REVIEW PAPER

SORPTION PHENOMENA IN SUBSURFACE SYSTEMS: CONCEPTS, MODELS AND EFFECTS ON CONTAMINANT FATE AND TRANSPORT*

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Abstract—The behavior, transport and ultimate fate of contaminants in subsurface environments may be affected significantly by their participation in sorption reactions and related phenomena. The degree to which the resulting effects can be quantified and predicted depends upon the extent to which certain fundamental aspects of sorption are understood, and upon the accuracy with which these phenomena can be characterized and modeled in complex subsurface systems. Current levels of understanding of the reactions and processes comprising sorption phenomena are discussed in this paper, as are the forms and utilities of different models used to describe them. Emphasis is placed on concept development, on the translation of these concepts into functional models for characterizing sorption rates and equilibria, and on the application of these concepts and models for explaining contaminant behavior in subsurface systems. Examples are provided to illustrate the impacts of sorption phenomena on contaminant transport.

Key words—sorption, partitioning, soils, groundwater, subsurface systems, rate and equilibrium models, mass transfer, contaminant tranport

NOMENCLATURE

A = area (L^2)
a_i = chemical activity of species i
b = Langmuir isotherm coefficient corresponding to the enthalpy of adsorption (L^3/M)
$C_{e,i}$ = equilibrium solution phase concentration of species i (M/L^3)
$C_{e,i}^*$ = equilibrium solution phase concentration of species i in a single-solute system at the same spreading pressure as that of a mixture (M/L^3)
$C_{i,j}$ = concentration of species i associated with phase or interface j (M/L^3)
D_e = effective diffusion coefficient (L^2/t)
D_h = hydrodynamic dispersion coefficient (L^2/t)
$\mathbf{D_h}$ = second-rank hydrodynamic dispersion tensor (L^2/t)
$D_{h,a}$ = apparent dispersion coefficient (L^2/t)
D_l = free liquid diffusion coefficient (L^2/t)
D_m = minimum energy in the Morse potential model (ML^2/t^2)
E = Coulombic constant of proportionality ($ML^3/t^2 \cdot Q^3$)
e = minimum energy level for attractive forces in Lennard–Jones potential (ML^2/t^2)
$f_{i,j}$ = activity coefficient of species i in phase j
$F_{i,x}^0$ = flux of species i in direction x ($M/L^2 \cdot t$)
HSA = hydrocarbonaceous molecular surface area (L^2)
$\mathbf{k}$ = Boltzman's constant 1.38×10^{-16} erg/degree Kelvin ($ML^2/t^2 \cdot T$)

k' = psuedo-first-order rate constant ($1/t$)
K_B^A = ion-exchange selectivity coefficient between ions A and B
k_α = overall mass transfer coefficient for diffusion into an adjacent solute accumulating phase ($1/t$)
K_D = distribution coefficient (L^3/M)
K_D^j = distribution coefficient in phase j (L^3/M)
k_e = effective mass transfer coefficient (L/t)
K_{eq} = equilibrium constant
K_F = Freundlich isotherm constant $[(L^3/M)^n]$
k_F = forward rate constant ($L^3/M \cdot t$)
k_f = film transfer coefficient (L/t)
K_{oc} = organic carbon-normalized linear isotherm coefficient (L^3/M)
K_{ow} = octanol/water partition coefficient (dimensionless)
K_P = partition coefficient (dimensionsless)
k_R = reverse rate constant ($1/t$)
m = Morse potential constant ($1/L$)
N = total number of species in solution
n = Freundlich isotherm exponent (dimensionless)
%OC = percent soil organic carbon content
q = mass of solute sorbed per unit mass of sorbent (M/M)
q_r = mass of solute sorbed per unit mass of sorbent at radial distance r (M/M)
$q_{e,i}$ = mass of solute i sorbed per unit mass of sorbent at equilibrium (M/M)
$q_{e,i}^*$ = solid-phase concentrations of species i in single-solute system with the same spreading pressure as that of the mixture (M/M)
$q_{i,j}$ = solid-phase concentration of species i associated with phase or interface j (M/M)
Q = charge

Q^0 = Langmuir isotherm coefficient corresponding to the mass of sorbate per unit mass of sorbent at monolayer coverage (M/M)

q_T = total mass of solutes sorbed per unit mass of sorbent (M/M)

R = gas constant $8.314\,\text{J/K-mol} = 8.314 \times 10^7\,\text{erg/K-mol}$ ($L^2/t^2\text{-}T$)

r = radial distance (L)

r_e = Morse potential minimum separation distance (L)

R_f = retardation factor (dimensionless)

R_p = particle radius (L)

T = absolute temperature degrees Kelvin

t = time (t)

V = volume (L^3)

$\mathbb{V}$ = volume of solute-accumulating phase adjacent to a mass transfer domain (L^3)

v = reaction velocity (M/L^3-t)

$\mathbf{v}$ = the pore-velocity vector (L/t)

$V_{m,j}$ = the molar volume of phase j (L^3)

v_z = one dimensional fluid-phase pore (interstitial) velocity in the z direction (L/t)

$x_{i,j}$ = the mole fraction of solute i in phase j (dimensionless)

$z_{e,i}$ = the mole fraction of solute i in the sorbed phase (dimensionless)

z_i = charge species $i(Q)$

α = empirical coefficient relating sorption to the cosolvent content of the solvent (dimensionless)

β^c = volume fraction of a cosolvent in an aqueous phase (dimensionless)

γ = surface tension (M/t^2)

$\Delta\gamma'$ = difference in HSA/solvent interfacial tensions (M/t^2)

ϵ = porosity, void volume per unit total volume (dimensionless)

ϕ_{oc} = mass of organic carbon per unit mass of solid (dimensionless)

ϕ_{SM} = mass of solid phase associated with the mobile fluid per unit total mass of solid (dimensionless)

ρ_i = density of phase i (M/L^3)

θ_j = volume of phase or region j per unit total volume (dimensionless)

ψ_C = Coulombic potential energy (ML^2/t^2-Q)

ψ_{LJ} = Lennard–Jones potential energy (ML^2/t^2)

ψ_M = Morse potential energy (ML^2/t^2)

ψ^0 = electrochemical potential at the near approach plane in a surface complexation model (ML^2/t^2-Q)

ψ^β = electrochemical potential at the β plane in a surface complexation model (ML^2/t^2-Q)

σ = parameter in the Lennard–Jones potential relationship (L)

Γ = surface excess (M/L^2)

Π_i = spreading pressure of species i (M/t^2)

μ_i = chemical potential of species i (ML^2/t^2)

μ_i^0 = standard chemical potential of species i (ML^2/t^2).

1. INTRODUCTION

Sorption processes involve an array of phenomena which can alter the distribution of contaminants between and among the constituent phases and interfaces of subsurface systems. The interchanges of mass associated with such processes impact the fate and transport of many inorganic and organic substances. The effects can be complex, given the diversity, magnitude and activity of chemical species, phases and interfaces commonly present in contaminated subsurface environments. Each combination of solute, sorbing phase, interface, phase from which

sorption occurs and set of local conditions yields a unique mass distribution, which may be either stable or transient. Thermodynamic considerations govern contaminant mass distributions ultimately achievable, and thus "stable". The rates at which such distributions are approached involve separate but equally important considerations, considerations which frequently determine the relative significance of sorption with respect to other reaction and transport processes operating in subsurface environments. Prediction of contaminant fate and transport requires characterization and quantification of both energy balances and rates associated with sorption processes.

State-of-the-art "know-how" in this regard includes a reasonable understanding of parameters which influence rates and extent of reactions, an extensive base of empirical observations, and a comprehensive set of descriptive and predictive models predicated on various mechanistic representations of sorption phenomena. This paper explores our current level of understanding of sorption processes, and the form and utility of different models used to describe them and their effects. Particular emphasis is given to concept development, and the extent to which such concepts can be applied in understanding and explaining contaminant behavior in subsurface systems.

2. SORPTION PHENOMENA

Sorption interactions generally operate among all phases present in any subsurface system and at the interfaces between these phases. Solutes which undergo sorption are commonly termed sorbates, the sorbing phase the sorbent, and the primary phase from which sorption occurs the solution or solvent. Two broad categories of sorption phenomena, adsorption and absorption, can be differentiated by the degree to which the sorbate molecule interacts with and is free to migrate between the sorbent phase. In adsorption, solute accumulation is generally restricted to a surface or interface between the solution and adsorbent. In contrast absorption is a process in which solute transferred from one phase to another interpenetrates the sorbent phase by at least several nanometers. An additional variation of the process occurs if a sufficiently high accumulation of solute occurs at the interface to form a precipitate or some other type of molecular solute–solute association, e.g. a polymer or a micelle. Such processes differ from both adsorption and absorption in that they result in formation of new and distinct three-dimensional phases. Because adsorption processes generally yield surface or interface concentrations of solute greater than those in the bulk phase, it is possible for precipitation or association to occur on a surface in the absence of a solution phase reaction of the same type. Although such association reactions are often classified as separate processes, they must in fact be preceded by adsorption or absorption.

Sorption results from a variety of different types of attractive forces between solute molecules, solvent molecules and the molecules of a sorbent. Such forces usually act in concert, but one type or another is just as usually more significant than the others in any particular situation. Absorption processes, such as dissolution of a relatively immiscible phase into an aqueous phase or accumulation of a lipophilic substance in an organic phase, involve exchanges of molecular environments. In such cases, the energy of an individual molecule is altered by its interactions with the solvent and sorbent phases. The distribution of the solute between phases results from its relative affinity for each phase, which in turn relates to the nature of the forces which exist between molecules of the sorbate and those of the solvent and sorbent phases. These forces can be likened to forces which arise in classical chemical reactions. Adsorption also entails intermolecular forces, but in this case it is molecules at the surface of the sorbent rather than bulk phase molecules which are involved, and the former typically manifest a broader range of interactions. Accordingly, three loosely defined categories of adsorption—physical, chemical and electrostatic—are traditionally distinguished, according to the class of attractive force which predominates. Some significant features of these different interactions and classes of adsorption are summarized in Table 1.

Forces associated with interactions between the dipole moments of sorbate and sorbent molecules commonly underlie physical sorption processes. Dipole moments arise from charge separation within a molecule and can be either permanent or induced. Molecules possessing a permanent dipole moment are referred to as polar molecules. Interactions between polar molecules or between polar molecules and nonpolar molecules—in which dipole moments are thereby induced—represent one class of "physical" sorption. In most cases, such interactions are short range, the associated energy decreasing inversely with the sixth power of the distance separating the interacting molecules. There are cases, however, of longer range permanent dipole interactions in which the potential energy is inversely related to the third power of the distance between molecules; for example polar molecules which are specifically oriented (Hiemenz, 1986).

A more general class of physical sorption is associated with forces attributable to rapidly fluctuating or instantaneous dipole moments resulting from the motion of electrons in their orbitals; so-called London dispersion forces. Energies associated with interactions of this type also decrease inversely with the sixth power of the distance between molecules.

The magnitude of physical sorption forces can be estimated from measurements of differential heats of adsorption. Values for interactions of the London-dispersion type for small molecules are generally of the order of 1–2 kcal/mol (Kiselev, 1965). More specific interactions have higher heats of sorption.

The relatively weak bonding forces associated with physical sorption are often amplified in the case of hydrophobic (more generally, solvophobic) molecules by substantial thermodynamic gradients for repulsion from the solution in which they are dissolved. Although the sorption bond may still be attributable to dispersion-type interactions, the combined effect in aqueous system is often referred to as "hydrophobic bonding" (Haymaker and Thompson, 1972).

Table 1. Characteristic interactions associated with categories of adsorption

Category and Characteristic Interaction	Representation of Interaction	Interaction Range
CHEMICAL Covalent		Short Range
Hydrogen Bond		Short Range
ELECTROSTATIC Ion-Ion		$1/r$
Ion-Dipole		$1/r^2$
PHYSICAL Dipole-Dipole (Coulombic)		$1/r^3$
(Keesom energy)		$1/r^6$
Dipole-Induced Dipole (Debye energy)		$1/r^6$
Instantaneous Dipole-Induced Dipole (London dispersion energy)		$1/r^6$

*Adapted from Israelachvili, 1985.

The existence of an energy acting to drive hydrophobic molecules out of aqueous solution can be understood in the context of the structure of water. It is commonly envisioned that water molecules exist in one of two principal types of structural associations in aqueous phase. The first is one in which each water molecule is tetrahedrally coordinated to four others via hydrogen bonding, yielding a structure similar to that of crystalline ice. The second is an agglomeration of more densely packed but less well ordered molecules. A relatively non-polar dissolved solute molecule is held in aqueous solution by an arrangement of the ice-like water molecules, and the dissolution reaction is generally exothermic. This favorable enthalpy of solution is countered, however, by an unfavorable entropy resulting from the increased ordering of solvent molecules (Nemethy and Scheraga, 1962; Haymaker and Thompson, 1972). Solute molecules can thus be driven from solution at concentrations well below maximum solubility, that is at levels below those at which they could precipitate, if the system can achieve a state that is thermodynamically favorable to sorption. Chlorinated hydrocarbons, for example, tend to sorb readily to organic-rich soils because hydrocarbon–natural organic interactions are energetically preferred to hydrocarbon–water interactions.

To this point the discussion has focused primarily on attractive forces. At near approach, or small intermolecular separation, repulsive forces may well dominate. Repulsive forces—variously referred to as exchange, hard core or Born repulsion forces—become negligible beyond an extremely small and characteristic intermolecular distance referred to as the van der Waals radius. Empirical descriptions of repulsive forces have generally employed relationships in which the energy varies inversely with the twelfth power of distance (Israelachvili, 1985). Summation of the attractive and repulsive forces leads to a total intermolecular pair potential relationship known, in the case of dispersion forces, as the Lennard–Jones or "6–12" potential:

$$\psi_{\text{LJ}} = 4e[(\sigma/r)^{12} - (\sigma/r)^6]. \tag{1}$$

The term ψ_{LJ} represents the potential energy between a pair of molecules separated by a distance of $2r$, e the minimum energy level for which attractive forces correspond to negative potential, and σ the half-distance between molecules when $\psi_{\text{LJ}} = 0$. As noted previously, the potential energy between molecules attributable to other types of physical interactions may vary in magnitude, but the general shape of the potential energy relationship remains the same. Moreover, extension of the Lennard–Jones potential, which was derived for interactions between two molecules, to the interaction of a molecule and a surface necessitates summing the pairwise interactions between the molecule and surface atoms. Although the resulting relationship will obviously have different values for the exponents than those of the Lennard–Jones relationship, its graphical form will be similar.

Forces of greater intensity and longer range exist between discretely charged entities. These forces derive from specific electrostatic interactions between localized charges, and exhibit much higher heats of sorption than those associated with physical sorption. Electrostatic forces extend over long distances, varying inversely with the square of the distance between molecules and directly with the product of the charges. The relationship between potential energy and distance between charges is defined by Coulomb's law:

$$\psi_{\text{C}} = E\frac{z_1 z_2}{r}. \tag{2}$$

The magnitudes of the charges associated with each of two interacting species are represented by z_1 and z_2, respectively, and E is a constant dependent on the properties of the solvent. As shown by equation (2), these forces can be attractive in the case of oppositely charged species or repulsive between those having like charges.

The final category of sorption defined according to predominant surface–solute interaction is chemical sorption or chemisorption. The bonds that form between solute molecules and specific surface chemical groups in this type of sorption have all of the characteristics of true chemical bonds and are characterized by relatively large heats of sorption. The reactions may involve substantial activation energies and be favored by high temperatures. Chemical bonding between a sorbate molecule and a sorbent site can be represented in terms of the Morse potential energy relationship, which was developed for a covalent bond between two identical molecules, and has the functional form (Gasser, 1985):

$$\psi_{\text{M}} = D_{\text{m}}[1 - e^{-m(r - r_e)}]^2. \tag{3}$$

The term D_{m} in equation (3) is the minimum energy, r_e is the equilibrium separation of the molecules and m is a constant. The variation of the Morse potential energy with separation distance exhibits a form similar to that of the Lennard–Jones potential, although the former yields a much greater minimum energy and a smaller separation between molecule and surface sites at the minimum.

