

Modeling Organic Contaminant Partitioning in Ground-Water Systems

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ABSTRACT

Effective management of a ground-water system requires description and prediction of the transport and fate of contaminants in that system. This can be facilitated by using mathematical models which accurately represent the physical phenomena operative in the system. One of the most significant phenomena impacting the transport of many organic pollutants is partitioning between the solid (soil) and aqueous (ground-water) phases.

The tendency of a contaminant to partition may be roughly approximated from measurements of such constitutive properties as the octanol:water partition coefficient of the contaminant and organic carbon content of the soil. Such rough approximations provide a basis for cursory appraisal, but are inadequate for quantitative system descriptions, particularly where nonlinear equilibrium sorption, kinetically dependent partitioning, or irreversible and/or hysteretic phase distribution phenomena are operative. Accurate simulation of solute transport frequently requires the incorporation of kinetic parameters and/or a nonlinear isotherm relationship to define transport phenomena in the fundamental equations governing mass transport. Laboratory measurements may be utilized to assess sorptive factors of importance, kinetic properties of an organic solute and a soil system, and equilibrium partitioning relationships. Such measurements can be utilized to provide more accurate modeling of contaminant transport.

INTRODUCTION

Extensive ground-water contamination by persistent organic pollutants has precipitated an urgent need for evaluation of cleanup alternatives, short- and long-term contaminant risks, and methods for safe disposal of potential contam-

inants. Such evaluations require a thorough understanding of the behavior of contaminants in ground-water systems, which in turn requires identification and quantification of all processes which influence overall transport and fate. These typically include mean bulk fluid movement, fluid dispersion, contaminant retardation and transformation, and inputs and outputs by and to contaminant sources and sinks, respectively. Management decisions frequently require prediction of conditions resulting from changes in the variables associated with these processes.

Such predictions may be accomplished through the use of mathematical models which account for each operative process. This paper presents a brief overview of a major subsystem process for organic contaminant transport in ground-water systems, sorptive partitioning, and a discussion of the significance of this process for overall contaminant transport modeling.

ROLE OF PARTITIONING

The movement of ground water is influenced by the properties of the media through which flow occurs and the location and magnitude of regions of recharge and discharge. When a contaminant (solute) is introduced it tends to move in a manner governed by the overall flow system. This movement is typically characterized by a bulk or advective flow component and a component relating to deviations from bulk flow. The latter, commonly referred to as the dispersive flow component or simply dispersion, results from microscopic-scale velocity variations and subsurface inhomogeneities. While the adequacy of the advection-dispersion approach to describing solute transport has been questioned (Anderson, 1979; Matheron and de Marsily, 1980; Sauty, 1980), the model suffices as a framework for

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discussion of contaminant retardation by partitioning.

The general form of the solute transport equation for saturated flow in porous media may be given as (Bear, 1979)

$$\frac{\partial C}{\partial t} = \underbrace{\text{div}(D_h \cdot \text{grad } C)}_{\text{(dispersion)}} - \underbrace{v \cdot \text{grad } C}_{\text{(advection)}} - \underbrace{\frac{\rho(1-\theta)}{\theta} \frac{\partial q}{\partial t}}_{\text{(sorption)}} + \underbrace{\left(\frac{\partial C}{\partial t}\right)_{\text{rxn}}}_{\text{(reaction)}} \quad (1)$$

where

C = liquid phase concentration of solute (M/L³);

t = time (t);

D_h = hydrodynamic dispersion coefficient (L²/t);

v = interstitial fluid velocity (L/t);

ρ = solid phase particle density (M/L³);

θ = volumetric fraction represented by the liquid phase (L³/L³);

q = normalized solid phase concentration of sorbed solute species (M/M); and

rxn = subscript denoting biological or chemical reaction of the solute in solution phase.

