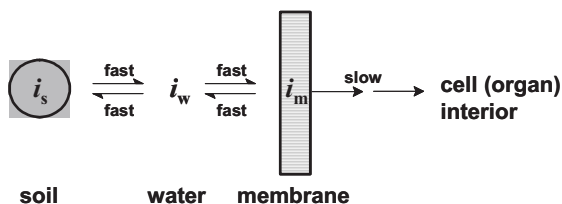
(Scheme 1)

This situation is realistic when sorption and membrane partitioning are rapid compared to intracellular steps, or if the receptor does not appreciably reduce the chemical concentration immediately surrounding it during the duration of exposure. Partitioning of contaminant into the vapor phase in Scheme 1 is omitted for simplicity. Vapor-phase concentration is related to solution-phase concentration by the Henry's law coefficient.

It is widely accepted that sorption of most neutral organic compounds occurs predominantly to the soil organic matter (SOM) fraction. The model historically (and still most frequently) used to describe sorption to SOM is in the linear partition model:

$$C_s / f_{oc} = C_{oc} = K_{ocw} C_w \qquad (1)$$

where C_s [mol/kg$_s$] is the sorbed concentration in the whole soil; f_{oc} is the fraction of soil organic carbon (OC); C_{oc} is the OC-based sorbed concentration [mol/kg$_{oc}$], C_w is the aqueous solute concentration [mol/L$_w$], and K_{ocw} is OC-water partition coefficient [L$_w$/kg$_{oc}$].

Likewise, the equilibrium expression for partitioning between water and the biomembrane is given by:

$$C_m = K_{mw} C_w \qquad (2)$$

where C_m is the membrane-phase concentration [mol/kg$_m$ or mol/L$_m$] and K_{mw} is the membrane-water partition coefficient [L$_w$/kg$_m$ or L$_w$/L$_m$].

We may now define the Biomembrane-Soil Organic Carbon Concentration Factor (BS$_{oc}$CF) [kg$_{oc}$/kg$_m$] as the ratio of concentrations in the membrane and the soil, obtained by combining eqs 1 and 2:

$$\text{BS}_{oc}\text{CF} = \frac{C_m}{C_{oc}} = \frac{K_{mw}}{K_{ocw}} \qquad (3)$$

We will see in subsequent discussion how the BS$_{oc}$CF is affected by various factors influencing the sorption process.

2.1   Effect of Contaminant Structure

Extensive literature is available on the effect of solute structure on sorption by soils from aqueous solution. The most useful correlation is the linear free energy relationship (LFER) between OC sorption and 1-octanol-water partitioning:

$$\log K_{ocw} = a_{oc} \cdot \log K_{ow} + b_{oc} \tag{4}$$

where K_{ow} is the 1-octanol-water partition coefficient and a_{oc} and b_{oc} are regression coefficients. This correlation is strong for a related set of compounds. A linear relationship with a similar slope may also be constructed between log K_{ocw} and the solute molar volume. The K_{ow} and the solute molar volume primarily reflect 'hydrophobic effects,' which have to do with expulsion of organic molecules from the less favorable environment of the aqueous phase into a more favorable environment of the organic phase. When the dataset includes compounds that are not closely related—especially when it includes a mix of polar and apolar compounds—it is more accurate to use multi-parameter LFERs that take into account the net effects of all possible weak interactions (London, Keesom, Debye, H-bonding, etc.) that occur between the molecule and its surroundings in the sorbed and dissolved states (Goss and Schwarzenbach, 2001; Nguyen et al., 1995). However, for our purposes the simpler single-parameter model is satisfactory.

Values of K_{ocw} have been determined for many compounds in many different soils and sediments. Regression curves for "polycyclic aromatic hydrocarbons (PAHs)," "halogenated hydrocarbons," and "polar compounds" collected from the literature by Nguyen et al. (2005) are shown in Figure 1.

A LFER may likewise be constructed between biomembrane-water partitioning and 1-octanol-water partitioning:

$$\log K_{mw} = a_m \cdot \log K_{ow} + b_m \tag{5}$$

where a_m and b_m are regression coefficients. Chemical partitioning in real biomembranes is experimentally difficult and instead researchers have used models. The simplest and most widely accepted models are artificial bilayer phospholipid vesicles based on phosphatidylcholine monomers known as *liposomes*. Partitioning of nonionic compounds (or the neutral form of ionogenic compounds) in liposomes is characteristically linear with concentration, except at aqueous concentrations approaching solubility (Escher and Schwarzenbach, 1996). Figure 1 includes the regression curves for selected liposome systems. The log K_m-log K_{oc} relationship is essentially linear for a closely-related set of chemicals up to about log K_{ow} ~7. Above log Kow ~7, the slope of the relationship for polychlorinated biphenyl (PCB) partitioning in liposomes seems to decline, and even become slightly negative. This has been attributed to steric effects in packing of the highly chlorinated congeners (Dulfer and Govers, 1995).

Combining eqs 4 and 5 with eq 3 gives an expression for the BS$_{oc}$CF as a function of K_{ow}:

$$\log(\text{BS}_{oc}\text{CF}) = (a_m - a_{oc}) \cdot \log K_{ow} + (b_m - b_{oc}) \tag{6}$$

Figure 2 plots eq 6 for selected combinations of data sets represented in Figure 1. Similar plots can be made by substituting solute molar volume for log K_{ow}. From the graph in Figure 2 it can be seen, first, that there is little dependence of BS$_{oc}$CF on K_{ow} below log K_{ow} ~7. This means that among neutral compounds of the same type in a given soil, the equilibrium bioavailability is almost independent of hydrophobic character or molecular
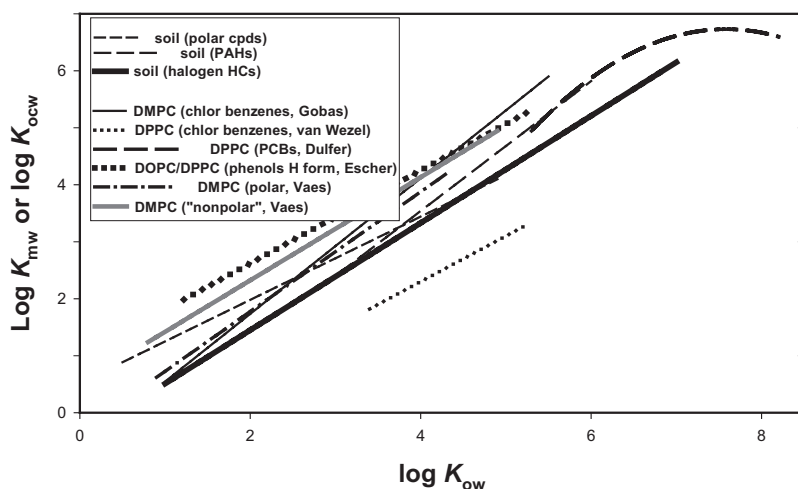