Categorization of the primary classes of interactions leading to sorption reaction provides a useful means to bridge the gap between detailed enumerations of intermolecular forces and working descriptions of observed sorption phenomena. In reality, however, such forces do not act independently; it is, rather, the effect of their action collectively and in concert which dictates the sorptive separation of substances in any system. As such, there are two predominant means by which the sorption is motivated. The first derives from the net forces of affinity between the sorbate and the sorbent, here defined as "sorbent-motivated" sorption. Cation exchange

reactions with clays, for example, are sorbent-motivated sorptions in which the electrostatic charge characteristics of the sorbent are overwhelmingly attractive to the sorbate. The second involves the sum of adverse interactions of the sorbate with its solution phase, yielding "solvent-motivated" sorptions. The repulsion by water of an oil or other hydrophobic contaminant leading to its accumulation at a soil–water interface, which may or may not be indifferent to the sorbate, constitutes a principally solvent-motivated sorption. As expected, the combined influence of all intermolecular forces in complex systems usually leads to sorption processes which are not as easily categorized as specifically or exclusively either sorbent motivated or solvent motivated, but rather which fall somewhere in the interlying continuum.

3. SORPTION EQUILIBRIA

3.1. Absorption processes

The eventual equilibrium distribution of contaminant mass between solution phase and a sorbent or interface is dictated by a corresponding energy balance, and thus may be categorized thermodynamically. This characterization is somewhat more obvious for absorption than for adsorption, in that the former relates more to issues of classical chemistry and energy balances within and between discrete phases, whereas the latter often involves ill-defined surfaces and interfaces.

The differences in molecular environments of a contaminant in aqueous and sorbent phases which manifest themselves in absorption processes can be described using classical thermodynamics. At equilibrium, there is no driving force for further net chemical change and the chemical potential, μ_i, of a solute i must be equal in the solvent and sorbent phases:

$$\mu_{i, \text{solvent}} = \mu_{i, \text{sorbent}}. \quad (4)$$

The chemical potential is a function of the chemical activity, a_i, and the standard state chemical potential, μ_i^0, of species i:

$$\mu_i - \mu_i^0 + RT \ln a_i. \quad (5)$$

Chemical activity is dimensionless, but its value depends on the units of concentration and on the choice of a standard state. The activity of a solute can be related to its mole fraction, x_i, through an activity coefficient, f_i:

$$a_i = f_i x_i. \quad (6)$$

The activity coefficient is defined with respect to a reference state. Two reference states are common: the infinitely dilute state, where f_i approaches unity as x_i approaches 0, and the pure solute state, where f_i approaches unity as x_i approaches 1. The best choice for the reference state depends on the system to be examined. For liquid–liquid partitioning of organic compounds it is common to take the pure solute as the reference state with correction for pure solutes which are solid at the temperature of interest (Yalkowsky and Valvani, 1980). For purposes of this discussion, however, the activity coefficient may be taken to reflect the extent to which intermolecular interactions in the solution (solute–solvent and solute–solute) differ from those in the standard state (solute–solute) (Karickhoff, 1984).

The partitioning of a solute between two phases can be expressed in terms of the ratio of its respective concentrations, C_i, in each phase. Assuming the same standard state for i in both the solvent (1) and sorbent (2) phases and low concentrations of solute in each phase, this ratio has a constant value given by:

$$\frac{C_{i,2}}{C_{i,1}} = \frac{V_{\text{m},1} x_{i,2}}{V_{\text{m},2} x_{i,2}} = \frac{V_{\text{m},1} f_{i,1}}{V_{\text{m},2} f_{i,2}} = K_{\text{p}}. \quad (7)$$

The term V_{m} is the molar volume of each phase, and K_{p} is termed the phase "partitioning" coefficient for the solute. Equation (7) relates the distribution of solute between the phases to the ratio of the respective activity coefficients, reflecting the relative intermolecular interactions of the solute in those two phases. In aqueous phases, the hydrophobic interactions described earlier coupled with the choice of reference state can lead to activity coefficients much greater than unity, a reflection of the significant difference in interactions which arise between the solute and the aqueous solvent and the solute in the pure solute reference state.

3.2. Adsorption processes

The properties of a system most significant for this type of sorption process are those related to the surface at which accumulation occurs. Driving forces for attainment of chemical equilibrium in homogeneous phases relate to reduction of the free energies of bulk systems, whereas the driving force for a surface reaction is a reduction in surface energy. One common manifestation of surface energy occurs when a drop of liquid placed on a flat solid surface resists spreading, and attempts to gain or retain a nearly spherical shape. The liquid in this case is attempting to minimize its free surface energy. This phenomenon, the development of a tension at the surface, results from attractive forces between molecules of the solid plate or molecules of liquid within the drop. Because molecules of the liquid are attracted more strongly to one another by cohesion forces than they are to molecules of the solid plate at the liquid–solid interface, molecules of liquid at the surface will be pulled mainly toward the interior of the drop. The same effect applies to the air–liquid interface, which thus tends to decrease its exposed surface as a result of the surface tension developed by the intradrop molecular cohesion forces. This imbalance of intermolecular forces is illustrated schematically in Fig. 1.

A pure liquid always tends to reduce its free surface energy through the action of surface tension. From a
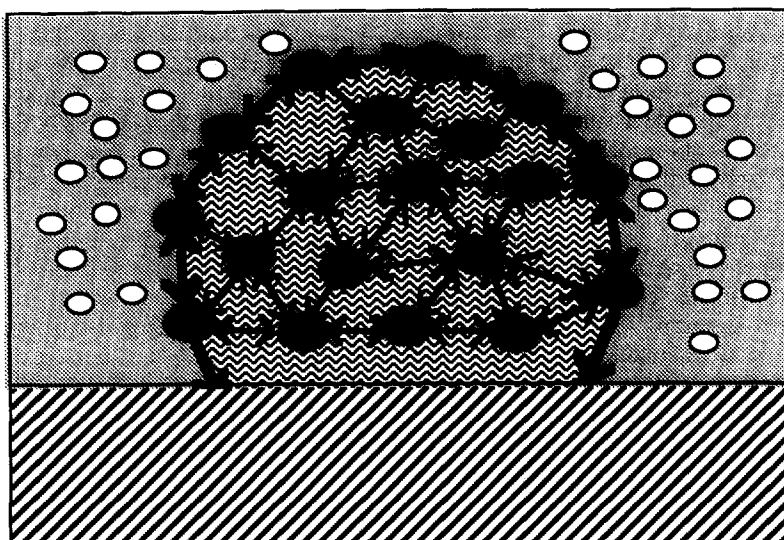
Fig. 1. Illustration of surface tension arising from the imbalance of molecular attraction forces in a liquid drop (adapted from Weber, 1972).

molecular point of view, enlarging a surface requires the breaking of bonds between surface molecules of the liquid phase, and the forming of bonds between these molecules and those of adjacent phases.

A wide variety of soluble substances can alter the surface tension of a liquid. Surfactants, for example, lower the surface tension of water and cause it to spread on a solid surface, resulting in a wetting of that surface. Such substances are therefore termed wetting agents. If a surface active solute is present in a liquid system, a decrease in the surface tension of that liquid will occur upon movement of the substance to the surface. Stated another way, any solute known to lower the surface tension of a liquid will migrate to, and adsorb at, the interface of that liquid with some other phase.

It is possible to define rigorous relationships for conditions in which equilibrium interfacial tension is reduced with increasing concentration of a solute sorbed at an interface. Such relationships are rooted in the fundamental expression developed by J. Willard Gibbs in 1878 for relating a change in the interfacial tension, γ, at the surface of a phase to the adsorption of solutes at the surface. If Γ_i is defined as the equilibrium amount of solute, i, adsorbed per unit area of surface in excess of its concentration in the bulk solution (i.e. the "surface excess"), the Gibbs equation at constant temperature and pressure has the form (Weber, 1972):

$$d\gamma = -\sum_{i=1}^{n} \Gamma_i d\mu_i. \qquad (8)$$

For dilute solutions of one solute of concentration C, the Gibbs equation may be approximated by:

$$d\gamma = -RT\Gamma \frac{dC}{C}. \qquad (9)$$

Equation (9) states that any solute which reduces the interfacial tension (i.e. $d\gamma/dC < 0$) results in an increase in Γ and thus will be present at the interface in higher concentration than in bulk solution. For $d\gamma/dC > 0$, negative adsorption is experienced. Water has a relatively high surface tension (73 dynes/cm for a pure water–air interface at 20°C; Weber, 1972) which can be reduced by the presence of other solutes. Typical changes in surface tension at water–vapor interfaces are depicted in Fig. 2 for three classes of solutes, an inorganic electrolyte (e.g. a calcium chloride salt), a relatively simple organic chemical such as a chlorinated ethene (e.g. trichloroethylene) and a surface active organic compound (e.g. an alkyl sulfate). It is apparent that both organic solutes act to decrease surface tension and tend to adsorb at the water–vapor interface, although, just as apparently, to different degrees. In contrast, the inorganic electrolyte increases the surface tension and tends to migrate away from the water–vapor interface.
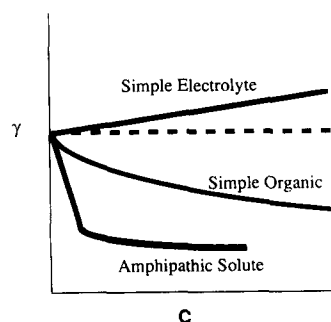

Fig. 2. Examples of variations in surface tension at water–air interfaces with changes in the aqueous phase concentrations of different solutes (adapted from Hiemenz, 1986).

4. EQUILIBRIUM MODELS

4.1. Phenomenological models

Models for characterizing the equilibrium distribution of a solute among the phases and interfaces of an environmental system typically relate the amount of solute, q_e, sorbed per unit of sorbing phase or interface to the amount of solute, C_e, retained in the solvent phase. An expression of this type evaluated at a fixed system temperature constitutes what is termed a sorption "isotherm".

Examples of phenomenologically different equilibrium patterns are illustrated graphically in Fig. 3. A number of conceptual and empirical models have been developed to describe these various adsorption patterns. The most simple is the linear model, which describes the accumulation of solute by the sorbent as directly proportional to the solution phase concentration:

$$q_e = K_D C_e. \tag{10}$$

The constant of proportionality or distribution coefficient, K_D, is often referred to as a partition coefficient. However, C_e and q_e are typically expressed in terms of mass per unit volume and mass per unit mass, respectively, and thus K_D, unlike the K_p presented earlier, is not dimensionless.

An example of a linear isotherm is depicted in Fig. 4 for a particular set of experimental equilibrium data obtained in our laboratories for sorption of tetrachloroethylene (TTCE), a moderately hydrophobic, volatile compound, by a moderately low organic content soil, Ann Arbor II (%OC = 0.5), in completely mixed batch reactors (CMBRs). The linear isotherm is appropriate for sorption relationships in which the energetics of sorption are uniform with increasing concentration and the loading of the sorbent is low ("Henry's region" sorption). It accurately describes absorption and has been found to adequately describe adsorption in certain instances, most commonly at very low solute concentrations and for solids of low sorption potential. When justified, linear approximations to sorption equilibrium data are particularly useful in modeling contaminant fate
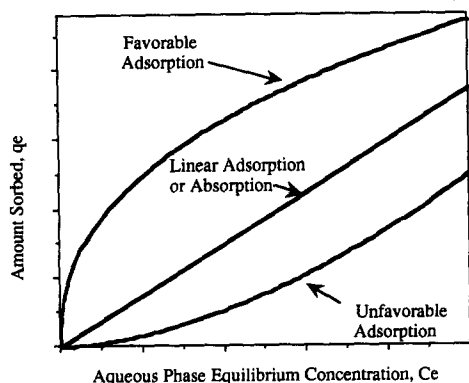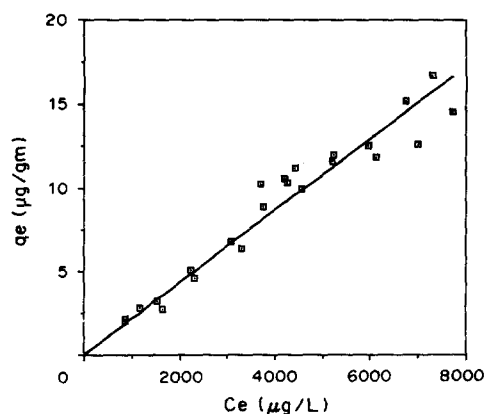

Fig. 4. Linear isotherm model fit to experimental equilibrium data for sorption of tetrachloroethylene (TTCE) by Ann Arbor II soil in CMBR systems.

and transport because they substantially reduce the mathematical complexity of the modeling effort. Even when a particular set of data are reasonably well described by a linear model, however, caution should be exercised in application of the model because it may not be valid over concentration ranges beyond those represented by the data to which it is calibrated.

The Langmuir model, perhaps conceptually the most straightforward non-linear isotherm model, was developed originally for systems in which sorption leads to the deposition of a single layer of solute molecules on the surface of a sorbent. This model is predicated on the assumptions that the energy of sorption for each molecule is the same and independent of surface coverage, and that sorption occurs only on localized sites and involves no interactions between sorbed molecules. Given these assumptions, the Langmuir model can be derived variously by mass action, kinetic, or statistical thermodynamic approaches. The resulting expression is in each case:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}. \tag{11}$$

The parameter Q^0 represents the sorbed solute concentration on the sorbent corresponding to complete monolayer coverage, i.e. a "limiting capacity", and b is a sorption coefficient related to the enthalpy of adsorption. At low surface coverage the Langmuir isotherm reduces to a linear relationship. Calibration of the model to a set of experimental data can be accomplished either by nonlinear regression or by simple regression of a linearized form of the model, the most common of which results from inversion of equation (11):

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0} \frac{1}{C_e}. \tag{12}$$

An example of an application of equation (12) to description of experimental CMBR equilibrium data obtained in our laboratories for sorption of trichlorobenzene (TCB) by Ann Arbor I soil (%OC = 1.14) is presented in Fig. 5. Note by comparison of Figs 4 and

Fig. 3. Illustration of general types of sorption isotherms.

5 that the soil of higher organic content and higher sorptive potential (Ann Arbor I) yields a distinctly non-linear sorption pattern, while that of lower organic content and lower sorptive potential (Ann Arbor II) yields a pattern which is reasonably described by a linear isotherm model.

The Freundlich isotherm is perhaps the most widely used nonlinear sorption equilibrium model. Although both its origins and applications are for the most part empirical, the model can be shown to be thermodynamically rigorous for special cases of sorption on heterogeneous surfaces. This model has the general form:

$$q_e = K_F C_e^n. \tag{13}$$

The parameter K_F relates to sorption capacity and n to sorption intensity. For determination of these empirically derived coefficients, data are usually fit to the logarithmic form of equation (13):

$$\log q_e = \log K_F + n \log C_e. \tag{14}$$

An example of such a fit is presented in Fig. 6 for equilibrium data we have obtained for sorption of trichlorobenzene (TCB) on Wagner soil (%OC = 1.2) In CMBR systems. It is not uncommon for the Langmuir and Freundlich models to have roughly equal utility for describing nonlinear sorption phenomena over moderate ranges of solution concentration, but major differences between the models are usually apparent over wide ranges and high levels of concentration.

In multiple solute systems competition between solutes for sorption may occur as a result either of differences in sorption energies (sorbent or solute heterogeneity) or because of site limitations. Models based on adaptations of the Langmuir and Freundlich isotherms have been used to describe multi-solute sorption, but these adaptations are restricted in their applicability by the limiting assumptions of the elementary models. More accurate characterization of multicomponent adsorption equilibria is often provided by the ideal adsorbed solution theory (IAST) model.
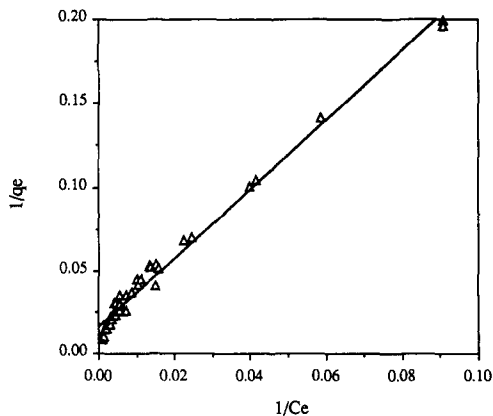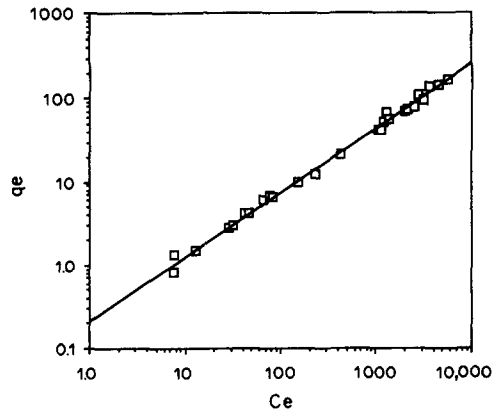

Fig. 6. Freundlich isotherm model fit to experimental equilibrium data for sorption of trichlorobenzene (TCB) by Wagner soil in CMBR systems.