For this discussion the general form of the transport equation may be reduced to its one-dimensional (z) form

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{\rho(1-\theta)}{\theta} \frac{\partial q}{\partial t} + \left(\frac{\partial C}{\partial t}\right)_{\text{rxn}} \quad (2)$$

or, for conservative (resistant) contaminants which do not undergo reaction in solution phase

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{\rho(1-\theta)}{\theta} \frac{\partial q}{\partial t} \quad (3)$$

Many organic contaminants are hydrophobic (water-disliking) in character, and their movement in ground-water systems is thus affected by sorption phenomena. Sorption, represented by the third term on the right-hand side of equations (1)-(3) consists of the transfer of solute (contaminant) from the liquid phase (ground water) to the solid phase (soil particles). This phase partitioning process may be fully or partially reversible (desorption). It is evident from equations (1)-(3) that sorption functions to retard the mean rate of solute movement relative to the advective rate of movement of the water. The impact of sorption/desorption on the transport of an organic contaminant is influenced by many variables, including the physical and chemical characteristics of the soil,

the physical and chemical properties of the organic contaminant in question, the presence of competing solutes, and levels and types of background organic matter in solution. These factors result in net effects that may range from indistinguishable to retardation of contaminant movement to a rate several orders of magnitude less than that of the water.

The objective of sorption subsystem modeling is to characterize the term $(\partial q/\partial t)$ in equations (1)-(3). One common approach to modeling the effects of sorption on contaminant transport is to assume that the sorption process achieves an instantaneous equilibrium, and usually to further assume that the solid phase concentration at equilibrium, q_e , is a linear function of the solution phase concentration, C_e . Incorporating these assumptions in equation (3) yields the familiar linear-isotherm retardation equation (Anderson, 1979)

$$r_f \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (4)$$

where the retardation factor, r_f , is given by

$$r_f = 1 + \frac{\rho(1-\theta)}{\theta} K_p \quad (5)$$

and the linear partition coefficient, K_p , by

$$K_p = \frac{q_e}{C_e} \quad (6)$$

The validity of the linear-isotherm retardation equation is dependent on the validity of the underlying assumptions of local equilibrium and of a linear and completely reversible liquid/solid phase distribution of solute. The first assumption relates to sorption kinetics or rate of attainment of an equilibrium condition. The second relates to sorption/desorption equilibria—specifically, the characteristics of the solute distribution at equilibrium and the reversibility of that equilibrium. Each of these aspects of sorption of contaminants in ground waters is considered in turn in ensuing sections of this paper.

SORPTION KINETICS

The rate at which the sorption or desorption of a contaminant by soil structures approaches equilibrium in a ground-water system is an important consideration in assessing the transport of the contaminant in that system. If the rate is rapid, it may be adequate to assume that the inter-phase (water/soil) distribution is governed by

equilibrium relationships appropriate to that system. The assumption of instantaneous achievement of local sorption/desorption equilibria for solutes in soil systems is widespread practice in solute transport modeling (Back and Cherry, 1976; Anderson, 1979; Freeze and Cherry, 1979; Faust and Mercer, 1980; Prickett, *et al.*, 1981; and Enfield, *et al.*, 1982). There is, however, substantial evidence that the behavior of many organic solute/soil systems deviates significantly from that suggested by this assumption (Kay and Elrick, 1967; Leenheer and Ahlrichs, 1971; Boucher and Lee, 1972; and Karickhoff, 1980).

Several different types of subsystem rate models have been used in cases where the assumption of local equilibrium has been found inappropriate. Oddson and coworkers (1970) applied a simple first-order reversible rate model to describe sorption of nonionic surfactants

$$\frac{\partial q}{\partial t} = k_s \frac{\theta}{\rho(1-\theta)} C - k_d q \quad (7)$$

where k_s and k_d are first-order rate constants (τ^{-1}) for sorption and desorption, respectively. Cameron and Klute (1977) employed a modeling approach predicated on the hypothesis that a portion of the sorption process is governed by rapidly achieved local equilibrium and the remainder by an independent reversible rate process such that

$$\frac{\partial q}{\partial t} = \frac{\partial q_r}{\partial t} + \frac{\partial q_e}{\partial t} \quad (8)$$

where q_r is the fraction of the total q determined by the rate process and q_e is the fraction determined independently by instantaneous local equilibrium. These investigators further assumed that the local equilibrium is linear [equation (6)], and that the rate process is a reversible first-order function [equation (7)] to deduce the relationship

$$\frac{\partial q}{\partial t} = k_s \frac{\theta}{\rho(1-\theta)} C - k_d q_r + K_e \frac{\partial C}{\partial t} \quad (9)$$

which was applied to sorption subsystem modeling for a variety of solutes including atrazine, phosphorus and silver, where K_e is the equilibrium governed partition coefficient.