Figure 1. Relationship liposome-water and soil organic carbon-water partition coefficients to n-octanol-water partition coefficient. DOPC = L-α-dioleylphosphatidylcholine; DPPC = L-α-dipalmitoylphosphatidylcholine; DMPC = dimyristoylphosphatidylcholine. The correlations for 33 halogenated hydrocarbons in soil (log K_{ocw} = 0.94 log K_{ow} − 0.43), 11 PAHs in soil (log K_{ocw} = 1.14 log K_{ow} − 1.02), and 21 polar compounds in soil (log K_{ocw} = 0.73 log K_{ow} − 0.52) are from Nguyen et al. (2005). The correlation for chlorinated benzenes in DMPC (log K_{mw} = 1.19 log K_{ow} − 0.645) is from Gobas et al. (1988), for seven chlorinated benzenes in DPPC at 23 °C (log K_{mw} = 0.80 log K_{ow} − 0.90) is from van Wezel et al. (1996), for fourteen PCBs in DPPC (log K_{mw} = -0.343 (log K_{ow})^2 + 5.20 log K_{ow} − 12.98) is from Dulfer and Govers (1995), for polar compounds in DMPC (log K_{mw} = 0.904 log K_{ow} + 0.515) is from Vaes et al. (1997), and for nonpolar compounds in DMPC (log K_{mw} = 1.05 log K_{ow} − 0.324) is from Vaes et al. (1997). The correlation for twenty neutral phenols in DOPC/DPPC (8:2 ratio) is the regression line (log K_{mw} = 0.815 log K_{ow} − 0.989; r^2 = 0.958) through data tabulated in Escher and Schwarzenbach (1996).
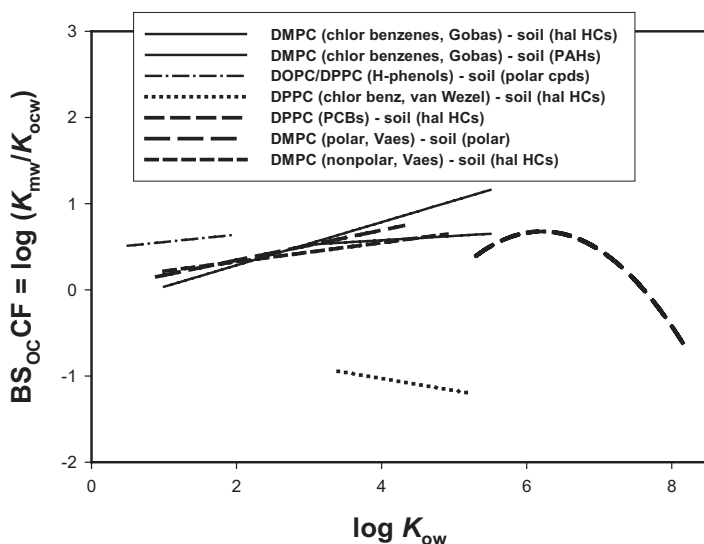
Figure 2. Relationship between Biomembrane-Soil Organic Carbon Concentration Factor and *n*-octanol-water partition coefficient for different series of compounds represented in Figure 1. For the PCB curve, the K_{oc}-K_{ow} LFER was extended a log unit beyond the included data set to log K_{ow} = 8.

size. For example, benzene and the four-ring PAH, pyrene are predicted to have nearly the same bioavailability under equilibrium conditions. Second, there is less than about a factor-of-three difference between polar and apolar compounds. Third, log $BS_{oc}CF$ ranges between 0 and 1 in most cases, which means that the distribution tends to modestly favor the membrane phase over the soil OC phase as a whole. An exception is the data set based on chlorinated benzene partition coefficients in DPPC (van Wezel et al., 1996) that is in substantial disagreement with the others.

2.2 Effect of Contaminant Concentration

Equation 3 assumes that sorption in both the membrane and soil is concentration-independent. While usually the case for liposomes, it is not generally the case for soils. An isotherm model that has been widely employed is the Freundlich model:

$$C_s / f_{oc} = C_{oc} = K_{F,ocw} C_w{}^n \tag{7}$$

where $K_{F,ocw}$ is the OC-based Freundlich coefficient and n is the Freundlich exponent, which can take on any value, but is usually less than 1. A value less than 1 indicates decreasing affinity for the solid with increasing concentration. The Freundlich model does not always fit the data perfectly, but it is useful for our purposes. The expression for $BS_{oc}CF$ incorporating nonlinearity of soil sorption is:

$$BS_{oc}CF = \frac{C_m}{C_{oc}} = \frac{K_{mw}}{K_{F,ocw}} C_w^{\,1-n} \tag{8a}$$

or

$$BS_{oc}CF = \frac{C_m}{C_{oc}} = \frac{K_{mw}}{K_{F,ocw}^{\,1/n}} C_{oc}^{\,\frac{1-n}{n}} \tag{8b}$$

depending on whether $BS_{oc}CF$ is expressed as a function of solute or sorbate concentration.
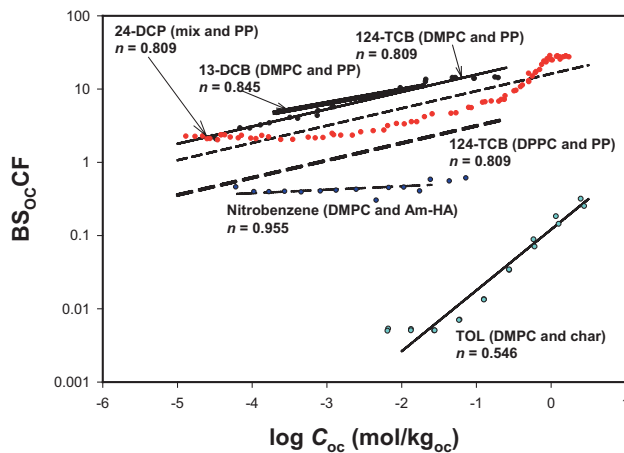

Figure 3. Biomembrane-Soil Organic Carbon Concentration Factor ($BS_{oc}CF$) for selected compounds. Given is n, the Freundlich exponent. 1,3-Dichlorobenzene and 1,2,4-trichlorobenzene in DMPC and DPPC liposomes used measured K_{mw} values listed in van Wezel et al. (1996). 2,4-Dichlorophenol used measured K_{mw} value from Escher and Schwarzenbach (1996). Toluene and nitrobenzene K_{mw} values were calculated by the liposome-octanol LFER expression of Gobas et al. (1988).

Figure 3 plots $BS_{oc}CF$ versus sorbate concentration for selected systems where the soil isotherms are known in detail and when the liposome-water partition coefficients have been measured or can be estimated by the K_m-K_{ow} LFERs in Figure 1. The examples displayed include both polar and apolar compounds and isotherms that vary from almost linear to highly nonlinear. Shown are actual data calculated as C_m/C_{oc} as well as the Freundlich model predicted curves. The $BS_{oc}CF$ is nearly constant for compounds whose isotherms are close to linear (e.g., nitrobenzene in a humic acid ($n = 0.955$). By contrast, compounds that give strongly nonlinear isotherms in soil have $BS_{oc}CF$ values that are correspondingly non-constant with concentration. By example we may consider partitioning of toluene between a liposome and charcoal, which is a form of "black carbon" present in many soils and believed to be an especially strong adsorbent of organic compounds. The isotherm of toluene on charcoal is highly nonlinear ($n = 0.546$); accordingly, the $BS_{oc}CF$ increases by two orders of magnitude over the experimental concentration range of slightly more than two orders of magnitude. Compounds with more typical Freundlich n values, such as 2,4-dichlorophenol and 1,2,4-trichlorobenzene in a peat soil ($n = 0.809$ in both cases) give intermediate results. In these cases, $BS_{oc}CF$ increases by about one order of magnitude over about five orders of magnitude in concentration.

