

Transport of Organic Chemicals by Gas Advection in Structured or Heterogeneous Porous Media: Development of a Model and Application to Column Experiments

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The use of soil venting or vacuum extraction for remediation of contaminated soil has led to an increased interest in modeling gas-phase processes. The majority of existing transport models have been developed assuming homogeneous porous media properties. It is well known, however, that the assumption of homogeneity will almost always be invalid for field systems. In addition, sorption has been described using the local equilibrium assumption. This assumption has also been shown to be invalid under certain conditions. A one-dimensional model is presented that accounts for a structured or heterogeneous porous medium and for rate-limited sorption. The model is designed for cases where transport occurs by advection and dispersion in the gas phase and where the liquid phase is immobile. A sensitivity analysis is presented, and parameter determination is discussed. The performance of the model was evaluated by comparing predicted simulations to data obtained from the literature. The model performed well, especially considering that the values for all input parameters were obtained independent of curve fitting.

INTRODUCTION

Interest in the fate of volatile organic chemicals in the vadose zone has resulted in the development of mathematical models designed to simulate solute transport in three-phase (gas, liquid, solid) systems. Gas-phase advective transport has been studied in relation to land disposal of waste gases [cf. Miyamoto *et al.*, 1974] and migration of gas from landfills [cf. Metcalfe and Farquhar, 1987]. However, the advent of "soil venting" or "vacuum extraction" as a popular means of remediating vadose zone contamination has greatly expanded interest in gas-phase processes, including gas-phase advection. The first generation of models designed to simulate gas-phase advective transport of organic chemicals were based on assumptions of ideal transport [cf. Johnson *et al.*, 1987; Wilson *et al.*, 1987, 1988; Baehr *et al.*, 1989]. For ideal transport it is assumed that properties of the porous media (e.g., hydraulic conductivity, sorption capacity) are spatially homogeneous at the macroscopic scale and also that sorption is instantaneous (the local equilibrium assumption). The heterogeneity of vadose zone systems has been established beyond doubt. In addition, the existence of secondary structures, including aggregates, fractures, and root channels, has been documented by numerous studies. Thus the assumption of homogeneity does not reflect reality.

Field observations inconsistent with the assumption of instantaneous sorption have been reported by several investigators. For example, analyses of soil and soil-gas samples taken from a contaminated field site indicated that the ratio of the concentration of trichloroethene in the soil gas to its soil-phase concentration was 1 to 3 orders of magnitude smaller than the ratio predicted by using an assumption of equilibrium conditions [Smith *et al.*, 1990]. The authors suggested that this apparent disequilibrium resulted from a slow desorption of trichloroethene from the soil phase.

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Observations of pesticide residues in agricultural fields long after application also support the invalidity of the local equilibrium assumption. For example, residues of 1,2-dibromoethane (EDB) were found to persist in fields as long as 19 years after application, even though EDB is volatile and readily degradable [Steinberg *et al.*, 1987]. Similar behavior was reported for DBCP (1,2-dibromo-3-chloropropane) by Buxton and Green [1987]. Considering the heterogeneous nature of porous media and the observations inconsistent with instantaneous sorption, it is improbable that gas-phase advective models based on ideal transport will accurately describe solute transport in the vadose zone.

A second generation of gas-phase advective models that incorporate nonideal phenomena are beginning to appear in the literature. Models based on the existence of two pore domains, macropore (gas-phase) and micropore (liquid-phase), were presented recently by Gierke *et al.* [1991] and Rasmuson *et al.* [1990]. Such models are likely to provide a more accurate representation of how fluid flow affects solute transport in the vadose zone. However, instantaneous, spatially invariant sorption was assumed for both models. Gas-phase advection models that included rate-limited sorption were presented by Brown and Rolston [1980] and van de Water [1989]. The models were developed, however, assuming homogeneous soil properties. It is likely that a model that includes both heterogeneity and rate-limited sorption will be required to accurately represent solute transport by gas-phase advection in the vadose zone. The purpose of this work is to present such a model.