The IAST model has theoretical roots in the Gibbs equation, and thus provides a useful thermodynamic approach to description of multisolute sorption behavior. The IAST model can be used to solve for the adsorbed quantities, $q_{e,i}$, of each of a mixture of solutes, requiring only the corresponding single solute isotherm relationships for each solute and sorbent of interest. The solution method described here summarizes the numerical aspects; a more rigorous exposition of the theory is available elsewhere (Radke and Prausnitz, 1972). The reduction in surface tension which accompanies adsorption is commonly termed the spreading pressure, Π. IAST equates the spreading pressure of each component, Π_i, with that of the system at equilibrium. The spreading pressure of a solute is computed from single solute isotherm data through integration of $q_{e,i}/C_{e,i}$ with respect to $C_{e,i}$ over the range from 0 to that concentration value, $C_{e,i}^*$, corresponding to the concentration required in a single-solute system to yield the same spreading pressure as the mixture, that is:

$$\Pi = \Pi_i = \frac{RT}{A} \int_0^{C_{e,i}^*} \frac{q_{e,i}}{C_{e,i}} \, dC_{e,i}. \tag{15}$$

When the equilibrium relationship between C_e and q_e can be expressed in a functional form such as one of the isotherm models discussed above, equation (15) becomes an analytic expression for the spreading pressure of each solute as a function of its solution phase concentration or, alternatively, the concentration of each solute as a function of the spreading pressure of the system. The IAST model assumes an ideal adsorbed phase (i.e. infinitely dilute sorbed phase) where the mole fraction, $z_{e,i}$, of each solute in the sorbed phase is equal to the ratio of the solute concentration in the mixture, $C_{e,i}$, to its concentration, $C_{e,i}^*$, in single-solute solution having the same spreading pressure as that of the mixture:

$$z_{e,i} = \frac{C_{e,i}}{C_{e,i}^*}. \tag{16}$$

Fig. 5. Langmuir isotherm model fit to experimental equilibrium data for sorption of trichlorobenzene (TCB) by Ann Arbor I soil in CMBR systems.

The mole fraction of sorbed solute is also equal to the ratio of the sorbed amount, $q_{e,i}$, of i to the total sorbed phase concentration of all species, $q_{e,T}$:

$$z_{e,i} = \frac{q_{e,i}}{q_{e,T}}. \tag{17}$$

The use of a set of solution phase solute concentrations to solve for the individual sorbed phase solute concentrations requires solving for the spreading pressure of the system (Π), the sorbed phase mole fractions of each solute ($z_{e,i}$) and the single solute solution phase concentrations for each solute at the system spreading pressure ($C^*_{e,i}$). The above equations can be solved simultaneously for these unknowns using a variety of techniques (see, for example, Weber and Smith, 1988).

Once the spreading pressure of the system and the sorbed phase mole fraction of each solute is known, the sorbed phase concentration of each solute is given by:

$$q_{e,i} = q_{e,T} z_{e,i}. \tag{18}$$

The total sorbed phase concentration of all species, $q_{e,T}$, is calculated from:

$$\frac{1}{q_{e,T}} = \sum_{i=1}^{n} \frac{z_{e,i}}{q^*_{e,i}}. \tag{19}$$

The single-sorption value corresponding to the same spreading pressure as that of the multi-solute solution, $q^*_{e,i}$, can be obtained from the isotherm–spreading pressure relationship.

An example application of the IAST model to equilibrium data we have obtained for sorption of TTCE and DCB from a bisolute mixture in CMBR systems is illustrated in Fig. 7.

It is important to note that the assumptions associated with the conceptual developments of the foregoing isotherm models are rarely satisfied in natural systems. Thus the fact that any one of them may provide a phenomenological description of a sorption process in any given situation should not be taken as
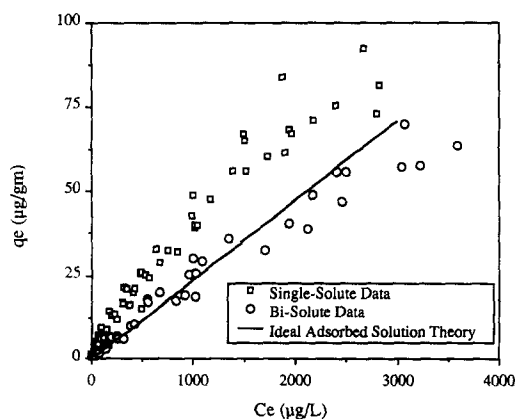

Fig. 7. Single-solute and bi-solute equilibrium data and IAST model prediction for sorption of tetrachloroethylene on Ann Arbor I soil in the presence of dichlorobenzene in CMBR systems.

verification of the concept or mechanism upon which it is based. The ability of any phenomenological model to describe observed data may establish its utility for a specific set of conditions, but the inherent lack of mechanistic rigor associated with such models dictates against extrapolation to ranges of system conditions not experimentally quantified. Indeed, none of the isotherm models discussed here or otherwise available has been demonstrated to be capable of describing data over a wide range of conditions without parameter recalibration. It is not uncommon for a model to describe observed sorption behavior for a given sorbate/sorbent combination under one set of conditions but fail to do so when the system conditions change.

4.2. Mechanistic models

Models providing "first principle" description of the energetics of intermolecular reactions underlying sorption have also been developed. These models include mechanistic characterization of the ion exchange, surface complexation and hydrophobic sorption reactions discussed at the outset of this paper. Such models can often provide insights into mechanisms controlling sorption reactions in particular types of systems, and thus aid in the analysis of anticipated system responses to changes in critical conditions.

4.2.1. Ion exchange and surface complexation

Soil materials typically contain a variety of surfaces which exhibit electrical charge characteristics, which in turn can exert strong influence on the sorption of ionic and polar species. Such surface charges are instrumental, for example, in the sorption of metal species in subsurface systems. The charge on the surface must be counterbalanced in the aqueous phase to maintain electroneutrality. As a result, an electrical double layer exists at interfaces. This double layer consists of the charged surface sites and an equivalent aqueous-phase excess of ions of opposite charge (counter-ions) which accumulate in the water near the surface of the particle. The counter-ions are attracted electrostatically to the interfacial region, giving rise to a concentration gradient, which in turn sets up a potential for random diffusion of ions away from the surface. The competing processes of electrostatic attraction and counter-diffusion spread the charge over a diffuse layer in which the excess concentration of counter-ions is highest immediately adjacent to the surface of the particle and decreases gradually with increasing distance from the solid–water interface. Such distributions are illustrated schematically in Fig. 8.

Several types of reactions can be attributed to forces associated with charged sites. Ion exchange reactions resulting from the action of electrostatic forces occur at fixed sites on soil surfaces (Stumm and Morgan, 1981; James and Parks, 1982). Fixed-charge sites, those not subject to change in solution phase concentration, result from isomorphic substitution of

Surface Stern   Diffuse   Bulk
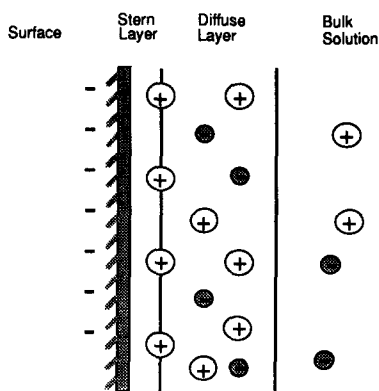   Layer   Layer   Solution

Fig. 8. Schematic representation of an electrical double layer.

ions in the lattice structure of clay-like minerals. A number of relationships have been developed to describe ion-exchange equilibria, including equations based on the Guoy–Chapman model for the diffuse double layer (Eriksson, 1952). The most common description is made by analogy to a chemical reaction. For example, the exchange of a cation A^{n+} of charge n, dissolved in solution, for a monovalent cation B^+, associated with an adsorbent surface, can be written in terms of simple stoichiometry for a fixed-charge site, S^-, as:

$$A^{n+} + n(S^-)B^+ = (S^-)_n A^{n+} + nB^+. \qquad (20)$$
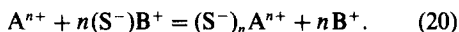
Continuing the analogy, a parameter corresponding in form to the mass law equilibrium constant but more correctly referred to as a "selectivity coefficient" can be defined in terms of the chemical activities of the species involved as:

$$K_B^A = \frac{(a_{S_n A})(a_B)^n}{(a_A)(s_{SB})^n}. \qquad (21)$$

Alternative formulations of this chemical reaction approach, such as the Gapon equation (Bolt, 1967), often employ concentrations instead of activities. Such formulations have been shown to agree with experimental data over narrow concentration ranges. The selectivity coefficients of the mass law approach are related to ion size, ion charge and mineral type. Exchange affinities for major soil cations generally increase with increasing charge and decreasing hydrated radius, often follow the Irving–Williams series (Sposito, 1984a), and are sensitive to molecular configuration.

Sorption reactions which occur on variable (*vis-à-vis* fixed) charged surfaces, such as soil organic matter, mineral oxides (SiO_2, Al_2O_3, TiO_2 and FeOOH) and on the edge sites of layered silicate minerals comprise another class of electrostatic interactions. The association of ions with these surfaces is hypothesized to occur through surface complexation or ligand exchange reactions analogous to those which occur in solution. The charges on these surfaces arise most commonly through protonation and

deprotonation reactions, and are thus highly pH dependent. Carboxyl and phenolic hydroxyl groups are the primary surface functional groups involved in surface complexation reactions on soil organic matter. The most abundant surface functional group participating in surface complexation reactions on oxide surfaces and clay minerals is the hydroxyl group, which is amphoteric and extremely reactive (Sposito, 1984a). It is the reactivity of such sites which induces a strong pH dependence for sorption of metal ions by natural solids.

A number of surface complexation models have been developed over the past several decades. These utilize mass law relationships and mass and charge balance equations to describe equilibria between solution species and surface complexes, and various hypotheses regarding the structure of the interfacial region to identify the location of surface complexes and describe the diffuse layer-charge potential relationship. General reviews are available in the literature (Sposito, 1984b; Barrow and Bowden, 1987). For purposes of illustration one such model, the Triple Layer Model (TLM), is briefly summarized here.

The triple layer model, in its current version (Hayes and Leckie, 1987), assumes that three planes of adsorption exist within the electrical double layer and that the charge at each plane results from surface complexation of ionic solutes. A schematic representation of the interfacial structure of the model is presented in Fig. 9. The σ^0 and σ^β planes shown in this figure are generally referred to as the inner and outer spheres, respectively. Metal ions are presumed to undergo either inner sphere or outer sphere reactions, depending on the affinity of these ions for the surface (Hayes and Leckie, 1987). In general, cations having lower hydrolysis constants and higher charge are more strongly adsorbed and undergo inner sphere reactions to form coordination bonds with surface sites. Cations which adsorb to a weaker extent, such as alkaline earth metals, undergo outer-sphere surface complexation reactions which result in ion-pair formation. Similarly, weak base anions form outer-sphere ion-pair bonds to surface sites and have the lowest affinity for oxide surfaces, adsorbing at relatively low pH values and only to the most acidic sites.
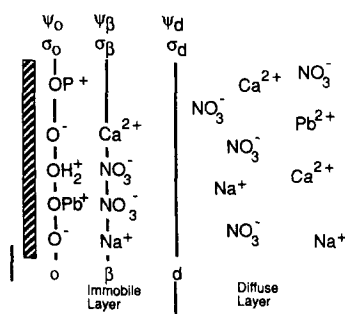

Fig. 9. Schematic representation of an electrical triple layer (adapted from Hayes and Leckie, 1987).

Conversely, strong base anions are postulated to undergo ligand exchange reactions with surface hydroxyl groups.

Examples of pertinent binding relationships are presented in Table 2. As shown, a diprotic representation of surface acidity has been assumed in which two inner sphere mass law equations can be written to describe the amphoteric properties of the surface sites. In conjunction with these, a number of outer-sphere electrolyte surface reactions have been proposed.

The TLM model utilizes the Stern–Grahame model (Grahame, 1947) for description of the electrical double layer and charge balances based on the reactions presented in Table 2 for each of the planes. Application of the model requires determination of the mass law constants, the surface density and the inner and outer layer capacitances. Methods for determination of these parameters have been summarized elsewhere (Kent et al., 1986).

Successful applications of ion association models for description of solution phase interactions have lent support to the notion that such an approach may provide an effective means for characterizing interactions between dissolved inorganic species and sorbent surfaces. Reservations exist, however, particularly with respect to how well the model corresponds to actual mechanism in stoichiometric and energetic relationships (Westall and Hohl, 1980; Morel et al., 1981) and because of the inherent complexity of natural surfaces.

4.2.2. Hydrophobic sorption

Hydrophobic interactions comprise the primary motivation for a large class of sorption reactions in the subsurface. The association of neutral, relatively nonpolar organic molecules with soils often results in quasi-linear equilibrium sorption patterns, and the magnitude of the associated coefficients often vary with the organic carbon content of the soil. The importance of soil organic matter in determining the extent of sorption of certain solutes, earlier evidenced by comparison of Figs 6 and 7, is dramatically illustrated in Fig. 10, which shows the sorption of lindane on a soil before and after the organic matter associated with that soil was removed with a strong oxidant (Miller and Weber, 1986). Such observations suggest that the sorption reaction may well arise from "partitioning" of the solute into an organic phase on the surface of or within soil particles or aggregates. The linear isotherm distribution coefficients (K_D) which result are often normalized by the fractional organic carbon content of the soil, ϕ_{oc}, to give an organic carbon normalized isotherm coefficient, K_{oc}:

$$K_{oc} = \frac{K_D}{\phi_{oc}}. \tag{22}$$

The K_{oc} then represents the hypothesized distribution coefficient for a sorbent composed entirely of organic carbon. Values for K_{oc} have been found to vary by a factor of only two or so for a wide range of soils and sediments (Schwarzenbach and Westall, 1981). This

Table 2. Triple Layer Model Reactions and Equilibrium Expressions

| Reaction	Equilibrium Expression
Surface protolysis reactions	
$SOH_2^+ \Leftrightarrow SOH + H^+$	$K_{a1}^{int} = \dfrac{[SOH][H^+]}{[SOH]_2^+} \exp(-F\Psi_0/RT)$
$SOH \Leftrightarrow SO^- + H^+$	$K_{a2}^{int} = \dfrac{[SO^-][H^+]}{[SOH]_2^+} \exp(-F\Psi_0/RT)$
Electrolyte surface reactions	
$SOH + Na^+ \Leftrightarrow SO^-\text{-}Na+ + H^+$	$K_{Na}^{int} = \dfrac{[SO\text{-}Na^+][H^+]}{[SOH][Na+]_2^+} \exp(-F(\Psi_0-\Psi_b)/RT)$
$SOH + H^+ + NO_3^- \Leftrightarrow SOH_2^+\text{-}NO_3^-$	$K_{NO3}^{int} = \dfrac{[SO\text{-}H_2^+\text{-}NO^{3-}]}{[SOH][H+][NO_3^-]_2^+} \exp(F(\Psi_0-\Psi_b)/RT)$
Outer-sphere surface reaction	
$SOH + Ca^{2+} \Leftrightarrow SO^-\text{-}Ca^{2+} + H^+$	$K_{Ca}^{int} = \dfrac{[SO\text{-}Ca^{2+}][H^+]}{[SOH][Ca^{2+}]_2^+} \exp(-F(\Psi_0-2\Psi_b)/RT)$
Inner-sphere surface reaction	
$SOH + Pb^{2+} \Leftrightarrow SOPb^+ + H^+$	$K_{Pb}^{int} = \dfrac{[SOPb^{2+}][H^+]}{[SOH][Pb^{+2}]_2^+} \exp(F\Psi_0/RT)$
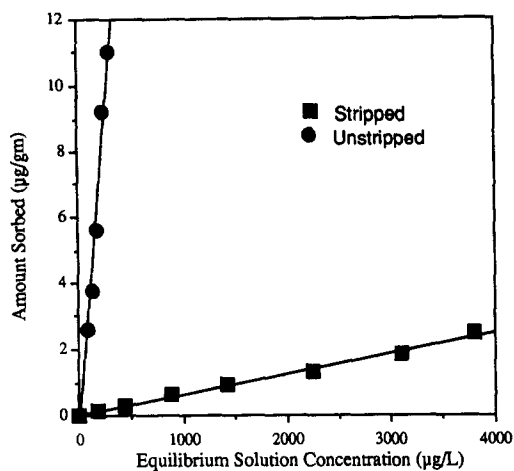
Fig. 10. Sorption of lindane on Ann Arbor I soil before (unstripped) and after (stripped) removal of soil organic matter in CMBR systems (after Miller and Weber, 1986).

variability has been linked to the nature of the organic material in the soil (Garbarini and Lion, 1986) and to concurrent mineral-site sorption (Karickhoff, 1984). The relative constancy of K_{oc} has strengthened the notion that the sorption of hydrophobic organic compounds onto soils may be likened to partitioning or absorption into a uniform organic phase (Chiou et al., 1983).