One can expect that as concentration falls during the course of degradation, uptake or through dilution of the liquid phase, the membrane becomes less and less effective from a thermodynamic standpoint in attracting contaminant molecules. Molecules sorbed to black carbon are less bioavailable than molecules sorbed to SOC as a whole, and become even less so as uptake or degradation proceeds.

2.3   Competition for Sorption by Co-Solutes

When a nonlinearly sorbing compound is present in a system containing one or more additional compounds there may be competition for mutually accessible "sites." This follows from the fact that nonlinear sorption is a form of self-competition. Competitive effects are important because contaminant mixtures occur far more commonly than single contaminants. Competitive equilibrium sorption seems to be fairly commonly observed in soil and sediment systems containing two or three organic solutes and can be predicted using established competitive sorption models (Pignatello, 1991; Xing et al., 1996; Xing and Pignatello, 1997, 1998; White et al., 1999; White and Pignatello, 1999; Zhao et al., 2001, 2002). In addition, competitive effects have been observed between contaminants and naturally-occurring aromatic acids (Xing et al., 1998). Competitive sorption in liposomes or real

biomembranes has not been addressed experimentally, but is expected to be absent for at least two reasons. First, the fluid-like nature of the membrane is conducive to sorption linearity, except possibly at concentrations approaching solubility. Second, active membrane transport, which could involve association at specific sites on the membrane, is widely believed unlikely for most pollutants.

An example of the potential effect of competitive sorption on equilibrium bioavailability is illustrated here. Zhao et al. (2002) reported the suppression of anthracene sorption in estuarine sediment in the presence of phenanthrene and pyrene. The isotherm of anthracene was displaced downward and became more linear in the presence of the other two solutes. Figure 4 shows that the $BS_{oc}CF$ of anthracene calculated for a DMPC-estuarine sediment system increases by an order of magnitude or more in the presence of the other two PAHs. The dependence of $BS_{oc}CF$ on phenanthrene concentration in the tri-solute system is almost eliminated, consistent with an increase in the linearity of its isotherm when the other PAHs are present.
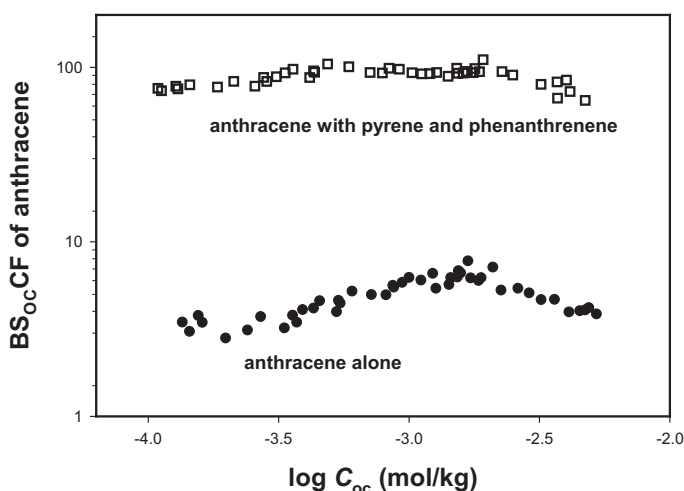

Figure 4. Effect of co-solute competitive sorption on Biomembrane-Soil Organic Carbon Concentration Factor calculated for anthracene. Model membrane: DMPC liposomes; soil: estuarine sediment from Long Island Sound (Zhao et al., 2002). Competing solutes: phenanthrene and pyrene. The K_m for anthracene in DMPC was calculated using the K_m-K_{ow} LFER of Gobas et al. (1988).

There is also direct evidence that bioavailability is enhanced when a competitor is present. Mineralization of phenanthrene in two different soils

by *Pseudomonas* Strain R, a culture grown up on phenanthrene, was enhanced when pyrene was added (White et al., 1999). Pyrene was non-biodegradable by this organism and probably did not induce the degradation of phenanthrene. In parallel sterile experiments, it was shown that pyrene added after equilibration of phenanthrene quickly displaced phenanthrene into solution, resulting in a reduction in the apparent soil-water distribution ratio of phenanthrene by up to 44 to 83% relative to a control (White and Pignatello, 1999).

A reduction in the distribution ratio of a principal solute by a competing co-solute results in an increase in the aqueous concentration of the principal solute, which, in turn, leads to a higher concentration in the biomembrane phase, and therefore enhanced bioavailability of the principal solute. One may anticipate that if the co-solute is consumed by organisms, or otherwise lost from the system, along with the principal solute, the bioavailability of the principal solute would decline accordingly.

2.4   Effect of Irreversible Sorption Behavior

Physi-sorption of organic compounds is commonly assumed to be reversible. It is becoming clear, however, that this assumption is not generally valid: sorption depends on the prior sorption history of the sample. This can be manifested in two ways: by *hysteresis* in the isotherm, i.e., the non-singularity of the sorption and desorption branches (Scheme 2a), or by the *conditioning effect*, which refers to the enhanced sorption observed in a repeated experiment on the same sample after a prior sorption-desorption cycle (Scheme 2b). When not due to artificial causes, these phenomena comprise *irreversible sorption*. The term irreversible is used in the thermodynamic sense to mean that the pathways for desorption and sorption are different. It does not necessarily imply irretrievability of the chemical. In both hysteresis and conditioning phenomena one can see that sorption is enhanced in a subsequent experiment, whether it be desorption or repeat sorption.

Hysteresis is observed after diluting the fluid phase of an equilibrated system to induce desorption and finding that the newly-equilibrated point does not fall back on the original sorption isotherm. While artificial causes of hysteresis are possible, Sander and Pignatello (2005b) have verified true hysteresis in several cases using isotope exchange techniques. In systems exhibiting hysteresis, they found complete exchange when a tiny amount of ^{14}C-labelled chemical was added or removed at the initial bulk-chemical

a) hysteresis
b) conditioning effect
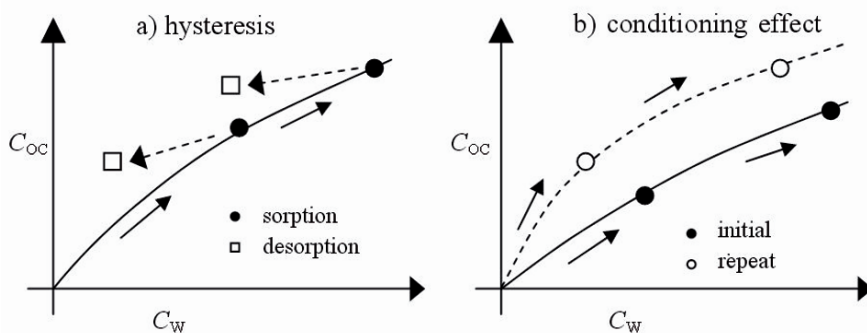
Scheme 2

sorption or desorption points, keeping bulk chemical concentration constant. This indicates that sorption is reversible for infinitesmal changes in concentration, but is irreversible (i.e., truly hysteretic) for large changes in concentration.