Karickhoff (1980), in describing the results of sorption experiments involving three bottom sediments and three hydrophobic organic solutes (phenanthrene, pyrene, and naphthalene) employed a two-step relationship in which a linear equilibrium controlled process and a first-order rate process are coupled; that is:

$$C \rightleftharpoons q_e \rightleftharpoons q_r \quad (10)$$

If the fraction of total sorption capacity of the solid accessed immediately by solute by virtue of the local equilibrium controlled process is represented by the term f , then the equilibrium-controlled component, q_e , is given by

$$q_e = fK_p C \quad (11)$$

and, at long periods of time, the rate-controlled component q_r by

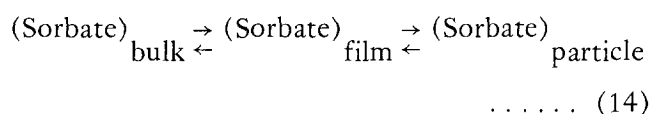
$$\lim_{t \rightarrow \infty} q_r = (1-f) K_p C \quad (12)$$

Karickhoff further assumed that the first-order sorption and desorption rates were equal to arrive at the following relationship for exchange between the equilibrium and rate controlled fractions of sorbed solute

$$\frac{\partial}{\partial t} \left(\frac{q_r}{1-f} \right) = k_{sd} \left(\frac{q_e}{f} - \frac{q_r}{(1-f)} \right) \quad (13)$$

where k_{sd} is the sorption/desorption rate constant (τ^{-1}). Karickhoff (1980) reported that the time required for the rate controlled process to reach completion ranged from minutes to weeks and was inversely proportional to K_p .

Other kinetic relationships involving more complex rate processes and nonlinear equilibrium relationships have been developed for related systems involving different adsorbents (e.g., activated carbon and ion exchange resins; see for example, Weber, 1972; Weber and Crittenden, 1975; and Crittenden and Weber, 1978). Miller and Weber (1983) have extended some of these more complex rate processes to sorption in ground-water systems. One of these methods is a two-resistance rate model consisting of an equation governing diffusive transport of solute from solution to the external surface of the solid phase across a hydrodynamic boundary layer (film transport) and a coupled equation governing subsequent diffusion of solute within the solid phase (intraparticle transport). This two-resistance approach to modeling sorptive transport phenomena may be depicted in a schematic fashion as



Equation (14) may be presented in a more rigorous manner as a set of equations with the necessary coupling boundary conditions by

$$\frac{\partial q}{\partial t} = D_s \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial q}{\partial r} \right] \quad (15)$$

where

$$k_f(C - C_s) = D_s \rho \frac{\partial q}{\partial r} \quad @ r = R \quad (16)$$

$$\frac{\partial q}{\partial r} = 0 \quad @ r = 0 \quad (17)$$

$$q_e = f(C_e) \quad (18)$$

r = radial dimension for a particle of radius R (L);

D_s = intraparticle diffusion coefficient (L^2/t);

k_f = external film transfer coefficient (L/t); and

C_s = equilibrium solution concentration corresponding to the solid phase concentration at the exterior of the particle (M/L^3).

Equation (18) is a general statement of an equilibrium solid phase/solution phase distribution. This equation may take the specific form of any of a number of isotherm models, some of which will be described in the discussion which follows.