The importance of solute hydrophobicity in sorption reactions on soils and sediments has been confirmed qualitatively by numerous observations that K_{oc} values for particular solutes on a wide variety of such natural sorbents can be correlated reasonably well with the octanol/water partition coefficients of those solutes. One such correlation developed by Schwarzenbach and Westall (1981) is compared in Fig. 11 to our own experimental data for several different solutes and soils. It is apparent that the

correlation provides an approximation to the data trend, but that significant differences exist between "predicted" and observed values.

More rigorous evaluations of the sorption of hydrophobic organic compounds by soils has related that sorption to the organic matter associated with the soils. The organic carbon normalized distribution coefficient has been related to the partitioning between the aqueous solvent phase and the organic phase [recall equation (7)]:

$$K_{oc} \propto \frac{f_{i,1}}{f_{i,2}}. \tag{23}$$

Because of the relative uniformity of solute–soil organic interactions compared to solute–aqueous phase interactions, differences that exist between the activity coefficients, $f_{i,1}$, of various solutes in aqueous phase are likely to be much more significant than differences in the activity coefficients, $f_{i,2}$, for the same solutes in the sorbed phase (Karickhoff, 1984). Partitioning analyses of this type have been employed to relate the sorption of hydrophobic organic compounds to their partitioning behavior in octanol–water systems (Chiou et al., 1982) and their retention patterns in reverse-phase liquid chromatography systems (Chin et al., 1988).

The predictability of sorbed phase activity coefficients using Flory–Huggins polymer theory has also been examined. The organic phase is considered as an ideal polymer and deviations from ideal behavior due to size disparities between solute and the polymer molecules can be quantified (Chiou et al., 1983). This calculation relates the sorbed phase activity coefficient to the properties of the solute and polymer and an interaction parameter.

Predictions based on traditional partitioning theory frequently suffer to some degree from failure to account for the presence and role of macromolecu-
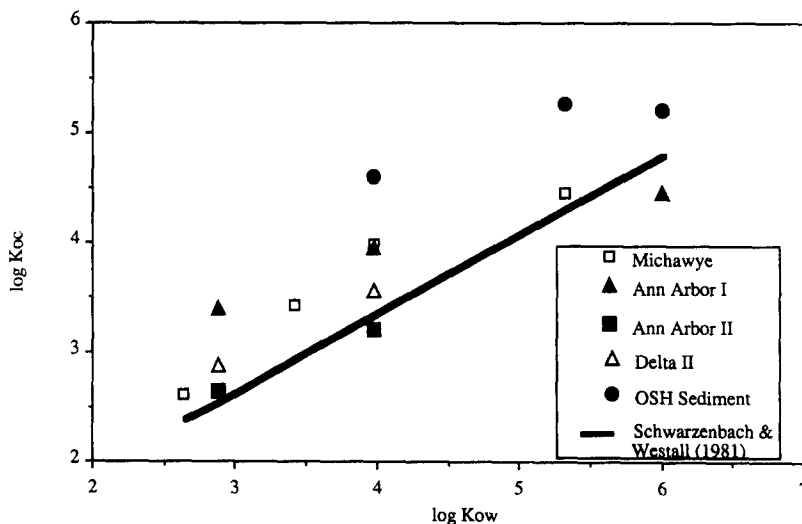

Fig. 11. Comparison for several different solutes of the relationship between partitioning coefficients for sorption by a variety of aquifer soils and sediments, normalized to organic carbon content, and the log octanol–water partition coefficient.

lar dissolved organic matter in the solvent phase. Natural "dissolved organic material" has been shown to increase the effective solubility of hydrophobic organic compounds (Carter and Suffet, 1983). This solubility enhancement has been ascribed to either alteration of the structure of the aqueous phase by the organic material or to a partitioning of solute into organic polymers (Chiou et al., 1986). This association can lead to a decrease in the extent of sorption of solutes on solid phases. Chin and Weber (1989) and Chin et al. (1991) have presented a three-phase binding model formulated on the basis of a modified Flory–Huggins equation for a dispersed polymer phase. Their comparisons of model predictions and experimental observations demonstrate, as might be expected, that decreases in sorption attributable to dispersed polymers in solution phase are most marked for relatively hydrophobic solutes.

The simple relationships discussed above for correlating hydrophobic solute sorption are applicable only to dilute aqueous systems. In severely contaminated subsurface systems, the properties of the solvent itself may change. Such changes in aqueous phase characteristics can be accounted for in the case of nonpolar molecules by relating the distribution coefficient in the mixed solvent system (K_D^M) to the coefficient in the pure aqueous system (K_D^W) through an expression developed from the general relationship between the magnitude of the "hydrocarbonaceous" surface area of the solute (HSA) and its aqueous phase incompatibility, according to the so-called "solvophobic theory" (Nkedi-Kizza et al., 1985):

$$\ln \frac{K_D^M}{K_D^W} = -\alpha \Delta \gamma' \frac{\text{HSA}}{kT} \beta^c. \qquad (24)$$

The term α is an empirical coefficient, $\Delta \gamma'$ is the difference between HSA/aqueous solvent, and HSA/co-solvent interfacial tensions, and β^c is the fraction of the organic co-solvent in the aqueous phase. Equation (24) describes the log-linear relationship which has been observed between solute sorption and the fraction of the co-solvent in the aqueous phase. It is difficult to apply the equation directly in many instances because the difference in these interfacial tensions must be determined experimentally. Values for this quantity for several co-solvent systems have been presented (Nkedi-Kizza et al., 1985).

Hydrophobic sorption models provide a convenient basis for prediction of sorption equilibria only for those classes of compounds which meet the assumed conditions. This implies relatively nonpolar, neutral solutes, and sorbents similar to those with which the correlations were developed; in general, soils and sediments with greater than 0.1% organic carbon content. The sorptive behavior of polar and ionic organic solutes often manifest significant deviations from the correlations presented, relating to differences in the forces responsible for the sorption reactions.

5. SORPTION RATE PROCESSES

Equilibrium relationships comprise a set of limiting conditions for sorption processes, a set of conditions predicated on there being sufficient time for a system to achieve thermodynamic stability. In practical systems, however, the time scales associated with attainment of this condition may approximate or exceed time scales associated with changes in solute concentrations due to macroscopic transport processes (i.e. advection and dispersion). Under such conditions, the rates at which equilibrium is approached may significantly affect the process and the distribution of contaminants among the phases of the system. Whereas the extent of sorption is dependent only on the initial and final equilibrum states, rates of sorption depend on the path leading from the initial to the final state. In porous media, these paths include events that are controlled either chemically or by molecular-level mass transport. Molecular-level mass transfer refers in this context to stationary phase diffusion processes, as differentiated from the fluid-associated macro-scale transport processes of advection (convection) and hydrodynamic dispersion. The influence of these latter processes is addressed in the final section of this paper. At this point, however, it is appropriate to consider in detail the two molecular processes that control rates of adsorption at the microscopic level; that is, reaction rate and local mass transfer.

5.1. Reaction rate control

Chemical reaction rates depend on the nature of specific interaction(s) that occur between the solute and sorbent in the sorption process. Physical sorption processes are generally rapid, with local (site) equilibrium being achieved within milliseconds or, at most, seconds. The larger activation energies associated with other types of sorption (e.g. chemisorption) may, however, lead to slower rates. The fundamental basis for molecular characterization of reaction kinetics is the law of mass action, which states that the rate of an elementary homogeneous chemical reaction is directly proportional to the product of the masses (more rigorously, activities) of the reacting species. While sorption reactions are clearly not homogeneous and rarely elementary, it is possible to draw a stoichiometric analogy. The stoichiometry for a reaction involving a sorbate molecule, A, and a sorbent site, S, may be characterized schematically as:

$$A + S \leftrightarrow A\text{–}S. \qquad (25)$$

The term A–S represents the sorbed complex, denoted in this particular case as the association of one mole of A with 1 mole of S. For the simple case in which only one reacting species and only one type of site are involved in a one-step chemical reaction, the law of mass action analogy suggests that the forward

rate or "velocity" of sorption, v_F, will be second order and of the form:

$$v_F = k_F C_A C_S. \tag{26}$$

The parameter k_F is the time-independent constant of proportionality or rate constant, and C_A and C_S represent the mass concentrations of A and S, respectively, at any time. Similarly, the rate of desorption, v_R, is defined in terms of a desorption rate constant, k_R, and the mass concentration of site-associated molecules of sorbent at any time, C_{A-S}:

$$v_R = k_R C_{A-S}. \tag{27}$$

The net rate of sorption, and thus the time rate of sorbate uptake in a completely mixed batch reactor (CMBR) system, is then given by the difference between the rates of the forward and reverse reactions, or:

$$v_{net} = \frac{dC_{A-S}}{dt} = -\frac{dC_A}{dt}$$

$$= v_F - v_R = k_F C_A C_S - k_R C_{A-S}. \tag{28}$$

It is evident that rate models based on the laws of thermodynamics must have an equilibrium boundary condition consistent with the assumptions underlying the rate law derivation. For the rate model expressed by equation (28), setting the left side to zero (i.e. the net rate of sorption is zero at equilibrium) yields:

$$k_F C_A C_S = k_R C_{A-S}. \tag{29}$$

Upon rearrangement equation (29) gives an effective "equilibrium constant" for the stoichiometric analogy [equation (25)] drawn for this sorption reaction:

$$\frac{k_F}{k_R} = \frac{C_{A-S}}{C_A C_S} = K_{eq}. \tag{30}$$

A mass balance on the total number of surface sites, C_T, gives:

$$C_T = C_{A-S} + C_S. \tag{31}$$

When equations (30) and (31) are then combined, an equation having the same general form as the Langmuir isotherm results [compare to equation (11) for $C_{A-S} = q_e$, $C_T = Q^0$, and $K_{eq} = b$]:

$$C_{A-S} = \frac{C_T K_{eq} C_A}{1 + K_{eq} C_A}. \tag{32}$$

A first-order approximation to the forward rate law given in equation (26) can be employed in cases where the number of surface sites is sufficiently greater than the number of solute molecules that C_S in equation (26) can be considered constant. Thus, a pseudo-first-order rate law is assumed for the forward reaction rate:

$$v_F = k_F C_S C_A = k_F' C_A. \tag{33}$$

The resulting expression for the overall rate of reaction, v_{net}, is then:

$$\frac{dC_{A-S}}{dt} = v_{net} = k_F' C_A - k_R C_{A-S}. \tag{34}$$

For an element of saturated porous media having a porosity ϵ and a solid phase density ρ_s, and letting q represent the quantity of sorbate, A, associated with a unit mass of sorbent, the rate of sorbate uptake can be expressed as:

$$\frac{dq}{dt} = k_F' \frac{\epsilon}{\rho_s(1-\epsilon)} C_A - k_R q. \tag{35}$$

Rate expressions derived from mass action analogies provide only first approximations to the true form of sorption rate relationships. Experimentally determined reaction orders and coefficients seldom correspond to those implied by the reaction stoichiometry and associated equilibrium energy state. The fact that experimental data for any particular system may be fit by a given rate expression is not sufficient evidence that the molecularity of the reaction is that implied by the rate expression.

The simplicity of the rate expressions given above results in part from the inherent assumption that chemically equivalent reaction rates obtain for all sorption sites. The fact that natural sorbents frequently exhibit functionally nonuniform surfaces means that empirical application of the simplified rate expressions frequently involves determination of sample-averaged coefficients, which may not be applicable beyond the condition of experimental measurement. To counter this potential deficiency, a number of heterogeneous reactive site rate models have been suggested. These take a variety of forms, some of which are summarized in equations (36)–(38) below.

(1) Two site models, for example, where rapid adsorption onto one type of site is accompanied by a slower reaction onto a second type of site:

$$\frac{dq}{dt} = k_{F1}' \frac{\epsilon}{\rho_s(1-\epsilon)} C_A$$

$$+ k_{F2}' \frac{\epsilon}{\rho_s(1-\epsilon)} C_A - k_R q. \tag{36}$$

(2) Models in which a continuous and specific range of site reactivities are hypothesized, such as the Elovich equation (Travis and Eitner, 1981):

$$\frac{d(q/q_e)}{dt} = B_1 \exp\left(-B_2 \frac{q}{q_e}\right). \tag{37}$$

(3) Expressions similar to the simple rate laws with additional parameters included, such as a nonlinear first-order rate equation:

$$\frac{dq}{dt} = k_F' \frac{\epsilon}{\rho_s(1-\epsilon)} C^n - k_R q. \tag{38}$$

These models usually derive from some presumed mechanism and set of related assumptions. As emphasized in the discussion of equilibrium isotherm models and reiterated above, however, the fact that they may give reasonable representation of experimental data in any given application does not necessarily mean that the associated assumptions and implied mechanisms are verified for the application.

5.2. Mass transfer

Effective rates of sorption in subsurface systems are frequently controlled by rates of solute transport rather than by sorption reactions *per se*. In general, mass transport and transfer processes operative in subsurface environments may be categorized as either "macroscopic" or "microscopic". In the content of this discussion, macroscopic transport refers to movement of solute controlled by movement of bulk solvent, either by advection or hydrodynamic (mechanical) dispersion. By distinction, microscopic mass transfer, the focus of the discussion, refers to movement of solute under the influence of its own molecular or mass distribution.

One of the fundamental steps involved in characterizing and modeling microscopic mass transfer is appropriate representation of associated resistances or impedances, including relevant distances over which solute is transferred and relevant properties of the medium through which transfer occurs. The nature and characteristics of such resistances vary with local conditions associated with particular combinations of sorbent, solute, fluid, and system configuration. Differences in local conditions and associated transport phenomena are typified in subsurface systems by differences between solute transport through the interstitial cracks and crevices of rocks or soil particles, through organic polymer matrices associated with soils, and through internal fluid regions of soil aggregates. Mathematical descriptions of microscopic impedances and mass transfer processes within fluid and sorbing phases are generally structured upon one of several different types of conceptual models, tailored as necessary for a particular circumstance by appropriate assumptions and constraints regarding initial and boundary conditions and system behavior or state.

These same conceptual models comprise the basis for a wide range of process descriptions in a variety of natural and engineered environmental systems. Mass transfer typically controls overall rates of aeration and reaeration in natural waters; evolution and dissolution of volatile compounds from solids and liquids; dissolution of solid substances and non-aqueous phase liquids into water; and treatment operations involving stripping, solvent extraction, membrane separations, ion exchange and adsorption processes. In such cases the specific modeling and/or design relationships for these processes are predicated on one or more of the several different conceptual models described below (see, for example, various process model developments in Weber, 1972).