The conditioning effect is observed by constructing a sorption isotherm on a sample that previously sorbed the chemical of interest or some other chemical serving as a "conditioning agent." (The conditioning agent is removed before the isotherm is constructed.) The conditioning effect is revealed by comparing the isotherm on the conditioned sample with that on a control sample that had no previous history of sorption, but was carried though the same physical manipulations (Xia and Pignatello, 2001; Lu and Pignatello, 2002, 2004; Sander et al., 2006).

It is not possible thermodynamically for a given solute concentration to correspond to multiple sorbed concentrations. It follows that irreversible sorption must arise from the generation of metastable states. The cause of hysteresis in sorption of organic compounds to natural organic matter has been attributed (Lu and Pignatello, 2002, 2004; Sander et al., 2005; Sander et al., 2006) to the same mechanism that generally causes hysteresis in glassy polymers and macromolecular organic solids. (The polymer analogy for natural organic matter is well accepted among environmental scientists.) This mechanism for hysteresis is referred to as "pore deformation."

Non-crystalline organic solids such as polymers may exist in the rubbery (flexible-chain) state or the glassy (stiff-chain) state. Which state the solid assumes depends on its chemical composition, temperature, and the concentration of plasticizers. Plasticizers are chemical absorbents —including the absorbing chemical of interest — that soften the polymer and increase the chain flexibility by virtue of forming plasticizer-chain interactions at the expense of chain-chain interactions. For example, phthalate esters are often added to stiff plastics to make them pliable.

The glassy state of an organic solid is perpetually metastable because the stiffness of its chains prohibits its complete relaxation to the thermodynamic state. As a result, the glassy state contains excess free – volume – essentially packing defects in the form of molecular-scale cavities, or "holes." In order to understand irreversible sorption in the context of the pore deformation mechanism one must realize that for absorption to occur in either rubbery or glassy solids, a cavity of appropriate size must pre-exist or be created inside the solid to accommodate the incoming sorbate molecule, as illustrated in Scheme 3.
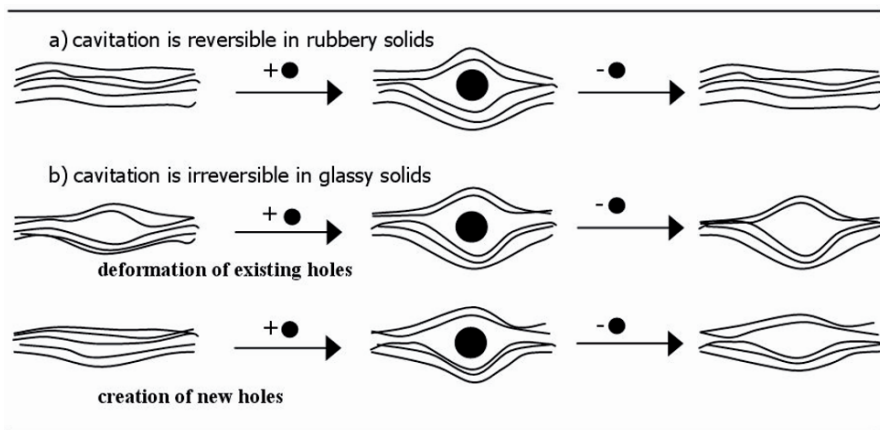
(Scheme 3)

In rubbery solids, cavitation is more-or-less reversible during a sorption-desorption cycle because the chains are sufficiently flexible and can relax on a timescale that is as short or shorter that the timescale of desorption. For glassy solids, however, cavitation is not always irreversible due to the inflexibility of the macromolecules. Molecules entering pre-existing holes that are too small may induce expansion of the hole that then does not fully relax when the molecule leaves; likewise, molecules entering areas lacking excess free volume may create a cavity that does not fully relax when the molecule leaves. In both cases, the solid is left with a higher free volume after desorption. Accordingly, this results in a higher affinity for sorbing molecules in a subsequent sorption experiment because the free energy of hole expansion/creation has already been invested by the previous sorption step. Annealing the conditioned soil or humic acid samples at temperatures up to $90^{\circ}C$ leads to a time- and temperature-dependent relaxation of the sorption distribution coefficient towards original values (Lu and Pignatello, 2002; Sander et al., 2006), indicating that matrix relaxation is activated, and providing convincing support for the pore deformation mechanism.

Figures 5 and 6 illustrate how sorption irreversibility can affect bioavailability. Figure 5a shows the hysteretic isotherm of 1,4-dichlorobenzene in a soil, which is one of several isotherms in various soils that has been identified as being truly hysteretic after rigorous experimentation to rule out artifacts (Sander and Pignatello, 2005b). Hysteresis in this example is considered to be moderate; that is, the Thermodynamic Index of Irreversibility (TII) is calculated to be 0.3-0.6, depending on concentration, on a scale of 0 to 1 (Sander et al., 2005). Figure 5b plots the $BS_{oc}CF$ for sorption and desorption data in Panel a and shows that hysteresis is expected to lead to a decrease of up to about a factor of two in thermodynamic bioavailability.

Figure 6a shows the isotherms of 1,2,4-trichlorobenzene in a soil before and after conditioning with chlorobenzene (Sander et al., 2006) one sees that the conditioning effect in these examples leads to up to a factor of three increase in sorbed concentration at a given solute concentration after conditioning. Similar results were obtained for 1,3-dichlorobenzene in a soil humic acid (Sander et al., 2006), for trichloromethane in a soil (Xia and Pignatello, 2001), and for chlorinated benzenes in glassy poly(vinyl chloride) (Sander et al., 2006). (As expected, the conditioning effect was not found for rubbery polyethylene (Sander et al., 2006).) Figure 6b shows that conditioning leads to a reduction of the $BS_{oc}CF$ for 1,2,4-trichlorobenzene in Pahokee peat by a factor of about two in the conditioned sample compared to the control.
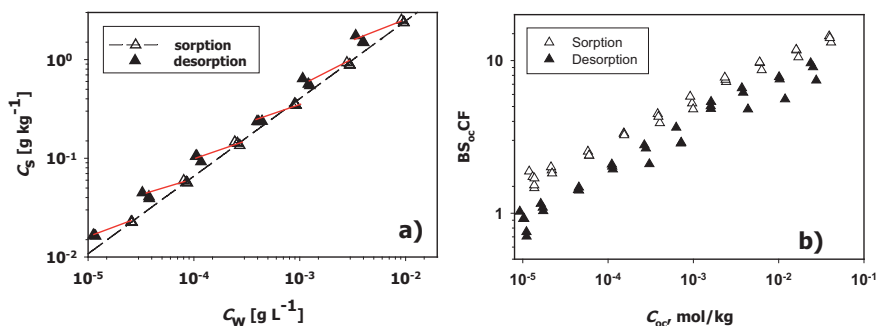

