

# THE MEASUREMENT AND INTERPRETATION OF SORPTION AND DESORPTION RATES FOR ORGANIC COMPOUNDS IN SOIL MEDIA

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Sorption controls the physical and biological availability of chemicals in soil. Most organic molecules undergo primarily weak physisorption interactions and the driving force for sorption is the hydrophobic effect. Sorption and desorption rates, therefore, are governed mainly by molecular diffusion through the fixed interstitial pores of particle aggregates and through the three-dimensional pseudophase of soil organic matter. Retardation in the fixed pore system is due to tortuosity, chromatographic adsorption to pore walls, and, in the smallest pores, steric hindrance.

Soil organic matter, which has the strongest affinity for most organic compounds, may exist in rubbery and glassy phases and retards sorption and desorption by its viscosity and by the presence of internal nanopores, which detain molecules and may sterically inhibit their migration. Soot carbon and/or ancient organic matter may be present in some soils but their roles are yet unclear. Desorption rates are correlated with the size and shape of the diffusant. Hysteresis is commonly observed but a satisfactory explanation for it has yet to emerge. Mathematical models based on bond energetics, driving force theory, diffusion, and stochastic analysis are discussed. These models have been used to describe batch experiments and have been coupled to advection–dispersion transport equations for use in flowing water systems. Diffusion models are the most realistic but also the most difficult to apply because diffusion is highly dependent on the geometry and composition of the sorbent. Soil heterogeneity impedes the mechanistic interpretation of rates. Particles span an extremely wide range of sizes. The appropriate diffusion length scale is often uncertain. The diffusion coefficient is expected to be concentration dependent in any diffusing medium in which sorption is nonlinear. Furthermore, the diffusant may alter the structure of soil organic matter. Bioavailability can be rate limited by desorption. Cells are believed to access only dissolved molecules, but organisms may affect sorption kinetics indirectly by steepening the concentration gradient or by altering soil properties through bioactivity. Coupled sorption–biodegradation models are necessary whenever nonequilibrium conditions prevail during exposure. Models coupling Monod or first-order biodegradation kinetics with “two-site,” driving-force, or diffusion models have been employed. Some have been used in conjunction with the advection–dispersion transport model. © 2000 Academic Press.

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## I. INTRODUCTION

Sorption is fundamental to the fate of organic chemicals in soil environments. In order to assess the influence of sorption, it is important to understand the nature of the bonding forces between the sorbing molecule (sorbate) and the solid (sorbent), the thermodynamic driving forces responsible for establishing the position of equilibrium, and the rates of association and dissociation of sorbate with time. The primary focus of this chapter is on sorption kinetics. Sorption kinetics is an important field of investigation in soil and environmental science because non-equilibrium sorption conditions often apply as other fate processes, such as vapor- or liquid-phase transport, uptake by organisms, and chemical reactions, are taking place. In fact, sorptive equilibrium may take as long as many months. Recent reviews (Alexander, 1995; Linz and Nakles, 1997; Pignatello and Xing, 1996) discussed the rate-limiting effects of sorption on mass transport and bioavailability and the ramifications thereof for the management and risk assessment of chemicals in soils and aquatic sediments.

Soil particles are typically porous or have phases, such as soil organic matter (SOM), that are penetrable by the sorbate. Hence, sorption usually consists of at

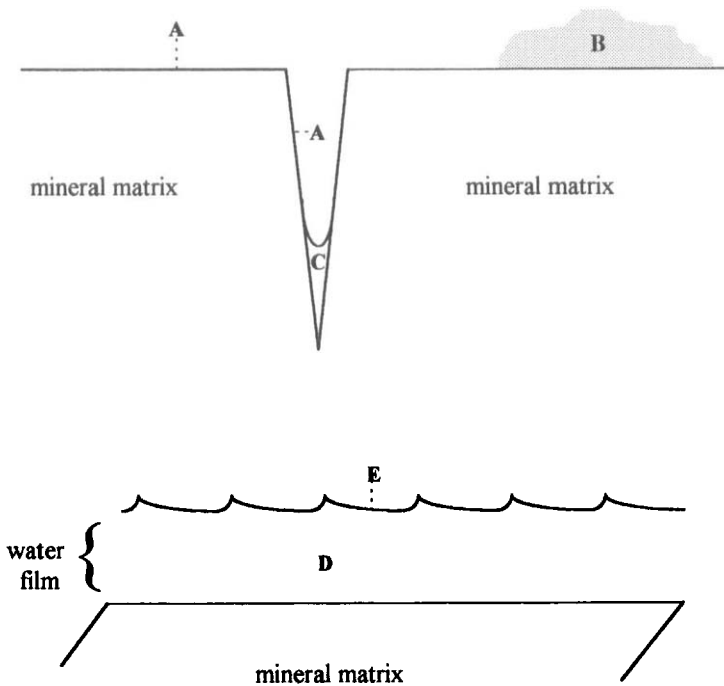
least three steps: (i) transport from the bulk fluid (vapor or liquid) to the vicinity of the external surface of the particle, (ii) transport through the pore structure or interstices of the particle, and (iii) formation of a “bond” at the “site” of sorption. This chapter will begin by discussing the properties of sorbate and sorbent and the nature of the sorption bond; in addition to providing a brief review of mechanisms, the purpose of this introductory material is to make the reader aware of the complexity of the sorption process, an essential prerequisite to understanding the kinetics of sorption. The chapter will then give an overview of the current state of our knowledge about the mechanisms that retard sorption and desorption. Next, mathematical approaches to describing sorption/desorption kinetics are discussed, followed by a discussion of the experimental techniques for measuring rates. The last section will address sorption kinetics in relation to bioavailability. The mathematical models discussed in this chapter will be presented only in their essential features to save space and spare the reader unnecessary mental toil; consequently, it is incumbent on an investigator to consult the original works before embarking on their use.

It should be noted that a full understanding of the mechanisms that retard sorption has not been attained. As a result, there is plenty of opportunity for advancement in the field. It is still not generally possible to predict a priori the entire uptake or release curve for any given soil–chemical system. The goal of this chapter is to lay a foundation for understanding the causes of sorption/desorption rate limitations. In this chapter, we will deal with systems in a hydrated state.

## II. THE NATURE OF ELEMENTARY SORPTION PROCESSES IN SOILS

Defined broadly, the terms *sorption* and *desorption* refer to bulk mass-transfer phenomena in which molecules leave the fluid phase and become associated with an immobile phase and vice versa. The terms imply nothing about the nature of the interaction nor about the transport of the sorbate molecules once in the confines of the immobile phase. We speak of *solution–solid* and *vapor–solid* sorption. Sorption of organic compounds may be broadly divided into the following categories (Fig. 1):

- *Adsorption* (A in Fig. 1) refers to association of molecules at the solid–fluid interface. The interface may exist on the external surface of the particle facing the bulk fluid or on the surface of a pore facing the fluid contained in that pore.
- *Absorption* (B in Fig. 1) occurs when molecules penetrate the solid surface and intermingle with its three-dimensional molecular or atomic matrix. In natural soils, SOM is the only component that is penetrable in this manner. Polluted soils



**Figure 1** Different types of sorption available to organic molecules. A, Adsorption; B, absorption in SOM or NAPL phase; C, capillary condensation; D, dissolution in water film; E, adsorption to water film.

may contain additional absorptive phases in the form of nonaqueous phase liquids (NAPLs)—solvents, oils, tars, and so on.

- **Condensation** (C in Fig. 1) refers to a phase change from the vapor or solution state to a nonaqueous liquid or solid state. Condensation may occur on any surface when the concentration is above the solubility or vapor pressure. However, it is facilitated in small pores (<50 nm): As a pore width decreases there is a progression from monolayer adsorption to capillary condensation owing to the effect of surface tension, which reduces the vapor pressure below the value of the pure liquid in accordance with the Kelvin equation (Ruthven, 1984). Water competes effectively with organics for condensation in pores of minerals because such surfaces are ordinarily polar; however, recent studies of aquifer sediments suggest that capillary condensation of compounds such as benzene may occur even from aqueous solution and even at concentrations lower than their bulk water solubility (Corley *et al.*, 1996).

- *Association with water films*: Depending on the relative humidity, unsaturated soils contain liquid water in pores and as coatings of surfaces. When organic vapors contact unsaturated soils, *dissolution in* (D in Fig. 1) and *adsorption on* (E in Fig. 1) water films may occur (Kim *et al.*, 1998; Ong and Lion, 1991; Petersen *et al.*, 1995). Molecules in such states are technically sorbed because they are removed from the surrounding vapor state.

## A. INTERMOLECULAR INTERACTIONS AVAILABLE TO ORGANIC MOLECULES

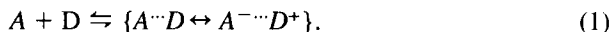
Organic compounds can undergo *chemisorption*, *physisorption*, or *ion pair formation* (ion exchange) with natural particles.

- *Chemisorption* involves significant atomic or molecular orbital overlap with the solid phase; that is, the formation of a covalent or coordination bond. Examples relevant to this chapter include “inner-sphere” coordination complexes between carboxylate, phenolate, amine, or sulfhydryl groups and metal ions; i.e.,  $\equiv M^{n+}-ZR$ , where  $\equiv M^{n+}$  is a structural or adsorbed metal ion. Such bonds have both ionic and covalent character. Sorption accompanied by formation of a true covalent bond (such as a C–C bond) is seldom reversible and thus is not considered relevant to this chapter.
- *Physisorption* involves weak intermolecular attractive forces between atoms and molecules, including “van der Waals,” hydrogen (H-) bonding, and charge transfer.

Van der Waals force encompasses the following interactions (Castellan, 1971; Israelachvili, 1992): (i) dipole–dipole forces, resulting from mutual attraction between permanent dipoles; (ii) induced dipole–induced dipole (dispersion) forces, resulting from the synchronization of electronic motion in each molecule producing momentary dipole moments in each; (iii) Dipole-induced dipole, resulting from the attraction of a permanent dipole with the dipole it induces in its neighbor. Forces (i–iii) involve no appreciable molecular orbital overlap, are randomly oriented in space, and are only a few kilojoules per mole in energy. Force (ii) is available to all atoms and molecules. The total van der Waals energy is the sum of all individual interactions between the sorbate and the site, and it depends on the distance of approach, the sorbate size, and the polarizabilities and polarities of both sorbate and site.

H-bonding (Schuster *et al.*, 1976) involves interactions between acids and bases of the type  $-AH\cdots B-$ , where A and B are ordinarily N, O, or S atoms. H-bonding is a combination of the dipole–dipole force and a small degree of molecular orbital overlap. It is oriented in space (A–H–B angle  $\leq \sim 15^\circ$ ) and ranges in strength from 10 to 25 kJ/mole.

Charge-transfer interactions (often referred to as donor–acceptor interactions) may occur when an electron-poor acceptor ( $A$ ) encounters an electron-rich donor ( $D$ ) and forms a complex in which one resonance structure represents transfer of an electron (Foster, 1969):



Charge-transfer complexes most relevant to soil systems are  $n \rightarrow \pi$  and  $\pi \rightarrow \pi$  types, where  $n$  refers to a nonbonding lone-pair electrons and  $\pi$  refers to an aromatic ring or other extended  $\pi$ -conjugated system (Foster, 1969). Haderlein *et al.* (1996) proposed  $n \rightarrow \pi$  charge-transfer complexation between permanent charges on clays (donor) and electron-deficient polynitroaromatic rings (acceptor).  $\pi \rightarrow \pi$  charge-transfer bonds are possible between appropriate functional groups on sorbate and SOM (Müller-Wegener, 1987).

- *Ion-exchange* force involves electrostatic attraction between an organic anion or cation and a charged group on the sorbent. It may be augmented by physisorption forces. For minerals, this type of sorption is best described as a concentration enhancement of the organic ion in the water near the surface, accompanied by depletion of the original (usually inorganic) ion. Ion exchange may also occur at charged sites in SOM, usually carboxylate or phenolate groups.

## B. PROPERTIES OF SOIL COMPONENTS AND MECHANISMS OF SORPTION

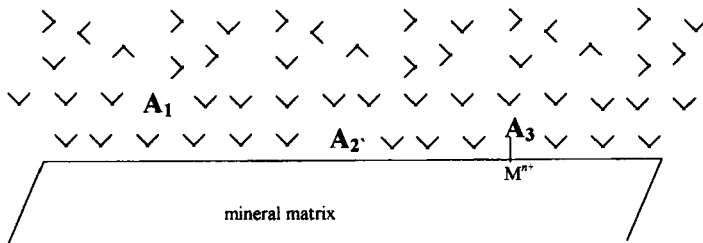
### 1. Mineral Surfaces

Two principal types of surface exist on natural minerals:

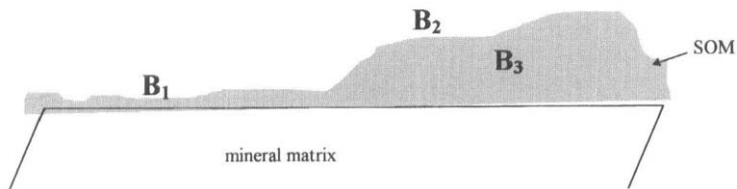
1. The *hydroxylated* surface consists of -OH groups protruding into solution from the topmost layer of metal ions ( $\equiv M^{n+}-OH$ ). It exists on all hydrous oxides of Si, Fe, and Al and on the edges of layer silicate clays. It has variable positive or negative charge density, depending on mineral, pH, and ionic strength. Regardless of charge, it is strongly hydrophilic; adsorption of water on this surface is more energetic than adsorption of nonpolar organic molecules (Curthoys *et al.*, 1974), and it is believed that at ordinary humidities one or more layers of ordered water ("vicinal water") are strongly under the influence of the surface.

2. The *siloxane* surface consists of oxygen atoms bridging underlying  $Si^{4+}$  ions. It exists on the faces of many layer silicate clays. It has permanent negative charge, depending on the degree of isomorphic substitution in the underlying lattice. The charged sites are closely associated with metal or organic cations and the surface in the vicinity of the charge is strongly hydrophilic. The neutral regions between charges are hydrophobic or only weakly hydrophilic (Chen, 1976; Jaynes and Boyd, 1991).

a



b



**Figure 2** Depiction of sorption. (a) Sorption to mineral surfaces:  $A_1$ , solvent-separated physisorption;  $A_2$ , physisorption with direct interaction with the surface;  $A_3$ , chemisorption by coordination with underlying metal ion. (b) Sorption to SOM:  $B_1$ , adsorption to the *SOM-coated mineral surface*;  $B_2$ , adsorption to the *extended organic surface*;  $B_3$ , absorption in the *random network polymer phase*.

Although not fully understood, several different modes of adsorption are believed occur on soil minerals (Fig. 2a).  $A_1$  in Fig. 2 refers to physisorption in which the sorbate is separated from the surface by solvent molecules (Goss, 1992). This occurs on hydroxylated surfaces for compounds that cannot displace adsorbed water. This type of adsorption might be best described as a concentration enhancement of the solute in the "vicinal water."  $A_2$  refers to physisorption in which the sorbate is in direct contact with surface atoms. Direct contact occurs on neutral siloxane surfaces, as well as on hydroxylated surfaces, provided water is scarce or the compound's H-bond ability is sufficiently great that it can displace tightly bound water.  $A_3$  refers to chemisorption through inner-sphere coordination with lattice or adsorbed metal ions. This mechanism requires appropriate coordinating functional groups on the molecule. D refers to pore condensation as discussed in reference to Fig. 1.

## 2. Soil Organic Matter

It is well established that sorption of hydrophobic compounds out of aqueous solution or at high relative humidity is dominated by the SOM fraction unless that fraction is very small (Schwarzenbach *et al.*, 1993). For example, sorption of chlorinated benzenes and polycyclic aromatic hydrocarbons (PAHs) to nonporous inorganic oxides is so weak that it is expected to be insignificant when the fraction of soil organic carbon ( $f_{oc}$ ) is  $\geq \sim 0.0001$  (Mader *et al.*, 1997)! Situations in which the predominance of SOM does not necessarily hold include (i) very dry conditions, when capillary condensation or adsorption can be important, and (ii) when chemisorption is important.

SOM consists of plant and microbial material in various stages of decomposition. Materials bearing little physical and chemical resemblance to their precursor biological polymers are called *humic substances* and make up the bulk of SOM (Hayes *et al.*, 1989). Knowledge about humic substances is mainly inferred from studies of *humic* and *fulvic acids*, which are humic substances isolated from natural waters or extracted from soil with dilute base or polar solvents. Humic and fulvic acids are a refractory mixture of polyanionic macromolecules ranging from hundreds (Novotny *et al.*, 1995) to hundreds of thousands of grams per mole (see Pellegrino and Piccolo (1999), however). Bearing in mind that each humic macromolecule may be unique, a hypothetical structure has been proposed on the basis of physical, spectroscopic, and fragmentation-identification studies (Schulten and Schnitzer, 1993) (Fig. 3a). It has both aliphatic and aromatic subunits and an abundance of oxygen functional groups. In solution, the macromolecules coil up in a random fashion and aggregate to form a spheroidal, water-swollen phase of entangled humic macromolecules (Fig. 3b). The density of the particle increases gradually from edge to center (Hayes and Himes, 1986; Swift, 1989).

The unextractable SOM—typically more than half the total—is called *humic*. Humic is separated from minerals only by drastic treatment such as hydrofluoric acid digestion which dissolves the minerals (Preston *et al.*, 1989). Humic may be separated into lipid-like and humic-like components (Rice and MacCarthy, 1990). Little is known about humic, even though it may have a greater affinity for organic compounds than whole SOM (Xing and Pignatello, 1997). The bulk of humic may consist simply of humic acid-like molecules of higher molecular weight and stronger affinity for mineral surfaces. Humic is more hydrophobic and more condensed than humic or fulvic acids.

In the native state, SOM is usually bound to mineral particles on a scale ranging from a monolayer organic film to a discreet organic phase. The nature of SOM as a sorbent of organic compounds—obviously crucial to its role in sorption kinetics—is controversial. SOM has been modeled as a *coating on mineral surfaces*, an *extended organic surface*, or a *random network polymer phase*. These are depicted in Fig. 2b.

As a coating, SOM is regarded to enhance the surface affinity for organic mol-



ecules by making it more “hydrophobic,” similar to the effect of alkyl chains attached to the surface of silica gel used in reverse-phase liquid chromatography. On such a surface, the sorbate may be under the simultaneous influence of the mineral and the organic matter. Mayer (1999) provides evidence, however, that even in low-organic carbon (OC) aquifer sediments SOM exists in multilayer patches rather than as monolayers on the surface. The extended organic surface concept regards SOM to be an impenetrable adsorptive surface. The external surface area of SOM measured by  $N_2$  adsorption at 77 K using the B.E.T. equation is on the order of  $\sim 10^0 \text{ m}^2/\text{g}$  (Chiou *et al.*, 1993), which appears to be too low to account for the high affinity of SOM for organic compounds, implying that little impenetrable surface exists.

The preponderance of evidence points to SOM behaving as a random network polymer phase that provides a three-dimensional hydrophobic environment for organic molecules. The “surface” of such a phase is expected to be diffuse rather than sharply defined due to more extensive solvation of the outer polar regions of the humic polymers that face the solvent (Hayes and Himes, 1986; Swift, 1989). If true, a long-lived surface-adsorbed state would be disfavored. Instead, the sorbate is expected to penetrate the phase and intermingle with the humic strands, much the same way in which small molecules interact with synthetic organic polymers (Rogers, 1965; Vieth, 1991; Frisch and Stern, 1983). The structure of lignin, the woody component of plant material and probably the main precursor of terrestrial humic substances, is also considered a “random network polymer” (Goring, 1989).