The sorption kinetic models presented [equations (7)-(17)] may be used to describe sorption in the standard advection-dispersion equation or may be applied to completely mixed batch reactor (CMBR) systems with the necessary revisions for solid and liquid phase description. CMBRs allow for isolation of the sorption reaction as completely mixed conditions cause the transport terms to vanish and leave concentration as a function of time, solids weight, solution volume, and initial conditions. Figure 1 is an example of measured CMBR sorption data fitted by several

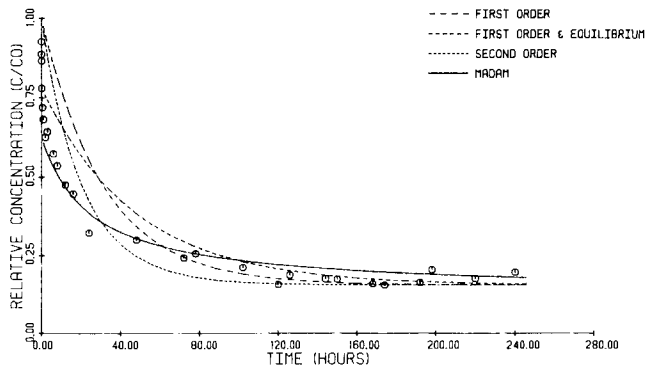


Fig. 1. Observed and kinetically modeled partitioning data (Miller and Weber, 1983).

different rate models from previous work by Miller and Weber (1983). The derivative data for Figure 1 were based on the partitioning of a lindane solute on a uniform granular soil and indicate that sorption is continuing at time in excess of five days. For this case the two-resistance rate model (MADAM, the Michigan Adsorption Design and Applications Model) predicated on equations (14)-(18) provided the best fit of the observed data.

The above treatments of sorption kinetics represent but a few examples of formulations that have been used for describing rate observations in different solute/soil systems. A complete description of available sorption rate models is beyond the scope and intent of this discussion; it suffices here to emphasize two major points. First, there is a large body of evidence which indicates that kinetics are indeed important in the partitioning of contaminants between the water and soil phases in many ground-water systems. Secondly, many different types of kinetic models have been used for description of observed rate phenomena in such systems. Approaches to the subsystem modeling of sorption processes are predicated on different phenomenological descriptions of the process, are subject to different assumptions, and therefore yield different mathematical expressions to describe the process. The validity of a given model for a particular system depends on the appropriateness for that system of the underlying assumptions of the model under consideration.

SORPTION EQUILIBRIA

Irrespective of whether a sorption process achieves immediate equilibrium or approaches equilibrium gradually, characterization and quantification of the sorption process require information relative to the nature and position of thermodynamic equilibrium to which it is driven. This equilibrium is manifest as the "final" distribution of contaminant between the soil phase (adsorbed state) and the water phase (dissolved state). The relationship describing the equilibrium is termed a sorption isotherm equation. In the foregoing discussion of sorption kinetics this relationship has been exemplified in its most simple form; linear partitioning [equation (6)]. Sorption isotherm measurements are integral to investigations of interphase distributions of contaminants in environmental systems, and different descriptive efforts have resulted in a variety of conceptual and mathematical descriptions of interphase partitioning equilibria. The relationships utilized most frequently are briefly summarized here.

The Linear Isotherm

As noted above, the most simple modeling approach to sorptive partitioning is to treat the distribution of solute between the soil and water as linear, or, by rearrangement of equation (6)

$$q_e = K_p C_e \quad (19)$$

Linear isotherms have been applied to a number of soil/solute/water systems (Oddson, *et al.*, 1970; Back and Cherry, 1976; Anderson, 1979; Karickhoff, *et al.*, 1979; Brown and Flagg, 1981; Roberts, *et al.*, 1982). However, caution must be taken not to employ linear relationships for systems or conditions which do not warrant such simple representation. This is particularly true in situations where experimental isotherm data are obtained for a limited solution phase concentration range. It is not unusual for approximately linear relationships to adequately describe data over narrow concentration ranges. Subsequent extrapolation of parameters derived from linear fits of narrow range data may, however, be totally inappropriate. Several investigators (O'Connor and Connolly, 1980; Voice, 1982; Weber, *et al.*, 1983) have noted that even very hydrophobic substances do not generally partition in a linear fashion over large ranges of equilibrium concentration. Figure 2 depicts two situations in which a linear partitioning relationship may be incorrectly inferred from limited experimental data.