Figure 5. Effect of sorption irreversibility manifested as hysteresis on the calculated biomembrane-soil organic carbon concentration factor ($BS_{oc}CF$) for 1,4-dichlorobenzene on Pahokee peat. (a) sorption and single-step desorption points; dashed line is fit of sorption data to the Freundlich equation and solid lines link desorption replicate points to their corresponding origin on the sorption branch. (b) $BS_{oc}CF$ versus solid-phase concentration for the system in panel a, using experimental data for DMPC liposomes (Gobas et al., 1988).
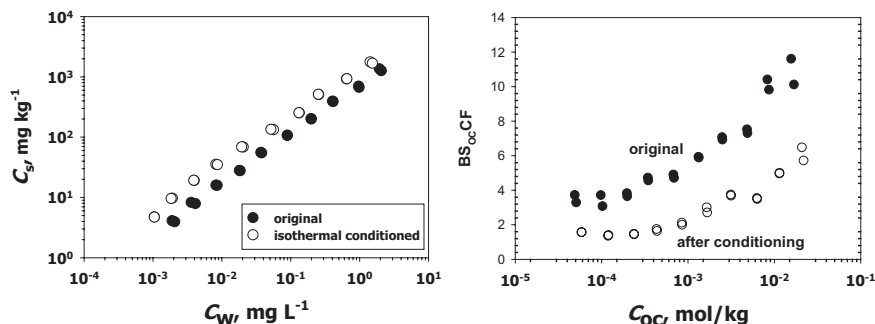
Figure 6. Effect of sorption irreversibility (manifested as the conditioning effect) on the calculated biomembrane-soil organic carbon concentration factor ($BS_{oc}CF$) for 1,2,4-trichlorobenzene on Pahokee peat soil. (a) sorption isotherms (Sander et al., in press). (b) $BS_{oc}CF$ with respect to DMPC liposomes corresponding to Panel a.

3.   MASS TRANSPORT LIMITATIONS TO BIOAVAILABILITY

When nonequilibrium conditions prevail during exposure it is necessary to consider mass transport rate laws describing the flux of chemical through the particle, across the particle-bulk fluid interface, across the fluid-biomembrane interface, and through the biomembrane phase. These fluxes are dictated by convection and/or diffusion rate laws applicable to each phase, which, in turn, depend on the geometry of the phase, the concentration gradient that exists within the phase at any given time, and the boundary conditions. All-encompassing rate laws are not easy to write given the heterogeneity of the system. Although few data are available, it may be predicted that intra-membrane mass transport is relatively rapid in view of the fluid nature of the membrane and its thickness. Experience indicates that intra-particle mass transport, by contrast, may be relatively slow; depending on the compound and soil, equilibrium in a spiked aqueous soil suspension may require as short as a few hours or as long as several months (Pignatello and Xing, 1996). It will often be the case, then, that that incorporation of a contaminant by an organism will eventually become rate-limited by intra-particle mass transport. This is illustrated in Scheme 4.
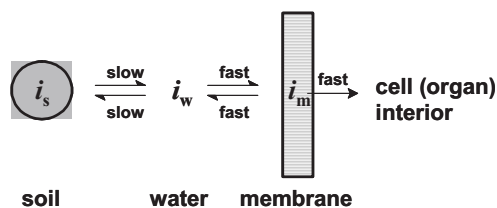
(Scheme 4)

3.1 Effect of Solute Structure

The most systematic studies in this regard were performed by Brusseau and co-workers using frontal analysis of elution profiles obtained in soil column experiments. The analysis was based on the "two-site" model, which postulates instantly-reversible and slowly-reversible compartments. While this distinction is artificial, the results can be used for comparative purposes. The log of the rate parameter for the slowly-reversible compartment for a given soil correlated inversely with the solute's equilibrium sorption affinity, such as log soil-water partition coefficient (Borglin et al., 1996), the first-order valence molecular connectivity index—a measure of molecular topology—(Piatt and Brusseau, 1998), or log K_{ow} (Piatt and Brusseau, 1998). Other studies with more limited data sets confirm these trends, at least qualitatively. Such behavior is consistent with the notion that the stronger the compound sorbs, the slower will be its progress of random migration through intraparticle pores or the organic matter matrix to/from the bulk water interface.

3.2 Effect of Solute Concentration

It is predicted theoretically that normalized sorption or desorption rate or the calculated diffusion rate parameter will be concentration-dependent for compounds showing a nonlinear isotherm, and concentration-independent for compounds showing a linear isotherm (Braida et al., 2001, 2002; Zhao et al., 2001, 2004). For example, for a compound with Freundlich $n < 1$, sorption becomes progressively weaker as concentration increases; thus, normalized rate or diffusion parameter is expected to increase with final concentration in the uptake direction or with starting concentration in the release direction.

In many cases we have found that the dual-mode model (DMM), originally proposed in connection with isotherms of gases and organic vapors in glassy polymers, fits sorption isotherms of chemicals in soil better than the Freundlich model (Xing and Pignatello, 1997; Xia and Pignatello, 2001). The DMM, which applies to natural organic matter as the sorbent, contains a dissolution domain (described by a linear term) and a hole-filling domain (described by a Langmuir term):

$$C_{OC} = K_D C_W + \frac{C_{OC}^{max} \cdot b \cdot C_W}{1 + b \cdot C_W} \tag{9}$$

where K_D is the dissolution-domain partition coefficient and C_{OC}^{max} and b are the hole-filling domain capacity and affinity coefficients, respectively. If one assumes—as in the polymer model—that molecular "jumps" between holes and the surrounding dissolution domain are much slower than jumps within the dissolution domain, the apparent diffusion coefficient (D_{app}) can be written as the product of a concentration-independent diffusion coefficient reflecting diffusion within the dissolution domain and a concentration-dependent term reflecting exchange between dissolution and hole sites (Zhao et al., 2002). Thus, D_{app} is expected to be independent of concentration at very low and very high concentrations, where as inspection of equation 9 reveals the isotherm is linear, and dependent on concentration at intermediate levels, where the isotherm is nonlinear.

The expectation of concentration-dependent kinetics is met experimentally, with some complications due to shifting boundary conditions (Braida et al., 2001, 2002; Zhao et al., 2001, 2004). In all these studies sorption or desorption is found to increase in rate with increasing final or initial concentration, respectively. Recently, isotope exchange experiments, in which ^{14}C-labelled chemical exchange rates were followed after equilibration of bulk chemical at two widely-spaced concentrations, clearly showed that sorption and desorption are both relatively slower at the lower concentration (Sander and Pignatello, 2005b). We have also shown that the normalized desorption rate increases in the presence of a competing co-solute, although it was not possible to apportion the rate increase between thermodynamic and kinetic effects (Zhao et al., 2002).

3.3   **Strongly Resistant Desorption**

Since the late 1980s there have been many published reports demonstrating biological effects that are apparently controlled by sorption-desorption kinetics (e.g., Pignatello and Xing, 1996; Alexander, 1995, 2000).

First, compounds that do not equilibrate rapidly with soil (e.g., polycyclic aromatic hydrocarbons) become less bioavailable to an organism (e.g., bacteria or earthworms) as the soil-chemical pre-contact time in the absence of the organism increases. This is due to continued diffusion of the contaminant to sites in the soil particles further and further removed from contact with the bulk fluid, where it becomes more and more resistant to desorption once the organism is introduced.