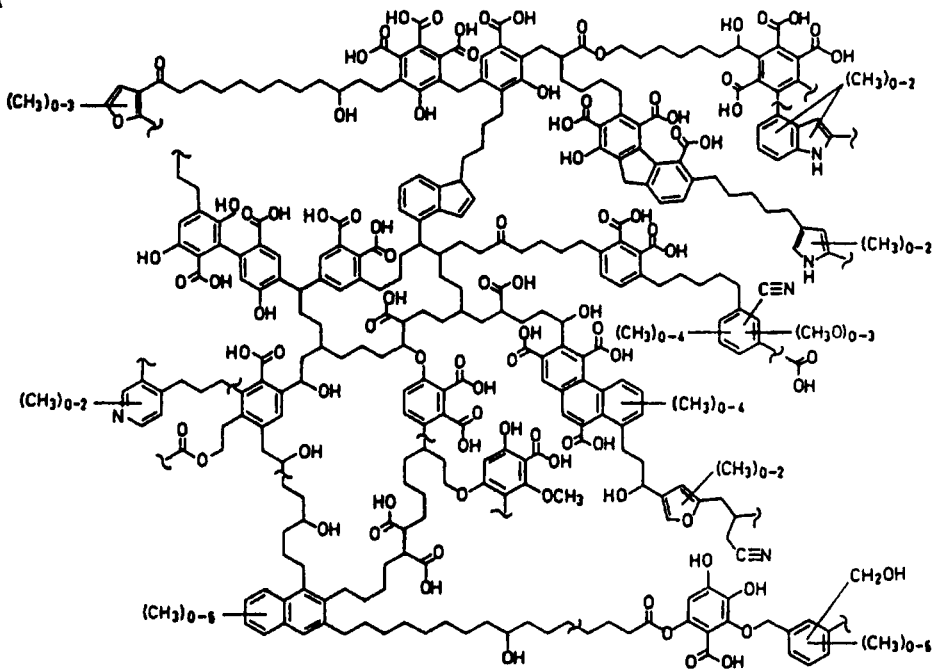
According to the polymer phase concept, sorption is attributed to dissolution (absorption) of the hydrophobic solute in the liquid-like, organophilic phase in order to escape the polar environment of water (Chiou, 1989). Unlike a liquid, however, the sorption potential of SOM is not uniform (Pignatello, 1998, 1999; Xing *et al.*, 1996; Xing and Pignatello, 1997; Young and Weber, 1995). Sorption isotherms tend to be nonlinear in the sense that sorption diminishes with increasing concentration. The isotherm can be fit to the Freundlich equation,

$$q_e = K_e C_e^n, \quad (2)$$

where  $q_e$  and  $C_e$  are the equilibrium sorbed and solution concentrations,  $K_e$  is the sorption coefficient, and  $n$  is a constant  $< 1$ . Moreover, sorption in bisolute and multisolute systems is competitive. These behaviors indicate a more specific mechanism than ideal solid-phase dissolution and can be reconciled by considering SOM as a composite of “rubbery” and “glassy” polymers. Accordingly, the properties of SOM vary continuously from rubbery-like phases that have an expanded, flexible, and highly solvated structure to glassy-like phases that have a condensed, rigid, and less solvated structure (Pignatello, 1998, 1999; Xing *et al.*, 1996; Xing and Pignatello, 1997). The glassy character has been suggested to increase with diagenetic alteration in the following natural progression: SOM  $\rightarrow$  kerogen  $\rightarrow$  coal and shale (Huang and Weber, 1997; Young and Weber, 1995).

The nature of sorption is postulated to change along the rubbery–glassy con-

A



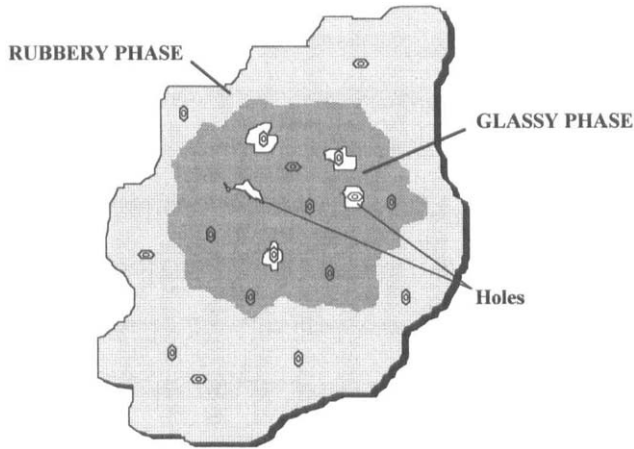
**Figure 3** Soil organic matter. (A) Hypothetical structure of a humic macromolecule (reprinted from Schulten and Schnitzer, 1993, with permission from Springer-Verlag). (B) Three-dimensional depiction of a natural organic matter colloid in aqueous solution. The colloid is an approximately spherical polymer mesh of entangled humic macromolecules that is swollen with water (water molecules not shown). The mass density increases toward the center. Some negative charges on the humic strands form ion pairs with metal cations, whereas others are balanced by counterions in solution. Cross-linking between strands is illustrated for the divalent cations  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . (Reprinted from Pignatello, 1998.)

tinuum in the same fashion as sorption of gases and organic molecules in polymers. In highly rubbery regions of SOM sorption occurs by solid-phase dissolution, whereas in glassy regions sorption occurs by a combined mechanism of solid-phase dissolution and site-specific, "hole-filling" processes. The holes are postulated to be nanometer-size pores made up of rigid humic segments, in which the guest molecules undergo an adsorption-like interaction with the pore walls. The sorption isotherm is thus given by the "dual-mode" equation (Eq. 3) (Pignatello, 1999; Xing *et al.*, 1996; Xing and Pignatello, 1997), in which total sorption ( $q_e$ ) is contributed by solid-phase dissolution ( $q_D$ ) and the sum of multiple site-selective processes ( $q_L$ ), each of which follows a Langmuir relationship:

B



Figure 3 Continued



**Figure 4** Rubbery-glassy polymer concept of soil organic matter. The perspective is intended to be three-dimensional. The rubbery and glassy phases both have dissolution domains in which sorption is linear and noncompetitive. The glassy phase, in addition, has pores of subnanometer dimension (“holes”) in which adsorption-like interactions occur with the walls, giving rise to nonlinearity and competitive sorption. The binding is analogous to host-guest inclusion complexes in chemistry. (Reprinted from Xing and Pignatello, 1997.)

$$q_e = q_D + q_L = K_D C_e + \sum_{i=1}^n \frac{b_i Q_i C_e}{1 + b_i C_e}, \quad (3)$$

where  $K_D$  is the (linear) dissolution domain coefficient made up of inseparable terms representing the rubbery phase and the dissolution domain of the glassy phases,  $C_e$  the equilibrium solution concentration, and  $b_i$  and  $Q_i$  are the Langmuir affinity and capacity constants for the  $i$ th unique site in the hole-filling or Langmuir domain. The dual-mode model is depicted in Fig. 4.

Gas adsorption studies confirm the existence of internal nanoporosity in SOM samples which increases the total surface area by at least two orders of magnitude (Xing and Pignatello, 1997; de Jonge and Mittelmeijer-Hazeleger, 1996). The nanoporosity is correlated with the degree of nonlinearity in the isotherms and the degree of competition between compounds of like structure (Xing and Pignatello, 1997). Conditions that favor the rubbery state—increased temperature, the presence of cosolvents such as methanol, and high concentrations of cosolute—tend to make the isotherm more linear. The degree of nonlinearity follows the order expected on the basis of the glassy character of the material: humic acid < humin. As will be shown, there is increasing evidence that the mass transfer rates depend on the rubbery-glassy character of SOM.

### 3. Carbonaceous Materials Other Than SOM

Soils may contain forms of carbon not usually classified as SOM. These include ancient materials such as kerogen, coal, and shale, and “black carbon” (also known as “soot”), which refers to incompletely combusted organic material. Such materials are widely distributed in the environment and, because they are hydrophobic, are expected to have a high affinity for organic compounds (Kuhlbusch, 1998; McGroddy *et al.*, 1996). The nature of these materials as sorbents of organic compounds is not well-known. Coal appears to have properties quite like glassy polymers—“internal microporosity” (Larson and Wernett, 1988) and demonstrable glass-to-rubber transition temperatures (above 300°C) (Lucht *et al.*, 1987). Soots are expected to have some impenetrable hydrophobic surface. If this is true, sorption may occur by adsorption and condensation in fixed pores, as occurs in familiar inorganic materials. However, they may also have tar-like phases which behave more like absorption domains. PAHs, being products of incomplete combustion themselves, may become occluded in the interstices of soot particles during their formation in a way that makes them extremely unavailable (Gustafsson *et al.*, 1997).

Sorption of chemicals by NAPLs occurs by simple liquid-phase dissolution analogous to organic solvents such as hexane and octanol. The partitioning between the fluid phase and NAPLs 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, respectively, of a pure reference state (Schwarzenbach *et al.*, 1993).

#### C. THERMODYNAMIC DRIVING FORCE FOR SORPTION

Upon sorption from solution, an organic molecule exchanges one set of interactions with the solvent for another set of interactions with the sorbent. The molar free energy change at constant temperature and pressure encompasses free energy changes in sorbate–sorbent, sorbate–solvent, sorbent–solvent, and solvent–solvent interactions of all components involved in the sorption process, including displaced molecules such as water from the surface, and any reorganization occurring on the surface. For nonpolar and weakly polar compounds capable of interacting only by nonspecific physisorption mechanisms, sorption from water to mineral surfaces (Goss, 1997), as well as to SOM (Chiou, 1989), is driven principally by the *hydrophobic effect*. The hydrophobic effect results from the gain in free energy when a molecule possessing hydrophobic surface area is transferred out of the polar medium of water. The hydrophobic effect plays the same dominant role in aqueous solubility. Surface tension studies show that the hydrophobic

effect is due almost entirely to the H-bonding cohesive energy of water (van Oss *et al.*, 1988; van Oss and Good, 1988). It is thought that water molecules form an ordered cage around the hydrophobic portions of the solute, costing enthalpy, entropy, or both (Schwarzenbach *et al.*, 1993; van Oss *et al.*, 1988). H-bonding and dipolar interactions with the sorbent will increase the thermodynamic driving force for sorption only if such interactions with the sorbent are stronger than those with the solvent.

#### D. RATES OF ELEMENTARY PROCESSES

It has been shown that sorption of organic compounds to soil particles usually involves the weak physisorption interactions. In solution, such interactions are practically instantaneous. For example, the lifetime of the  $\text{H}_2\text{O}\cdots\text{NH}_2\text{CH}_3$  hydrogen bond in water is only  $1.2 \times 10^{-11}$  s (Emerson *et al.*, 1960). Van der Waals interactions are even shorter lived. The situation on the surface is more complex, however. Consider the elementary collision of a gas molecule with an unhindered plane surface having a number of "sites" of identical energy. The energy profile versus distance from the surface is illustrated in Fig. 5. As the adsorbate approaches the surface it descends into a potential energy well of depth  $Q$ . The instantaneous rate of adsorption is proportional to the pressure  $p$  and the concentration of vacant sites  $S_v$ . The instantaneous desorption rate is proportional to the concentration of occupied sites  $S_o$ . In the Arrhenius formulation, the rate expressions are

$$\text{Rate of sorption} = A_a e^{(-E_a^*/RT)} p S_v, \quad (4)$$

$$\text{Rate of desorption} = A_d e^{(-E_d^*/RT)} S_o, \quad (5)$$

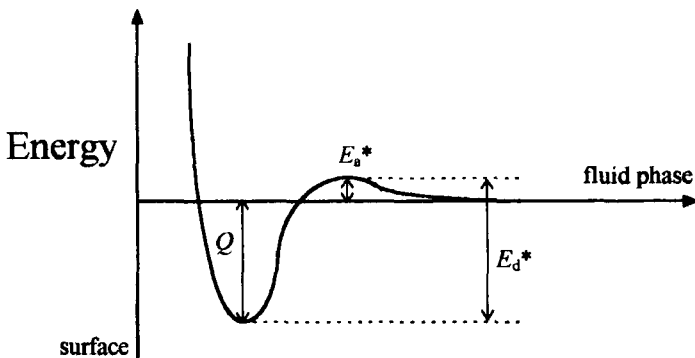


Figure 5 Energy diagram for a physisorbing molecule approaching the surface.

where  $E_a^*$  and  $E_d^*$  are the adsorption and desorption activation energies ( $\text{kJ mole}^{-1}$ ),  $R$  is the universal gas constant, and  $A_a$  and  $A_d$  are the preexponential constants reflecting the “sticking probability.”

Physisorption of a molecule from the vapor state to an unhindered surface is considered to be unactivated ( $E_a^*$  near zero) (Adamson and Gast, 1997). Physisorption from solution may be slightly activated due to reorganization of solvent molecules around the sorbate and the surface. Desorption, however, is always activated because it requires “ascension” from the potential energy well. Assuming the principle of microscopic reversibility (that desorption follows the reverse pathway of sorption),

$$E_d^* = -Q + E_a^* \quad (6)$$

The  $Q$  is approximately equal to the isosteric heat of adsorption  $-\Delta H$  (Ruthven, 1984). Values of  $-\Delta H$  for vapor sorption on dry, nonporous silica gel (which represents a hydroxylated mineral surface) range from 36 to 63 kJ/mol for small nonpolar molecules, such as *n*-hexane, tetrachloromethane, and benzene, as well as polar molecules containing ether, cyano, nitro, ketone, and ester groups (Curthoys *et al.*, 1974). Goss (1994) found that  $-\Delta H$  for  $C_1$ – $C_{10}$  compounds on moist surfaces of silica, quartz sand, and clays ranged from 28 to 50 kJ/mol. Adamson and Gast (1997) estimate the mean time of stay on the surface,  $\tau$ , of a molecule at 25°C, assuming  $E_a^* = 0$  and a sticking probability of unity. For  $-Q = 37.6$  kJ/mol,  $\tau = 10^{-6}$  s and for  $-Q = 83.7$  kJ/mol,  $\tau = 10^2$  s. Thus, we may expect that physisorption of typical compounds on a plane surface should occur in minutes or less. This is generally borne out experimentally (Adamson and Gast, 1997; Ruthven, 1984).

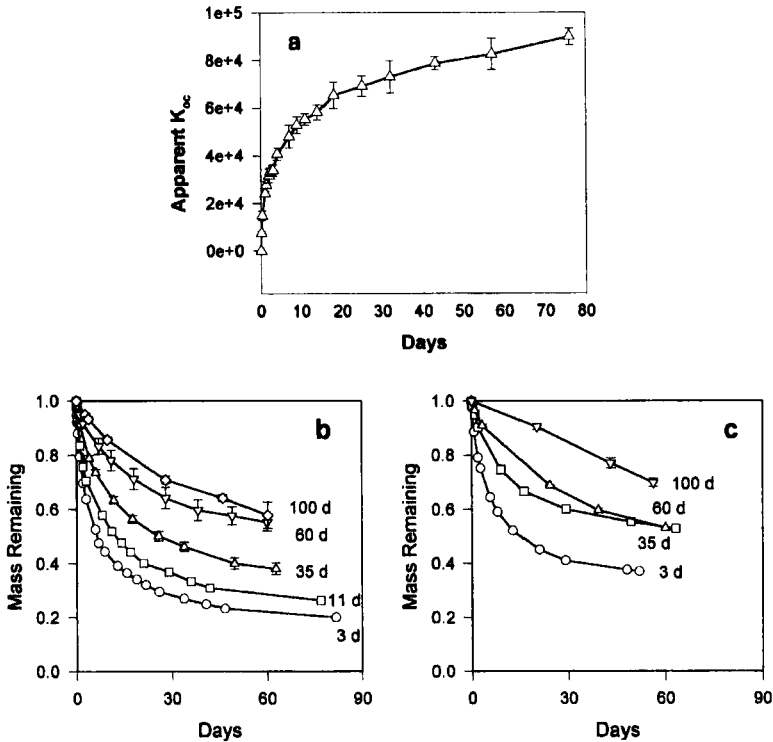
The same conclusion of rapid equilibrium does not apply, however, when the elementary reaction involves forces stronger than physisorption. For example, in ligand exchange,  $E_a^*$  may be appreciable due to such effects as orbital rehybridization and displacement of other ligands ( $\text{OH}^-$ ,  $\text{H}_2\text{O}$ , or organic ligand) from the inner coordination sphere of the metal ion (McBride, 1994). The  $E_d^*$  will reflect the energy of the coordination bond, which is especially strong when the molecule coordinates through two or more functional groups (the “chelate effect”). There is little quantitative information available on the forward or reverse rates of ligand-exchange reactions on soils or appropriate model sorbents.

Also, the conclusion of rapid equilibrium does not apply to sorption in a sterically hindered environment such as the interstices of SOM. There, from the standpoint of the sorbate molecule as it tries to weave its way around the humic strands, each elementary jump from site to site is sterically hindered. Depending on the flexibility of the humic matrix, a cooperative movement in the position of humic macromolecules may be required in order to allow the sorbate molecule to pass. Thus, an elementary jump is expected to involve the making and breaking of numerous interactions simultaneously and therefore may be highly activated.

### III. SLOW SORPTION AND DESORPTION

#### A. UPTAKE AND RELEASE PROFILES

Evidence for slow (“nonequilibrium”) sorption phenomena has come from many sources—the extended tailing of breakthrough curves in soil column experiments, the formation of so-called “resistant” fractions in batch experiments, and the unexpected persistence of pesticides in the environment (Alexander, 1995; Pignatello, 1989). Since the late 1980s there have been many reports of chemical residues in samples collected from the field that appear to desorb extremely slowly, as well as reports of laboratory-spiked compounds that undergo sorption or de-



**Figure 6** Sorption of phenanthrene in suspensions of Pahokee peat soil and derivatives. (a) Uptake by the peat soil showing slow approach to equilibrium. Apparent  $K_{oc}$  is the ratio of sorbed to solution concentration referenced to organic carbon. (b) Normalized desorption of 2  $\mu\text{g/g}$  phenanthrene from the peat soil a in the presence of Tenax adsorbent beads after 3- to 100-day aging periods. (c) Same as b from peat humin (a is from White and Pignatello, unpublished; b and c are reprinted from White *et al.*, 1999).



sorption over weeks or months. This subject has been reviewed by Pignatello (1989) and Pignatello and Xing (1996).

Figure 6a shows that phenanthrene, a three-ring PAH, required in excess of 110 days to reach equilibrium in a shaken suspension of a peat soil containing mostly organic matter (6.9% ash). Figure 6b shows the desorption of phenanthrene after various contact ("aging") periods of 3–100 days (White *et al.*, 1999). The desorptions were carried out in the presence of Tenax polymeric adsorbent, which rapidly sorbs phenanthrene as it leaves the soil, approximating conditions of zero concentration infinite bath and maximizing the driving force for desorption. One can see that the desorption rate slows with an increase in the aging period. It is worth noting that after only 3 days of sorption approximately 20% of phenanthrene strongly resists desorption over the subsequent 90 days in the presence of the infinite sink. Similar findings—that short-term contact can lead to formation of a strongly resistant fraction—have been reported by others (Kan *et al.*, 1997, 1998).

The following are observations pertaining to the resistant fraction:

1. Desorption is highly temperature dependent, being significantly enhanced by heating. For example, the apparent desorption activation enthalpy for aged 1,2-dibromoethane was 66 kJ/mol (Steinberg *et al.*, 1987) and that of aged chlorobenzenes, polychlorinated biphenyls (PCBs), and PAHs ranged from 60 to 70 kJ/mol (Cornelissen *et al.*, 1997b).

2. Desorption is accelerated by addition of cosolvents but only slightly by addition of surfactants (Deitsch and Smith, 1995).

3. Desorption is accelerated by breaking up particles (Steinberg *et al.*, 1987; Ball and Roberts, 1991b).

4. Resistant fractions may be formed in soils containing no appreciable mineral matter (e.g., Fig. 6), in strictly inorganic porous particles (Farrell and Reinhard, 1994a,b; Werth and Reinhard, 1997), and perhaps even in colloidal-size particles (Maguire *et al.*, 1995; Schlebaum *et al.*, 1998).

## B. RETARDATION MECHANISMS

Slow kinetics has been exhibited by aliphatic and aromatic hydrocarbons, halogenated aliphatic and aromatic hydrocarbons, and agricultural chemicals. Generally, only physisorption interactions are open to them. Chemical and biological transformations, although quite possible, are irreversible in the sense that the by-products cannot easily revert to starting compound and would not be identified as starting compound by the analyst using modern techniques. Therefore, the only reasonable explanation for slow kinetics for such compounds is mass transfer resistance—the resistance of the matrix to molecular diffusion.

Diffusion is the tendency of molecules to migrate against a gradient in concen-

tration (more correctly, a gradient in chemical potential) so as to achieve maximum entropy. Soil particles are characteristically porous and contain minerals such as SOM that can absorb small molecules within their interstices. These materials can provide resistance to diffusing molecules in many ways. Most suggested mechanisms for hindering the sorption process can be grouped into the following: pore diffusion (PD), and intraorganic matter diffusion (IOMD).

Variations exist within each group, and in some cases there is some overlap. Although investigators have argued the merits of one compared to the other, it is likely that both operate, depending on soil properties. Resistant fractions can be generated in purely inorganic sorbents such as porous silica gel (Farrell and Reinhard, 1994b; Werth and Reinhard, 1997) and in pure organic materials such as low-ash peat soils (White *et al.*, 1999).

### 1. Pore Diffusion

PD attributes slow rates to hindered diffusion of molecules through the fixed intraparticle pore system. Fixed pores are more or less permanent and unaffected in shape by the presence of the diffusant. Porosity exists in cracks, lattice discontinuities, along grain boundaries, and in the interlayers of expandable clays. Pore sizes are classified by IUPAC according to their aperture ( $d$ ):

$$\begin{aligned} \text{Macropores: } d &> 50 \text{ nm,} \\ \text{Mesopores: } 50 > d &> 2 \text{ nm,} \\ \text{Micropores: } d &< 2 \text{ nm.} \end{aligned}$$

In addition, there is a class of pores in the  $\sim 0.3$ - to 1-nm range referred to in the literature as "ultramicropores" or "nanopores." For perspective, the C–C bond is  $\sim 0.15$  nm long and  $\text{CCl}_4$  is  $\sim 0.5$  nm in diameter. Researchers have different views on the nature of the pores and the root causes of hindered sorption.