A model is presented that incorporates the effects of physical heterogeneity (e.g., structured porous media) and rate-limited sorption on the transport of chemicals by gas-phase advection and dispersion. The governing equations are presented, and the finite difference numerical solution is tested against an analytical solution. Methods for determining values for input parameters are discussed. Performance of the model is evaluated by comparing simulations to data obtained from the literature.

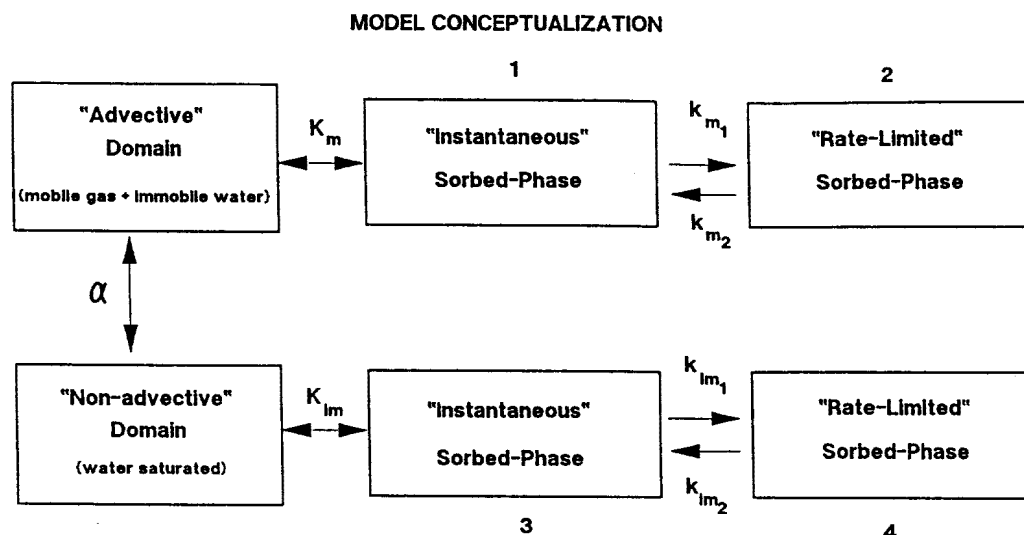


Fig. 1. Conceptual diagram of the MPNEG (multiprocess nonequilibrium transport by gas advection) model.

THEORY

The conceptual framework upon which the model is based is shown in Figure 1 and is similar to that developed by Brusseau *et al.* [1989] for solute transport by water flow. The processes included in the new model are as follows: (1) advective-dispersive transport in the gas phase, which resides in the "advective" domain (e.g., macroporosity), (2) equilibrium-governed partitioning to immobile water residing in the "advective" domain, (3) combined instantaneous and rate-limited mass transfer between water and solid phases residing in the "advective" domain, (4) rate-limited mass transfer between water residing in the "nonadvective" domain (e.g., microporosity) and the gas phase, and (5) combined instantaneous and rate-limited mass transfer between water and solid phases residing in the "nonadvective" domain. Each of the transport components will be discussed below, followed by the development of the governing equations.

Gas Flow

Three major differences exist between water flow and gas flow. First, the assumption of incompressibility that is used almost universally for water flow is typically not valid for gas flow. The dependency of gas density on pressure results in a nonlinear flow equation. Second, the assumption of zero flux at surfaces of solids, which is used for water flow, may not be valid for gas flow. Nonzero surface fluxes result in "slip flow" or the Klinkenberg effect. Third, much smaller pressure gradients are required to generate significant gas flow, in comparison to water flow, because of the lower viscosities of gases.

Although equations for gas flow must generally account for compressibility, there are conditions under which compressibility may be ignored. The assumption of incompressible gas flow is valid when the pressure difference inducing flow is approximately 20% or less [Alzayadi *et al.*, 1978; Krishnappa *et al.*, 1988; Wilson *et al.*, 1988; Croise *et al.*, 1989; Massmann, 1989; Johnson *et al.*, 1990]. Fortunately, soil-venting systems are operated using pressure differences of this magnitude or smaller [Payne *et al.*, 1987; Hutzler *et al.*, 1989; Massmann, 1989; Johnson *et al.*, 1990; McWhorter, 1990]. Hence models designed to simulate sol-

ute transport under conditions typical of soil venting can be based on the assumption of incompressible gas flow.