Second, contaminated soil or sediment collected from the environment often contains a fraction of the total extractable chemical present in a state that strongly resists desorption. In several cases a correlation exists between the desorption-resistant fraction and the fraction that is unavailable or much less available to a test organism.

Third, many studies examining sorption independently have shown that addition of a chemical to an initially clean soil often generates a minor fraction that strongly resists desorption. For example, Figure 7 shows the desorption profiles of phenanthrene from six different soils (Braida et al., 2002). Nine other soils showed similar behavior. The soils were pre-equilibrated with phenanthrene for 180 days under sterile conditions prior to initiating desorption. Uptake rate studies indicated apparent equilibrium (leveling off of the solution-phase concentration) occurred well within this timeframe. Desorption was carried out in the presence of Tenax polymer (beads) which rapidly and efficiently takes up desorbed molecules and, thus, serves as an infinite sink (Zhao and Pignatello, 2004). The Tenax was replaced at each desorption step, ensuring the steepest possible gradient in phenanthrene concentration across the soil-bulk water interface and, thus, the maximum rate of desorption. Except in the case of Mount Pleasant silt loam, a substantial fraction of phenanthrene resisted desorption after 500-600 days of desorption to infinite dilution. This fraction, which ranged from about 5 to 30% of the initial amount added, was recovered by hot-solvent extraction as unaltered phenanthrene. The desorption resistant fraction decreased with increasing applied phenanthrene concentration.

Plausible mechanisms for formation of strongly immobilized fractions in soils include: (i.) chemisorption, (ii.) entrapment during particle synthesis, (iii.) diffusion into remote sites, and (iv.) post-sorption rearrangement of the local matrix leading to sterically hindered desorption.

Chemisorption includes formation of covalent bonds with organic matter or coordination complexes with metal ions in the solid. Covalent linkage is possible if the sorbate undergoes chemical or biological transformation, and
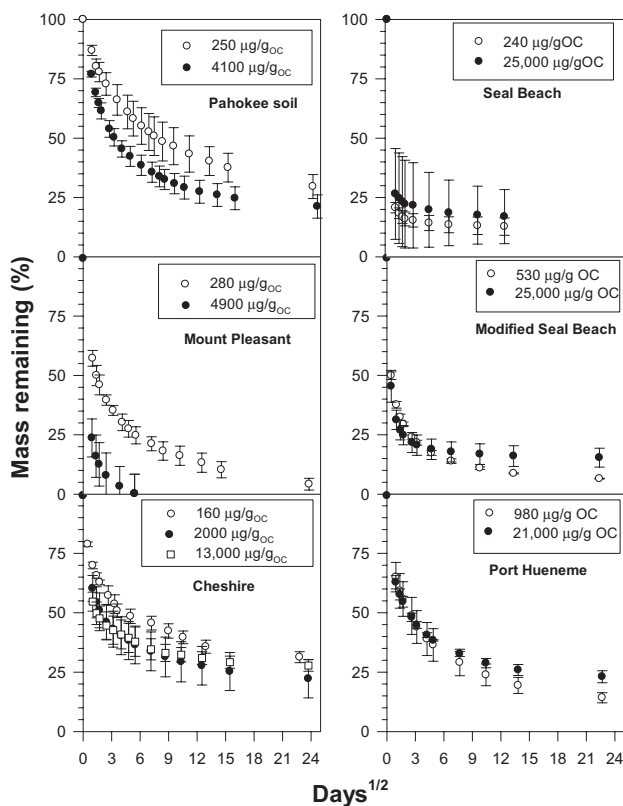
Figure 7. Desorption profiles of phenanthrene after 180 days pre-equilbration in soil-water suspension at indicated initial concentrations. Error bars represent cumulative uncertainty (95% level) of three to four replicates. Reprinted with some modification from Braida et al. (2002) with permission from the Society of Environmental Toxicology and Chemistry.

many examples of such reactions have been reported. In most cases, however, covalent bond formation leads to permanent loss of compound identity, even if any of the original atoms ultimately were to become bioavailable. Thus, covalent coupling cannot be said to lead to "desorption resistance." Coordination complexes require certain functional groups (e.g., a carboxyl or sulfhydryl) capable of forming inner-sphere bonds with the metal. Dissociation can be considerably slower than association. However, it should be realized that desorption resistance is broadly applicable, applying to compounds that do not contain any interacting functional groups whatsoever.

Entrapment during particle synthesis likely contributes to desorption resistance of PAHs in black carbon particles. Sediments rich in black carbon often contain a fraction of PAH compounds in a highly immobile state. Since PAHs are co-formed with soot during combustion of fuels, their apparent immobilization may result from entrapment in closed micropores during particle formation. Organic solvents are known to swell black carbon (Jonker and Koelmans, 2002; Braida et al., 2003), so such molecules can be counted as part of the total PAH because they would be liberated during analytical extraction.

Molecules may also be rendered desorption resistant if a fraction of them diffuse into sites at the ends of especially tortuous paths. In that case, transport to or from such sites would require much longer times than to or from more available sites. This is the classical explanation for desorption resistance. It is not hard to imagine the existence of such sites. Small bits of organic matter may be occluded within mineral aggregates (Kleineidam et al., 1999). Within the organic matrix there may be micro-domains that for steric reasons require longer times to access.

The last mechanism for sorbate immobilization (iv) requires a mechanism for matrix rearrangement. Random thermal motions of natural organic matter macromolecules do, of course, occur constantly, and some of these motions might lead to encagement of sorbed molecules that happen to be there. The same random motions could lead to their release, so one would expect to reach a steady state of a small fraction of temporarily-entrapped molecules. Kan et al. (1997) proposed that a fraction of sorbate molecules is transferred to "high-affinity" micro-environments "in equilibrium with the dissolved state" that are created by virtue of "conformational or physical rearrangement of a small fraction of the organic matter." However, this model was silent about the driving force for rearrangement and the underlying cause of enhanced affinity. Weber at al. (2002) observed strong hysteresis of the phenanthrene sorption isotherm in soil and shale in the presence of high concentrations of a co-solute. They postulated that the co-solute caused swelling of the solid; when desorption was initiated by dilution of the liquid phase, the abrupt change in sorbed concentration of the co-solute caused the matrix to collapse and stiffen around phenanthrene molecules still remaining in the solid (anti-plasticization effect). However, other explanations are possible, such as reduced competition for adsorption sites by the now-diluted co-solute, a purely artificial effect (Sander and Pignatello, submitted for publication). A similar matrix collapse mechanism was invoked by Braida et al. (2003) to explain pronounced sorption hysteresis of benzene in a wood charcoal (Scheme 6). They showed conclusively that benzene caused swelling of the char particles, but they gave no direct evidence for matrix entrapment.
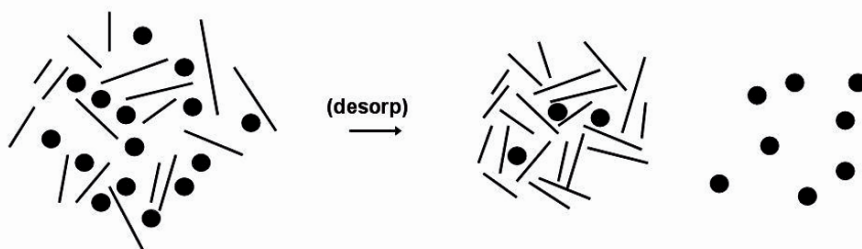
(Scheme 5)