The pore surface may be organic or inorganic. In most PD models it is assumed that molecules instantaneously equilibrate locally between the pore liquid phase and the surface ("local equilibrium"). Diffusion in pores may be hindered with respect to diffusion in a bulk fluid by any or all of the following mechanisms: (i) tortuosity, a term encompassing elongation of diffusion paths relative to a straight line, variations in pore diameter, and the degree of pore connectivity as reflected by the presence of "dead-end" pores; (ii) sorption to pore walls analogous to a "chromatographic effect"; and (iii) steric interference from pore walls, especially in pores approaching the diffusant diameter. These will be discussed in more detail in Section IV,C. In addition, diffusion in small pores may be hindered by the viscous nature of water near hydrophilic surfaces where water molecules are strongly under the influence of the surface.

Although the concept of pore diffusion is long known, Wu and Gschwend

(1986) appear to be among the first to employ it to describe intraparticle diffusion of chemicals in soils and sediments. Ball and Roberts (1991b) used the PD model to describe sorption of trichloroethane (TCE) and tetrachlorobenzene in aquifer solids over long periods. They often obtained superior fits by including an instantaneously sorbing fraction of up to 30% of total. In these (Ball and Roberts, 1991b; Wu and Gschwend, 1986) and other studies (Kleineidam *et al.*, 1999) the results were consistent with the nominal particle radius as the length scale over which diffusion occurs. By contrast, other studies (Carroll *et al.*, 1994; Cornelissen *et al.*, 1998b; Farrell and Reinhard, 1994b; Pignatello *et al.*, 1993; Pignatello and Xing, 1996; Steinberg *et al.*, 1987) found little or no dependence of diffusion rates on nominal soil particle radius, suggesting the appropriate diffusion length scale may be much smaller than the nominal particle radius, perhaps as small as 10–100 nm. The diffusion length scale likely depends on the micromorphology of the soil particles in the sample.

Pignatello (1990b) observed enhanced release of a portion of strongly resistant fractions of halogenated hydrocarbons by acidification of the suspension to  $\text{pH} < 3$ . This suggested that some SOM, in particulate or coating form, had been shielded by mineral grains that were subsequently dispersed when the materials cementing them were acid dissolved. The results of Holmén and Gschwend (1997) on PAH transport in aquifer sand columns support this idea. They suggested that diffusion in porous oxide coatings on quartzite sand particles controls the rate of diffusion. The coatings, which consisted of fine-grained iron oxide and aluminosilicate clay particles, had porosities of 0.4 or 0.5, thicknesses up to  $\sim 200 \mu\text{m}$ , and OC contents (0.7–1.6%) higher than the quartz substrate. Since the retardation of PAH transport was less than expected based on calculated  $K_{\text{oc}}$  values, they inferred that only a fraction of SOM was accessed during a compound's pass through the column. The flow velocities, however, were quite high—0.5–115 cm/h for a 7-cm column or 1.7–400 column pore volumes per day.

Farrell and Reinhard (1994b) and Werth and Reinhard (1997) desorbed TCE vapors from unsaturated silica gel columns or soils preequilibrated with TCE at fairly high relative pressures and 100% humidity. They observed biphasic kinetics (fast and slow phases). The small, highly resistant fraction of TCE that was formed was attributed to hindered diffusion in “hydrophobic micropores.” Corley *et al.* (1996) suggested that the resistant fraction of TCE and other volatile organic compounds (VOCs) might be associated with a neat VOC phase formed by capillary condensation in micropores or small mesopores during the sorption step.

In their study of chlorinated benzenes and biphenyls in freshwater sediment (2.8–6.3% OC), Lick and coworkers (Borglin *et al.*, 1996; Lick and Rapaka, 1996; Tye *et al.*, 1996) proposed that sorption/desorption rates are controlled by diffusion in the pore network of flocs. Flocs result from the aggregation of sediment grains suspended in water. Their size and density is a function of sediment con-

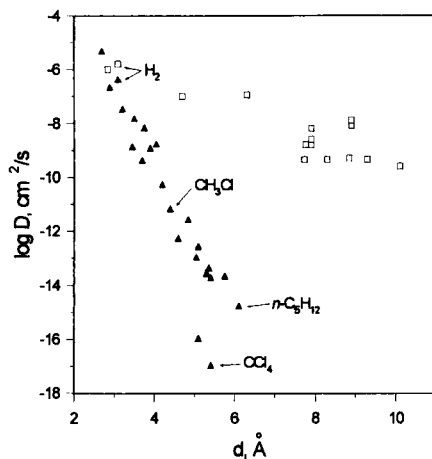
centration, fluid shear force, and water chemistry. Consistent with their mechanism, the effective diffusion coefficient depended on the floc size and porosity, sediment OC content, and (linear) partition coefficient of the sorbate.

Another location where diffusion might be hindered is the interlayers of expandable clays. The interlayer gap is typically  $< 1$  nm—small enough to provide steric hindrance to diffusion or even size exclusion of some compounds. An important question that has not been satisfactorily answered regards availability of clay interlayers in natural soils to pesticides and other chemicals. The small amount of published information suggests that diffusion in the interlayer, when it is accessible, is relatively fast. Sawhney and Gent (1990) sorbed TCE and 1,2-dibromoethane vapors onto various expandable and nonexpandable clays under dry conditions. Desorption from the (expandable) smectite gave among the fastest rates, and X-ray analysis did not support penetration of the interlayer. In desorption of TCE from moist packed columns, Farrell and Reinhard (1994b) found that montmorillonite gave the smallest resistant fraction among many model and natural sorbents, but they, too, argued that interlayer penetration had not occurred. Huang *et al.* (1996) found that sorption of phenanthrene to bentonite was complete in a few hours, but no evidence of interlayer processes could be found. The remaining literature on the subject is confined to organoclays. Organoclays have quaternary ammonium ions (e.g., hexadecyltrimethyl ammonium) as exchangeable cations that are believed to provide an organophilic phase, or surface, with high affinity for hydrophobic compounds. Studies of organoclays [e.g., naphthalene and di-uron (Nzengung *et al.*, 1997) and carbon tetrachloride and 1,2-dichlorobenzene (Deitsch *et al.*, 1998)] indicate that sorption equilibrium appears to be complete in hours and is much faster than sorption to SOM in the form of peat particles (Deitsch *et al.*, 1998). Moreover, the solute-sorbent aging time did not significantly affect the rate of desorption (Deitsch *et al.*, 1998). Questions remain, however, about how much sorption in these organoclays occurred in the interlayer versus on the edges (Nzengung *et al.*, 1997).

## 2. Intraorganic Matter Diffusion

### a. General Considerations

Since neutral organic compounds tend to associate predominantly with the SOM fraction, it is natural to consider whether SOM is the principal cause of hindered diffusion. SOM can hinder diffusion in at least two ways. First, even as a “rubbery” organic gel, SOM represents a highly viscous fluid that impedes molecular diffusion compared to water. Diffusion coefficients of small molecules in rubbery polymers compared to water are several orders of magnitude smaller and depend more strongly on the size and shape of the diffusant (Berens, 1989; Rogers, 1965). In the solid state, humic acid is believed to be a more rubbery form of organic matter than the SOM from which it was extracted (Xing and Pignatello, 1997). The



**Figure 7** Diffusion coefficient at 30°C for gases and organic vapors in glassy (▲) or rubbery (□) polyvinyl chloride. The rubbery state was obtained by adding phthalate ester plasticizers. (Redrawn from Fig. 9 of Berens, 1989, with permission.)

diffusion coefficients of toluene, *n*-hexane, and acetone in pressed humic acid disks range from  $10^{-8}$  to  $10^{-9}$   $\text{cm}^2 \text{s}^{-1}$  (Chang *et al.*, 1997), about the same as those in rubbery polymers at the same temperature, and may be compared to values of approximately  $10^{-5}$   $\text{cm}^2 \text{s}^{-1}$  in water.

Second, glassy SOM offers a much greater impediment to diffusion than rubbery SOM because it is more rigid and condensed and it contains holes (nanopores) in which organic molecules can momentarily be detained (Pignatello, 1998; Pignatello and Xing, 1996; Xing and Pignatello, 1997). Figure 7 shows that the diffusion coefficient of gases and organic molecules in glassy polyvinyl chloride (PVC) is smaller than that in rubbery PVC for a given molecular diameter. Furthermore, they sharply diverge as the molecular size of the diffusant increases (Berens, 1989). Hole filling (and hole emptying) becomes an increasingly activated process as steric constraints at the hole increase. Figure 6c shows that desorption of phenanthrene from peat humin—the insoluble organic matter after humic acid is removed—is slower than that from the original peat SOM for a given aging period, reflecting the more glassy character of the humin compared to the native SOM (White *et al.*, 1999). It has also been shown (White and Pignatello, 2000) that pyrene, a four-ring PAH, not only acts thermodynamically as a competing co-solute toward phenanthrene but also increases the *rate* of phenanthrene desorption, presumably by blocking nanopore sites ordinarily available to phenanthrene. This strongly suggests that the presence of nanopores impedes molecular diffusion inside SOM.

Similar conclusions about the effect of SOM structure on diffusion rates have been reached by Weber and coworkers in their studies of hydrophobic compound sorption on soils and model materials (Weber and Huang, 1996). They proposed a three-domain model of soil. The domains fill up in the following order:

Domain I: exposed inorganic surface

Domain II: "amorphous" SOM (equivalent to rubbery)

Domain III: "condensed" SOM (equivalent to glassy)

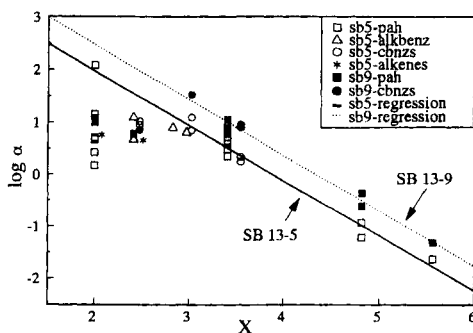
Domain I, which is minor for hydrophobic compounds, is filled in minutes (Huang *et al.*, 1996). The conclusion that domain III fills slowest is based on findings that the Freundlich exponent of phenanthrene ( $n$ ) decreases with approach to equilibrium, especially in the first hours. The nonlinearity is assumed due to sorption in domain III. Similar changes in  $n$  with time were reported by Xing and Pignatello (1996) for 2,4-dichlorophenol, metolachlor, and 1,2-dichlorobenzene in two soils, including the 93% SOM peat soil. The decrease in linearity is due to the combined effects of increasing contribution from the glassy SOM with time and the intrinsic concentration dependence of diffusion in the glassy state (see Section IV,C,4). In the glassy state, diffusivity increases with sorbate concentration due to the following: (i) the decline in hole-filling sorption (see Eq. 3)—i.e., as the holes fill up, there is less impedance for subsequent molecules as they pass through. This is confirmed by the competition experiments between phenanthrene and pyrene mentioned above. (ii) At high enough concentrations the sorbate can "plasticize" the polymer—that is, bring about its conversion to a more rubbery state.

#### b. Structure–Activity Relationships

On the assumption that IOMD is the important limiting mechanism, many researchers have tried to relate the desorption rate parameter to molecular structure. Carroll *et al.* (1994) found that the effective diffusion coefficient ( $D_{\text{eff}}$ ) of PCBs in a sediment decreased with molecular size; about an order of magnitude decline in  $D_{\text{eff}}$  occurred from monochlorinated to trichlorinated biphenyls. Brusseau and coworkers (Brusseau, 1993; Hu *et al.*, 1995; Piatt and Brusseau, 1998) studied the transport of various compounds in packed soil columns. Through analysis of solute breakthrough curves they obtained a desorption mass transfer coefficient ( $\alpha$ ) for the noninstantaneous fraction (see discussion of the "two-site" model in sections IV,A and V,B). Since the residency time of the solutes in the columns was only a few minutes to a few hours, their results apply to short-timescale phenomena; applicability to longer timescale sorption requires caution. They found a linear log–log relationship between  $\alpha$  and  $K_{\text{ow}}$ :

$$\log \alpha = a \log K_{\text{ow}} + b, \quad (7)$$

where  $a$  and  $b$  are regression constants. This constitutes a linear free energy relationship (LFER) between sorption rate and sorption strength since  $\log \alpha$  is proportional to activation energy,  $E_{\text{d}}^*$ , and  $\log K_{\text{ow}}$  is proportional to  $\log K_{\text{e}}$ , which in



**Figure 8** Linear free-energy relationship between the desorption mass transfer coefficient ( $\alpha$ ) and the first-order molecular connectivity index ( $^1X$ ) for PAHs, alkyl benzenes, chlorinated benzenes, and alkenes in two sandy aquifer samples (SB13-5 and SB-13-9) taken from a single bore hole at different depths. (Reprinted with permission from Piatt and Brusseau, 1998. Copyright 1998 American Chemical Society.)

turn is proportional to the thermodynamic free energy of sorption,  $\Delta G_{\text{sorp}}$ . The slope of Eq. (7) was negative, which means that the rate of desorption decreases with increasing affinity for the sorbent.

Brusseau and coworkers interpreted the LFER in terms of a polymer diffusion concept. Thus, increasing molecular size results simultaneously in increasing hydrophobicity and decreasing mobility in the viscous organic phase. Such interpretation has also been given for diffusion of small- and medium-size molecules in polymers (Rogers, 1965). Brusseau (1993) and Piatt and Brusseau (1998) actually obtained slightly better LFERs between  $\alpha$  and the molecular connectivity index  $X$ —a measure of topological size and degree of branching—than between  $\alpha$  and  $K_{\text{ow}}$ . Figure 8 presents such a correlation for hydrophobic compounds in two soils. They argued that diffusion through SOM is not just dependent on molecular polarity or hydrophobicity but also on size and shape. Such findings are consistent with diffusion limitations in an organic phase. They are not, however, inconsistent with diffusion limitations in fixed pore systems, as numerous studies of reference materials have shown (Kärger and Ruthven, 1992).

### 3. Effect of Soil Heterogeneity on Sorption Kinetics

When dealing with a heterogeneous mixture of particles, the rate of sorptive uptake will be dominated by the faster-sorbing particles at short times and the slower-sorbing particles at long times. Pedit and Miller (1994, 1995) showed that better fits to the pore diffusion model could be obtained by incorporating different size classes into the model (see Section IV,C,6). The size classes not only have different diffusive path lengths but also may have different equilibrium sorption ca-

capacities. Kleineidam *et al.* (1999) studied sorption to sands and gravels in southwest Germany and Switzerland. The samples, fragments of Triassic and Jurassic sedimentary rock, were separated according to size and lithographic type. They found that the rates of phenanthrene uptake depended on both particle size and properties. In general, dark-colored particles had the highest OC contents, lowest porosities, and highest sorption capacities while giving the slowest kinetics (e.g., 10% equilibrium in 500 days). The lighter-colored particles were just the opposite and showed the fastest kinetics (e.g., equilibrium in a few to 100 days). Most of the OC in these samples was ancient.

#### 4. Hysteresis

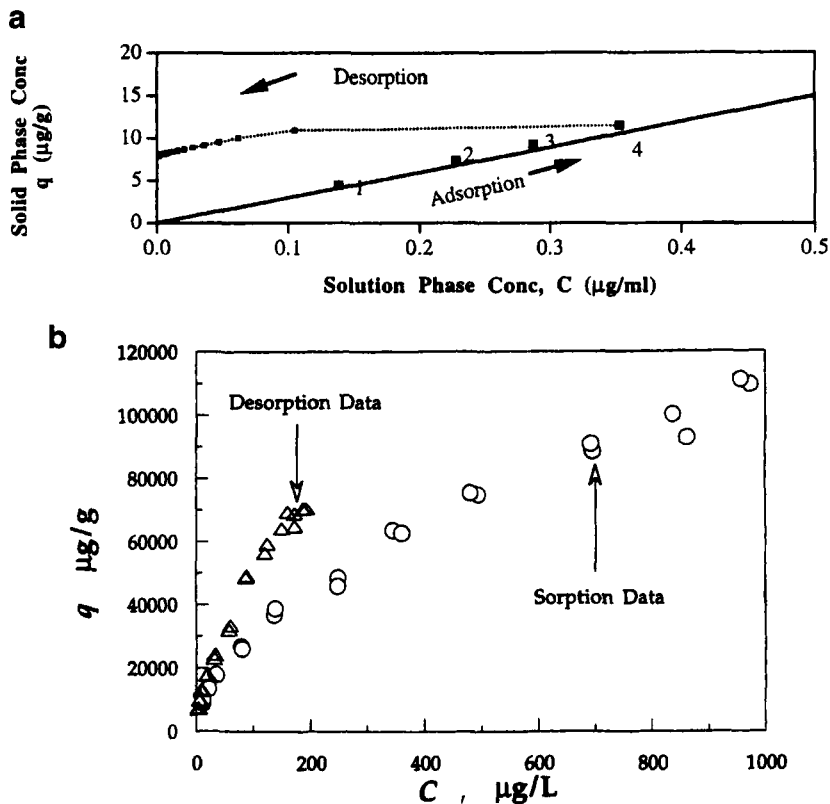
Hysteresis refers to the apparent asymmetry (nonsingularity) of the sorption/desorption process. There is reference in the literature to asymmetry in the isotherm, where the curve defining the relationship between sorbed and fluid-phase concentrations is different depending on whether it is determined in the forward (sorption) or the reverse (desorption) direction. There is also reference to nonsingularity in the rate parameters for sorption and desorption. Hysteresis has been observed in many soil-chemical systems but its causes have not been satisfactorily explained.

Provided sorption is reversible and true thermodynamic equilibrium is attained, isotherms constructed from the sorptive and desorptive directions are expected to be superimposable. Figure 9 shows two examples of isotherm hysteresis by phenanthrene—in a riverine sediment (Fig. 9a; Kan *et al.*, 1998) and in a shale material (Fig. 9b; Huang and Weber, 1997). In the former, a single sample was subjected to numerous desorption cycles, while in the latter, each sample was desorbed only once. As exemplified by Fig. 9a, the desorption curve often appears to intersect the ordinate at a nonzero value, indicating the presence of a “strongly resistant” fraction. Aside from method artifacts or chemical transformations (Rao and Davidson, 1980), there are several possible causes of isotherm hysteresis:

1. Formation of metastable states: Metastability plays an important role in the condensation/evaporation of gases in mesopores. The “hysteresis loop” commonly observed in gas adsorption isotherms is caused by formation of metastable films during uptake that abruptly coalesce to the condensed phase triggered by nucleation (Gregg and Sing, 1982). Hysteresis has also been observed in absorption of gases (e.g., CO<sub>2</sub> and small hydrocarbons) by glassy, but not rubber, polymers (Kamiya *et al.*, 1989, 1992). In this case the cause is believed to be slow volume-structural relaxation; that is, the microvoid volume which increases on sorption does not instantly relax to the original value on desorption. A mechanism involving metastable states in the context of sorption of dilute chemicals from soil solution, however, has not been articulated.

2. Insufficient time allowed for equilibrium: Nonattainment of equilibrium due





**Figure 9** Hysteretic isotherms of phenanthrene in two soils. Experiments were done in decant-reseal batch cycles with replacement of most of the fluid after each cycle. (a) Lula sediment. Adsorption: four cycles lasting 1–4 days each; desorption: 49 cycles lasting 1–59 days each. (b) Norwood shale. Adsorption: 28 days; desorption, 14 days. [(a) Reprinted with permission from Kan *et al.*, 1998. Copyright 1998 American Chemical Society. (b) Reprinted with permission from Huang and Weber, 1997. Copyright 1997 American Chemical Society.]

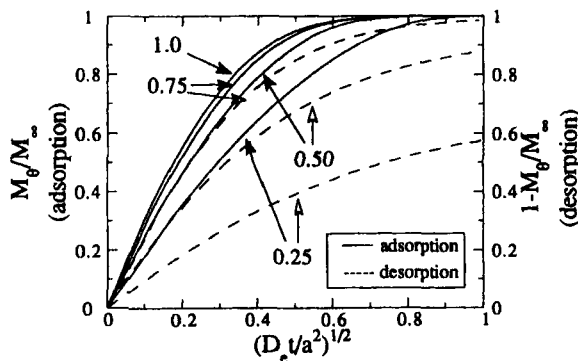
to rate-limited diffusion can lead to an underestimation of equilibrium sorbed concentration in the sorption direction and an overestimation in the desorption direction. A likely explanation for hysteresis in many cases, this is a vexing problem experimentally because true equilibrium can require very long times and may be concentration dependent.