5.2.1. Conceptual models

Models for describing microscopic mass transfer are generally predicated on assumptions regarding predominant or controlling transport mechanisms operating within specific types of media or domains. Microscopic mechanisms of mass transport in fluid phases include diffusion of solute molecules through elements of fluid and solute transport facilitated by molecular-scale movement of fluid elements at or within fluid phase interfaces (surface renewal) and across microscopic velocity gradients (Taylor dispersion). The particular mass transfer mechanism which predominates in any situation depends on the properties of the solute and the medium comprising the domain, and on the microscopic hydrodynamics of the flow regime. Under fluid flow conditions typical of subsurface systems, molecular diffusion generally dominates microscopic mass transfer. Molecular diffusion can be either random ("Fickian") or constrained ("Knudsen") by the boundaries of the medium, such as surfaces bounding pore spaces. Knudsen diffusion occurs when both molecular velocities and ratios of longitudinal to radial pore lengths are high, and can be significant in gas phase mass transfer operations. Molecular diffusion in liquid phase is, however, generally controlled by Fickian motion. In this type of diffusion, the velocity at which solute migrates along a linear path within a particular coordinate system is directly proportional to the gradient in its chemical potential, μ_i, along the path; that is, to the thermodynamic "driving force". As noted previously, the chemical potential of a substance is directly related to its activity and, in dilute aqueous solutions, to its concentration, C_i. It follows then that the time rate of solute mass flow by diffusion along a path, x, and across a normal (perpendicular) unit cross-sectional area (i.e. a one-dimensional flux) is directly proportional to the solute velocity, and thus to the gradient concentration. For point-wise instantaneous diffusion, this flux, $F_{i,x}^0$, is then given by:

$$F_{i,x}^0 = -D_1 \frac{\partial C}{\partial x}. \tag{39}$$

Equation (39) expresses Fick's first law for diffusion under non-steady state conditions. For liquid phase diffusion the constant of proportionality, D_1, is termed the free liquid diffusion coefficient, most commonly referenced to the aqueous phase.

The driving force, $\partial C/\partial x$, in equation (39) may relate to either a constant or instantaneous difference in mass concentration across a homogeneous layer or "film" of fixed size (i.e. $\Delta x = \delta$), or to a time-variable concentration profile along a continuous path of variable length. The proportionality constant or

diffusion coefficient is affected by various factors which relate to molecular interactions between the solute and the solvent, including the size, configuration and chemical structure of the diffusing molecule and the chemical structure and physical properties (e.g. viscosity) of the liquid. Values of D_1 for diffusion of typical organic contaminants in pure aqueous solutions generally fall in the range 0.5–5.0×10^{-5} cm^2/s. It should be noted, however, that the diffusion of any solute through interfacial aqueous regions between fluid and/or sorbent phases may involve resistances or impedances which differ from those of pure water. These differences arise because the properties of interfacial regions often reflect molecular interactions between adjacent bulk phases. The magnitude of the diffusion coefficient for a solute in an interfacial domain reflects these variations. For example, the accumulation of molecules other than those of the diffusing solute in an interface can increase resistance to transfer and yield a decreased diffusion coefficient, or drag forces near surfaces may effect reductions in diffusion coefficients in interfacial regions between liquid and solid phases.

Models depicting microscopic molecular transport of conservative (non-reactive) substances in homogeneous or single-phase domains involve relatively straightforward applications of equation (39). These are referred to here as Type I models. If the domain is homogeneous but also involves a reaction of the species being transported, the transport is described by a Type II model. Transport in heterogeneous domains (multi-phase) is described by either Type III or Type IV models, depending upon whether solute reactions are involved.

5.2.1.1. Type I domains and models

Models to describe mass transfer rates in any particular system typically incorporate the instantaneous point-form description of diffusion given in equation (39) in the appropriate mass balance or continuity equation for that system. For transport of a conservative solute through a diffusion domain such as that depicted schematically in Fig. 12, the mass continuity relationship states that the time rate of change in mass within the domain is given by the

difference between the mass fluxes into and out of that domain. Thus, for a domain of volume V, length Δx, and unit cross-sectional area:

$$V\left(\frac{\Delta C}{\Delta t}\right)_V = F^0_{i,x}|_x - F^0_{i,x}|_{x+\Delta x}. \qquad (40)$$

In the limit ($\Delta x \to 0$, $\Delta t \to 0$), equation (40), takes the form:

$$\left(\frac{\partial C}{\partial t}\right)_V = \frac{\partial}{\partial x}(-F^0_{i,x}). \qquad (41)$$

In Type I models the only impedance to mass transfer arises from the uniform resistance of a homogeneous medium over a straight-line distance of travel. Adaptation of the general schematic given in Fig. 12 to this particular type of mass transfer is represented by Fig. 13. In this case the flux associated with the microscopic mass transfer process is defined by Fick's first law, equation (39), and equation (41) can be written:

$$\left(\frac{\partial C}{\partial t}\right)_V = \frac{\partial}{\partial x}\left(D_1 \frac{\partial C}{\partial x}\right). \qquad (42)$$

If there is no net accumulation of solute in the diffusion domain (i.e. steady-state) the left-hand side of equation (42) is zero and integration yields a constant gradient in concentration across the domain; that is, a linear driving force for mass transfer. If in a given system the spatial integration applies to a fixed distance $\Delta x = \delta$, then a steady-state constant flux over this distance can be represented in terms of the upgradient and downgradient boundary concentrations, C_0 and C_δ respectively, and a solute velocity or mass transfer coefficient, k_f, as follows:

$$(F^0_{i,x})|_{x=0} = -D_1 \frac{(C_\delta - C_0)}{\delta}$$

$$= \frac{D_1}{\delta}(C_0 - C_\delta) = k_f(C_0 - C_\delta). \qquad (43)$$

It is apparent from equation (43) that this "linear driving force" model for mass transfer is similar in form to a first-order reaction rate equation, and its solution can be approached in similar fashion.
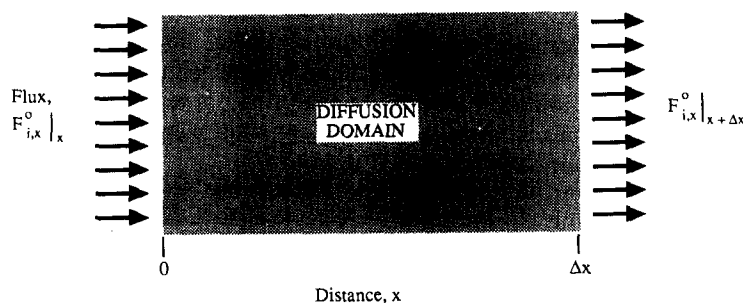

Fig. 12. Schematic depiction of a diffusion domain for application of the mass continuity equation.
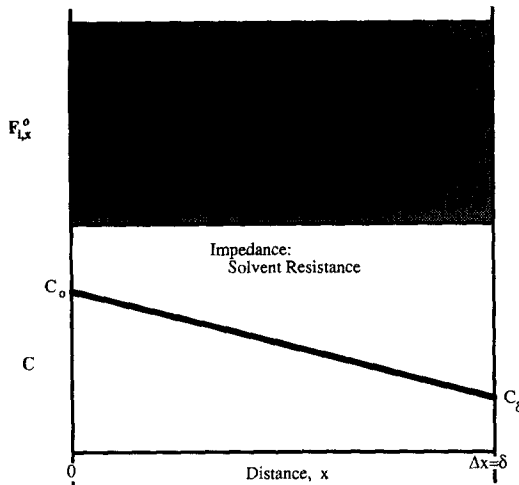
Fig. 13. Schematic representation of solute migration and steady-state concentration profile for a Type I diffusion domain.

It is imperative to note that the mass transfer coefficient and concentration relationship given in equation (43) have been developed for, and apply strictly only to, steady-state diffusion in a homogeneous medium in which there is no impedance to diffusion other than that provided by resistance of the medium to movement of solute molecules. Other types of solute diffusion involving non-steady conditions, concurrent reactions, sorption and accumulation, and/or tortuous paths around obstacles, involve additional impedances and require different model formulations. This is emphasized here because expressions of the same general form as that given in equation (43) are often employed as expedients to estimate mass transfer in more complex systems. When this is done, the gradient in concentration in the more complex system may in fact not remain constant, and the mass transfer coefficient may implicitly include factors other than just the free liquid diffusion coefficient and a fixed diffusion distance, factors not specifically identified and/or quantified. Under such circumstances the model, even if it can be fitted well to a particular data set, becomes a condition-specific relationship which may have limited utility for any application other than characterizing that data set.

5.2.1.2. Type II domains and models

In some cases of mass transfer a solute may be subject to depletion by reactions such as hydrolysis or oxidation during the course of its diffusion through a particular domain. These reactions can be included in the continuity expression developed above, leading to Type II models of the general form:

$$\left(\frac{\partial C}{\partial t}\right)_V = \frac{\partial}{\partial x}\left(D_1 \frac{\partial C}{\partial x}\right) - \left(\frac{\partial C}{\partial t}\right)_r \qquad (44)$$

where $(\partial C/\partial t)_r$ is a reaction velocity rate relationship of one of the types discussed previously in the section

on chemical kinetics. For a first-order irreversible reaction with a rate constant, k, for example $(\partial C/\partial t)_r = v = kC$.

As illustrated in Fig. 14 for steady-state conditions and boundary conditions identical to those given in Fig. 13 for the Type I model, the gradient in concentration, and thus the flux, varies across the domain as a result of the continued depletion of solute. For steady-state transfer across a fixed diffusion domain, δ, coupled with a complete depletion of solute by first-order irreversible reaction within the domain, solution of the flux relationship at the upgradient boundary of the domain yields:

$$(F^0_{i,x})|_{x=0} = \frac{D_1 C_0}{\delta}\left[\frac{\delta(k/D_1)^{0.5}}{\tanh \delta(k/D_1)^{0.5}}\right] \qquad (45)$$

where $\delta(k/D_1)^{0.5}$ in equation (45) is the Thiele modulus and the ratio $[\delta(kD_1)^{0.5}/\tanh \delta(k/D_1)^{0.5}]$ is the dimensionless Hatta number, which characterizes the relative significance of the reaction and diffusion processes. As the Hatta number increases with increasing values of the reaction rate coefficient, k, the denominator in equation (45) approaches unity and the flux at the boundary becomes:

$$(F^0_{i,x})|_{x=0} = (kD_1)^{0.5}C_0. \qquad (46)$$

Comparison of equation (46) to equation (43) for a value of $C_\delta = 0$ indicates that the reaction term effectively renders the flux, and therefore the mass transfer coefficient, proportional to the square root of the free liquid diffusion coefficient rather than to the diffusion coefficient itself. This underscores the level of error which might be introduced by using a Type I model formulation to represent a Type II mass transfer process without specifically characterizing the relative effects of reaction(s) and mass transfer.
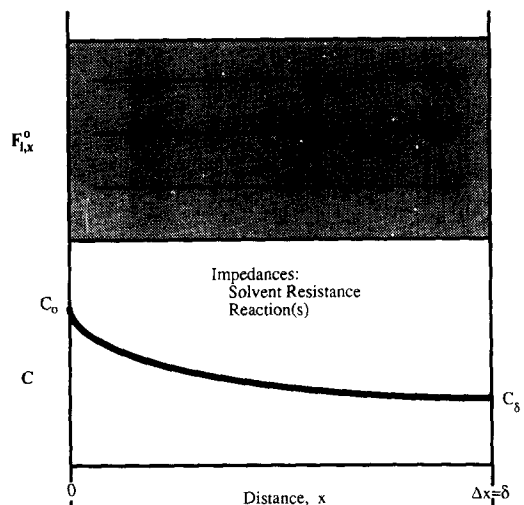

Fig. 14. Schematic representation of solute migration and steady-state concentration profiles for a Type II diffusion domain.

5.2.1.3. Type III domains and models

Transport of a solute across a diffusion domain can also be altered by constraining movement of the solute to specific flow paths. These conditions generally occur when diffusional transport through a heterogeneous (multiple phase) medium is restricted to certain regions or is more rapid through particular pathways, as illustrated schematically in Fig. 15. The mass transfer expression for diffusion in a Type III domain is similar to that for Type I, with the notable exception that the mass transfer coefficient now becomes a composite or "effective" parameter that reflects both the increased path length and the path constrictions which alter transport of the solute in the domain. The increased path length can be quantified as the ratio of the actual to the shortest path through the domain, a ratio frequently termed the "tortuosity" (Giddings, 1965). Constrictions of flow paths can further increase impedance to transport. When solute transport is restricted to the fluid-filled fraction of the domain (volumetric water content), θ_w, and both tortuosity and constriction effects are lumped in an apparent or effective diffusion coefficient, D_e, application of the mass continuity expression to the Type III domain leads to a modified form of equation (42):

$$\left(\frac{\partial C}{\partial t}\right)_{V,\theta_w} = \theta_w \left(\frac{\partial C}{\partial t}\right)_V = \frac{\partial}{\partial x}\left(\theta_w D_e \frac{\partial C}{\partial x}\right). \quad (47)$$

If the void space is saturated with water, then the value of θ_w is equal to the porosity, ϵ, and equation (47) can be expressed as:

$$\left(\frac{\partial C}{\partial t}\right)_V = \frac{1}{\epsilon}\frac{\partial}{\partial x}\left(\epsilon D_e \frac{\partial C}{\partial x}\right). \quad (48)$$

If the spatial gradient of porosity is very small, which is most commonly the case, ϵ can be brought out of the derivative term and cancelled out in equation (48). The concentration profile shown in Fig. 15 for diffusion to a Type III domain under steady-state
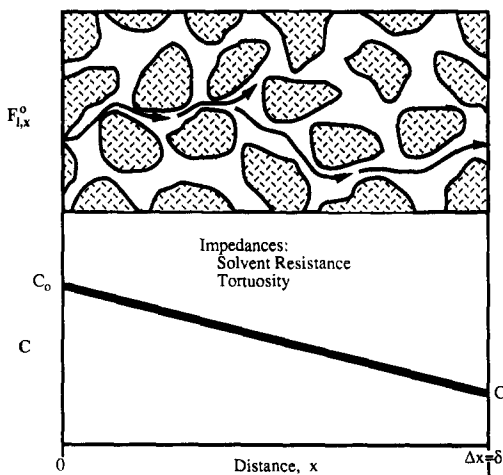
conditions is similar to that of Fig. 13 for diffusion in a Type I domain, and the flux relationship can be obtained in a manner analogous to that used to develop equation (43), yielding:

$$(F^0_{i,x})|_{x=0} = k_e(C_0 - C_\delta). \quad (49)$$

The effective mass transfer coefficient, k_e, in equation (49) now combines the effective diffusivity of the solute and the characteristic length of the domain.

5.2.1.4. Type IV domains and models

The heterogeneous domains associated with Type IV mass transfer processes involve combinations of the interactions described for Type II and Type III models. As depicted in Fig. 16, the diffusion paths are tortuous and constricted and there are reactions such as sorption and catalyzed transformation with the surfaces of impermeable or semi-permeable phases in the domain which further impede solute transport. For the case of transport through a Type IV domain in which the only reaction is sorption of solute by a solid phase of density ρ_s, the steady-state continuity equation can be expressed in a form analogous to equation (44) for the Type II domain, but the reaction term $(\partial C/\partial t)_r$ is now related to, and expressed in terms of, the rate of change of the solid phase concentration, q, as follows:

$$\left(\frac{\partial C}{\partial t}\right)_r = \frac{(1-\epsilon)}{\epsilon}\rho_s \frac{\partial q}{\partial t}. \quad (50)$$

The mass continuity expression for diffusion in a Type IV domain then combines equation (50) with the expression developed in equation (48) for the Type III domain, yielding:

$$\left(\frac{\partial C}{\partial t}\right)_V = \frac{1}{\epsilon}\frac{\partial}{\partial x}\left(\epsilon D_e \frac{\partial C}{\partial x}\right) - \frac{(1-\epsilon)}{\epsilon}\rho_s \frac{\partial q}{\partial t}. \quad (51)$$

Again, ϵ can be factored out of the first term on the right side of equation (53) if the spatial gradient of

Fig. 15. Schematic representation of solute migration and steady-state concentration profile for a Type III diffusion domain.
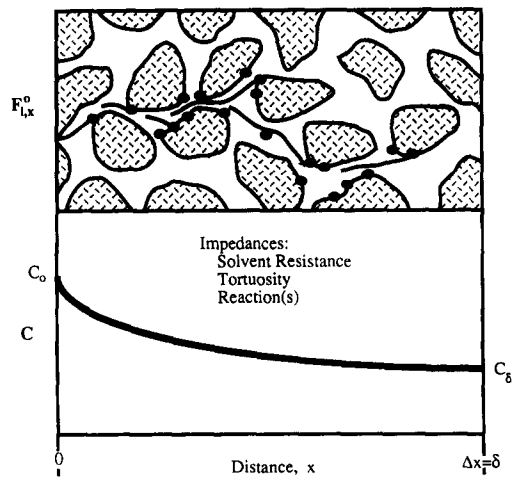

Fig. 16. Schematic representation of solute migration and steady-state concentration profile for a Type IV diffusion domain.

porosity is very small. A general schematic concentration profile for steady-state diffusion in a Type IV domain is shown in Fig. 16. It is apparent from equation (51) that the relative rates of solute sorption and diffusion dictate the extent to which the concentration profile, and therefore flux, decreases with distance through the domain pictured in Fig. 16. It is also apparent that more strongly sorbed solutes will exhibit a greater retardation in overall rates of migration through such domains.