The 'matrix collapse' hypothesis has now been given some credence by recent studies of 1,4-dichlorobenzene (DCB) sorption in two soils (Sander and Pignatello, submitted for publication). Isotope exchange in both the forward and reverse directions was followed at the bulk sorption and bulk desorption points at two widely-spaced points on the isotherm. The mass of isotopically-labelled ^{14}C-DCB added or removed was miniscule relative to the concentration of existing bulk DCB. In all cases, the label re-equilibrated to exactly the same place (i.e., same distribution coefficient within experimental error) as the bulk after 35 days, remaining so over more than 100 days total. From this result it could be estimated that at most 3% of sorbed molecules could have been rendered out of free exchange with the solution state after either the bulk sorption or bulk desorption steps. Next, the samples were desorbed in three 21-day extractions in the presence of Tenax, renewed at each step. These exhaustive desorptions left significant amounts of ^{14}C-DCB in the solid ranging from 1.7 to 18.6% of initial, as given in Table 1. The data in Table 1 are corrected for a minor amount of chemically- or biologically-transformed DCB formed during the lengthy experiment. Most ^{14}C-DCB was removed in the first Tenax extraction, with declining yields in the second and especially third Tenax extraction. The fraction finally remaining was considerably greater at lower of the two concentrations. The fraction finally remaining at the low concentration was well outside the limits of uncertainty determined in the isotope exchange experiment. This means that it is possible ^{14}C-DCB became entrapped as a result of physical collapse of the matrix induced by abrupt Tenax extraction. However, as 418 days had passed in the interim between the initial spike of ^{14}C-DCB and initiation of Tenax extraction it is possible that during this lengthy time these fractions had penetrated remote sorption sites, even though penetration to these sites could not be detected in 100-day isotope exchange experiments. Further work is required to assess this important mechanism.

Table 1. Fraction of total initial UL-14C-1,4-dichlorobenzene remaining after desorption in each of three 21-day Tenax extraction steps.

Step	Pahokee peat		Beulah-Zap	
	initially 2.34 g/kg	initially 0.042 g/kg	initially 6.21 g/kg	initially 0.19 g/kg
1	0.059 ± 0.003^a	0.186 ± 0.0066	0.0951 ± 0.007	0.101 ± 0.004
2	0.0268 ± 0.0006	0.143 ± 0.007	0.036 ± 0.003	0.065 ± 0.004
3	0.017 ± 0.001	0.120 ± 0.007	0.0230 ± 0.0008	0.051 ± 0.003

[a] Mean and standard deviation from triplicate experiments. The mean values are corrected for a small amount of label not identified as ^{14}C-DCB after hot-solvent extraction of the solid and comparison of ^{14}C-DCB concentrations determined by gas chromatography and liquid scintillation counting.

4.   FACILITATED BIOAVAILABILITY

Facilitated bioavailability refers to the ability of organisms to directly access sorbed molecules or to promote desorption by altering the properties of the soil particles or the surrounding liquid.

Many ways can be envisioned by which organisms could alter the chemistry of the fluid or even the properties of the solid. Particles entering the digestive or respiratory tracts of organisms may be subjected to desorption-inducing conditions such as, a) higher temperatures than the surroundings, b) aqueous fluids that may include dissolved biosurfactants (e.g., bile acids, Voparil et al., 2003) or competitive adsorbates, or c) abrasion that breaks up particles—for example, in the gizzards of birds. Microorganisms may exude biosurfactants that can increase the apparent dissolved concentration. Plant roots can affect soil solution chemistry. Addition of chelating agents like citrate, oxalate or pyrophosphate was found to enhance desorption of hydrophobic compounds such as PAHs from soil organic matter by solubilizing metal ions that are essential for cross-linking humic substances or bridging humic substances to mineral surfaces (Yang et al., 2001; Subramaniam et al., 2004). Solubilization of humic substances accompanied mobilization of PAHs. Some evidence suggests that exudation of chelating agents by plant roots may facilitate uptake of chlorinated hydrocarbon insecticides by this mechanism (White et al., 2003), although other explanations are possible. Natural organic acids exuded by plants can also plausibly increase bioavailability by competitively displacing contaminants from sorption sites (Xing and Pignatello, 1998).

Single-cell organisms may lie in close contact with soil surfaces and the question has arisen whether or not they may have "direct access" to molecules in the sorbed state. While some studies suggest they do not, others indicate that some microorganisms may have facilitated access to sorbed

molecules (Guerin and Boyd, 1992; Crocker et al., 1995; Dean et al., 2001; Li et al., 2005). The mechanism of facilitated access is unclear at this time. Bacterial cells are on the order of 10^{-6} m in diameter; therefore, they cannot penetrate mesopores (2-50 nm) or micropores (< 2 nm), which contribute nearly all the surface area of soil particles. Nor can they penetrate the internal matrix of natural organic matter, where sorbed molecules of nonionic organic compounds are primarily located. While it is true that the concentration of a contaminant on the particle surface on an absolute scale may be orders of magnitude higher than it is in solution, the chemical potential is identical if local equilibrium is assumed (Pignatello, 2000). Thus, at a given solution concentration, the equilibrium uptake by cell membrane is independent of whether soil is present or not.

We have attempted to address the question of facilitated access of desorption-resistant residues by bacteria. Braida et al. (2004) spiked phenanthrene to 15 different sterilized soils and allowed them to equilibrate for 180 days. Then, in separate experiments each lasting 30 days, replicate flasks were amended with either–Tenax to initiate desorption—still under sterile conditions—or with an inoculum of a bacterial culture grown on phenanthrene as the sole C and energy source. Braida et al. (2004; their Figure 4) showed the relationship between the biotransformation-resistant fraction and the Tenax desorption-resistant fraction. Most of the points lie near the 1:1 line. Two or three soils show a significantly smaller desorption-resistant fraction than biodegradation-resistant fraction, indicating that biology, not desorption was rate-limiting. Only one soil shows the opposite result consistent with facilitated desorption. In another study of phenanthrene in two soils using two bacterial cultures, White et al. (1999) showed that the normalized desorption and biodegradation rates decreased with a similar slope with pre-test sterile aging period, as did total amount desorbed and total amount biodegraded within a specified period. The results of these studies (White et al., 1999; Braida et al., 2004) underscore the link between physical availability and biological availability and point away from the facilitated bioavailability hypothesis.