3. Changes in the properties of the sorbent on sorption such that desorption takes place from a different molecular environment than sorption. For SOM it may be hypothesized that some sorbed molecules experience a conformational rearrangement of the local humic matrix, resulting in engagement or at least an enhancement of the activation barrier for subsequent escape. An analogy has been

made between sorbate-induced changes in the conformation of humic molecules and substrate-induced changes in the conformation of enzymes (Pignatello and Xing, 1996). Rearrangement has been observed in computational simulations of pollutant molecules [e.g., atrazine (Schulten, 1995) and pentachlorophenol (Schulten, 1996)] interacting with the hypothetical humic acid macromolecule shown in Fig. 3a.

In order to explain isotherm hysteresis, Kan *et al.* (1998) proposed that total sorption includes *reversible* and *irreversible* components. The term *irreversible*, rather than implying permanent immobilization, is intended to mean that molecules leave a site by a different microscopic pathway than that by which they enter because of some kind of change of state taking place in the meantime (Adamson and Gast, 1997). Such behavior has been discussed in regard to adsorption of surfactants and polymers on oxides (Adamson and Gast, 1997, pp. 404–405) but without resolution of the cause. According to Kan *et al.* (1998), the “irreversible” compartment has a fixed maximum capacity for sorbate and fills in one or more steps in response to the solution-phase concentration. They proposed that the SOM matrix rearranges to trap the sorbate. Huang and Weber (1997) suggested that, in addition to nonattainment of equilibrium, hysteresis may be contributed by sorbate-induced expansion of condensed SOM to form pores that may “have no exits” once configurational changes in humic molecules occur.

There are numerous examples of kinetic hysteresis, in which sorption appears to be faster than desorption (Connaughton *et al.*, 1993; Farrell and Reinhard, 1994b; Harmon and Roberts, 1994; Pignatello *et al.*, 1993). Harmon and Roberts (1994), for example, found the diffusion coefficient to be two to five times small-



**Figure 10** Sorption and desorption rate curves for a hypothetical case. The cumulative mass gained or lost ( $M_0$ ) relative to the mass gained or lost after infinite time ( $M_\infty$ ) is shown for different Freundlich  $n$  values. The abscissa is the square root of dimensionless time. (Reprinted with permission from Lin *et al.*, 1994. Copyright 1994 American Chemical Society.)

er for desorption than sorption. “Thermodynamic” and “kinetic” hysteresis may have the same underlying cause; in studies of TCE and benzene vapor uptake by soil grains using an intragrain diffusion model, Lin *et al.* (1994) suggested that much of the diffusion asymmetry can be explained simply by nonlinearity of the isotherm. The results of the hypothetical case appear in Fig. 10. Note that the effect of nonlinearity is relatively minor unless the Freundlich exponent is less than about 0.75. Also, Farrell and Reinhard (1994b) found that the “slow fraction” of TCE remaining after  $N_2$  sparging was not well simulated by taking into account only equilibrium nonlinearity. A common assumption in many studies is that the rate parameter pertaining to sorption or desorption is single valued when in fact, because of the heterogeneous nature of soils, it is more likely to take on a range of values, depending on position along the uptake or release curve. Because most studies to date have focused on the behavior of the bulk of the chemical (first 80% sorbed or desorbed), much useful information has been missed.

## IV. SORPTION KINETIC MODELS

### A. MODELS BASED ON BOND ENERGETICS

The simple rate laws in Eqs. (4) and (5) seldom apply to real particles for two reasons. First, diffusion (mass transfer) is intrinsic to sorption kinetics because most sites are located in pores or within the SOM matrix and thus not directly accessible by molecules in the bulk fluid phase. Second, sites vary energetically because soils are heterogeneous. Nevertheless, kinetic models based on bond energetics, particularly those modified to account for soil heterogeneity, serve a purpose because, unlike diffusion models, they do not require knowledge about particle geometry. Only the essential features are presented for the models that follow: Readers are urged to consult the original papers for details about their application.

The Langmuir kinetic model, reviewed by Adamson and Gast (1997), posits a collection of sites of uniform energy. Combining Eqs. (4) and (5) (since sorption and desorption events occur concurrently) and recognizing that the exponentials are constant at constant temperature,

$$\begin{aligned} \frac{dS_o}{dt} &= \left[ A_a e^{(-E_a^*/RT)} \right] pS_v - \left[ A_d e^{(-E_d^*/RT)} \right] S_o \\ &= k'_a p(S_T - S_o) - k'_d S_o \end{aligned} \quad (8)$$

where total sorption  $S_T = S_v + S_o$ , and  $k'_a$  are the adsorption and desorption rate constants. Equation (5) may be put into a relevant soil–water frame of reference

by replacing  $p$  with aqueous concentration  $C$  [ $M L^{-3}$ ]; replacing  $S_o$  with sorbed concentration  $q$  [ $M M^{-1}$ ]; and letting  $Q$  [ $M M^{-1}$ ] be the capacity constant—the sorbed concentration when all sites are occupied. This gives

$$\frac{dq}{dt} = \frac{k_a \theta}{\beta} C(Q - q) - k_d q \quad (9)$$

where  $k_a$  is in units of [ $L^3 M^{-1} T^{-1}$ ] and  $k_d$  is in units of [ $T^{-1}$ ]. The Langmuir kinetic model is the basis for the familiar Langmuir isotherm since at equilibrium ( $dq/dt = 0$ ) Eq. (9) reduces to

$$q_e = \frac{bQC_e}{1 + bC_e}, \text{ where } b = \frac{k_a \theta}{k_d \beta} \quad (10)$$

Site nonuniformity has been dealt with customarily by including multiple sites. The two-site model (Hu and Brusseau, 1998) envisions an instantly reversible site  $S_1$ , comprising a fraction  $f$  of the total sites, and a slower kinetic site  $S_2$ :



The equilibrium expressions are as follows.

$$S_{1e} = f K_e C_e^n, \quad (12)$$

$$S_{2e} = (1 - f) K_e C_e^n, \quad (13)$$

where  $K_e$  is determined on the basis of total sorbed concentration,  $q$ . The overall rate is the sum of the rates for each of the sites;

$$\frac{\partial q}{\partial t} = \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \quad (14)$$

Sorption at site 1 is governed by the equilibrium expression in Eq. (12), whereas site 2 follows a first-order reversible rate law in which the forward rate is proportional to  $S_1$  and the reverse rate is proportional to  $S_2$ .

$$\frac{\partial S_2}{\partial t} = k_2 S_1 - k_{-2} S_2. \quad (15)$$

After differentiation and substitution to eliminate  $S_1$ , and realizing that  $k_2/k_{-2} = (1 - f)/f$ , the overall rate law becomes

$$\frac{\partial q}{\partial t} = n f K_e C^{n-1} \frac{\partial C}{\partial t} + k_2 f K_e C^n - (1 - f) \quad (16)$$

A Dutch group (Cornelissen *et al.*, 1997a; 1998; 1999; Ten Hulscher *et al.*, 1999) used a multicompartmental model (either two or three compartments) for desorption of polychlorinated benzenes and PAHs from sediments in the presence of Tenax TA polymeric beads as a third-phase adsorbent sink. The initial sorbed concentration  $q_0 = \sum f_i q_{i0}$ , where  $f_i$  is the fraction in the  $i$ th compartment. Desorption in each compartment was regarded to occur in a first-order manner:

$$\frac{dS_i}{dt} = -k_i S_i, \quad (17)$$

$$S_i = S_{i,0} e^{-k_i t}. \quad (18)$$

Since the beads sorbed PAHs faster than does soil, the rate of resorption by the soil was assumed negligible. Thus,

$$\frac{q_t}{q_0} = f_r e^{-k_r t} + f_s e^{-k_s t} + f_{vsl} e^{-k_{vsl} t} \quad (19)$$

where  $f_r$ ,  $f_{sl}$ , and  $f_{vsl}$  refer to rapid, slow, and very slow fractions of initial chemical demarcated, somewhat arbitrarily, on the basis of discontinuities in the desorption curve.

One could add as many different types of sites as one wanted. The “multireaction” model tested by Xue and Selim (1995) on alachlor sorption considers up to four sorption domains: an equilibrium domain  $S_e$  obeying a Freundlich isotherm ( $n$ ,  $K_e$ ), a reversible kinetic domain  $S_1$ , a “consecutive” irreversible kinetic domain  $S_2$  accessible only from  $S_1$ , and a “concurrent” irreversible domain  $S_{irr}$  accessible only from solution.

## B. DRIVING FORCE MODELS

Several models are based on the idea that the rate is related to the degree that the system has reached equilibrium. The reversible model reviewed by Travis and Etnier (1981) assumes the rate is proportional to the difference between the equilibrium amount sorbed and the amount already sorbed:

$$\frac{dq}{dt} = \alpha_R (q_e - q) = \alpha_R (K_e C^n - q) \quad (20)$$

where  $\alpha_R$  is a rate parameter [ $T^{-1}$ ]. Equation (20) is the reversible linear model or reversible nonlinear model, depending on the value of  $n$ . The reversible linear model is identical in form to the Langmuir model at very low concentration.

The film resistance model (Eq. 21) assumes mass transfer resistance of molecules across a stagnant boundary layer (“film”) at the interface. The rate of sorp-

tion is controlled by the difference between bulk solution concentration  $C$  and the concentration  $C^*$  in equilibrium with the surface,

$$\frac{dq}{dt} = \alpha_{FR}(C - C^*) \quad (21)$$

where  $\beta$  is the solids concentration [ $\text{ML}^{-3}$ ] and  $\theta$  is the volumetric water content [ $\text{L}^{-3}\text{L}^{-3}$ ].

One can see that if  $C^*$  is related to  $q$  by the linear Freundlich isotherm then the film resistance model is of the same form as the reversible linear model. On the other hand, if  $C^*$  is related to  $q$  by the Langmuir isotherm then it is of the same form as the Langmuir model.

The second-order driving force model (Hendricks and Kuratti, 1982) regards the rate to be proportional to solution concentration times the difference between the equilibrium amount sorbed and the amount sorbed at time  $t$ :

$$\frac{dq}{dt} = \alpha C(q_e - q) \quad (22)$$

where  $\alpha$  is now in units of [ $\text{L}^3\text{M}^{-1}\text{T}^{-1}$ ]. In sorption of a dye to Dowex 50 ion-exchange resin or to activated carbon, Hendricks and Kuratti (1982) found this model to be superior to the reversible model, the Langmuir model, and two other models conceptually similar to the second-order and reversible models.

The Fava–Eyring model (Fava and Eyring, 1956) is a nonlinear driving force model in which the rate is related to  $\phi(t)$ , defined as the distance from equilibrium divided by the initial distance from equilibrium; that is,  $\phi(t) = (q - q_e)/(q_0 - q_e)$ , where  $q_0$  is the initial amount sorbed. The rate expression is given by Eq. (23), where  $a$  and  $b$  are constants. The hyperbolic sine term accounts for diminishing affinity for the sorbate with increasing loading:

$$\frac{d\phi}{dt} = 2\alpha\phi \sinh(b\phi) \quad (23)$$

## C. DIFFUSION MODELS

### 1. General Considerations

Soil particles are typically porous and contain highly viscous sorptive phases (i.e., SOM). Any mechanistic-based depiction of sorption would have to take diffusion of one kind or another into account. The form that the diffusion model takes is critically dependent on the geometry of the diffusing medium and the boundary conditions. To understand diffusion in heterogeneous systems such as soils we

must consider studies of model sorbents. These studies are covered well by Kärger and Ruthven (1992) for fixed-pore sorbents and Frisch and Stern (1983) and Vieth (1991) for the organic solid state. The mathematics of diffusion is dealt with by Crank (1975).

*Transport diffusion* is the nonequilibrium migration of molecules along the concentration gradient. *Self-diffusion* is scrambling of molecules due to their Brownian motions under equilibrium (no gradient) conditions and may be approximated by adding a tiny amount of radiolabeled tracer. Transport and self-diffusion are not necessarily equal. The fundamental diffusion equations are known as Fick's first and second laws, which are given in Eqs. (24) and (25), respectively, for one-dimensional diffusion in the  $z$  direction and the general case:

$$J = -D(c) \frac{\partial c}{\partial z}; \quad \mathbf{J} = -D(c) \text{ grad } c \quad (24)$$

$$\frac{\partial c}{\partial t} = D(c) \frac{\partial^2 c}{\partial z^2}; \quad \frac{\partial c}{\partial t} = D(c) \text{ div}(\text{grad } c) \quad (25)$$

where  $J(\mathbf{J})$  is the flux ( $\text{E L}^{-2} \text{T}^{-1}$ ),  $c$  is the total local volumetric concentration in the diffusing medium [ $\text{M L}^{-3}$ ], and  $D(c)$  is the diffusion coefficient, or diffusivity [ $\text{L}^2 \text{T}^{-1}$ ]. Equation (26) gives Fick's second law in radial coordinates for a  $\nu$ -dimensional sample ( $\nu = 1$  for a slab,  $\nu = 2$  for a cylinder, and  $\nu = 3$  for a sphere),

$$\frac{\partial c}{\partial t} = \frac{1}{r^{(\nu-1)}} \frac{\partial}{\partial r} \left( r^{(\nu-1)} D(c) \frac{\partial c}{\partial r} \right) \quad (26)$$

where  $r$  is the thickness (slab) or radius (cylinder, sphere). The equations apply as long as the sample is isotropic and homogeneous and not appreciably changed by the penetrant. The equations for the slab and cylinder assume no edge effects.

In Eqs. (24)–(26),  $D$  is expressed as a function of concentration, although in many cases it may be constant at a given temperature;  $D$  is concentration dependent when

1. The diffusant alters the sorbent properties of the solid. For example, high loadings of an organic diffusant may cause an organic solid to soften and swell (Frisch and Stern, 1983; Lyon, 1995; Lyon and Rhodes, 1993; Vieth, 1991). This increases diffusivity because it makes the macromolecular chains more flexible, allowing the diffusant to pass more easily.

2. Sorption is nonlinear with concentration. Since the gradient in chemical potential is related to the logarithm of concentration, the transport diffusivity  $D$  is related to the self-diffusivity  $\mathcal{D}$  (also called "corrected diffusivity") (Kärger and Ruthven, 1992) by

$$D = \mathcal{D} \frac{d \ln p}{d \ln c} \quad (27)$$

where  $p$  is the pressure of diffusant in the external fluid. It can be seen from Eq. (27) that  $D = \mathcal{D}$  when  $c$  is linear in  $p$ . If the isotherm is Langmuir-type, then  $D = \mathcal{D}(1 - \Phi)^{-1}$ , where  $\Phi$  is the fractional coverage,  $q_e Q^{-1}$ . Sorption is always linear at infinite dilution; thus,  $D \rightarrow \mathcal{D}$  as  $c \rightarrow 0$ .

Diffusion is an activated process analogous to any elementary chemical reaction. In the Arrhenius formulation,

$$D = D_o e^{-E_D^*/RT}, \quad (28)$$

where  $E_D^*$  is the diffusion activation energy and  $D_o$  is the preexponential constant.

Analytical solutions to the diffusion equation are available for a variety of simple situations that might be encountered, including

- sorption/desorption in an infinite bath of constant or variable concentration;
- sorption/desorption in a finite bath; and
- “evaporation” at the surface to an infinite bath.

The solutions are available for plane-sheet, cylinder, and sphere geometries in Crank (1975) and for cube geometry in Kärger and Ruthven (1992). They are too cumbersome to present here. Obviously, soil particles are not perfectly round; however, since the diffusion curves for the cylinder and cube cases are quite similar to that of the spherical case, except at long times, it is common practice to use the simpler spherical expression, whereupon the radius corresponds to that of a sphere having the same volume to external surface ratio.

Analytical solutions are useful; however, the researcher must be aware that they come at the expense of many assumptions and simplifications. Some of the common ones include the following:

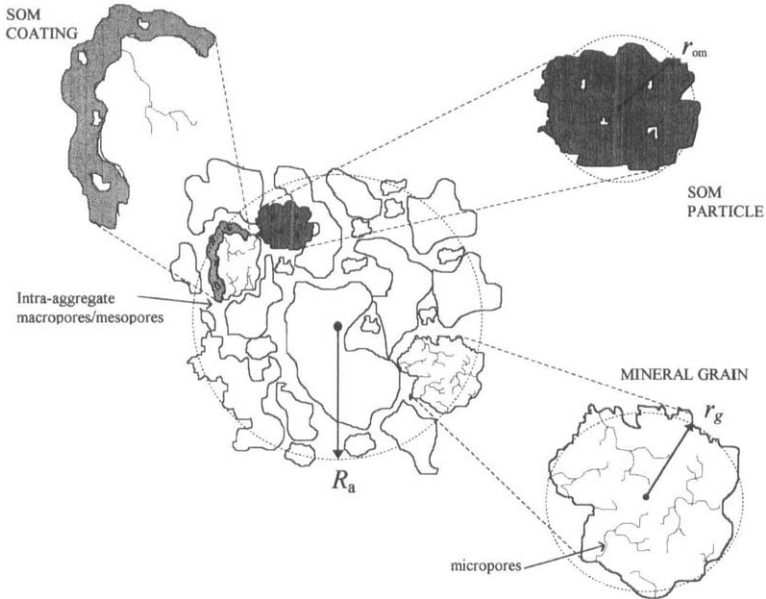
1. Diffusion obeys Fick’s laws.
2. The diffusion coefficient is concentration independent.
3. The sample consists of particles of uniform size.
4. The diffusant concentration is uniform throughout the particle at equilibrium.
5. Local equilibrium exists in a finite element of the particle.

Assumption (1) may be invalid if the properties of the sorbent change in response to sorption, as could occur for SOM. Assumption (2) is not always valid but may be regarded to be valid over a narrow concentration range. Assumptions (3) and (4) are typically invalid for soils. Assumption (5) requires that, e.g., steric hindrance at the entrance/exit to sites is not rate limiting.

## 2. Diffusion in Fixed-Pore Systems

Soil particles are aggregates of smaller grains that are cemented together with organic or inorganic matter (Greenland and Hayes, 1981). Figure 11 shows a rea-





**Figure 11** Soil particle aggregate with spherical-equivalent radius  $R_a$  made up of smaller grains of minerals of radius ( $r_g$ ) and organic matter ( $r_{om}$ ). Illustrated is a micropore structure within grains and macropore/mesopore structure between grains.

sonable depiction of a soil aggregate having an equivalent spherical radius  $R_a$ . The aggregate consists of SOM particles, SOM coatings, mineral particles, and mineral particles coated with finer grains. It has a macropores/mesopores between the grains and a micropore network within individual grains.

#### a. Macropores and Mesopores

Diffusion is similar in macropores and mesopores in many respects and it is convenient to discuss the two sizes simultaneously. At relative humidities most relevant to the environmental (i.e.,  $> \sim 50\%$ ) the following conditions hold: (i) at least a monolayer of water is present on external mineral surfaces, (ii) micropores and mesopores are filled with water, and (iii) macropores are empty or only partially filled with water. As the humidity approaches 100%, the bulk  $K_e$  of a chemical is close to that observed under saturated conditions (Chiou, 1989).

Diffusion of small molecules in macropores and mesopores is affected principally by tortuosity and sorption. For a particle of radius  $R$ , consider a volume element of that particle in which  $c_p$  [ $M L^{-3}$ ] is the local pore fluid concentration and

$s_p$  [ $\text{M L}^{-3}$ ] is the local sorbed concentration (i.e.,  $c = \varphi c_p + (1 - \varphi)s_p$ , where  $\varphi$  is the particle porosity). The governing equation in radial coordinates is

$$\varphi \frac{\partial c_p}{\partial t} + (1 - \varphi) \frac{\partial s_p}{\partial t} = \varphi D_p \left[ \frac{\partial^2 c_p}{\partial R^2} + \frac{2}{R} \frac{\partial c_p}{\partial R} \right] \quad (29)$$

and  $D_p$  is the local pore diffusivity which includes diffusion along the pore surface and diffusion in the pore fluid. Equation (29) assumes  $D_p$  to be concentration independent. By further assuming instantaneous local equilibrium, Eq. (29) becomes

$$\frac{\partial c_p}{\partial t} = D_{\text{eff}} \left[ \frac{\partial^2 c_p}{\partial R^2} + \frac{2}{R} \frac{\partial c_p}{\partial R} \right] \quad (30)$$

If the isotherm is linear— $s_p = K c_p$ , where  $K$  [dimensionless] is the local sorption coefficient—the effective diffusivity is given by

$$D_{\text{eff}} = \frac{\varphi D_p}{\varphi + (1 - \varphi)nK\epsilon} \quad (31)$$

Pore diffusivity taking into account surface diffusion can be expressed as

$$D_p = D_{\text{pf}} + \left( \frac{1 - \varphi}{\varphi} \right) K D_{\text{ps}} \quad (32)$$

where  $D_{\text{pf}}$  is the pore fluid diffusivity and  $D_{\text{ps}}$  is the pore surface diffusivity. Surface diffusion may be important in pores with a large surface to volume ratio. Surface diffusivities are generally determined by the difference between observed pore diffusivity and the estimated value of pore fluid diffusivity. Surface diffusivity tends to increase with diffusant concentration and temperature. Surface diffusivities have been determined for gases in activated carbons and mesoporous glasses (Kapoor *et al.*, 1989; Kärger and Ruthven, 1992). The contribution of surface diffusion in water-filled soil pores, however, is not well established.