Linear partitioning relationships provide ease of mathematical manipulation and facilitate comparison of sorption responses for various solute-solid systems based on measurement of constitutive properties. One such method suggests that equilibrium partitioning may be estimated by relating sorption to soil organic matter content and the octanol:water partition coefficient of the solute in question. Karickhoff *et al.* (1979) empirically derived the following equation from partitioning observations of soils and hydrophobic solute combinations

$$\log K_{oc} = \log K_{ow} - 0.21 \quad (20)$$

where K_{oc} is a partition coefficient normalized for the weight fraction of organic carbon comprising the solid phase (soil), and K_{ow} is the octanol:water partition coefficient of the solute.

The above relationships provide a convenient basis for describing and estimating sorptive partitioning for certain classes of contaminants; specifically, nonpolar, neutral, and hydrophobic compounds. A distinct advantage of the octanol:water partitioning approach is the breadth of

attendant literature reporting experimental values for a wide range of compounds (Verschuere, 1977; Kenaga and Goring, 1980; Banerjee, *et al.*, 1980; and Leo, *et al.*, 1971). Hansch and Leo (1979) have summarized reported values and have presented methods for estimating partition coefficients for different solutes in different solvent systems.

Nonlinear Isotherms

Two of the most commonly used isotherm relationships for systems which exhibit nonlinear partitioning behavior are the Langmuir and Freundlich isotherms. The Langmuir isotherm has the form

$$q_e = \frac{Q^\circ b C_e}{1 + b C_e} \quad (21)$$

where Q° is the limiting concentration of solute adsorbed on the solid phase ("monolayer" capacity) (M/M), and b is an enthalpy-related sorption constant (L^3/M). The Freundlich isotherm is given by

$$q_e = K_F (C_e)^n \quad (22)$$

where K_F is a constant relating to sorption capacity and n is a constant relation to sorption intensity. The conceptual basis and underlying assumptions for each of these nonlinear sorption models have been discussed in detail by Weber (1972).

Evaluation of the isotherm parameters for the Langmuir and Freundlich equations is somewhat more difficult than for the linear isotherm. Parameter evaluation may be facilitated by the use of a linearized form of either equation for data analysis. One such linearized form for the Langmuir equation is

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \frac{1}{b Q^\circ C_e} \quad (23)$$

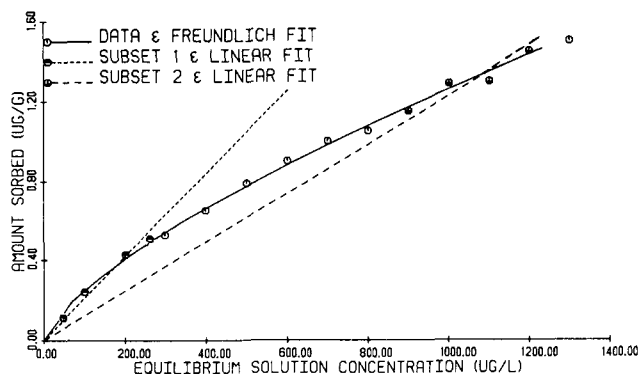


Fig. 2. Potential for inference of erroneous partitioning relationships from limited subsets of data.

variety of soil organic solute systems (Hamaker and Thompson, 1972; Weber *et al.*, 1983).

DESORPTION

Desorption is the reversal of the sorption process. Solute molecules sorbed to a solid phase may be released back into solution as a result of changes in system conditions. Changes which can result in desorptive shifts in phase distribution include decreases in solution phase solute concentration, increases in solids concentration, and changes in the background solution composition or temperature. Many modeling approaches assume that sorption and desorption isotherms are coincident; i.e., that the sorption process is completely reversible. This assumption greatly simplifies data collection and modeling but may not be warranted for some organic solute/soil systems. A number of investigators have reported desorptions that display hysteresis relative to their corresponding sorption reactions (Bailey and White, 1970; Boucher and Lee, 1972; Swanson and Dutt, 1973; Carringer, *et al.*, 1975; DiToro and Horzempa, 1982).