5.2.2. Application considerations

Subsurface systems are often comprised by multiple diffusion domains of different types and degrees of impedance. As a consequence, mass transfer processes associated with sorption reactions in such systems frequently involve two or more consecutive diffusion steps. It is generally the case, however, that one of these steps is significantly slower than the others, and is therefore "rate determining" or "rate limiting". Identification and characterization of the step which controls overall rate in any given situation greatly facilitates the process of modeling. Indeed, because of the potential mathematical and parameter evaluation complexities otherwise involved, it is in many cases an imperative aspect of model implementation. Once a rate determining step has been identified, models of the type presented above can be adapted to the particular boundary and state conditions appropriate for the system in question.

A further complication of real systems is that solute concentrations in domains of interest in such systems are generally time dependent, thus application of the steady-state forms of the various models developed above are seldom rigorously applicable. While departures from the boundary conditions associated with development of these models take various forms and yield different degrees of non-steady-state in real systems, practical approximations can frequently be made using certain quasi-steady-state approaches.

5.2.2.1. Quasi-steady-state models

The condition of true steady-state requires that the boundary concentrations of a domain, as well as the contributions of all sink and source terms, remain constant in time. If this requirement is not met, it may still be reasonable to assume a quasi-steady condition over time periods and/or for other specific conditions for which the solute flux through the domain is large compared to the rate of change in boundary concentrations. Quasi-steady-state modeling approaches are predicated on the assumption that the concentration profile remains approximately linear throughout the domain, even though the concentration at one or both of the boundaries varies with time. The rate of change of concentration at a domain boundary is usually dependent on the rate of concentration change in the phase adjacent to the domain, which may relate either to advective flow in/out of, or

accumulation/depletion within, the adjacent domain. This discussion focuses on situations involving accumulation in the downgradient domain because that condition pertains most directly to microscopic transport processes associated with sorption reactions in subsurface systems.

A simplified representation of diffusion through a Type I domain of fixed depth δ, cross-section A, and constant upgradient boundary concentration into an absorbing domain of volume $\forall$ is shown in Fig. 17. The instantaneous rate of change in solute concentration, q, in an absorbing domain having a density $\rho_\forall$ is given by:

$$\frac{\partial q}{\partial t} = \frac{A}{\forall \rho_\forall} \frac{D_1}{\delta} (C_0 - C_\delta). \tag{52}$$

The accumulation of solute in the absorbing domain results in a change in its concentration at the interface between the two domains; that is, the downgradient concentraion of the diffusion domain, C_δ. If the sorption process is linear and a local equilibrium state is maintained between the two domains, then the instantaneous rate of change in C_δ can be related to $\partial q/\partial t$ by a simple distribution coefficient, K_D [see equation (10) and ensuing discussion]. Thus:

$$\frac{\partial C_\delta}{\partial t} = \frac{A}{\forall} \frac{D_1}{\delta K_D \rho_\forall} (C_0 - C_\delta) = \frac{k_\alpha}{K_D \rho_\forall} (C_0 - C_\delta). \tag{53}$$

The effective mass transfer coefficient, k_α, in equation (53) incorporates the cross-sectional area of the diffusion domain, the diffusivity of the solute and the volume of the absorbing domain, and has the dimensions of inverse time. If the sorption process is not
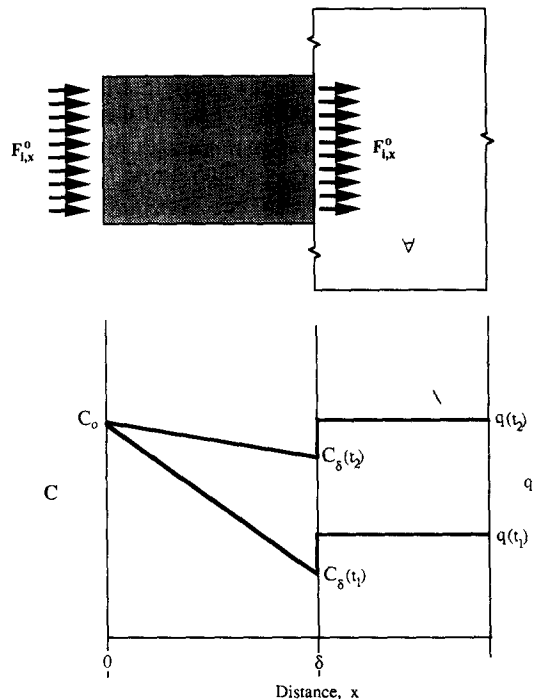

Fig. 17. Schematic representation of solute migration and temporal concentration profiles for a Type I domain with absorption in an adjacent region.

specifically characterized, experimentally measured values of k_α may also incorporate by default the effect of solute partitioning. In any case, this coefficient, which generally must in fact be determined empirically, is highly system-specific and thus restricted in applicability.

It is apparent from equation (53) that a number of concentration-independent factors impact the magnitude of $(\partial C_\delta / \partial t)$. If these factors are such that the change in C_δ over the period of interest is small relative to the difference in upgradient and downgradient concentrations (i.e. large K_D, small k_α), then solute migration through the diffusion domain can be approximated as a quasi-steady-state process. If this approach is applied to systems for which the assumption is inappropriate, the effective mass transfer coefficient k_α (or k_α / K_D) typically will be found to vary with time, and thus be even further restricted in applicability to other than the exact circumstances for which it was measured. Models which incorporate such parameters are necessarily limited in their ability to predict mass transfer behavior for alternative conditions, and are essentially restricted to data analysis and event simulation applications.

Quasi-steady-state mass transfer models based upon assumptions similar to those discussed above have been applied to describe the transfer of solute between two different phases, the transport of solute between fluid regions through relatively small pores, and solute transfer into intraparticle or aggregate regions. These models generally relate the flux through and out of one of the types of domains discussed to the rate of change in the solute concentration of the adjacent phase, whether the phase is a fluid or a solid.

Application of this modeling approach to description of solute mass transfer across a hypothesized Type I immobile "boundary" layer of fluid immediately adjacent to the external surfaces of a sorbent yields the so-called "external film model". This particular mass transfer step has been taken as rate determining in many modeling descriptions of solute uptake from bulk solution by liquid and solid sorbents. As illustrated in Fig. 18 for adsorption from solution at the exterior surfaces of a spherical solid sorbent, "film" transport is governed by a combination of an effective boundary layer thickness and a molecular diffusivity of the solute within the layer. In practice, the concentrations, C_0 and C_δ, of solute at the boundaries of the film in a modeling scenario similar to that depicted in Fig. 18 are typically taken as the solute concentration in the adjacent bulk fluid phase and the solute concentration corresponding to instantaneous equilibrium with the solid phase at the sorbent surface, respectively. The flux through the film is then expressed using a quasi-steady-state model for a Type I domain of thickness δ and cross-sectional area controlled by the dimensions of the particle surface. If the spherical solid particle shown in Fig. 18 has a radius R_p and density ρ_s, then the time
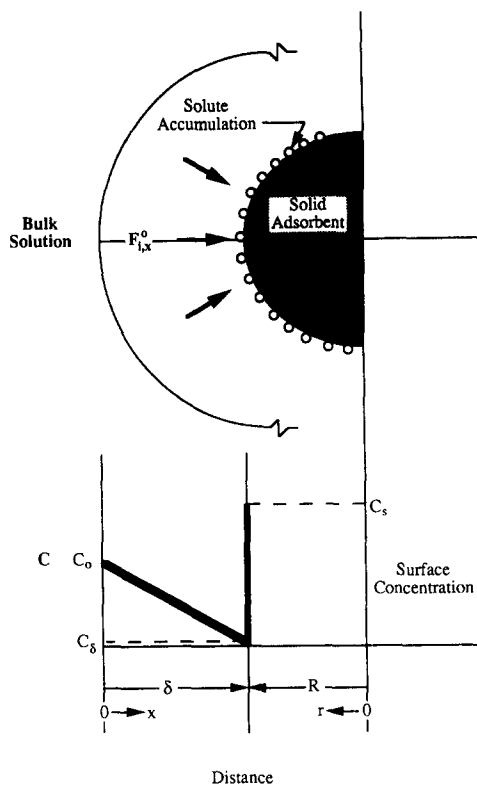

Fig. 18. Schematic representation and concentration profile for a film model to describe adsorption of solute by a spherical solid adsorbent.

rate of change of the mass averaged (mass/mass) sorbent phase concentration, q, can be expressed as:

$$\frac{dq}{dt} = \frac{3}{R_p \rho_s} k_f (C_0 - C_\delta). \tag{54}$$

The driving force for mass transfer will obviously vary as sorption proceeds, but if the gradient in concentration across the film is steep and the sorbent strongly sorbing, the use of a quasi-steady-state model for describing flux across the film region is not unreasonable.

In this application the film transfer coefficient, k_f, incorporates the diffusion of the solute in the medium surrounding the sorbent and the thickness of the film separating the sorbent surface from the bulk solution. When the boundary layer is a Type I domain comprised by the same material (e.g. water) as the bulk liquid, then the free liquid diffusivity can be employed. The film thickness, however, is ill defined and not readily determinable. Indeed, in many ways "film thickness" is more a conceptualization than a true physical dimension. The combined form, the mass transfer coefficient, k_f, can in some cases be measured experimentally, or otherwise estimated by means of semi-empirical correlations which define functional relationships between k_f and such physical system properties as mass flow rate, free liquid diffusivity of the sorbate, particle dimensions and in the case of porous media, ϵ, or porosity.

Quasi-steady-state models have been applied to estimate solute flux into the internal voids of porous non-sorbing solids and other heterogeneous domains. Goodknight *et al.* (1960) and Coats and Smith (1964), for example, have employed such models to describe solute transfer into regions internal to an aggregated soil. In these instances, rates of change in concentration in the "immobile" internal fluid regions of the aggregates were described in terms of mass transfer through a Type III domain. A conceptualization of this type of model, sometimes termed a "bicontinuum model", is given in Fig. 19.

It is apparent that the representation given in Fig. 19 assumes no preferential partitioning of solute between the mobile and immobile fluids, although that condition can be accommodated by incorporating an appropriate partitioning relationship [(again, see equation (10) and related discussion]. Conceptual representations similar to that pictured in Fig. 19 have been applied to describe contaminant sorption and related transport in soil columns by assuming the overall rate limitation for removal of solute from bulk mobile fluid to be diffusion into immobile fluid regions associated with interstitial spaces or internal regions of soil aggregates (van Genuchten and Wierenga, 1976). In such cases, the flux into the immobile regions under quasi-steady-state conditions is equal to the rate of change in the sum of the immobile fluid and sorbed phase concentrations. If the contaminant is distributed uniformly throughout the immobile region, the fluid phase concentration of the region is characterized by the concentration, C_δ, at its interface with the diffusion domain. The solute accumulation in an immobile solute sorbing region having a porosity ϵ, a solid-

phase density ρ_s and a sorbed phase concentration q_δ can then be written

$$\frac{k_e A_e}{V}(C_0 - C_\delta) = k_\alpha(C_0 - C_\delta)$$

$$= \epsilon \frac{\partial C_\delta}{\partial t} + \rho_s(1 - \epsilon)\frac{\partial q_\delta}{\partial t}. \quad (55)$$

The overall mass transfer coefficient, k_α, incorporates the effective cross-sectional area, A_e, of the diffusion domain; that is, the portion of the total cross-section of the domain available for fluid phase diffusion. It also incorporates the volume, $V_{IM} = V$, of the immobile region, and thus has the dimensions of inverse time (similar in this regard to a first-order rate coefficient). This coefficient is dependent on the physical characteristics of the internal region (i.e. internal tortuosity) and the solute diffusivity, in accordance with the Type III domain through which solute is transferred to the immobile region.

A characteristic feature of the mobile/immobile region models discussed above is that they assume a linear concentration gradient across the diffusion domain and a uniform internal concentration. In reality, however, when the dimensions of the internal region and the flow path are of similar magnitudes, for example, it is unlikely that the dual assumptions of steady-state transport within the diffusion domain and uniform concentration within the internal region will be met (Coats and Smith, 1964). In such instances, the overall mass transfer coefficients associated with models which do not specifically accommodate these conditions will vary with time as continued transport into the immobile region continues (Rao *et al.*, 1980a). The same limitations apply to models structured on the basis of transport in Type IV domains. Application of quasi-steady-state assumptions are in these instances further constrained to situations in which either the reaction rates or thermodynamics yield only small changes in solute concentrations in the immobile region relative to the flux across the domain. As an approximation for either Type III or Type IV domains, it may be reasonable to consider the flux into the heterogeneous domain within regions of a particle or aggregate proportional to the difference between the external or mobile concentration and a volume averaged internal or immobile concentration (Gluekhauf and Coates, 1947). While this approximation may be valid for certain situations, sorption and/or accumulation must be taken into account. As a result, applications of quasi-steady-state models in such situations again often yield highly system-specific approximations.

5.2.2.2. Non-steady-state models

More accurate and general representations of complex mass transfer processes may be obtained by employing non-steady-state models to describe solute transport. The continuity expression for mass transfer by diffusion within the domain leads to
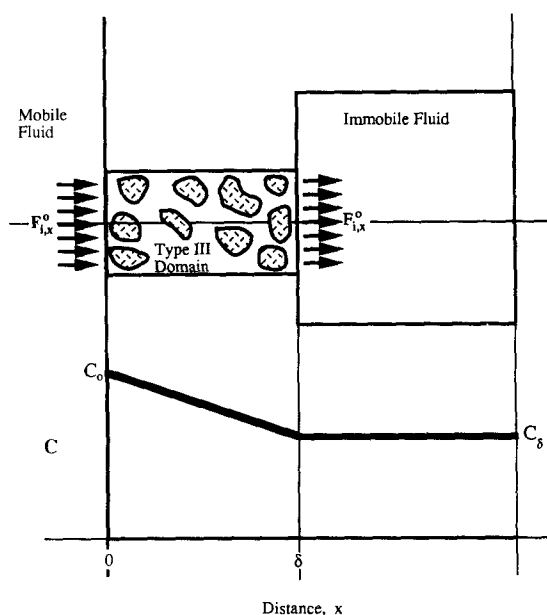

Fig. 19. Schematic representation and concentration profile for a "mobile/immobile" domain or bicontinuum model.

expressions similar to equation (44). Analytical solutions to such equations under non-steady-state conditions are available for certain applications and boundary conditions (Crank, 1975). In many cases, however, numerical solutions are required.