Pore fluid diffusivity is reduced with respect to bulk fluid diffusivity by a tortuosity factor  $\tau$  ( $\geq 1$ ) that reflects deviation from straight-line paths and pore interconnectedness and by a steric parameter  $\kappa$  ( $\leq 1$ ) that reflects steric hindrance by the pore walls:

$$D_{\text{pf}} = \kappa D_b / \tau. \quad (33)$$

Theoretical models predict  $\tau$  to be proportional to  $\varphi^{-1}$  (Currie, 1960; Kärger and Ruthven, 1992; Wakao and Smith, 1962). Currie (1960) studied  $\text{H}_2$  diffusion in

beds of glass beads, sand, carborundum, several soils, and sodium chloride packed at various bulk densities. The beds had porosities between 0.18 and 0.65 consisting primarily of macropores and mesopores. Currie found the exponent of  $\phi$  to vary with the material and with  $\phi$ . Columns of high porosity gave an exponent of  $\phi$  close to  $-1$ , but this exponent became less negative with decreasing porosity to values as high as  $-0.38$ . For lower porosities and smaller pore sizes, tortuosity appears to be greater than predicted on the basis of  $\tau \propto \phi^{-1}$ . For example, for intraparticle diffusion of chlorinated hydrocarbons in aquifer sediments,  $\tau$  was  $10^2$  or  $10^3$  times greater than predicted (Ball and Roberts, 1991b; Grathwohl and Reinhard, 1993). This can be attributed in part to incomplete interconnectedness of pores and in part to steric hindrance of diffusion.

Steric effects begin to show when the ratio ( $\lambda$ ) of the minimum critical molecular diameter to the pore diameter reaches  $\sim 0.1$  and become severe as  $\lambda$  approaches unity. Most molecules of interest are  $< \sim 1.5$  nm in their smallest dimension. Hence, steric effects are important in micropores and smaller mesopores. Many theoretical models have been presented for steric hindrance that fit specific data reasonably well (Kärger and Ruthven, 1992; Lee *et al.*, 1991). Satterfield *et al.* (1973) found  $\kappa = \lambda^{-2.0}$  ( $0.09 < \lambda < 0.5$ ) for nonsorbing sorbates in microporous (3.2 nm diameter) silica-alumina beads. For sorbing compounds, the effects of tortuosity and steric hindrance are difficult to separate. The diffusivities of  $\text{Cd}^{2+}$  ion vs the larger  $\text{SeO}_e^{2-}$  ion in aluminas were consistent with a greater steric effect in micropores than in mesopores (Papelis *et al.*, 1995).

Combining Eqs. (31–33), we get

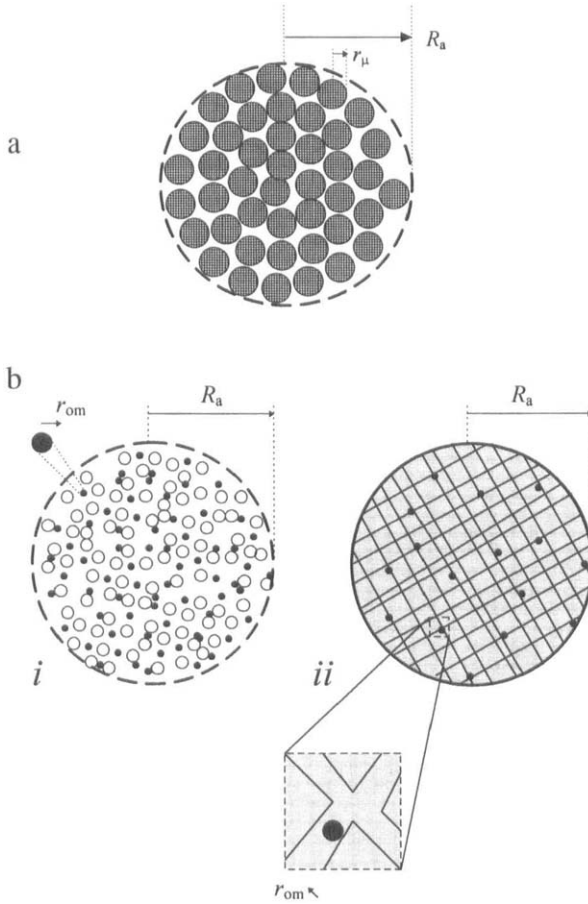
$$D_{\text{eff}} = \frac{\phi \kappa \tau^{-1} D_{\text{pf}} + (1 - \phi) K D_{\text{ps}}}{\phi + (1 - \phi) K} \quad (34)$$

To simplify modeling it has been customary to (i) neglect surface diffusion; (ii) combine tortuosity and steric hindrance into a single “effective tortuosity” parameter ( $\kappa/\tau = \tau_e$ ); and (iii) relate the local sorption coefficient to the bulk equilibrium sorption coefficient ( $K = \rho K_e/\phi$ , where  $\rho$  [ $\text{M L}^{-3}$ ] is the particle density inclusive of intraparticle porosity).

#### b. Micropores

In the narrow confines of a micropore the diffusant is always under the influence of the surface; therefore, it is meaningless to distinguish between fluid and sorbed concentrations. The following is the governing equation in a spherical particle of radius  $r_\mu$ :

$$\frac{\partial s}{\partial t} = D_\mu \left[ \frac{\partial^2 s}{\partial r^2} + \frac{2}{r} \frac{\partial s}{\partial r} \right], \quad (35)$$



**Figure 12** (a) Schematic of biporous diffusion model: microporous spherical grains inside a mesoporous or macroporous spherical aggregate. (b) Coupled pore-intraorganic diffusion model: (i) completely mixed aggregate of uniform mineral microparticles and uniform spherical SOM microparticles or (ii) a porous mineral particle in which SOM microparticles are uniformly distributed throughout the internal surface. (Reprinted from Yiacoumi and Tien, 1994, with permission from the American Geophysical Union.)

where  $s(r)$  is the local concentration and  $D_\mu$  is the effective micropore diffusivity. Equation (35) is a restatement of Eq. (26) for a sphere and concentration-independent  $D_\mu$ .

### c. Dual-Resistance Models

One may consider the case in which diffusion takes place in a biporous particle such as the one shown in Fig. 12a, which depicts a macroporous (or mesoporous)

aggregate ( $R_a$ ) made up of individual microporous grains ( $r_\mu$ ). This model combines Eqs. (29) and (35) and has the following boundary conditions:

$$s(r, 0) = c_p(R, 0) = 0 \quad (36a)$$

$$\frac{\partial s}{\partial r}(0, t) = \frac{\partial c_p}{\partial R}(0, t) = 0 \quad (36b)$$

$$s(r_\mu, t) = Kc_p(R_a, t) \quad (36c)$$

$$\bar{s}_p(R, t) = \bar{s}(R, t) = \frac{3}{r_\mu^3} \int_0^{r_\mu} s(r)r^2 dr \quad (36d)$$

$$(36e)$$

where  $C(t)$  [ $\text{ML}^{-3}$ ] is the external solution concentration.

An analytical solution of the biporous dual-resistance model is found in Ruckenstein *et al.* (1971) and Lee (1978) for linear sorption under two types of well-mixed batch conditions: (i) a step change in surface concentration, in which the external fluid concentration is kept constant, and (ii) variable surface concentration, in which diffusion occurs from a finite medium. The mathematics are similar for two other conceptual systems: particle-scale independent macropore and micropore networks (not realistic for natural particles) and a particle with in-series macropore and micropore networks. Arocha *et al.* (1996) describe a numeric solution to cases in which sorption in the macroporous and microporous systems is nonlinear and obeys different Freundlich equations; they applied this nonlinear biporous dual-resistance model to toluene vapor sorption to dry soil crumbs and Na-montmorillonite. The diffusivity of toluene in the micropore zone was approximately  $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ , which is consistent with values reported for zeolites (Kärger and Ruthven, 1992).

### 3. Diffusion in Organic Matter

Rubbery SOM, in which diffusant molecules are considered to be dissolved, is analogous to a highly viscous fluid. Equation (35) applies if the particle is spherical. However, as discussed previously, SOM may have both a dissolution domain and a Langmuir domain in which adsorption-like interactions occur, with an overall isotherm given by the dual-mode model [Eq. (3)]; for polymers, it is commonly assumed that  $n = 1$ . In this case, diffusion is more complex.

The model of Vieth and Sladek (1965) assumes that diffusion occurs only in the dissolution domain ( $D_D$ ) and that molecules at Langmuir sites are totally immobile ( $D_L = 0$ ). For diffusion through a planar sheet of polymer,

$$J = D_{\text{eff}} \frac{\partial s}{\partial z} = -D_D \frac{\partial s_D}{\partial z} \quad (37)$$

$$\frac{\partial (s_D + s_L)}{\partial t} = D_D \frac{\partial^2 s}{\partial z^2} \quad (38)$$

Analogous equations can be written for other geometries. If we assume local equilibrium exists between  $s_D$  and  $s_L$ , then

$$s_L = \frac{(bs_L^0/K_D)s_D}{1 + (b/K_D)s_D} \quad (39)$$

Therefore, we can eliminate  $s_L$  in Eq (38). After derivativizing we find that

$$D_{\text{eff}} = \left[ 1 + \frac{K'}{(1 + \alpha s_D)^2} \right]^{-1} \quad (40)$$

where  $K' = bs_L^0/K_D$ , and  $\alpha = b/K_D$ . Note that  $D_{\text{eff}}$  is a function of the local dissolution domain concentration and thus changes as sorption or desorption progresses.

The model of Paul and Koros (1976) considers dual but independent diffusivities. This means that molecular jumps are allowed within the dissolution domain and between sites in the Langmuir domain, but cross-jumps are ignored. For diffusion through a planar sheet of polymer,

$$J = D_{\text{eff}} \frac{\partial s}{\partial z} = -D_D \frac{\partial s_D}{\partial z} - D_L \frac{\partial s_L}{\partial z} \quad (41)$$

where  $s$  is the total local volumetric concentration in the polymer. Assuming local equilibrium and performing the mathematics in the analogous manner, it can be shown that

$$D_{\text{eff}} = D_D \left[ \frac{1 + \frac{K'(D_L/D_D)}{(1 + \alpha s_D)^2}}{1 + \frac{K'}{(1 + \alpha s_D)^2}} \right] \quad (42)$$

The models of Barrer (1984) and Fredrickson and Helfand (1985) allow cross-jumping between the Henry and Langmuir domains. The expression for effective diffusivity then becomes

$$D_{\text{eff}} = \frac{D_{DD} + \frac{(D_{DL} + D_{LL})K'}{(1 + \alpha s_D)^2} + D_{DL} \left[ 1 - \frac{s_D K'}{(1 + \alpha s_D)s_L^0} + \frac{s_D K'^2}{(1 + \alpha s_D)^3 s_L^0} \right]}{1 + \frac{K'}{(1 + \alpha s_D)^2}} \quad (43)$$

where  $D_{DD}$  and  $D_{LL}$  are the intradomain diffusivities, and  $D_{DL}$  is the cross-domain diffusivity.

For SOM, it must be assumed that there are many different kinds of sites. This makes the solution very complicated, indeed. Horas and Nieto (1994) derived an expression for  $D_{\text{eff}}$  for the general case in which the energy is distributed:

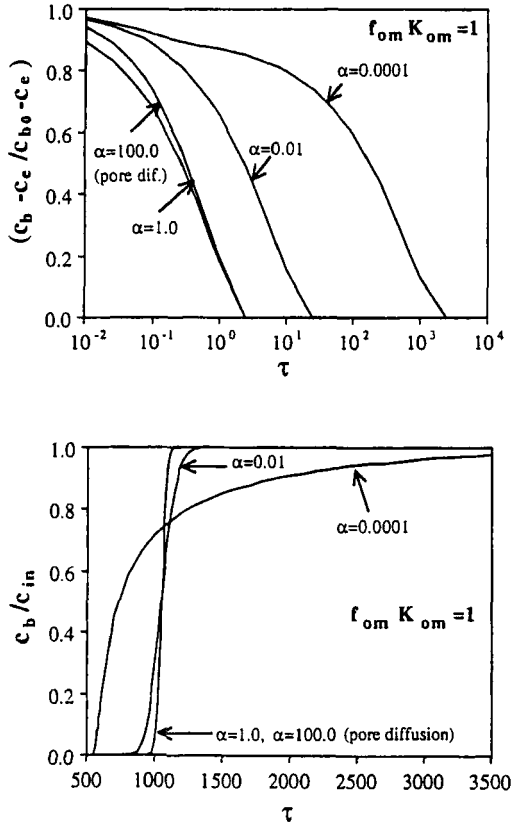
$$D_{\text{eff}} = f \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ell_{ij}^2 \frac{\partial}{\partial S} \left[ S_i v_{ij} (S_i^0 - S_j) \exp(-E_{ij}/kT) \right] dE_i dE_j \quad (44)$$

where  $f$  is the fraction of jumps in the direction of the macroscopic flux,  $S_i$  is the concentration of occupied sites of type  $i$ ,  $S_i^0$  is the total number of sites of type  $i$ ,  $\ell_{ij}$  is the average distance between sites  $i$  and  $j$ ,  $v_{ij}$  is the vibrational frequency of the molecule at site  $i$ ,  $E_{ij}$  is the potential energy barrier between sites  $i$  and  $j$ ,  $T$  is the temperature ( $^{\circ}\text{K}$ ), and  $k$  is the Boltzman constant ( $1.38044 \times 10^{-16}$  erg/deg).

The derivation of Eq. (44) requires many assumptions, some of which are debatable when applied to soils: (i) Only one molecule can occupy each site; (ii) the values of  $\ell_{ij}$ ,  $f$ , and  $v_{ij}$  are constant for a given system; (iii) the approximate jump frequency of molecules from site  $i$  to site  $j$  is a function of  $v_{ij}$ , the probability of finding a vacancy at  $j$ , and  $E_{ij}$  (this follows from statistical mechanics and transition-state theory); and (iv)  $E_{ij}$  is assumed to be equal to the thermodynamic depth of the potential energy well of site  $i$  (see Fig. 5), which is equivalent to saying that the energy level of the transition state is the same throughout the sorbent. Equation (44) has been integrated for the case in which the energy distribution is Gaussian. The solution is not presented here due to space limitations. Horas and Nieto have shown that it simplifies to Eq. (42) or Eq. (43) when the corresponding assumptions intrinsic to those models are employed.

#### 4. Combined Pore Diffusion/Organic Matter Diffusion Model

Yiacoumi and coworkers (Yiacoumi and Rao, 1996; Yiacoumi and Tien, 1994, 1995) developed a model that includes both pore and intraorganic matter processes simultaneously. It is mathematically equivalent for either of the situations depicted in Fig. 12b in which the particle aggregate of radius  $R_a$  is (i) a completely mixed aggregate of uniform mineral microparticles and uniform spherical SOM microparticles (radius  $r_{\text{om}}$ ) or (ii) a porous mineral particle in which SOM microparticles are uniformly distributed throughout the internal surface. The model takes into account pore diffusion ( $D_p$ ) composed of pore fluid ( $D_{\text{pf}}$ ) and pore surface ( $D_{\text{ps}}$ ) terms; adsorption on the mineral surface, assuming linearity and local equilibrium ( $s_p = K_{\text{mf}} c_p$ ); pore surface diffusion ( $D_{\text{ps}}$ ); sorption in SOM, assuming SOM is a homogeneous Henry's law partition medium ( $s_{\text{om}} = K_{\text{om}} c_p$ ); and radial diffusion in SOM ( $D_{\text{om}}$ ). The model also assumes that mass transfer across the bulk solution–macroparticle interface, as well as across the pore liquid–SOM interface, is never rate limiting.



**Figure 13** Sorption predicted by the combined pore–intraorganic matter diffusion model of Yiacoymi and coworkers. (Top) Approach to equilibrium in completely mixed batch experiment. (Bottom) Column breakthrough curve. (Bulk solution concentrations:  $c_b$ , time  $\tau$ ;  $c_{b0}$ , time zero;  $c_e$ , equilibrium;  $c_{in}$ , input eluent concentration.  $\tau$  is dimensionless time.). The  $\alpha$  refers to the ratio of diffusion time scales in pores vs OM (Eq. 43). Small  $\alpha$  reflects dominance of intraorganic matter diffusion resistance. (Reprinted from Yiacoymi and Tien, 1994, with permission from the American Geophysical Union.)

The governing equation is

$$[\varphi + (1 - \varphi)K_{mf}] \frac{\partial c_p}{\partial t} + \frac{\partial N}{\partial t} = [\varphi D_{pf} + (1 - \varphi)K_{mf} D_{ps}] \left( \frac{\partial^2 c_p}{\partial R^2} + \frac{2}{R} \frac{\partial c_p}{\partial R} \right) \quad (45)$$

Equation (45) is identical in form to Eq. (29) except that it includes a term for up-take of solute in pore liquid by SOM:



$$\frac{\partial N}{\partial t} = f_{\text{om}} \frac{\partial \bar{c}_{\text{om}}}{\partial t} = \frac{3f_{\text{om}}}{r_{\text{om}}} D_{\text{om}} \left( \frac{\partial c_{\text{om}}}{\partial r} \right)_{r=r_{\text{om}}} \quad (46)$$

where  $f_{\text{om}}$  is the fraction of organic matter and  $\bar{c}_{\text{om}}$  is the average sorbed concentration in SOM. The solution to Eqs. (45) and (46) for typical initial and boundary conditions was found by applying the method of Laplace transforms. The Laplace transform and the numerical techniques for inverting it are described in the original papers by Yiacoymi and coworkers cited previously. The solution was then used to provide aqueous solute concentration as a function of time in batch experiments and aqueous solute concentration as a function of both time and position in columns.

On the basis of calculations, Yiacoymi and Tien (1994) examined the influence of pore diffusion resistance vs intraorganic matter diffusion resistance. The ratio of diffusion timescales  $\alpha$  in pores vs OM is

$$\alpha = \frac{D_{\text{om}}/r_{\text{om}}^2}{(D_p/\varphi)/R_a^2} \quad (47)$$

In batch systems (see Fig. 13, top), they found that  $\tau$ , the dimensionless time for equilibrium, increased as intraorganic matter resistance increased in importance (i.e., as  $\alpha$  decreased). In column experiments (Fig. 13, bottom), the breakthrough curves became more spread out (less like piston flow) as the intraorganic matter resistance increased in importance. The mentioned effects were more pronounced at low  $f_{\text{om}}K_{\text{om}}$  (i.e., at low SOM concentrations or for compounds with low affinity for SOM). They also applied their model to data existing in the literature on short-term sorption desorption studies. When the model was applied to the data of Nkedi-Kizza *et al.* (1989) on transport of atrazine and diuron in columns of Eustis soil, Yiacoymi and Tien concluded that diffusion resistance in SOM rather than the pore system was rate controlling. When applied to batch desorption of tetrachlorobenzene from Charles River and North River sediments by Wu and Gschwend (1986), the results were inconclusive in this respect.

## 5. Mixtures of Particle Sizes

Particle size distributions in soil span many orders of magnitude. For a distribution of sphere sizes whose probability density function is  $\delta(a)$ , where  $a$  is  $R_a$  or  $r_{\mu}$ , the average concentration is obtained by mass balance as

$$\left( \frac{M_t}{M_{\infty}} \right)_{\text{mix}} = \left( \frac{q - q_0}{q_{\infty} - q_0} \right)_{\text{mix}} = \frac{\int_0^{\infty} \delta(a) \left[ \frac{M_t}{M_{\infty}} \right] (a) a^3 da}{\int_0^{\infty} \delta(a) a^3 da} \quad (48)$$

where the quantity  $[M_t/M_\infty](a)$  is the functional expression for the fractional mass of chemical taken up or released for each discrete particle size  $a$ . For narrow particle size fractions, Eq. (48) may be approximated as

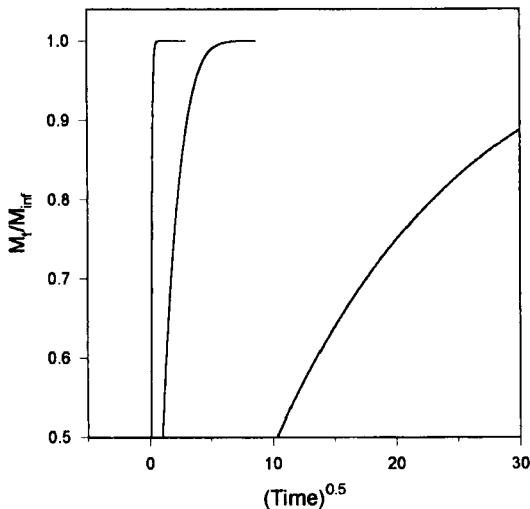
$$\left(\frac{M_t}{M_\infty}\right)_{\text{mix}} = 1 - \sum_i X_i \sum_{n=1}^{\infty} \left[\frac{M_t}{M_\infty}\right](a) \quad (49)$$

where  $X_i$  is the mass fraction of particles having geometric average radius  $a = \bar{R}_{ai}$  or  $\bar{r}_{\mu,i}$ . If experiments are done on pooled size fractions, the Sauter mean radius is recommended (Ball and Roberts, 1991b; Pedit and Miller, 1995):

$$a_s = \left[ \frac{\sum_{i=1}^n F_i}{\sum_{i=1}^n \frac{F_i}{a_i}} \right]^{-1} \quad (50)$$

where  $F_i$  and  $a_i$  are the mass fraction and geometric mean radius of each of the  $n$  subfractions pooled.