The Klinkenberg effect is generally negligible for silts, sands, and gravels [Massmann, 1989] and when the pressure difference is less than 20% [McWhorter, 1990]. Hence the Klinkenberg effect can be excluded from models designed for simulating transport under conditions typical of soil venting.

The net result of assuming that the pressure difference driving gas flow is small enough such that compressibility effects are negligible and that slippage effects are minimal is that Darcy's equation can be used for gas flow. Thus models developed for water flow can be used for gas flow. This approach has been used by several investigators for the development of gas-phase advective transport models [cf. Brown and Rolston, 1980; Johnson *et al.*, 1987; Gierke *et al.*, 1991; Rasmuson *et al.*, 1990], albeit without explicit justification. The assumptions of incompressibility and negligible slippage will be used herein.

Gas flow can be induced by density gradients as well as by pressure gradients. Density-driven flow may be of special concern for many of the organic chemicals found at contaminated sites because of the relatively high vapor pressures and molecular weights associated with these chemicals. The occurrence and significance of density-driven flow has been investigated recently. Density-driven flow will be of significance only in the vicinity of a large source (e.g., nonaqueous phase liquid) and when the hydraulic conductivity is high (i.e., coarse sand or gravel) [Falta *et al.*, 1989; Sleep and Sykes, 1989; Mendoza and Frind, 1990]. In addition, factors that reduce the gas-phase concentration, such as partitioning to pore water and sorption, will reduce the significance of density-driven flow [Falta *et al.*, 1989]. Density-driven flow is expected to be of significance therefore under only a few limited conditions. Density-driven flow will not be considered in the model to be developed herein.

Advective Transport in Heterogeneous/Structured Porous Media

In a two-fluid-phase system composed of gas and water, the gas will reside in the largest-diameter pores, whereas the

water will reside in the smaller pores. For structured porous media this means, generally, that the "macropores" will contain gas and possibly water films and that the "micropores" will be saturated with water. Mass transfer of solute between the gas (and water) residing in the macropores and the micropore water occurs by aqueous diffusion through the micropores. Many investigators have shown that physical nonequilibrium or nonideal transport occurs when mass transfer between the macropore and micropore domains is rate limited [cf. Davidson and Chang, 1972; van Genuchten and Wierenga, 1977; Rao et al., 1980; Nkedi-Kizza et al., 1984]. These studies were for water flow; moreover, Gierke et al. [1991] have shown recently that diffusion within water-saturated micropores caused nonideal transport for a system where gas was mobile and water was immobile.

The presence of media of differing hydraulic conductivity will also affect gas flow and thus solute transport. Gas will flow primarily through regions composed of coarser materials because of the differences in water retention capacities and pore sizes between coarse and fine-grained materials. Under these conditions the finer-grained regions act as sink/source components wherein mass transfer of solute between these nonadvective domains and the advective domain occurs by diffusion [Gillham et al., 1984; Goltz and Roberts, 1988; Brusseau and Rao, 1989a]. The effect of layered porous media on gas flow was demonstrated by Krishnappa et al. [1988] and Croise et al. [1989], who showed that gas does flow primarily through the layers of higher-hydraulic conductivity. They did not, however, investigate the effect on transport of solute.

The mobile-immobile concept, where advective transport occurs in the mobile domain and diffusive transport occurs in the immobile domain, has been used for systems influenced by dead-end pores [cf. Coats and Smith, 1964], water films [cf. Skopp and Warrick, 1974], aggregates [cf. Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976], channels [cf. Scotter, 1978], fractures [cf. Scotter, 1978; Grisak and Pickens, 1980], stagnant water pockets in (water) unsaturated media [cf. Gaudet et al., 1977], and regions of varying hydraulic conductivity [cf. Gillham et al., 1984; Goltz and Roberts, 1988; Brusseau, 1991]. Mass transfer of solute between the advective and nonadvective domains can be described by using a diffusion equation based on Fick's law or by some form of a mass transfer approximation. Models using the mass transfer approximation usually produce results that match those produced with a diffusion-based model [cf. Rao et al., 1980; Parker and Valocchi, 1986; Goltz and Roberts, 1988]. The first-order mass transfer approach will be used herein to describe mass transfer of solute between the advective and nonadvective domains.