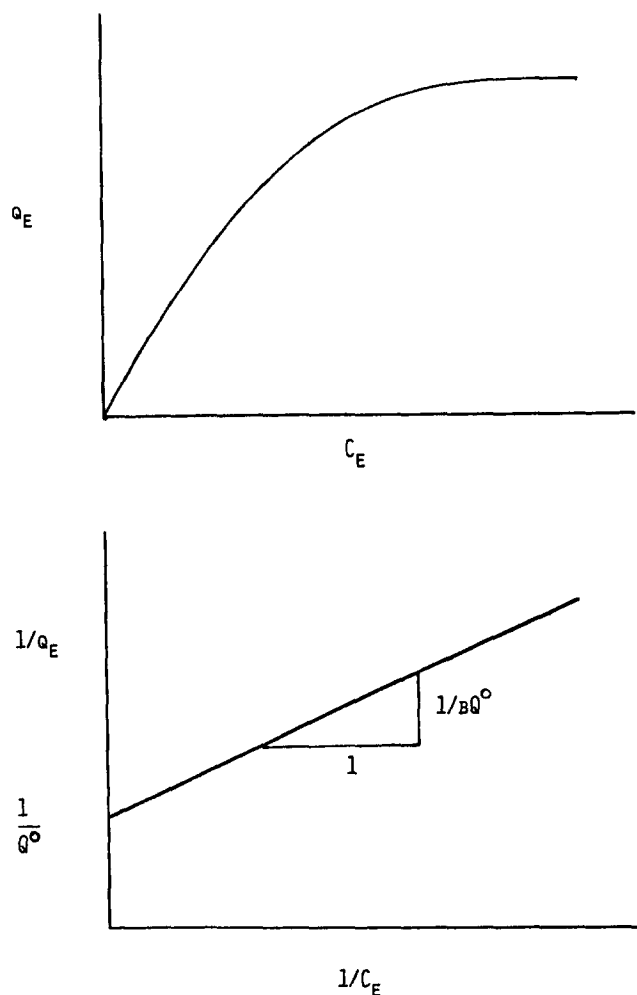


Fig. 3. (a) Langmuir isotherm. (b) Linearized Langmuir form.

Figure 3 illustrates an isotherm of the Langmuir type along with a graphical representation of the linear form given by equation (23).

The parabolic Freundlich equation may be logarithmically linearized for coefficient determination to give

$$\log q_e = \log K_F + n \log C_e \quad (24)$$

Figure 4 illustrates a typical Freundlich type isotherm and corresponding linearization of the equation. Because Freundlich coefficients determined by analysis of data plotted according to equation (24) are dependent on the origin chosen for reference, that origin must be noted and the concentration limits of the data defined. Extrapolation of any isotherm equation beyond the range of observed data is dangerous, but, because the Freundlich expression is parabolic in nature, special care should be employed in its case. In practice, the Freundlich equation has been found to fit data for a variety of systems ranging from powdered activated carbon (Weber, 1972) to a