Particle size can have an enormous effect on the diffusion curves (Fig. 14). The approach to equilibrium in a finite bath at fixed  $D$  is shown for uniform particles whose radii span a range of 100 arbitrary units. The small, medium, and large particles reach 95% equilibrium at approximately 0.14, 14, and 1400 units of time,



**Figure 14** Effect of spherical particle radius on uptake or release of a solute in a mixed finite bath.  $M_t/M_{\text{inf}}$  is mass of solute taken up or released divided by mass taken up or released at equilibrium. Radius (left to right): 1, 10, and 100 and time are in arbitrary units. Equations in Chapter 6 of Crank (1975) were used. Final mass taken up was 50% of total present.

respectively. Multiple-particle class models better represented long-term sorption rates than did single-particle class models (Pedit and Miller, 1995). Some researchers have used a two-compartment model, with one instantaneous and the other diffusion limited (Ball and Roberts, 1991b; Lorden *et al.*, 1998; Pignatello *et al.*, 1993) (see Section V,C,2,c); in this case, the instantaneous compartment may partially account for the smaller particles if the nominal particle radius is indeed the appropriate length scale for diffusion.

## D. STOCHASTIC MODELS

Researchers are well aware of the high degree of spatial variability of soils and the difficulty of applying models designed for homogeneous systems. Several investigators have therefore attempted to model sorption kinetics stochastically. In such models it is assumed that sorption rate can be described with an array of first-order rate constants  $k$  that are continuously distributed according to a probability density function (PDF).

A useful PDF is the *gamma function* (Chen and Wagenet, 1995; Connaughton *et al.*, 1993; Gustafson and Holden, 1990; Pedit and Miller, 1994, 1995), which expresses the frequency distribution of  $k$  as

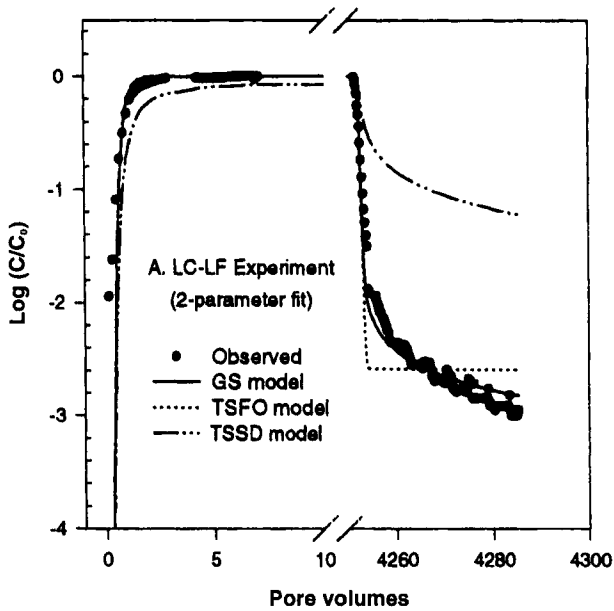
$$f(k) = \frac{\beta^\alpha k^{\alpha-1} e^{-\beta k}}{\Gamma(\alpha)} ; \quad \Gamma(\alpha) = \int_0^\infty x^{\alpha-1} e^{-x} dx \quad (51)$$

where  $\alpha$  and  $\beta$  are the shape and scale parameters, respectively, of the PDF curve, and  $\Gamma(\alpha)$  is a mathematical statistical function. The mean of  $k$  is  $\alpha\beta^{-1}$  and the variance of  $k$  is  $\alpha^{1/2}\beta^{-1}$ . The shape of the PDF ranges from Gaussian at  $\alpha \geq \sim 10$  to positively skewed (i.e., high frequency of small  $k$  values) at  $\alpha \leq \sim 1$ . The fraction of initial mass remaining after time  $t$  in any compartment having rate constant  $k$  is simply  $e^{-kt}$ . Thus, the mass remaining after  $t$  for all compartments is

$$\frac{M_t}{M_i} = \int_0^\infty f(k) e^{-kt} dt = \left( \frac{\beta}{\beta + t} \right)^\alpha \quad (52)$$

The values of  $\alpha$  and  $\beta$  are obtained by regression. The time  $t_{1-y}$ , necessary for the concentration to reach the fraction  $y$  of the initial concentration is  $t_{1-y} = \beta[y^{-1/\alpha} - 1]$ .

The gamma model has been applied to sorption/desorption of naphthalene in a freshly equilibrated soil and a field soil long contaminated with coal tar (Connaughton *et al.*, 1993), spiked lindane in a soil (Pedit and Miller, 1994), diuron in an aquifer sand (Pedit and Miller, 1995), and TCE during transport of its vapors in an aquifer soil column (Lorden *et al.*, 1998). Interestingly, Gustafson and Holden



**Figure 15** TCE vapor elution curves from an aquifer sand at 90% relative humidity and under “low concentration, low flow” (LC-LF) conditions (Lorden *et al.*, 1998) showing the superiority of the gamma stochastic model (GS) over the two-site first-order (TSFO) model and the two-site spherical diffusion (TSSD) model. The latter two assumed one of the sites to be instantaneous with a sorption distribution coefficient  $K_D$  determined experimentally; when  $K_D$  was included as a third fitting parameter, both TSFO and TSSD fit better but still not as good as the GS model. (Reprinted with permission from Lorden *et al.*, 1998. Copyright 1998 American Chemical Society.)

(1990) successfully applied the gamma PDF to field and laboratory “dissipation” data of 45 different pesticide–soil systems, where dissipation means all fate processes including sorption.

Pedit and Miller (1994, 1995) investigated a *log-normal PDF*, which is given by

$$f(k) = \frac{1}{(2\pi)^{1/2} \sigma k} \exp\left[-\frac{1}{2} \left(\frac{\ln k - \mu}{\sigma}\right)^2\right] \quad (53)$$

where the arithmetic mean of  $k$  is  $\bar{k} = \exp(\mu + \sigma^2/2)$  and the variance of  $k$  is  $V = \bar{k}^2 \exp(\sigma^2 - 1)$ . The log-normal PDF simulated lindane uptake by soil more accurately than did the gamma PDF.

Not surprisingly, stochastic models often outperform other models, given the same number of adjustable parameters. They outperform the single-site first-order model (Pedit and Miller, 1994), the two-site first-order model (Connaughton *et al.*,

1993; Lorden *et al.*, 1998), and the two-site diffusion model (one instantaneous and one diffusion controlled) (Lorden *et al.*, 1998; Pedit and Miller, 1994). Figure 15 shows the superiority of the gamma model in describing the tailing of TCE elution curves observed by Lorden *et al.* (1998).

The value of a stochastic approach depends on if and how well it can predict behavior under different conditions or different soil–chemical systems than the one in which the model parameters were obtained. Lorden *et al.* (1998) demonstrated predictive capability of the gamma function for elution of TCE vapors at different flow rates and TCE pressures. The ability of stochastic models to translate to different soil–chemical systems has not been established, however. Also, these models do not offer much mechanistic insight.

## V. EXPERIMENTAL METHODS

In a review such as this, it is worth discussing the methodology used in sorption/desorption rate studies. The sorption time frame may be *transient* or *steady state*. In the transient time frame one observes a changing concentration gradient, whereas in the steady-state time frame one establishes a stable concentration gradient and measures the mass of chemical entering or leaving the system. The transient time frame is the one most often used for soils.

Popular techniques for measuring transient processes include *batch*, *column*, *zero-length column* (ZLC), and *stirred-flow cell* (SFC). Batch techniques measure phenomena on the intraparticle scale since the external surfaces are exposed to a mixed fluid of uniform concentration. Column techniques measure phenomena on intra- and interparticle scales concurrently. The column's effluent concentration profile depends on both dispersion (longitudinal mixing) and sorption/desorption processes. Column techniques avoid abrasion of particles and can be more realistic. ZLC and SFC are hybrid techniques that attempt to combine the advantages of each.

### A. BATCH TECHNIQUES

In solution–solid systems, agitation (stirring or shaking) is usually required to achieve uniform conditions, whereas in vapor–solid systems bulk gas diffusion is rapid enough to maintain uniformity at all but the fastest uptake rates, provided the sorbent bed is sufficiently thin. Sorption may be carried out under *infinite* or *finite* source conditions, which require different approaches. Under infinite source conditions, the fluid-phase concentration is not reduced by sorption and uptake has to be measured by analysis of the solid. This approach is commonly used in vapor–

solid studies in which uptake is followed gravimetrically. When the source is finite, the bulk fluid-phase concentration changes, providing a convenient way to follow uptake, assuming no chemical transformations occur.

### 1. Measurement Techniques

Batch solution–solid experiments are commonly performed by mixing the components in sealed flasks and, at predetermined times, measuring solution concentration after first separating the phases. In estimating  $K_p$ , the optimal degree of sorption is about 55% (McDonald and Evangelou, 1997); the same degree of final sorption would apply to an uptake kinetic experiment if the objective is to quantify changes in  $K_p$  with time. Although this methodology appears simple to manage, the researcher must be aware of the following potential complications:

1. “Bottle losses”: Adsorption on glass walls can be important if it is more than a few percent of sorption to the soil. It is seldom an issue except for highly hydrophobic compounds and may be corrected by running controls. Diffusion through polymer materials is greater for small molecules and occurs regardless of whether the chemical comes into contact with the material via the solution or vapor phase (the chemical potentials in the two phases are equal). Little or no loss through Teflon cap liners was reported for lindane during 84 days (Miller and Pedit, 1992) or for phenanthrene over several weeks (White *et al.*, 1999). Polymer vessels and soft polymer stoppers or cap liners (e.g., “butyl” rubber or “phenolic”) should be avoided. Polymer materials can be avoided altogether by using flame-sealed glass ampules (Ball and Roberts, 1991a) or screw-cap vials with foil stretched tightly over the lip of the vial before the cap with its liner is screwed on (Huang *et al.*, 1997; Xia and Ball, 1999). Piercing the septum liner with a needle to remove sample will expose hydrophobic septum material (usually silicone rubber) to the flask contents, resulting in noticeable extraction even within hours; thus, most researchers use the “bottle point” method in which replicates are sacrificed at time points.

2. Phase distribution artifacts, such as headspace partitioning of volatile compounds and sorption to colloidal particles not removed by centrifugation or filtration: The former can be assessed by considering Henry’s law. The latter is potentially significant for highly hydrophobic compounds ( $\log K_{ow} > \sim 4$ ) or compounds that otherwise interact strongly with colloids (Schwarzenbach *et al.*, 1993). Assay of the liquid phase may not distinguish between colloid-bound and truly dissolved fractions. Moreover, one cannot assume the concentration of nonsettling colloids will remain constant throughout an experiment. The problem of sorption to colloids can be avoided by retaining the soil in dialysis tubing (Allen-King *et al.*, 1995), provided a correction can be made for sorption to the tubing.

3. Artifacts caused by agitation: Shear forces generated by vigorous agitation may change the particle size distribution and expose additional surface area, thus

affecting rates. Stir bars grind particles (Wu and Gschwend, 1986). The minimum degree of agitation necessary to achieve rapid mixing on the timescale of sorption is recommended; slow end-over-end tumbling seems to be the best technique.

4. Method of analyte introduction: Strongly sorbing compounds tend to sorb to the first surfaces encountered and may not readily redistribute to other particles; therefore, attention must be paid to the way in which initial contact between particle and chemical is achieved. Homogeneous particle coverage requires fast dispersion of particles into a large volume of a solution. When spiking bulk soils in preparation for desorption studies the method of Karickhoff *et al.* (1979) is recommended: First, the compound is deposited on the walls of the flask by evaporating a solution in a volatile carrier (e.g.,  $\text{CH}_2\text{Cl}_2$ ) and then the soil suspension is added, followed by agitating for 24–48 h.

5. Biodegradation: Sterilization may be accomplished by heat, irradiation, or chemical treatment. Wolf *et al.* (1989) compared sterilization techniques based on plate counts of bacteria and fungi. The following were completely effective on three soils: double or triple autoclaving, propylene oxide (48-h exposure),  $^{60}\text{Co}$   $\gamma$ -irradiation (0.05 MGy), and  $\text{HgCl}_2$  (500  $\mu\text{g/g}$ ). The remaining treatments were less effective and followed the order: once-autoclaving > oven-drying  $\gg$   $\text{NaN}_3 \sim \text{CHCl}_3 \sim$  microwave treatment > control  $\sim$  antibiotics. Autoclaving is generally avoided because of concerns it can affect soil chemistry, particularly SOM structure. Propylene oxide may react chemically with SOM, potentially affecting sorption of the compound of interest. [The same holds for formaldehyde, which was not tested by Wolf *et al.* (1989) but is widely known to be effective.]  $^{60}\text{Co}$   $\gamma$ -irradiation equipment is not widely available. Mercuric chloride had the least effect of all treatments on soil CEC, pH, and extractable metal ions. Xing *et al.* (1996) showed that  $\text{HgCl}_2$  had no effect on the 48-h Freundlich sorption parameters of metolachlor. Mercury presents a disposal problem, however. Sodium azide ( $\text{NaN}_3$ ) is a popular bacteriostat that binds to cytochromes, inhibiting terminal electron transport. However, its efficacy cannot be taken for granted since it may not inhibit enzymatic transformations that require little energy, and because bioactivity may be revived if dilution of the  $\text{NaN}_3$  occurs in subsequent steps [e.g., as it did in the protocol of Wolf *et al.* (1989)].

To separate the solid and liquid phases, centrifugation is not suitable for sampling frequencies more often than about one per 10 minutes. Filtration through a microporous filter (e.g., 0.2  $\mu\text{m}$ ) can increase sampling frequency to perhaps one per minute. Filtration has been employed in experiments at temperatures other than ambient in order to minimize temperature effects during sample handling (Xing and Pignatello, 1997). Wu and Gschwend (1986) used an air-stripping apparatus which constantly recirculated air through the soil suspension and then through a detector. This technique, which is suitable for sorption occurring over a few seconds to 48 h, avoids the colloid problem because activities are measured in the gas phase and related to solution-phase concentration via Henry's law. Similar appa-

ratures are described by Brusseau *et al.* (1990) and Benzing *et al.* (1996). For semi-volatile compounds Karickhoff and Morris (1985) designed a gas purge cell in which air was passed through glass frits in contact with the suspension and the vapors were collected in external traps containing Tenax, a polymeric hydrophobic resin. Harmon and Roberts (1994) describe a purge apparatus that fits around a glass ampule after the flame-sealed top is broken off. The apparatus of Benzing *et al.* (1996) can operate in both recirculate and purge modes.

A popular way to monitor desorption is by use of the *successive-dilution* technique, in which a known volume of the supernatant is replaced with "clean" water. The mathematical model that one uses needs to take into account the stepped boundary conditions that this technique entails.

Pignatello and coworkers (Pignatello, 1990a,b; White *et al.*, 1999) and Cornelison *et al.* (1997a,b, 1998a) used an *in situ trap* of Tenax polymeric adsorbent beads. Tenax has a high affinity for nonpolar compounds, even  $C_1$  and  $C_2$  halogenated hydrocarbons (Pignatello, 1990b). The beads are readily separated from the soil after centrifugation because they float. Soil particles have little tendency to adhere to the beads and are easily rinsed off. Carroll *et al.* (1994) used XAD-4 resin as an *in situ trap*; however,  $K_2CO_3$  had to be added prior to sampling to increase the solution density in order to make the beads float.

The purge gas or *in situ* polymer trap rapidly lowers the solution concentration to near zero. Hence, diffusion kinetics can be modeled using equations that describe "diffusion with surface evaporation" (Crank, 1975). These equations take forms that depend on the extent of diffusion and the sorbent shape. If the particle is a sphere of radius  $R_a$  and initially at uniform concentration, the surface boundary condition uses the linear driving force assumption

$$-D \frac{\partial c}{\partial R} = \alpha_{if}(c_s - c_o) \quad (54)$$

where  $c_s$  is the concentration just within the sphere,  $c_o$  is the concentration required to maintain equilibrium with the solution, and  $\alpha_{if}$  is the interfacial mass transfer coefficient [ $L T^{-1}$ ]. Provided that enough time has passed so that the rate of purging from the solution is equal to the rate of desorption, the governing equation for the fractional amount of substance leaving the particle at any time is

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 \exp(-\beta_n^2 Dt/a^2)}{\beta_n^2 \{\beta_n^2 + L(L-1)\}}, \quad (55a)$$

where  $L = \alpha a/D$  and the  $\beta_n$  values are the roots of

$$\beta_n \cot \beta_n + L - 1 = 0. \quad (55b)$$



In their studies of tetrachloroethane (PCE) desorption from aquifer sediments, Harmon and Roberts (1994) purged the suspension only intermittently during desorption; therefore, they used a model combining boundary conditions for diffusion with surface evaporation and diffusion to a solution of finite volume.

O'Dell *et al.* (1992) describe a *static batch reactor* in which nearly saturated soil containing a herbicide (imazethapyr) was placed in syringe barrels. At predetermined times the soil solution was displaced with saturated  $\text{CaSO}_4$  when the syringe was placed under vacuum. By including a tracer in the  $\text{CaSO}_4$ , they verified that the recovered soil solution was uncontaminated with the displacing solution.

Direct analysis of the solid is sometimes carried out. Sorbed concentration is conveniently measured by solvent extraction after correcting for solute in the water removed along with the solid. However, resistant sorbed fractions may not be completely recovered unless extraction is fairly vigorous. Sawhney *et al.* (1988), Pignatello (1990a), and Huang and Pignatello (1990) found that complete solvent extraction of even weakly sorbing compounds required several hours at 75°C. Similarly, Ball *et al.* (1997) found that a 16-h methanol extraction at 70°C was required to remove volatile organic contaminants in field aquifer sediments. A water-miscible solvent (e.g., acetone, methanol, or acetonitrile) will more effectively penetrate SOM and intraparticle pores than an immiscible solvent. Harmon and Roberts (1994) found that extraction of [ $^{14}\text{C}$ ]PCE from aquifer sediments by non-miscible scintillation cocktail required tens of days.

Tognotti *et al.* (1991) describe a *single-particle* technique in which the particle is suspended in a vapor-laden gas stream within an electrodynamic thermogravimetric analyzer (EDTGA). Uptake or release of toluene or carbon tetrachloride was measured by the voltage required to keep the particle stationary in the EDTGA as a function of time. To determine the effect of temperature, a  $\text{CO}_2$  laser was used to heat the particle.

## B. COLUMN TECHNIQUES

### 1. General Considerations

Glass columns with perforated Teflon end plates and Teflon adjustable plunger are commercially available. Stainless-steel preparatory-scale liquid chromatography columns have also been widely used. Column packing techniques apparently have not undergone systematic investigation. Typically, columns are packed by layering dry material a little at a time in an attempt to create a uniform bed. The investigator should be aware, however, that dry soil has a tendency to segregate by particle size, making it difficult to scoop up a representative sample from the container from which the soil is taken. Moistening the soil (e.g., to 5 or 10% wa-

ter by weight), if appropriate for the experiment, helps alleviate this problem. Pignatello *et al.* (1993) filled the column with air-dry soil, allowing about one-fourth of the volume to be free of soil; the soil was then homogenized by manually rocking and rotating the column axially for several minutes. After packing, the column is then slowly saturated from the bottom with eluent. Most investigators use dilute (e.g., 0.01 *M*)  $\text{CaCl}_2$  as the eluent to help prevent dispersion of clays and mobilization of colloids. The column is often "conditioned" by passing through many pore volumes of eluent prior to injecting the solute solution.

Eluent is pumped through the column with a constant-volume displacement pump such as the kind used in liquid chromatographic systems. A three-way valve is installed before the column to allow switching between reservoirs containing eluent with or without solute. The effluent may be collected with a fraction collector for later analysis or passed through a UV-visible, scintillation counter, fluorescence, or other type of flowthrough detector. For vapor-elution studies, Lorden *et al.* (1998) describe an apparatus that diverts flow to a gas chromatograph through a programmable automatic switching valve.