Equation (44) is in fact the continuity expression which obtains upon application of the non-steady-state diffusion equation to a homogeneous Type I domain. For a constant concentration boundary condition, $C = C_0$ at $x = 0$, and a negligible concentration at a large distance into the mass transfer region (a condition which may be met at the early stages of mass transfer), the concentration at a distance x into the region at any time, t, after initiation of diffusion is (Crank, 1975):

$$C = C_0 \left[1 - \mathrm{erf}\left(\frac{x}{(4D_l t)^{0.5}} \right) \right]. \qquad (56)$$

The concentration profile for this solution to the non-steady-state condition, depicted in Fig. 20, is non-linear. The concentration profile reflects a mass flux which varies temporally and spatially within the phase. It can be shown by substitution of equation (56) into Fick's law [equation (39)] that shortly after initiation of diffusion the flux of solute at the upgradient boundary of the domain ($x = 0$) is:

$$F_i^0 \big|_{x=0} = -D_l \frac{\partial C}{\partial x} = \left(\frac{D_l}{\pi t} \right)^{0.5} C_0 = k_e (C_0 - 0). \qquad (57)$$

In contrast to the flux relationship for steady-state diffusion in a Type I domain [equation (43)], the effective mass transfer coefficient, k_e, for non-steady-state diffusion is proportional to the square root of the free liquid diffusion coefficient. The time dependence of the mass transfer coefficient reflects the decrease in the local concentration gradient as the solute accumulates, a condition which was presented earlier as a possible shortcoming of the steady-state model.
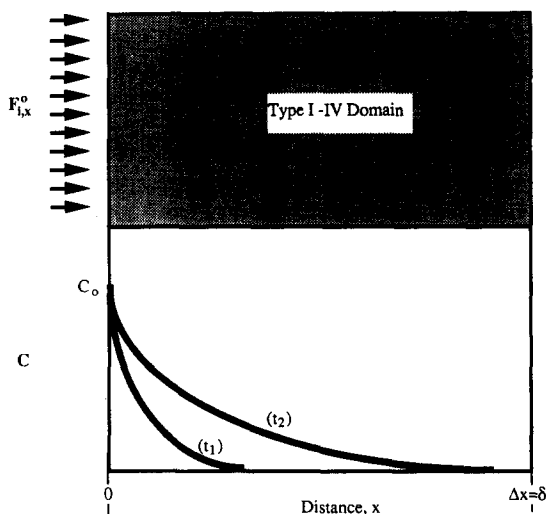

Fig. 20. General representation of concentration profiles for non-steady-state models.

In application of the non-steady-state representation to a Type II domain, which is characterized by a homogeneous diffusion medium and a solute reaction, the flux will represent a superposition of the effects of diffusion and reaction. Solution of equation (46) for the non-steady-state condition for a first-order reaction with rate constant, k, and for boundary conditions equivalent to those used to obtain equation (56) (i.e. a constant concentration, C_0, at $x = 0$) can be expressed (Crank, 1975):

$$C = \frac{C_0}{2} \left\{ e^{-x(k/D_1)^{0.5}} \mathrm{erfc}\left(\frac{x}{(4D_1 t)^{0.5}} + (kt)^{0.5} \right) \right.$$
$$\left. + e^{x(k/D_1)^{0.5}} \mathrm{erfc}\left(\frac{x}{(4D_1 t)^{0.5}} + (kt)^{0.5} \right) \right\}. \qquad (58)$$

Under several limiting conditions, the flux into a Type II domain reduces to one of the solutions presented earlier. When the solute reacts very rapidly after it enters the domain, the corresponding solution for the flux at the boundary can be closely estimated by:

$$F_i^0 \big|_{x=0} = (kD_1)^{0.5} C_0. \qquad (59)$$

This is identical to the steady-state solution for the Type II domain presented in equation (46). When the product kt is very small, the flux at the boundary can be expressed as:

$$F_i^0 \big|_{x=0} = (1 + kt) \left(\frac{D_1}{\pi t} \right)^{0.5} C_0. \qquad (60)$$

Equation (60) reduces to the solution for diffusion in a Type I domain without reaction [equation (57)] as k approaches zero.

Solute transport in subsurface systems often includes non-steady-state movement into particles or aggregates. A heterogeneous Type III domain representation, with an effective diffusion coefficient which accommodates the tortuous flow paths which occur within such a domain, can be applied to describe this transport. In these instances, the geometry of the domain must also be incorporated into the non-steady-state model because accumulation within the domain, and subsequent decreases in the local concentration gradient, will be affected by changes in fluid volume along the mass transfer path. Particles and aggregates in subsurface systems are commonly idealized as spheres in sorption rate models. In spherical coordinates, the non-steady-state continuity expression for non-reactive diffusion in a Type III domain of porosity ϵ has the form:

$$\left(\frac{\partial C}{\partial t} \right)_V = \frac{1}{\epsilon} \frac{1}{r^2} \frac{\partial}{\partial r} \left(\epsilon r^2 D_e \frac{\partial C}{\partial r} \right). \qquad (61)$$

As indicated above, the effective diffusion coefficient, D_e, in equation (61) reflects the properties of the medium through which the transfer is occurring. Solutions to equation (61) have been presented by Crank (1975) for several different conditions. While Type III domain models such as that given in equation (61) have been applied for description of the

non-steady-state transport of non-reactive solutes in soil systems (Rao et al., 1980b), sorbing contaminants require application of Type IV domain models. As discussed earlier, fluxes across Type IV domains reflect solute accumulation and retardation due to sorption by the solid phase, and expressions to describe non-steady-state diffusion in such domains must account for the solute in both sorbed and solution phases throughout the geometry of interest. The non-steady-state continuity expression for diffusion and adsorption in a Type IV domain is, in spherical coordinates:

$$\left(\frac{\partial C}{\partial t}\right)_V = \frac{1}{r^2\epsilon}\frac{\partial}{\partial r}\left(\epsilon r^2 D_e \frac{\partial C}{\partial r}\right) - \frac{(1-\epsilon)}{\epsilon}\rho_s \frac{\partial q}{\partial t}. \quad (62)$$

As noted in earlier discussions of steady-state models for Type III and IV domains, ϵ can usually be brought out of the spatial derivative and cancelled out of that term in equations (61) and (62).

Movement of solute in Type IV domains can occur both through diffusion of solute in liquid-filled regions and migration of sorbate along sorbent surfaces. When sorbed phase concentrations are sufficiently high, transport of solute by the latter route can be a significant, or even dominant, part of the overall intraparticle or intraaggregate solute flux. Because pore and sorbed phase diffusion act in parallel, that process which results in the greater flux is generally rate determining. Pore and sorbed phase (surface) diffusion models have been used singly and in combination to describe organic sorption rates for microporous sorbents, individual soil particles and soil aggregates (Weber and Crittenden, 1975; Weber, 1984; Crittenden et al., 1986; Roberts et al., 1987; Miller and Weber, 1988). Other descriptions of simultaneous diffusion and sorption in microporous sorbents and soil systems have been made using generalized expressions to represent both pore and sorbed phase diffusion (Weber and Rumer, 1965; Wu and Gschwend, 1986). Attempting to distinguish rigorously between sorbed phase and pore liquid intraparticle or intraaggregate diffusion may in fact be problematic for many combinations of soils and solutes, in part because neither the pore nor sorbed phase diffusion coefficient has a significant concentration dependence when the sorption isotherms are only weakly non-linear (Crittenden et al., 1986). Thus in many cases a microporous particle is treated as a homogeneous entity, the q expressed as a bulk particle value, and the effective diffusion coefficient, D_e, treated as a bulk particle property.

In many cases the overall mass transfer of solute into and through Type II and Type IV domains can be controlled by a combination of resistances, and more accurate descriptions of sorption rates are therefore obtained by combining two (or more) mass transfer models. A common conceptualization of sorption processes involving microporous soil particles and aggregates combines an external model for film transfer with an internal model for diffusion/sorption

within the particle or aggregate. Such "dual" resistance models have been employed successfully to describe sorption of organic contaminants on soils at both the particle level (Miller and Weber, 1986) and the aggregate level (Hutzler et al., 1984; Roberts et al., 1987). A schematic representation of the series domain concept and the concentration profiles associated with this type of model are shown in Fig. 21. The application of a dual resistance model can incorporate both equation (43) for an external or film transfer and equation (61) to describe the internal transfer. The flux across the external film must be equated to the internal flux at the particle or aggregate surface. Combining equation (43) with the general expression for internal flux leads to the condition:

$$k_f(C_0 - C_\delta) = D_e\rho_s \frac{\partial q_r}{\partial r} \quad \text{at } r = R_p. \quad (63)$$

This condition must be met at the exterior of the particle or aggregate, and thus comprises a boundary condition for interfacing the solid and liquid material balance equations.

It is evident from the foregoing that various adaptations of one or more of the basic "domain" models discussed at the outset of our consideration of microscopic mass transfer have been employed to characterize rate-limited sorption processes in different theoretical and experimental investigations. The choice of any particular model, the most "appropriate" model, is generally predicated on the level of detail available regarding a given application, and the level of "correctness" with which sorption processes must be characterized and evaluated. These same considerations of course govern whether any microscopic mass transfer model is to be preferred over a more simple "reaction rate" model; indeed, whether it is even necessary or appropriate to account for the time dependence of sorption processes in a particular application. Such issues go beyond considerations of microscopic mass transfer. They are crucial issues
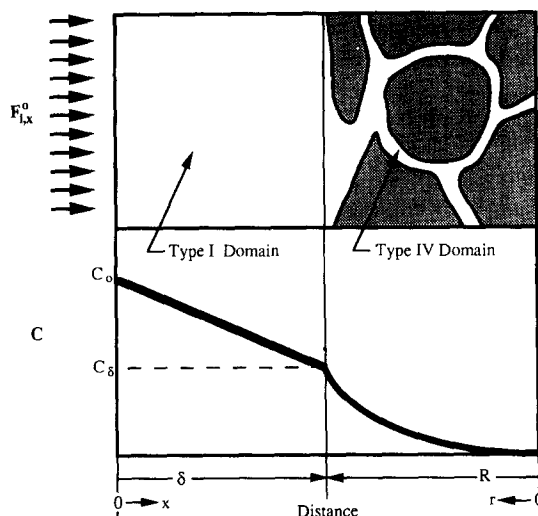
Fig. 21. Schematic representation and concentration profile for a dual resistance model.

with respect to the ultimate goal of characterizing and quantifying contaminant behavior in subsurface environments, however, and must be considered in that context. To that end, the final section of the paper addresses the potential effects of sorption processes on contaminant fate and transport in several typical circumstances.

6. SORPTION PROCESSES IN A FATE AND TRANSPORT PERSPECTIVE

The sorption rate and equilibrium models presented above, whether mechanistic or phenomenological, have been developed on what may be termed a local or microscopic scale; that is, by describing processes at a molecular or particle level. Their ultimate utility for characterizing and predicting the behavior and eventual fate of contaminants in subsurface systems depends on: (1) the relative importance of sorption processes in the context of other reaction and transport processes operative in subsurface environments; and (2) our ability to determine the level of complexity required to describe accurately the impact of microscopic processes on overall fate and transport at the macroscopic scale. It is not within the scope of this paper to examine macroscopic transport models in detail, but there is value in considering different levels of model sophistication required to capture the effects of sorption processes and reflect them in predictions or estimations of solute transport under field-scale conditions. To do this, several examples are selected to demonstrate that adequate macroscale characterization of solute behavior in typical subsurface environments requires thoughtful consideration and choice of appropriate microscale sorption models.

Macroscopic models for tranport in subsurface systems incorporate advection and dispersion processes, and are generally structured on principles of mass conservation applied on a "volume average" or otherwise statistically averaged basis. Generated on a differential scale, the continuity relationship yields the following advection–dispersion equation:

$$\frac{\partial C}{\partial t} = -\mathbf{v} \cdot \text{grad } C + \text{div}(\mathbf{D}_h \cdot \text{grad } C) + S(C). \quad (64)$$

The term $\mathbf{D}_h$ in equation (64) is a second-rank hydrodynamic dispersion tensor, $\mathbf{v}$ is a pore-velocity vector, C is the solution-phase concentration of solute, and $S(C)$ is a fluid-phase solute source term. When microscale processes are significant, equation (64) is expanded to include descriptions of reactions which affect solute concentration, yielding the so-called advection–dispersion–reaction (ADR) equation:

$$\frac{\partial C}{\partial t} = -\mathbf{v} \cdot \text{grad } C + \text{div}(\mathbf{D}_h \cdot \text{grad } C)$$

$$+ \left(\frac{\partial C}{\partial t}\right)_r + S(C). \quad (65)$$

The right-hand term subscripted with an r in equation (65) denotes the time-rate of change in concentration associated with a microscale reaction process, such as adsorption, which may in turn be represented by reaction rate models or by models describing microscale mass transfer processes. The significance of any particular microscale reaction on macroscopic solute transport can be estimated by: (1) conducting controlled investigations to determine rate and equilibrium parameters for that reaction; and (2) incorporating these parameters into the reaction term in the ADR equation and performing field-scale sensitivity analyses to determine the relative impact of the reaction, vis-à-vis the advection and dispersion processes.

In laboratory and controlled field-scale investigations of transport and transformation processes the experimental design is commonly structured in a manner that will allow close approximation of system behavior with a one-dimensional form of equation (65). There are certain field applications in which use of a one-dimensional form of the ADR equation may also be justified, although this simplification generally does not provide sufficiently accurate representations of field-scale transport. Nonetheless, the one-dimensional simplification does afford a convenient means for evaluating the relative effects of reaction and macrotransport processes in various contamination scenarios. Consider, for example, the finite control volume, V, represented schematically in Fig. 22 for a system of fluid flow through a porous matrix com-
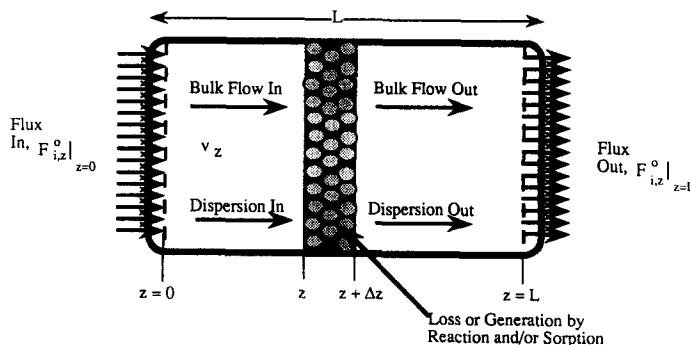

Fig. 22. Control volume for one-dimensional transport through porous media.

prised by a stationary sorbent phase. The flux of dissolved fluid-phase component, i, entering or leaving the control volume includes advective and dispersive components. Within the control volume, the component or solute of interest may undergo reaction (transformation) and/or sorption (phase transfer/exchange) with the sorbent phase. If equation (50) is used to describe the sorption reaction term, and no other fluid-phase reaction or source terms are considered, the ADR relationship given in equation (64) simplifies in one-dimensional (z) form to an advection–dispersion–sorption (ADS) model:

$$\left(\frac{\partial C_i}{\partial t}\right)_z = -v_z \frac{\partial C_i}{\partial z} + D_h \frac{\partial^2 C_i}{\partial z^2} - \frac{\rho_s(1-\epsilon)}{\epsilon}\left(\frac{\partial q_i}{\partial t}\right)_z. \quad (66)$$

The hydrodynamic dispersion term, D_h, in equation (66) is now a simple numerical coefficient, v_z is the component of fluid-phase pore velocity in the z direction and q_i is the volume averaged sorbed-phase solute concentration of component i expressed as a mass ratio.