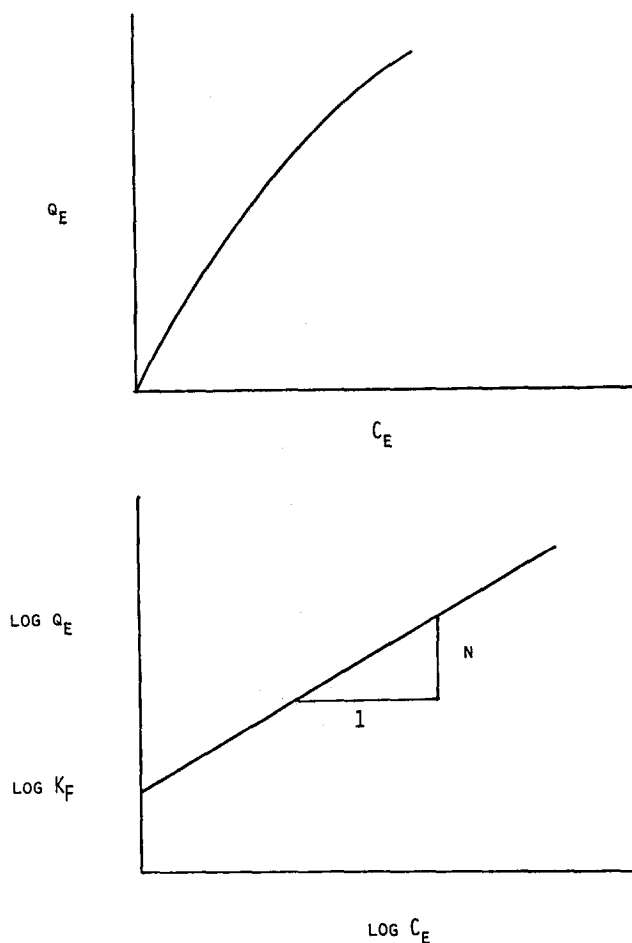


Fig. 4. (a) Freundlich isotherm. (b) Linearized Freundlich form.

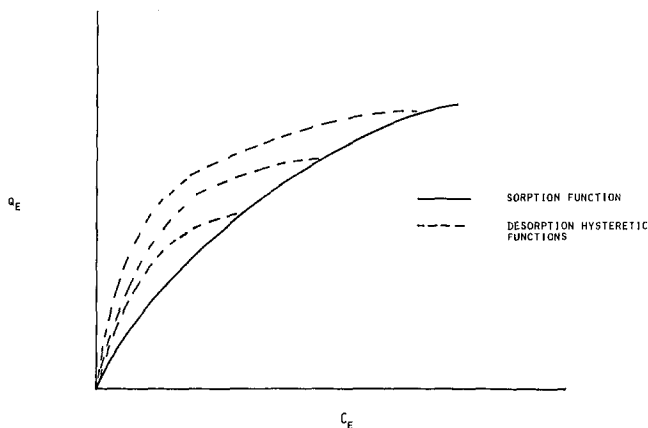


Fig. 5. Freundlich sorption-desorption isotherm.

Sorption relationships involving hysteresis are more difficult to define experimentally and add complexity to simulation procedures, but for certain systems the added complexity may be required if accurate system modeling is desired. Swanson and Dutt (1973) found for an atrazine solute and two contrasting soils that both sorption and desorption equilibria could be described for the Freundlich equation, but with different values for the corresponding isotherm coefficients. Van Genuchten *et al.* (1974) found that in applying the Freundlich equation for description of sorption/desorption data for a picloram solute on Norge loam soil that the exponent for desorption was not constant but rather a function of the maximum sorbed solute level. In both cases description of the observed hysteretic sorption/desorption behavior requires two separate isotherm equations

$$q_{e,s} = K_{F,s} (C_{e,s})^{n_s} \quad (25)$$

and

$$q_{e,d} = K_{F,d} (C_{e,d})^{n_d} \quad (26)$$

where the subscripts *s* and *d* represent sorption and desorption related parameters, respectively.

At equilibrium $q_{e,s}$ must equal the initial $q_{e,d}$ prior to desorption. If $q_{e,m}$ is used to denote the maximum solid phase concentration achieved in a given system, and $C_{e,m}$ the corresponding solution phase concentration, then

$$q_{e,m} = K_{F,s} (C_{e,m})^{n_s} = K_{F,d} (C_{e,m})^{n_d} \quad (27)$$

Swanson and Dutt found that the exponent for sorption, n_s , was 2.3 times as large as the desorptive exponent, n_d . Conversely, Van Genuchten, *et al.* (1974) did not find a single valued relationship for sorption and desorption

exponents, but rather observed the following dependence on the maximum solid phase concentration

$$\frac{n_s}{n_d} = 2.105 + 0.062 (q_{e,m})^{-1.076} \quad (28)$$

Figures 5 and 6 illustrate the character of hysteresis phenomena relative to the Freundlich and linear partitioning relationships, respectively.