Injection of the solute may occur according to a step function or a pulse function. For a step function, the concentration of solute is increased abruptly from an initial value (usually zero) to a second value, and the solute "breakthrough curve" at the terminus is observed until the concentration reaches the stepped value. Desorption may be observed at some later time by switching the inflow to clean eluent. For pulse injection, the solute is introduced over a finite period and the effluent concentration is monitored at the terminus.

Many reviews are available that discuss contaminant transport in soil columns (Brusseu and Rao, 1989; Parker and van Genuchten, 1984; van Genuchten and Wagenet, 1989). Solute transport when no decomposition occurs is described by the advection–dispersion (A–D) equation with sorption:

$$\theta \frac{\partial C}{\partial t} + \beta \frac{\partial q}{\partial t} = \theta D_h \frac{\partial^2 C}{\partial x^2} - \theta v \frac{\partial C}{\partial x} \quad (56)$$

where  $\theta$  is bulk porosity [ $\text{L}^3 \text{L}^{-3}$ ],  $\beta$  is bulk solids density [ $\text{M}^3 \text{L}^{-3}$ ],  $D_h$  is the hydrodynamic dispersion coefficient [ $\text{L}^2 \text{T}^{-1}$ ],  $v$  is the linear average flow velocity [ $\text{L} \text{T}^{-1}$ ], and  $x$  is longitudinal distance [ $\text{T}^{-1}$ ]. The term of focus,  $\partial q/\partial t$ , represents the rate of change in average sorbed concentration as seen by the flow regime.

In addition to the complicating effects of dispersion, another limitation of column studies is that the degree of sorption that occurs depends on the residency time of the solute in the column and hence the flow rate. That is, slow sorption states may not be fully accessed by solute molecules in a fast-moving fluid. For example, Brusseu (1992), using the two-site model, showed more than an order of magnitude decrease in the sorption rate parameter for several compounds with a decrease in flow rate from  $\sim 45\text{--}90$  to  $\sim 5$  cm/h (13 to 0.7 pore volumes per hour).

Likewise, Lorden *et al.* (1998) showed a decrease in the characteristic time for sorption of TCE vapors with increasing flow rate. It is difficult to achieve flow rates of less than one pore volume per day; however, batch studies show that a substantial fraction of sorption may require weeks or months to complete. Obviously, in the above-cited studies the equilibrium and kinetic fractions of the two-site formalization are accommodating to a shift in timescale of elution.

One must also be aware that significant amounts of injected chemical may reach slow sites but not desorb on the timescale of the experiment. For all practical purposes, such amounts are "irreversibly" sorbed and thus missed by the model. For example, Spurlock *et al.* (1995) carried out delayed elution experiments with monuron and fenuron, relatively polar compounds with high water solubilities, in a soil (3.4% OC). They found that the elution curves were affected little by the length of the prior contact period (8, 80, or 240 days). However, appreciable amounts (10–30%) remained sorbed after the effluent concentration declined to  $C/C_o < 0.01$ . This residual sorbed herbicide increased with contact time, became increasingly greater than predicted on the basis of the equilibrium law, and was uniform along the length of the column.

## 2. Transport Models with Sorption Kinetic Term

### a. Two-Region Model

In this model (van Genuchten and Wierenga, 1976, 1977; van Genuchten *et al.*, 1977), the pore space is divided into mobile water (*m*) and immobile water (*im*) regions, with advection and dispersion occurring only in the mobile region. The A–D equation is thus

$$\theta_m \frac{\partial C_m}{\partial t} + \beta f \frac{\partial S_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + \beta(1-f) \frac{\partial S_{im}}{\partial t} = \theta_m D_h \frac{\partial^2 C_m}{\partial x^2} - \theta_m v \frac{\partial C_m}{\partial x} \quad (57)$$

where *f* is the fraction of sorption occurring in the mobile region. Suppose sorption is locally instantaneous and obeys the Freundlich equation  $S_m = fK_c C_m^n$  and  $S_{im} = (1-f)K_c C_{im}^n$ . Upon differentiating  $S_m$  and  $S_{im}$  with respect to *t* and substituting into Eq. (57), one obtains

$$\left(\theta_m + \beta f n K_c C_m^{n-1}\right) \frac{\partial C_m}{\partial t} + \left(\theta_{im} + \beta(1-f) n K_c C_{im}^{n-1}\right) \frac{\partial C_{im}}{\partial t} = \quad (58)$$

The relationship between  $C_m$  and  $C_{im}$  is established by assuming that the driving force for mass transfer between the regions is simply proportional to the difference in their respective liquid-phase concentrations; thus,

$$(\theta_{im} + \beta(1-f)K_e n C_{im}^{n-1}) \frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}) \quad (59)$$

where  $\alpha$  is a mass transfer coefficient. An analytical solution to Eqs. (58) and (59) for the linear sorption case is available (van Genuchten and Wierenga, 1976). For the nonlinear case the solution must be obtained numerically. If  $K_e$  is known, the fitting parameters are  $\alpha$ ,  $f$ , and  $\theta_{im}$ . A reasonable assumption is that  $f$  and  $\theta_{im}$  are equal (Nkedi-Kizza *et al.*, 1984) or  $\theta_{im}$  may be obtained by fitting the model to the elution curve of a nonsorbing tracer (Spurlock *et al.*, 1995).

#### b. First-Order Models

A widely used model is the *two-site* (equilibrium and kinetic) one, described in Section IV,A (Eqs. 11–15) (Cameron and Klute, 1977; Nkedi-Kizza *et al.*, 1984; van Genuchten and Wagenet, 1989). The appropriate expression for  $\partial q/\partial t$  is Eq. (16). The A–D equation becomes

$$\left(1 + \frac{\beta}{\theta} f n K_e C^{n-1}\right) \frac{\partial C}{\partial t} + \frac{\beta}{\theta} \alpha (f K_e C^n - (1-f)q) = D_h \frac{\partial^2 C}{\partial x^2} - \quad (60)$$

Ordinarily,  $K_e$  is determined in separate batch experiments or calculated by moments analysis (Valocchi, 1985), and  $D_h$  is determined by eluting a nonsorbing tracer, such as  $^3\text{H}_2\text{O}$ . Thus, Eq. (60) has two fitting parameters,  $k_{-2}$  and  $f$ . An analytical solution is available for the linear case only (van Genuchten and Wagenet, 1989).

#### c. Diffusion Models

Diffusion concepts have been used directly or in conjunction with other models. Pignatello *et al.* (1993) and Lorden *et al.* (1998) used a two-compartment model having a rapid equilibrium compartment ( $S_1, f$ ) and a second slow compartment ( $S_D, 1-f$ ) governed by radial diffusion so that  $q = S_1 + S_D$ :



The model regards the diffusion domain as being a collection of idealized equal spheres (radius,  $a$ ) in which diffusion obeys a Fickian diffusion law Eq. (62a) (analogous to Eq. 26) with boundary conditions as given in Eq. (62b):

$$\frac{\partial s}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial s}{\partial r} \right) \quad (62a)$$

$$\left. \frac{\partial s(r)}{\partial r} \right|_{r=0} = 0 \quad \text{and} \quad s(r = a, t) = (1-f)K_e C \quad (62b)$$

The volume-averaged sorbed concentration in the diffusion domain is given by

$$\bar{S}_D = \frac{3}{\delta a^3} \int_0^a s(r,t) r^2 dr \quad (63)$$

where  $\delta$  is the particle density ( $\text{g}/\text{cm}^3$ ). Curve fitting requires numerical techniques.

A two-region diffusion concept was proposed by Nkedi-Kizza *et al.* (1982) for inorganic solutes and later used by Young and Ball (1994) to simulate breakthrough of PCE in aquifer sediments. In this conceptualization, the “immobile zone” is the intraparticle porosity ( $\varphi$ ) and its associated sorption capacity, and the “mobile zone” is the interparticle porosity and its associated sorption capacity. The same two-region A–D equation (Eq. 57) applies, except that  $\theta_{im}$  is replaced by  $\varphi$ , and  $C_{im}$  is replaced by the volume-averaged concentration *inside* the particles  $\bar{C}_{im}$  (spherical,  $R_a$ ):

$$C_{im} = \frac{3}{R_a^3} \int_0^{R_a} C_{im}(R,t) R^2 dR \quad (64)$$

The term  $\partial \bar{C}_{im}(R,t)/\partial t$  is expressed in terms of intraparticle radial diffusion laws (Eq. 30;  $c_p = \bar{C}_{im}$ ) and the series of equations solved numerically. This model assumes that particles are uniform in size, porosity, and chemistry; that  $K_e$  is the same in the mobile and immobile regions; and that  $C_m = c_{im}$  at the particle/mobile–water interface. The  $\varphi$  was determined (Ball *et al.*, 1990) by mercury porosimetry which measures intraparticle porosity down to pore widths on the order of  $\sim 10$  nm (mesopore to macropore range).

Piatt and Brusseau (1998) analyzed elution curves using the two-site model and then related the  $S_2$  site first-order desorption rate constant  $k_{-2}$  (see Section IV,A, Eq. 11) to an organic matter diffusivity  $D_{om}$ , a particle shape factor  $\eta$ , and a diffusion length scale,  $l$ :

$$k_{-2} = \eta D_{om} / l^2 (1 - f). \quad (65)$$

A solution for solute transport through a bed of uniform porous pellets for a step function change in solute concentration in the influent is provided by Yiacoymi and Rao (1996) and Yiacoymi and Tien (1994). Diffusion occurs within the pellet pore system and SOM microparticles contained therein, as described in Section IV,C,5. The solute uptake per pellet is given by

$$M = \int_0^t 4\pi R_a^2 D_p \left( \frac{\partial c_p}{\partial R} \right)_{R_a} dt \quad (66)$$

where the  $(\partial c_p / \partial R)_{R_a}$  term is from Eq. (45). Upon considering solute uptake on a per-gram sorbent basis, the rate of sorption is given by

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial t} \left[ \frac{1-\theta}{\delta \frac{4}{3} \pi R_a^3} M \right] = \frac{\partial}{\partial t} \left\{ \frac{3(1-\theta)}{\delta} \frac{D_p}{R_a} \int_0^t \left( \frac{\partial c_p}{\partial R} \right)_{R_a} dt \right\} \quad (67)$$

where  $\delta$  is the particle density ( $\text{g/cm}^{-3}$ ). Equation (67) is then substituted into the A–D equation (Eq. 56). The combined equations were solved by Yiacoymi *et al.* by the method of Laplace transforms. This gives a complex expression (not reproduced here) relating the observed bulk solute concentration in the Laplace domain  $\bar{C}$  as a function of the following: initial bulk solute concentration  $C_o$  (if other than zero), the input concentration  $C_{in}$ , diffusivities ( $D_{pf}$ ,  $D_{ps}$ , and  $D_{om}$ ), partition coefficients ( $K_{mf}$  and  $K_{om}$ ), pellet and SOM microparticle radii ( $R_a$  and  $r_{om}$ ), bulk moduli ( $\varphi$ ,  $\theta$ , and  $\delta$ ), flow velocity ( $v$ ), dispersion coefficient ( $D_h$ ), and distance along the column. Inversion of the Laplace transform was performed by a Fourier series approximation algorithm (Yiacoymi and Tien, 1992).

### C. STIRRED-FLOW CELL TECHNIQUE

The SFC is known in engineering as a “continuous-flow stirred tank reactor.” Eluent is passed through a chamber of volume  $V_R$  [ $\text{L}^3$ ] containing a well-mixed suspension of soil and out to a fraction collector, adsorbent cartridge, or flow-through detector (Deitsch and Smith, 1995; Eick *et al.*, 1990; Miller *et al.*, 1989; Seyfried *et al.*, 1989; Sparks, 1989; Zhang and Sparks, 1993). Frits are positioned at either end of the cell to hold in particles. As a hybrid of batch and column techniques, the SFC eliminates hydrodynamic dispersion but has the sampling advantages of a column. The method is capable of measuring sorption or desorption with “half-lives” as short as  $\sim 1$  min or desorption with characteristic times of a few tens of hours.

Uptake rates are measured by pumping influent of solute concentration  $C_{in}$  [ $\text{M L}^{-3}$ ] at flow rate  $u$  [ $\text{L}^3 \text{T}^{-1}$ ] through the suspension and measuring the effluent concentration  $C_{eff}$  [ $\text{M L}^{-3}$ ]. Release rates are measured likewise by pumping clean liquid through the suspension of known initial sorbed and aqueous concentrations,  $q_0$  [ $\text{M M}^{-1}$ ] and  $C_0$  [ $\text{M L}^{-3}$ ]. Provided adequate mixing occurs in the cell, the mass balance equation is

$$\beta \frac{\partial q}{\partial t} + \theta \frac{\partial C}{\partial t} = \frac{u}{V_R} (C_{in} - C_{eff}) \quad (68)$$

where  $q$  and  $C$  represent the instantaneous sorbed and aqueous concentrations in the cell,  $\beta$  is the bulk solids density [ $\text{M L}^{-3}$ ], and  $\theta$  is the volumetric liquid content [ $\text{L}^3 \text{L}^{-3}$ ]. Under well-mixed conditions  $C = C_{eff}$ . The  $C_{eff}$  is made up of a component  $c_s$

representing uptake or release from the sorbent plus a component  $C^*$  representing the liquid phase of the chamber that would be observed in the case of no sorption:

$$C_{\text{eff}} = c_s + C^* \quad (69)$$

$$C^* = (C_0 - C_{\text{in}}) \exp\left(\frac{-ut}{\theta V_R}\right) + C_{\text{in}} \quad (70)$$

The value of  $C^*$  is obtained by solving Eq. (68) for the case of no sorption. Verification of Eq. (70), which signifies thorough mixing conditions in the cell, can be performed using a nonsorbing solute such as  $^3\text{H}_2\text{O}$ . After subtracting  $C^*$  from  $C_{\text{eff}}$  (it can be seen that  $C^*$  approaches a constant value at long times), Eq. (68) in terms of  $c_s$  becomes

$$\frac{\partial q}{\partial t} = -c_s \frac{u}{V_R} - \frac{\theta}{\beta} \frac{\partial c_s}{\partial t} \quad (71)$$

The first term on the right in Eq. (71) represents efflux from the chamber due to the sorption process, whereas the second represents solution-phase chemical inside the cell due to the sorption process.

If an in-line detector is used and concentrations are measured at intervals of  $\Delta t$ , then the finite difference approximation of Eq. (71), correct to terms of order  $\Delta t^2$ , is

$$\frac{\Delta q}{\Delta t} = -\frac{u(c^{j-1} + 2c^j + c^{j+1})}{4V_R} - \frac{\theta}{\beta} \frac{(c^{j+1} - c^{j-1})}{2\Delta t} \quad (72)$$

where the superscript  $j$  represents the  $j$ th measurement. If samples are collected, reactor efflux is known exactly from  $c^j$  and, therefore, the analogous approximation is

$$\frac{\Delta q}{\Delta t} = -\frac{uc^j}{4V_R} - \frac{\theta}{\beta} \frac{(c^{j+1} - c^{j-1})}{2\Delta t} \quad (73)$$

The cumulative sorbed concentration is given by

$$q = q_0 + \sum \Delta t (\Delta q / \Delta t). \quad (74)$$

For measurements with natural soils, the SCF technique suffers from many problems. It is not very well suited for long-term uptake experiments because the differences between  $C_{\text{in}}$  and  $C_{\text{eff}}$  quickly become too small. Some cells have built-in stirring mechanisms: Magnetic stir bars grind particles and propeller seals have a finite life because of continual abrasion from particles. Deitsch and Smith (1995)

simply placed the cell on a rotary shaker to effect mixing. There is always a trade-off between loss of particles from the cell and clogging of the frits. Small particles can be generated from large particles over time owing to particle-particle and particle-wall collisions.

#### D. ZERO-LENGTH COLUMNS

ZLCs (Eic and Ruthven, 1988; Ruthven and Eic, 1988) are columns that are short enough (or the flow rate is fast enough) that dispersion is insignificant and thus the response is sensitive only to sorption processes. The method is most suitable for desorption experiments. Basically, a short column of preequilibrated material is swept with a stream of gas or liquid at a rate fast enough to maintain "zero" concentration at the external particle surfaces, and desorbed chemical in the effluent is monitored with a sensitive detector or is trapped. This method is useful because it retains the advantages of columns in terms of relevance and ease of measurement while eliminating the effects of longitudinal dispersion. Its advantage over batch experiments is that it eliminates the need for agitation.

For a bed of spherical particles of radius  $a$  the total amount of diffusing substance leaving the column compared with the initial amount is given by Eq. (55) (see Section V,A,1) provided the ratio of the rate parameter for external mass transfer to the diffusivity is large. The observation that verifies this condition is that the rate of efflux from the column is independent of flow velocity. The derivative of Eq. (55) with respect to time is the desorption rate.

The ZLC technique has been employed in studies of TCE desorption from columns of soil and silica sorbents (Farrell and Reinhard, 1994b; Grathwohl and Reinhard, 1993).

### VI. SORPTION KINETICS AND BIOAVAILABILITY

#### A. ASSIMILATION OF CHEMICALS IN SOIL SYSTEMS

It is well-known that bioavailability of chemicals (uptake, toxic effect, etc.) is lower in a soil-water mixture compared to water alone. Bioavailability is reduced for both thermodynamic and kinetic reasons: thermodynamic because a fraction of the chemical is partitioned to the soil and is not available there; kinetic because desorption can be rate limiting to uptake by the organism from the fluid phase. Although the terms "available" and "sequestered" are often used in the literature in regard to fractions of a sorbed chemical in soil, realistically there is a continuum from instantly available to completely unavailable. Furthermore, the term se-

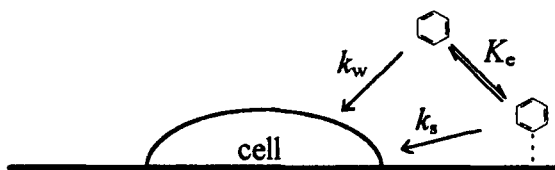


questered has meaning only in the context of a given receptor, chemical, soil environment, mode, and duration of uptake.

Clearly, large multicell organisms assimilate chemicals only through the fluid phase (liquid or vapor) and not directly from the particle surface or interior, although they may be able to indirectly affect the flux of chemical from the particle. For single-cell organisms the situation is less clear. Cells may attach to surfaces by molecular forces or via extracellular exudates. Whether attached cells are able to abstract sorbed organic molecules *directly from the surface* is inconclusive but the preponderance of evidence is in the negative, at least for soil particles (Crockner *et al.*, 1995; Shelton and Doherty, 1997). Experimental results are supported by logic: (i) Most sorption sites lie within SOM interstices, which are physically inaccessible to cells; (ii) most of the surface area of a particle is contained in mesopores and micropores (i.e., <50 nm), where even the smallest cells cannot fit; and (iii) if we assume rapid local equilibrium sorption at the solution–solid interface in the vicinity of the cell ( $K_e$ ), the chemical potential, and therefore the activity, of substrate is the same for dissolved and adsorbed forms. The following rate expressions apply,

$$\text{Rate of uptake from solution} = k_w a^* f_w \sigma \quad (75)$$

$$\text{Rate of uptake from surface} = k_s a^* (1 - f_w) \sigma \quad (76)$$



where  $k_w$  and  $k_s$  are the rate constants for uptake from water and surface,  $a^*$  is the activity of the chemical in solution or on the surface (in equivalent units), and  $f_w$  is the fraction of cell surface area,  $\sigma$ , exposed to the water. A surface abstraction mechanism can enhance bioavailability only if  $k_s(1 - f_w) > k_w f_w$ , which is doubtful because molecules on the surface are likely to be less mobile than molecules in solution.