A different result was obtained in another study, however. That study examined biodegradation by native microorganisms of a set of 15 PAH compounds in coal-tar residues in the soil surrounding a former manufac-tured gas plant (MGP) in Connecticut, U.S.A. (Li et al., 2005). Samples were suspended in deionized water and incubated under non-sterile conditions allowing the native organisms to degrade the PAHs. Desorption was monitored in separate sterile flasks containing Tenax and including 0.01 M citrate in solution, which was added to maximize the rate of desorption (Yang et al., 2001; Subramaniam et al., 2004). After about 100 days in each case, the remaining PAH was quantified. The results (Figure 8) show scatter

about the 1:1 line defining the relationship between biodegradation resistance and desorption resistance consistent with no facilitated bioavailability, and concordant with the studies of Braida et al. (2004) and White et al. (1999), among others. In some experiments, a suite of macro- (NH_4^+, P, K) and micro- (Mg, Ca, Fe, Co, Zn, Cu, Ni, Mo, Se, W) nutrients was included in the live flasks. Nutrient amendment was found to greatly stimulate biodegradation of PAHs in this coal tar soil. When nutrients were included, the biodegradation-resistant fraction was found to be generally smaller than the desorption-resistant fraction (Figure 9). This result suggests that microorganisms can, indeed, facilitate desorption.
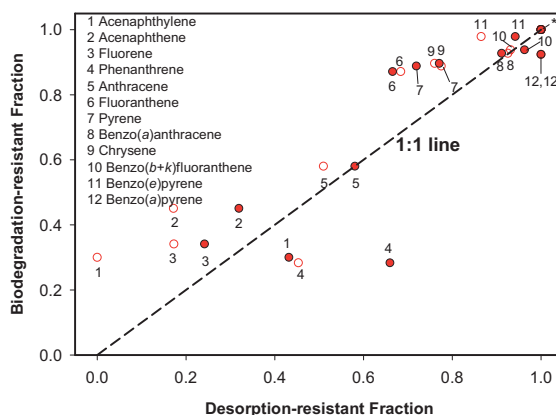

Figure 8. Comparison of biodegradation-resistant fraction (99 days) and desorption-resistant fraction (after 106 days) of PAHs in a coal tar contaminated soil. Biodegradation was carried out in soil suspension in deionized water and no supplemental culture of microorganisms. Desorption was carried out in 0.01 M citrate (open symbols) or 0.01 M pyrophosphate (filled symbols) solution and in the presence of Tenax beads to extract desorbed PAHs. Data from Li et al., 2005.

It appears that the persistence of PAHs for many decades at this MGP site is due, in part, to nutrient limitations of the native microorganisms. Exactly which nutrients are limiting is unknown. Had we not included nutrients in the experiment we would have falsely concluded no facilitated bioavailability.
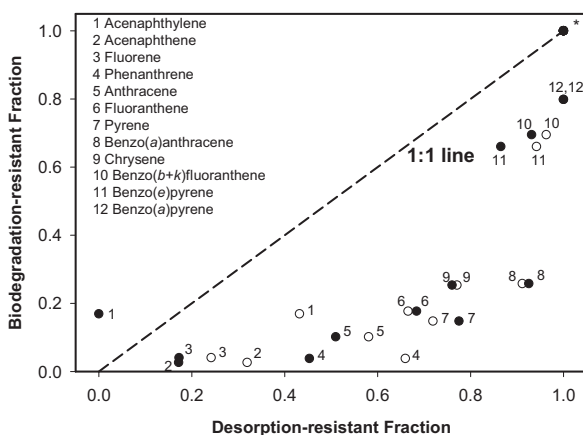
Figure 9. Same as Figure 8 except live samples contained a mixture of inorganic nutrients. Li et al., 2005; reprinted with permission from the Society of Environmental Toxicology and Chemistry.

The condition that distinguishes the coal tar case (Li et al., 2005) from the phenanthrene cases (Braida et al., 2004; White et al., 1999) is that the former followed substrate degradation by existing native organisms, while the latter two used enrichment culture amendments. (All experiments included nutrient amendment.) Thus, it is possible that native phenotypes possess unique adaptations that allow them to access pollutant mass that is unavailable to other organisms. It is also possible that the colonies are essentially different in the two experimental systems: the degraders in the coal tar soil contained established biofilms while the degrader inoculum in the phenanthrene-spiked soils was initially present as free-living cells (the degree of cell attachment was undetermined). It is possible that established biofilms extend deeper into pore structures, thus steepening the concentration gradient at the interface between the external surfaces of the particle and the bulk water. Further work is necessary to clarify the mechanism of facilitated bioavailability for microorganisms.

5.   SUMMARY

Sorption to particles in soil or sediment determines the immediate biological availability of chemicals to potentially affected organisms, the dispersion of contaminants within an ecosystem, and the transport of

contaminants to other ecosystems. Thus, sorption plays a role in the assessment of present and future risks to humans and ecosystems, and often enters into strategic decisions about remediating a contaminated site. The focus of this paper was on the role of sorption in regulating bioavailability.

The influence of sorption thermodynamics has been evaluated by considering equilibrium partitioning between soil, water and biomembrane phases. The Biomembrane Soil Organic Carbon Concentration Factor ($BS_{OC}CF$) may be defined as the ratio of biomembrane-water to soil OC-water distribution coefficients. Based on abundant sorption data and limited data on partitioning of chemicals in liposomes as model membranes one can make predictions about equilibrium bioavailability. $BS_{OC}CF$ is predicted to increase with contaminant concentration or the concentration of a competing co-solute due to the typically nonlinear nature of sorption to soil OC. Bioavailability enhancement by a competing, non-metabolized co-solute is validated experimentally for microorganisms. However, at constant concentration, the $BS_{OC}CF$ is predicted to be only weakly dependent on solute polarity or hydrophobicity indices.

Sorption exhibits "irreversible" phenomena, including hysteresis and conditioning effects caused by irreversible pore expansion of the glassy natural organic matter solid phases by the penetrating chemical. Irreversible behaviors are expected to result in a decrease in $BS_{OC}CF$. Because irreversible sorption always results in enhanced sorption affinity in a subsequent experiment, it is predicted to result in a decrease in equilibrium bioavailability.

The influence of sorption kinetics is discussed for circumstances in which desorption from particles is rate limiting. The characteristic sorption/desorption rate parameter (or normalized rate of uptake or release) decreases with solute molecular size, increases with solute concentration, and increases with concentration of a competing co-solute. Collected field samples often contain a strongly desorption-resistant fraction. Also, such a fraction may be generated when a contaminant is added to a clean sample. Mechanisms for sequestration include entrapment by co-condensation during particle synthesis (i.e., PAHs in soot particles), diffusion to 'remote' sites, and matrix collapse following sorption. The matrix collapse mechanism is a possible outcome of the irreversible pore deformation mechanism of sorption irreversibility and is a result of swelling-shrinking processes caused by the contaminant itself.

Some studies support the hypothesis of facilitated bioavailability in which cells either have access to sorbed molecules or are able to promote desorption by altering the chemical or physical properties of the soil particle

or surrounding liquid. In studies of phenanthrene degradation with added cultures we have found little support for facilitated bioavailability. However, in a study of PAH degradation by native organisms in a coal tar contaminated soil we observed a markedly smaller biodegradation-resistant fraction than the corresponding desorption-resistant fraction when biodegradation was stimulated with inorganic nutrients. This suggests that facilitated bioavailability is possible for adapted native populations when nutrient limitations are absent.

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