DATA REQUIREMENTS

The several approaches to modeling sorption kinetics and equilibrium relationships presented in the preceding discussion are not all inclusive, and other approaches may be more appropriate for some systems. Indeed, it is safe to say that no one modeling approach is ideal for all circumstances. Selection of an appropriate model for a given application should be based on desired accuracy, the nature and extent of available data, economic constraints, and time limitations. The degree of sophistication utilized for a given modeling approach should be consistent with the detail and accuracy of available background data.

The modeling of contaminant transport in a ground-water system requires a variety of data over and above that related to system hydrodynamics. This should include, as a minimum: the chemical structure, concentration range, aqueous solubility and octanol:water partition coefficient of the contaminant; and the organic carbon content, cation exchange capacity (for cationic organic solutes), and grain size distribution of the soil. In addition to these basic data requirements, information should be collected relative to equilibrium sorption behavior and the kinetic approach to

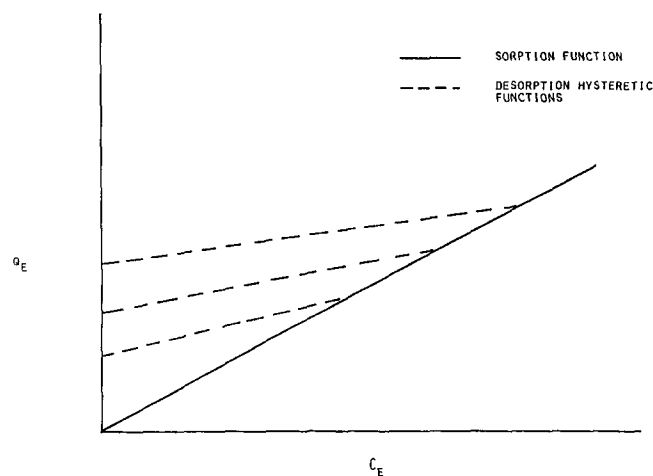


Fig. 6. Linear sorption-desorption isotherm.

equilibrium to facilitate accurate and thorough modeling methodologies. Kinetic and equilibrium data form the basis for selection and use of a particular subsystem sorption model and for determination of related coefficients for input to the model. Laboratory investigations offer economical, time, and constraint advantages as compared to field tests for determination of sorption model parameters, but these should be conducted under conditions similar to those encountered or anticipated for a specific field application; i.e., temperature, the character of the background solution, concentration range, competing solutes, and similar factors which are known to affect sorption kinetics or equilibria.

CONCLUSIONS

Organic contaminants tend to sorb from ground waters onto soil particles. This phase partitioning is motivated by solute/solvent/soil interactions which are both thermodynamically and kinetically influenced. While the soil phase concentration of contaminant is a function of its equilibrium solution phase concentration, the exact nature of this relationship is not described universally by a single model. Variations in the characteristics of both the soil and the contaminant impact equilibrium partitioning, a function roughly described by such factors as the organic carbon content of the soil and the octanol:water partition coefficient of the contaminant. Subsequent desorption of a contaminant from a soil frequently displays hysteretic behavior, further impacting the phase distribution of the contaminant and the selection of appropriate models to represent that distribution. Models which assume an instantaneous local equilibrium which is both linear and reversible are most widely cited and utilized for field scale investigations because of their ease of adaptation and mathematical manipulation. In many cases, however, accuracy in solute transport modeling requires that rate phenomena be taken into account and that nonlinear relationships be employed to describe observed equilibrium distributions. Desk top and experimental analyses can be used to assess the proper modeling approach for a given soil/contaminant system. These can be accomplished using available contaminant characteristics, information regarding the properties of the soil in question, and a series of rather straightforward laboratory measurements for the determination of equilibrium and kinetic sorption behavior and appropriate values for model coefficients.

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