It follows from earlier sections of this paper that the sorption term, $\partial q_i/\partial t$, can assume a variety of forms comprising different rate and equilibrium components. Several examples of one-dimensional macroscopic transport models incorporating various equilibrium and microscopic rate models are summarized in Table 3. The most simplistic approach to representation of sorption phenomena in a contaminant transport model is to assume that the time scales associated with the microscopic processes of diffusion and sorption are very much smaller than those associated with the macroscopic processes of fluid transport. This effectively assumes that equilibrium prevails locally; that is, that the time rate of change of the sorbed phase concentration, q_i, at any point z is instantaneously reflected in the time rate of change of the solution phase concentration, C_i, at that point. This yields the so-called local equilibrium model (LEM). A further simplification is to assume that the relationship between q_i and C_i involves a direct proportionality of the type typically associated with simple partitioning or absorption processes. Expressing this proportionality in terms of the distribution coefficient, K_D, defined by equation (10) gives the following relationship:

$$\left(\frac{\partial q_i}{\partial t}\right)_z = K_{D,i}\left(\frac{\partial C_i}{\partial t}\right)_z. \quad (67)$$

The macroscopic transport model which results upon rearrangement of equation (66) and substitution of the relationship for $(\partial q/\partial t)_z$ given in equation (67) is termed the linear local equilibrium model (LLEM):

$$\left(1 + \frac{\rho_s(1-\epsilon)}{\epsilon} K_D\right)\left(\frac{\partial C}{\partial t}\right)_z = R_{f,i}\left(\frac{\partial C_i}{\partial t}\right)_z$$

$$= D_h \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z}. \quad (68)$$

Table 3. Forms of the one-dimensional advection–dispersion equation incorporating sorption equilibria and rate expressions

General equation

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \rho_s \frac{(1-\epsilon)}{\epsilon}\frac{\partial q}{\partial t} \quad (i)$$

Local equilibrium

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \rho_s \frac{(1-\epsilon)}{\epsilon}\frac{\partial q}{\partial C}\frac{\partial C}{\partial t} \quad (ii)$$

with linear isotherm

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \rho_s \frac{(1-\epsilon)}{\epsilon} K_P \frac{\partial C}{\partial t} \quad (iii)$$

with Freundlich isotherm

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \rho_s \frac{(1-\epsilon)}{\epsilon} K_F n C^{n-1}\frac{\partial C}{\partial t} \quad (iv)$$

First-order sorption/desorption

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - k_F C + \rho_s \frac{(1-\epsilon)}{\epsilon} k_R q \quad (v)$$

Equilibrium and first-order sorption/desorption

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \rho_s \frac{(1-\epsilon)}{\epsilon}\frac{\partial q}{\partial C}\frac{\partial C}{\partial t} - k_F C + \rho_s \frac{(1-\epsilon)}{\epsilon} k_R q \quad (vi)$$

Mobile/immobile with quasi-steady-state linear driving force and sorption

$$\theta_M \frac{\partial C_M}{\partial t} = \theta_M D_h \frac{\partial^2 C_M}{\partial z^2} - \theta_M v \frac{\partial C_M}{\partial z}$$

$$- \rho_s \frac{(1-\epsilon)}{\epsilon}\theta_M \frac{\partial q_M}{\partial t} - \frac{\theta_{IM}}{\epsilon} k_\alpha(C_M - C_\delta) \quad (vii)$$

where

$$k_\alpha(C_M - C_\delta) = \rho_s(1-\epsilon)\frac{\partial q_\delta}{\partial t} + \epsilon \frac{\partial C_\delta}{\partial t}$$

and

$$(\epsilon)_M = (\epsilon)_{IM} = \epsilon$$
$$(\rho_s)_M = (\rho_s)_{IM} = \rho_s$$

Internal diffusion

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \rho_s \frac{(1-\epsilon)}{\epsilon}\frac{\partial q_{avg}}{\partial t} \quad (viii)$$

where

$$q_{avg} = \frac{3}{R_P^3}\int_0^{R_P} q_r r^2 \, dr$$

and

$$\frac{\partial q_r}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_e \frac{\partial q_r}{\partial r}\right)$$

Dual resistance

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{3}{R_P}\frac{(1-\epsilon)}{\epsilon} k_f(C - C_\delta) \quad (ix)$$

and

$$\frac{\partial q_r}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_e \frac{\partial q_r}{\partial r}\right)$$

where

$$\frac{k_f}{\rho_s}(C - C_\delta) = D_e \frac{\partial q_r}{\partial r} \quad \text{at} \quad r = R_p$$

and

$$C = C|_{x=0} \quad \text{in Fig. 21}$$

Equation (68) provides a reasonable means for first-cut assessment of the potential impact of sorption processes under field-scale conditions. For example, Fig. 23 presents an LLEM field-scale simulation
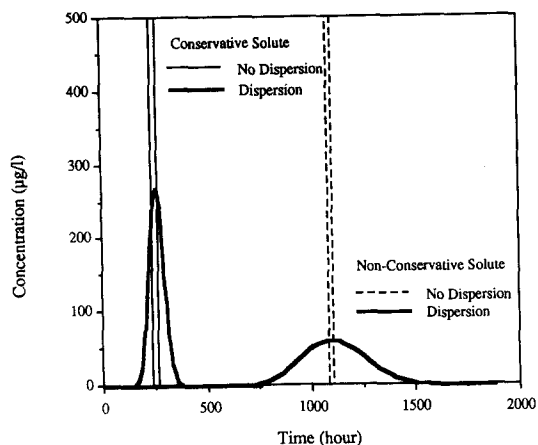
Fig. 23. Ten-meter field-scale simulations for a moderately hydrophobic contaminant using simplified forms of the ADS transport model.

of the concentration profiles for subsurface transport of a moderately hydrophobic solute through a moderately low organic content soil under representative conditions of fluid flow and hydrodynamic dispersion. The fluid velocity and dispersivity are assumed constant thoughout the domain to further simplify the evaluation. These profiles represent concentration patterns at a point 10-m downgradient of a pulse input of contaminant as a function of time after addition of that input. Parmeter values utilized in this 10-m simulation are tabulated in Table 4. Concentration–time profiles simulated by neglecting sorption and/or dispersion with all other conditions the same are also presented in Fig. 23. Comparison of these several profiles demonstrates that both sorption and dispersion must be accounted for in the one-dimensional ADS equation to adequately describe contaminant distribution in systems where these processes are operative at the levels represented in this simulation, which are reasonably typical of field-scale circumstances.

Although the LLEM version of the ADS equation has been widely employed for describing solute retardation by sorption in subsurface systems (Faust and Mercer, 1980; McCarty et al., 1981; Pinder, 1984), it has become increasingly apparent that this model frequently fails to provide adequate represen-

tation of the effects of sorption processes on contaminant transport. Inclusion of more sophisticated non-linear equilibrium models often provides better representation of sorption phenomena. Consider, for example, the potential error associated with macroscopic transport model predictions employing linear partitioning models in a system for which the actual equilibrium data are better characterized by a non-linear isotherm model. For this particular example we will assume that local equilibrium conditions prevail; this to examine singly the effects which accrue to the choice of the equilibrium model itself. The solute–soil system selected for analysis is comprised of tetrachloroethylene (TTCE) and Wagner soil, for which CMBR equilibrium data obtained in our laboratories are presented in Fig. 24(a). TTCE, a slightly polar chlorinated solvent of high volatility, has a moderate degree of hydrophobicity ($\log K_{ow} = 2.8$) and the Wagner soil an organic carbon content of 1.2%. Figure 24(a) shows the "best fits" to the equilibrium data afforded by linear regression with a simple partitioning model and by non-linear regression with the Freundlich model. Clearly the Freundlich model provides a better overall representation of the data, although portions of that data are reasonably well fit by the linear model. Projection of TTCE transport in a 1-m field-scale simulation made using two different forms of the ADS transport model incorporating these two alternative isotherm models [see equations (iii) and (iv) in Table 3] calibrated with the data given in Table 4 are presented in Fig. 24(b). It is apparent from comparison of these simulations that the use of a linear relationship to represent the equilibrium sorption behavior of the TTCE with respect to the Wagner soil results in a substantially different projection for contaminant transport than does the use of the Freundlich isotherm model. The most significant difference between the two projections is the slower rate of travel of the center of mass when the Freundlich model is employed. This is reflective of the model's ability to account for the higher sorption capacities observed at lower solution-phase concentrations [Fig. 24(a)]. The increased retention at low concentrations and the decreased slope of the Freundlich model fit leads to greater asymmetry or "tailing" of the solute pulse. It is important to note

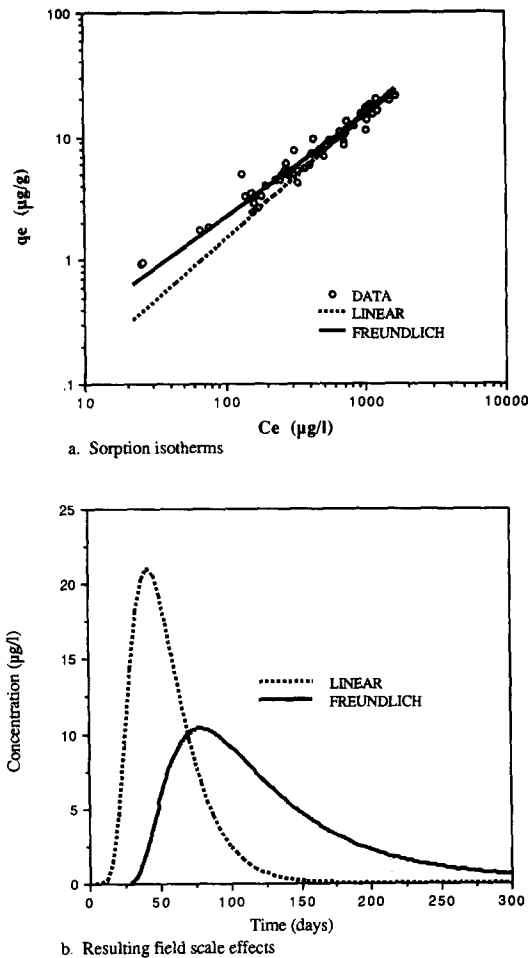| Table 4. Field Scale Case Model Input Parameters		
Parameter	Value	Units
Inital Concentration	1000	μg/l
Velocity	1	meter/day
Dispersion Coefficient	0.1	$meter^2$/day
Time of Solute Input	1	day
Soil Density	2.67	gr/cm^3
Void Fraction	0.4	

Fig. 24. Sorption isotherms (a) and 1-m field-scale simulations (b) for TTCE and Wagner soil using these isotherms in the ADS transport model.

that these effects are significant even though the data are not grossly ill-fit by the linear model. Indeed, the linear model would seem quite adequate had the experimental data set been limited to a narrow range, say to only those data above about 150 μg/l. The importance of both measuring and accurately representing equilibrium sorption data over the entire range of interest in any given situation should thus be abundantly clear.

The second consideration to be made here relates to the validity of assuming that sorption time scales are not important with respect to transport time scales. A number of investigations have shown that field-scale contaminant transport may be rate controlled (for a review see Brusseau and Rao, 1989). In such cases, overall contaminant dispersion is due to a combination of macroscopic and microscopic effects. The most simplistic approach for incorporating rate phenomena into model descriptions of contaminant transport is to assume that macroscopic and microscopic effects on front spreading are additive, and that an effective or apparent dispersion coefficient, $D_{h,a}$, can be incorported into equation (68)

to take account of these additive effects. The relative contributions of the reaction rate and hydrodynamic dispersion mechanisms are dependent on flow velocity and microporous particle or aggregate radius. The sensitivity of this apparent dispersion coefficient to particle or aggregate size and the related effective internal diffusion coefficient, D_e, for a Type IV domain is shown in Fig. 25, which was generated from a mathematical relationship between internal diffusion and hydrodynamic dispersion developed by Parker and Valocchi (1968). This relationship demonstrates that dispersion due to mass transfer will dominate for systems comprised of large microporous particles or aggregates. In a similar manner, it can be shown that mass transfer dominates at higher flow velocities. Sensitivity analyses performed by a number of investigators have shown that use of an apparent dispersion coefficient reasonably reproduces contaminant breakthrough profiles for large Peclet numbers. In contrast, this approach fails to describe accurately the asymmetry due to mass transfer effects for systems dominated by hydrodynamic dispersion.

The effect of rates on concentration profile asymmetry is apparent for chemically controlled rate phenomena as well as for mass transfer controlled sorption. These effects are illustrated in Fig. 26(a). Equilibrium conditions for this particular example were described using a linear isotherm model, and a range of first-order rate constants was tested. The ADS equations corresponding to the linear local equilibrium and first-order rate representations for this system are equations (iii) and (iv), respectively, in Table 3 (Miller and Weber, 1988). These models, calibrated for the conditions described in Table 4, yield the 1-m field-scale simulations presented in Fig. 26(a). Comparison of the simulations clearly demonstrates the potential error that might be associated with the use of a local equilibrium model for a system in which sorption rates are not truly negligible
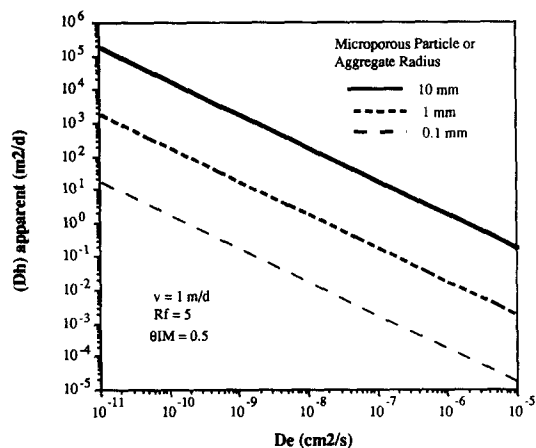

Fig. 25. Relationship between effective intraparticle molecular diffusion (D_e) and hydrodynamic dispersion (D_h) to give equivalent effects on initial spreading.

at the time scale of associated transport processes. It is readily apparent that rate limitations for the sorption process result in earlier arrival of the contaminant front at the 1-m downgradient point, as well as increased tailing of the front to increase the amount of total "dispersion" of the contaminant plume compared to the LLEM model, which accounts only for macroscopic or hydrodynamic dispersion.

The conditions employed in developing the simulations for Fig. 26(a) represent reasonable values for assessing the anticipated effects of rate-controlled sorption under typical background flow conditions. Such non-equilibrium effects may play an even more important role in flow situations associated with typical "pump and treat" remediation strategies. Consider, for example, the impact of rate-limited sorption on the volume of water to be treated in a remediation scheme in which the fluid velocity is increased by pumping to 10 m/d. As shown in Fig. 26(b), the effect of non-equilibrium conditions at a particular rate constant are even more significant in this scenario, and the potential error associated with erroneously employing a LLEM even greater. The

rate-controlled sorption process in this case translates into more than a 100% increase in the volume of contaminated water which must be treated.
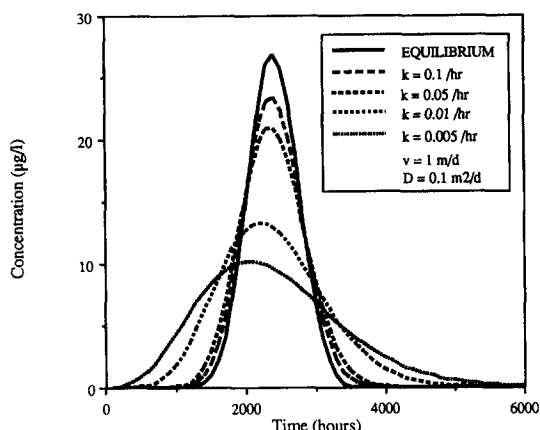
6.1. Closure

Sorption processes in subsurface systems are complex, often involving non-linear phase relationships and rate-limited conditions. We have demonstrated that these processes impact reactive solute behavior under typical field-scale conditions, and must therefore be considered in attempts to model or otherwise predict contaminant fate and transport in the subsurface. It is further apparent from the examples we have considered that the thoughtful selection of appropriate microscopic equilibrium and rate models, models which adequately describe the inherently complex and system-specific dynamics of sorption processes, is an imperative for accurate fate and transport modeling.
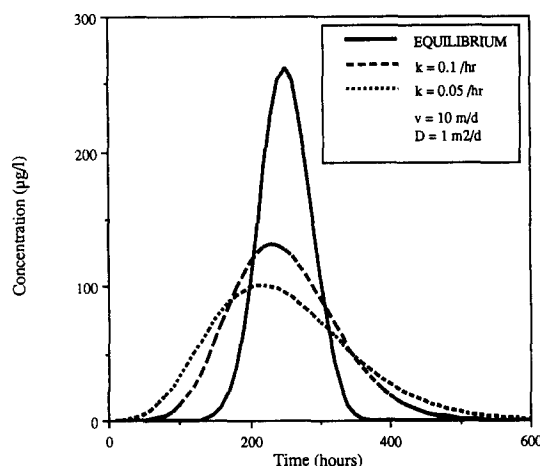
a. Background flow conditions

b. Pump and treat remediation conditions

Fig. 26. One-meter field-scale simulations showing effects of first-order reaction rates in typical flow (a) and remediation flow (b) situations.

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