An organism may affect the flux of chemical from soil particles *indirectly* in various ways. First, it can do so by steepening the concentration gradient across the particle–fluid interface as a result of uptake from the fluid. This will accelerate desorption and may explain why some bacteria seem able to access sequestered fractions (Guerin and Boyd, 1992; Schwartz and Scow, 1999). Second, it can do so by causing changes in soil properties through biological activity in ways that affect  $K_e$ . Such change may result through direct action on the particle or through

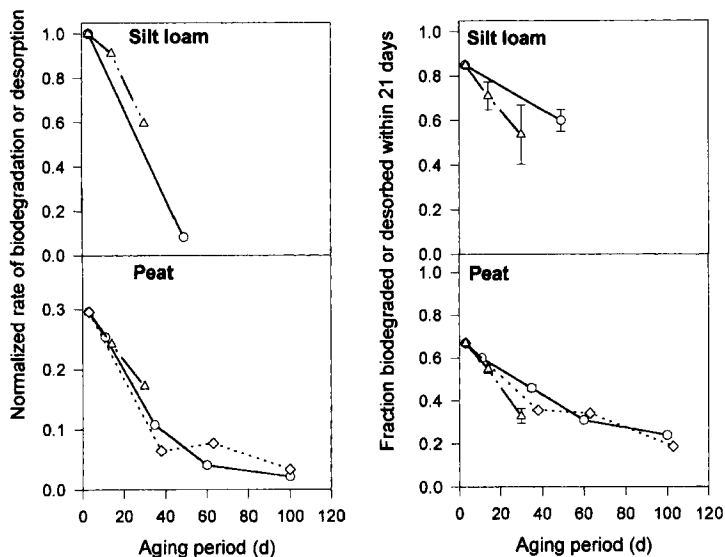
effects on the surrounding medium. For example, dermal contact may involve transfer of skin or hair oils to the particle that can facilitate uptake of hydrophobic chemicals. Ingestion may expose particles abruptly to biosurfactants and radically different pH regimes. Weston and Mayer (1998) found that stomach fluids increase bioavailability of PAHs in soil. Solution pH affects soil mineralogy and SOM structure; acidification of a soil to below pH  $\sim 2$  released sequestered fractions of halogenated hydrocarbons possibly by dissolving metal oxide cements (Pignatello, 1990b). Soil ingested by birds may be pulverized in the gizzard resulting in shorter diffusion path lengths. Grinding in a ball mill has been shown to release resistant fractions (Ball and Roberts, 1991b; Pignatello, 1990a; Steinberg *et al.*, 1987). Plant exudates may increase desorption by a surfactant effect or by a competitive sorption effect; natural aromatic acids that are produced by living and decomposing plants were shown to increase desorption of chlorinated aromatic hydrocarbons and phenols by competitive displacement (Xing and Pignatello, 1998). Recent studies show that competitive solutes increase sorption and desorption rates of the principal solute (J. White and J. Pignatello, submitted for publication).

## B. COUPLED SORPTION-BIODEGRADATION KINETIC MODELS

### 1. General Considerations

When biological uptake is relatively slow, or when the receptor moves rapidly through the contaminated medium, the solution concentration is not altered appreciably and bioavailability may be controlled simply by the existing solution concentration. The equilibrium partition model being considered by the U.S. Environmental Protection Agency for setting sediment quality criteria (Ankley *et al.*, 1996; Di Toro *et al.*, 1991) is based on the assumption that bioavailability, or biological effect, can be predicted knowing the equivalent pore water concentration. The pore water concentration is calculated from the total concentration present in the solids (determined by exhaustive extraction) and the  $K_{oc}$  determined experimentally or calculated from established  $K_{ow}$ - or solubility-based LFERs (Schwarzenbach *et al.*, 1993). Although the database of  $K_{oc}$  values and LFERs is extensive, the values are primarily based on short equilibration times ( $< 48$  h). Their relevance to aged-contaminated systems, therefore, is highly questionable. In many cases, the apparent  $K_{oc}$  in historically contaminated samples has been as much as two orders of magnitude greater than values obtained in freshly spiked samples (Pignatello and Xing, 1996). Ronday (1997) found that, although the toxicity of pesticides to the springtail (*Folsomia candida*) correlated well with the pore water concentration, the toxicity decreased over time and did not correlate well with short-term  $K_{oc}$  values.

When nonequilibrium conditions prevail during exposure it is necessary to consider mass transfer rate laws describing the flux of chemical through the par-



**Figure 16** The fraction or initial rate of phenanthrene desorbed (in the presence of Tenax infinite sink) or mineralized to  $\text{CO}_2$  by two bacteria. The coincidence indicates that phenanthrene metabolism is rate limited by desorption. The soils contained 1.4% OC (silt loam) and 44.5% OC (peat) (—○—) Desorption, (---△---) strain R biodeg, (---◇---) strain P5-2 biodeg. (Reprinted with permission from *Environmental Toxicology and Chemistry*, 1999. Correlation between the biological and physical availabilities of phenanthrene in soils and soil humin in aging experiments, by J. C. White, M. Hunter, K. Nam, J. J. Pignatello, and M. Alexander, **18**, 1720–1727. Copyright Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, FL, 1999.)

ticle, across the particle–bulk fluid interface, and across the fluid–biomembrane interface. An accurate bioavailability model will require linkage of uptake/deposition kinetics with sorption/desorption kinetics. Some coupled models will be discussed in this section. The discussion is restricted to the most widely researched systems—those involving degradation of chemicals by microorganisms. In the models we assume that the substrate is available only through the aqueous phase.

There are many studies showing that biodegradation is rate limited by desorption of the substrate (White *et al.*, 1999; Bosma *et al.*, 1997; Rijnaarts *et al.*, 1990). For example, Fig. 16 shows the results of experiments (White *et al.*, 1999) in which phenanthrene was allowed to “age” in contact with soil for various times before either adding bacterial degraders or carrying out desorption in the presence of the infinite sink, Tenax. Normalized plots of initial desorption rate or initial biodegradation rate, each as a function of aging time, coincide. Likewise, normalized plots of the amount desorbed or mineralized vs aging time coincide. This indicates that the degraders metabolize phenanthrene molecules as they desorb.

Substrate is supplied to the solution by desorption and consumed via the solution phase by biodegradation:

$$\theta \frac{\partial C}{\partial t} = -\beta \frac{\partial q}{\partial t} - \theta \left( \frac{\partial C}{\partial t} \right)_{\text{bd}} \quad (77)$$

Biodegradation of substrate when no other nutrient limitations exist is governed by Monod kinetics:

$$-\theta \left( \frac{\partial C}{\partial t} \right)_{\text{bd}} = \frac{\mu_{\text{max}} C}{K_m + C} \cdot \frac{X(t)}{Y_s} \quad (78)$$

where  $C$  is the solution concentration experienced at cell surfaces [ $\text{M L}^{-3}$ ],  $\mu_{\text{max}}$  is the maximum growth rate [ $\text{T}^{-1}$ ],  $K_m$  [ $\text{M L}^{-3}$ ] is the "half-saturation constant" (the substrate concentration at which the rate is 50% of maximum),  $X$  the cell mass concentration [ $\text{M L}^{-3}$ ], and  $Y_s$  [ $\text{M M}^{-1}$ ] is the specific bioconversion factor for growth on the substrate (i.e., biomass produced per mass substrate consumed). The values of  $\mu_{\text{max}}$ ,  $K_m$ , and  $Y_s$  are obtained in separate soil-free growth experiments, assuming the surface has no influence. When  $C$  is well below  $K_m$  substrate utilization is simplified to an expression that is first order in  $C$ :

$$-\theta \left( \frac{\partial C}{\partial t} \right)_{\text{bd}} = \frac{\mu_{\text{max}}}{K_m} \frac{X(t)}{Y_s} C \quad (79)$$

The cell mass concentration is a function of the rates of growth and decay, including death and inactivation by the soil. Cells may grow on the chemical and on utilizable natural organic matter (UOM). The general expression for the change in cell mass is

$$\frac{\partial X}{\partial t} = \frac{\mu_{\text{max}} CX}{K_m + C} + Y_{\text{UOM}} \left( \frac{\partial [\text{UOM}]}{\partial t} \right) - \lambda X \quad (80)$$

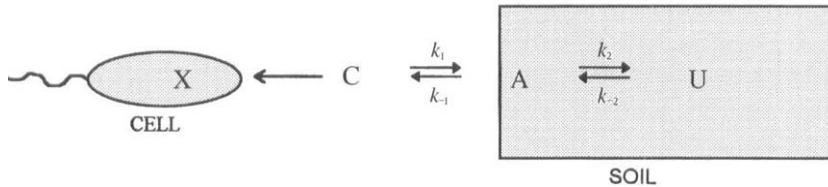
where  $Y_{\text{UOM}}$  [ $\text{M M}^{-1}$ ] is the corresponding bioconversion factor for growth on UOM, and  $\lambda$  [ $\text{T}^{-1}$ ] is a first-order decay coefficient.

If degradation by indigenous organisms is being considered, natural growth and decay may be assumed to have reached a steady state and the last two terms on the right of Eq. (80) cancel out. If, however, degradation by cultured organisms is being considered, the last two terms—especially the decay term—may be significant. Growth on UOM and decay processes in soils are complex and poorly understood. The values of  $Y_{\text{UOM}}$ ,  $\partial[\text{UOM}]/\partial t$ , and  $\lambda$  are thus difficult to acquire, especially since accurate assays for active cell population in the presence of soil particles are lacking. [Somewhat better than order-of-magnitude estimates of active degrader population may be made by a  $^{14}\text{C}$ -most-probable-number technique

if radiolabeled compound is available (Lehmiche *et al.*, 1979).] If cells can be accurately monitored, it may be possible to establish an empirical growth and decay curve in the absence of substrate and input it into the model.

## 2. Biodegradation Coupled with First-Order-Type Sorption Models

In their study of 2,4-dichloroacetic acid (2,4-D) degradation by a 2,4-D degrading *Alcaligenes* species in unsaturated soils, Shelton and Doherty (1997) employed a four-compartment model: the biomass (X), the solution (C), sorbed available (A), and sorbed unavailable (U) compartments:



Mass transfer between the compartments obeyed the following Monod and simple first-order expressions:

$$\frac{dX}{dt} = \frac{\mu_{\max} C}{K_m + C} X \quad (81a)$$

$$\frac{dC}{dt} = -k_1 C + k_{-1} S_A - \frac{\mu_{\max} C}{K_m + C} \frac{X}{Y_S} \quad (81b)$$

$$\frac{dA}{dt} = -k_1 C - (k_{-1} + k_2) S_A + k_{-1} S_U \quad (81c)$$

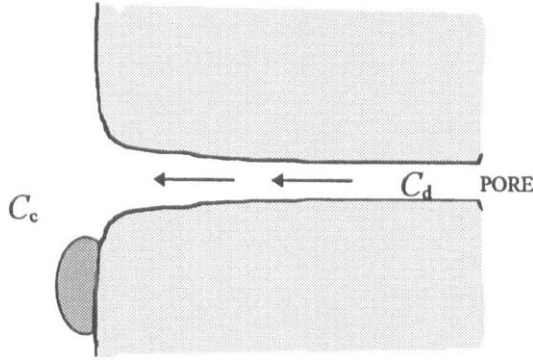
$$\frac{dU}{dt} = k_2 S_A - k_{-1} S_U \quad (81d)$$

They assumed that the pesticide is the primary growth substrate and limiting nutrient, that there was no interference from indigenous organisms, and (apparently) that there was no natural decay or growth. The sorption rate constants ( $k_1$ ,  $k_{-1}$ ) and ( $k_2$ ,  $k_{-2}$ ) were obtained in independent experiments performed over 3- and 48-h periods, respectively. Hence, the model is specific to the time frame of the experiment.

## 3. Biodegradation Coupled with Linear Driving Force Sorption Model

Bosma *et al.* (1997) studied the biodegradation of  $\alpha$ -hexachlorocyclohexane residues in field-contaminated soil. They assumed that the rate of desorption was

proportional to the concentration gradient of solute between liquids in distant pores, where cells cannot enter, and the sites of bacterial colonies (0.8 to 3- $\mu\text{m}$  macropores):



$$-\frac{\beta}{\theta} \frac{\partial q}{\partial t} = \alpha(C_d - C_v) \quad (82)$$

where  $C_d$  is the distal and  $C_c$  is the vicinal concentration with respect to the cell surface, and  $\alpha$  [ $\text{T}^{-1}$ ] is a desorption rate parameter. Under steady-state conditions Eqs. (78) and (82) are equal, and through further manipulation it is possible to obtain the so-called Best equation:

$$v = v_{\max} \frac{C_d + K_m + v_{\max} \alpha^{-1}}{2v_{\max} \alpha^{-1}} \left\{ 1 - \left[ 1 - \frac{4C_d v_{\max} \alpha^{-1}}{(C_d + K_m + v_{\max} \alpha^{-1})^2} \right]^{1/2} \right\} \quad (83)$$

where  $v$  is the specific degradation velocity [ $\text{M T}^{-1}$ ];  $v_{\max}$  ( $= \mu_{\max} X/Y_S$ ) is the maximum degradation velocity [ $\text{M T}^{-1}$ ], and the other variables are as defined previously. The Best number ( $Bn$ ),

$$Bn = \alpha/(v_{\max} K_m^{-1}), \quad (84)$$

is the index of mass transfer to biodegradation; the reaction is rate limited by biodegradation when  $Bn > 1$  and rate limited by mass transfer when  $Bn < 1$ . The  $Bn$  for  $\alpha$ -hexachlorocyclohexane in soil slurry was 0.016–0.03, indicating mass transfer limitation.

#### 4. Biodegradation Kinetics Coupled with Radial Diffusion Laws

These models (Rijnaarts *et al.*, 1990; Scow and Alexander, 1992; Scow and Hutson, 1992) employ a simple radial pore diffusion law such as the one in Eq. (30)

in order to calculate an effective diffusivity using analytical (Crank, 1975) or numerical solutions. It is normally assumed that the substrate concentration at the cell surface is near zero.

Rijnaarts *et al.* (1990) used the measured mean particle diameter (122–182  $\mu\text{m}$ ) to obtain  $D_{\text{eff}}$ ; however, this value of  $D_{\text{eff}}$  resulted in poor fits in the coupled model. Running the coupled model instead with a fitting parameter  $\delta$  representing the average “intraparticle diffusion distance” resulted in good fit when  $\delta = 14\text{--}18 \mu\text{m}$ . Rijnaarts *et al.* hypothesized that the bacteria were able to slightly penetrate the particle. However, it is more likely that the length scale over which diffusion occurs is simply smaller than the actual particle radius.

### 5. Biodegradation Coupled with Transport

With biodegradation the A–D equation for solute transport (Eq. 56; see Section IV,A) becomes

$$\theta \frac{\partial C}{\partial t} + \beta \frac{\partial q}{\partial t} = \theta D_h \frac{\partial^2 C}{\partial x^2} - \theta v \frac{\partial C}{\partial x} - \underbrace{\frac{\partial}{\partial t} (\sum \theta_i C_i)}_{\text{biodegradation term}}, \quad (85)$$

where  $i$  refers to each solution compartment if more than one is applicable. Models published to date have assumed first-order biodegradation kinetics; that is, that substrate concentration falls in the low-concentration region of the Monod curve and the degrader population is at steady state.

The two-region (mobile–immobile) A–D model (Eq. 58) incorporating degradation is thus

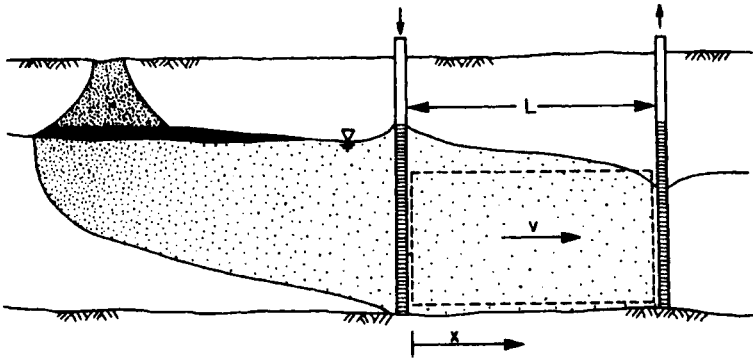
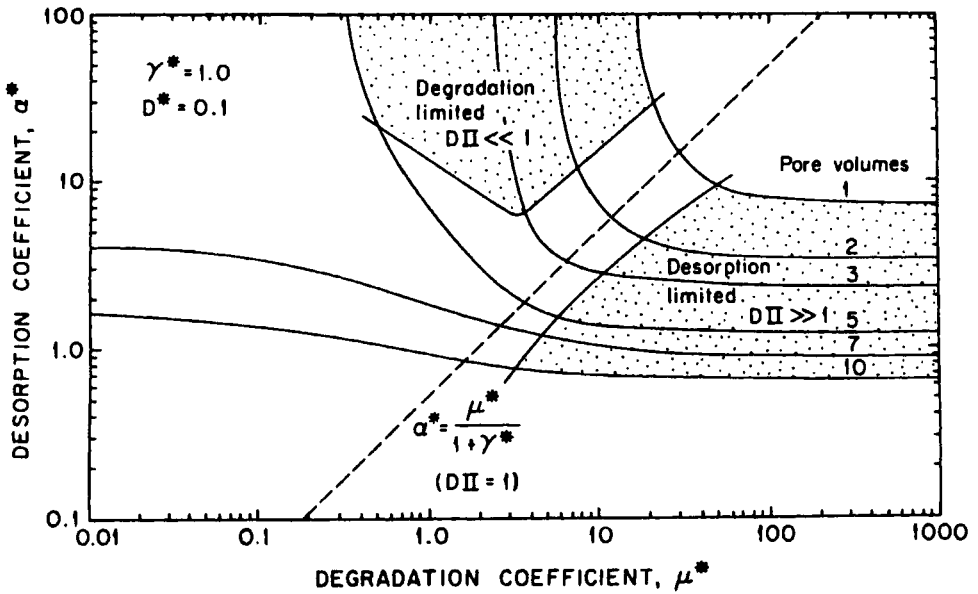
$$\begin{aligned} \left( \theta_m + \beta f n K_e C_{\text{im}}^{n-1} \right) \frac{\partial C_m}{\partial t} + \left( \theta_{\text{im}} + \beta (1-f) n K_e C_{\text{im}}^{n-1} \right) \frac{\partial C_{\text{im}}}{\partial t} = \theta_m D_h \frac{\partial^2 C_m}{\partial x^2} \\ - \theta_m v \frac{\partial C_m}{\partial x} - \theta_m \mu_m C_m - \theta_{\text{im}} \mu_{\text{im}} C_{\text{im}}, \end{aligned} \quad (86)$$

where the first-order biodegradation rate constants [ $\text{T}^{-1}$ ] in the mobile ( $\mu_m$ ) and immobile ( $\mu_{\text{im}}$ ) regions may be different due to nutrient availability, different populations, or other factors.

Likewise, the two-site (equilibrium–kinetic) A–D model of Eq. (60) is given by

$$\left( 1 + \frac{\beta}{\theta} f n K_e C^{n-1} \right) \frac{\partial C}{\partial t} + \frac{\beta}{\theta} k_{-2} (K_e C^n - q) = D_h \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \mu C, \quad (87)$$

where  $\mu$  is the first-order biodegradation rate constant [ $\text{T}^{-1}$ ]. An analytical solution to Eq. (86) or Eq. (87) is readily obtained in the linear sorption case (van Genuchten and Wagenet, 1989).



**Figure 17** Effect of dimensionless desorption rate parameter ( $\alpha^*$ ) and biodegradation rate parameter ( $\mu^*$ ) on the number of pore volumes needed to decrease the initial contaminant mass by a factor of  $10^3$  in an aquifer. Here,  $\alpha^* = \alpha L/v, \mu^* = \mu L/v, \gamma^* = \beta K_c/\theta$ , and  $D^* = D_v/vL$ .  $D_{II}$  is the Damkohler number II, the ratio of degradation rate to mass transfer rate. (Reprinted from Fry and Istok, 1994, with permission from the American Geophysical Union.)

Researchers have used these models experimentally with some success (Angley *et al.*, 1992; Gamberinger *et al.*, 1990; Hu and Brusseau, 1998). Degradation delays the breakthrough of the solute (Angley *et al.*, 1992; Hu and Brusseau, 1998) and, of course, decreases the amount recovered. Angley *et al.* studied alkylben-



zene transport in columns of nonsterile aquifer material, taking sorption to be linear. Predicted elution curves using the nonequilibrium two-site model were superior to the corresponding equilibrium single-site model ( $f = 1$ ). The  $\mu$ 's were highly dependent on flow velocity, however, increasing by a factor of three to eight with increasing flow velocity from 5.76 to 65.8 pore volumes per day. Even at the slowest flow velocity, the  $\mu$ 's were an order of magnitude greater than those in nonagitated batch microcosm studies. This result underscored the "pseudo, or non-constant nature of  $[\mu]$ " and rendered extrapolation to the field "problematic" (Anglely *et al.*, 1992).

The relationship between desorption and bioavailability in an aquifer remediation scenario was examined theoretical by Fry and Istok (1994). They assumed first-order biodegradation and the existence of a single sorption domain having a linear isotherm and first-order desorption rate coefficient. Figure 17 shows the number of pore volumes needed to decrease the initial contaminant mass in the aquifer by three orders of magnitude as a function of the dimensionless desorption coefficient,  $\alpha^*$ , and the dimensionless biodegradation rate coefficient  $\mu^*$ . When degradation is rate limiting ( $\alpha^*$  is large relative to  $\mu^*$ ), increasing the degradation rate decreases the number of pore volumes needed to remediate the aquifer. However, when desorption is rate limiting ( $\alpha^*$  is small relative to  $\mu^*$ ), increasing the degradation rate is predicted to be futile.

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