Gas-Phase Diffusive/Dispersive Transport

For water flow, mechanical dispersion is usually much more significant than diffusion. Conversely, both dispersive and diffusive transport may contribute to total flux for gas-advection systems. Diffusion is of greater significance in the gas phase because gas-phase diffusion coefficients are much larger than aqueous-phase diffusion coefficients. On the basis of the few sets of experimental data available [cf. Rolston et al., 1969; Brown and Rolston, 1980; Gierke et al., 1991; Roberts, 1990], it appears that diffusion predominates over mechanical dispersion for gas-phase transport except, perhaps, when velocities are very high.

Diffusion in the gas phase is generally more complex than aqueous-phase diffusion. Gas-phase diffusion can occur not only by molecular diffusion but also by Knudsen diffusion and nonequimolar diffusion (see Youngquist [1970] and Thorstenson and Pollock [1989] for reviews of gas-phase diffusion). Equations based on Fick's law are not adequate for representing diffusion in systems where contributions of Knudsen and nonequimolar diffusion are significant. In these systems the "dusty gas" model is more appropriate [Thorstenson and Pollock, 1989]. Equations based on Fick's law are also not appropriate for systems where the concentration in the gas phase is not dilute or where evaporative fluxes (mass transfer from organic liquid to gas phase) occur [Baehr and Bruell, 1990].

The contribution of Knudsen diffusion will be negligible except for very fine grained materials [Youngquist, 1970; Thorstenson and Pollock, 1989]. The assumption of dilute concentrations in the gas phase will be valid except when large sources of a chemical with a high vapor pressure are present. Molecular diffusion may therefore be the predominant form of diffusion for vadose zone systems. For soil-venting applications a detailed description of diffusion is probably unnecessary because the contribution of advective flux will overwhelm that of diffusive flux when pressure differences are of the order of 1% [Thorstenson and Pollock, 1989]. Hence the use of equations based on Fick's law to represent diffusive flux should be adequate. Models using Fick's law to describe gas-phase diffusion have been used successfully to simulate gas-phase advective transport of solute in soil columns [Rolston et al., 1969; Brown and Rolston, 1980; Gierke et al., 1991].

Gas-Liquid and Film Mass Transfer

In the development of the model, mass transfer between gas and liquid (i.e., water) phases will be assumed to be essentially instantaneous and governed by Henry's law. Experiments have shown that the assumption of local equilibrium for gas-liquid mass transfer is usually good [cf. Baehr et al., 1989; Brusseau et al., 1990; Gierke et al., 1990, 1991], especially when other nonideality factors are present.

Rate-limited mass transfer of solute across stagnant water films solvating surfaces of solid phases will not be considered in developing the model. Several experiments have shown that film mass transfer has negligible effect on transport of solute in soils [cf. Hutzler et al., 1986; Roberts et al., 1987; Gierke et al., 1990, 1991].

Sorption

Sorption (both adsorption and desorption) of organic chemicals by soils, sediments, and aquifer materials is often rate limited, apparently by a diffusion-related mechanism [cf. Hamaker and Thompson, 1972; Karickhoff and Morris, 1985; Wu and Gschwend, 1986; Brusseau and Rao, 1989a; Ball and Roberts, 1991; Brusseau et al., 1991]. Rate-limited sorption has been modeled by using diffusion equations based on Fick's law [cf. Wu and Gschwend, 1986; Ball and Roberts, 1991] and by using chemical reaction equations [Selim et al., 1976; Cameron and Klute, 1977]. The first-order bicontinuum sorption model of Selim et al. [1976], wherein sorption is assumed to be instantaneous for a fraction of the sorbent and rate limited for the remainder,

will be used to describe sorption dynamics for the model being developed. The bicontinuum model can be used to represent systems where rate-limited sorption is caused by chemical reaction or by diffusion [Brusseau and Rao, 1989a].

For the development of the model it will be assumed that vapor-phase sorption is negligible. Several investigators have shown that sorption of organic vapors on surfaces is insignificant when relatively small amounts of water are present [cf. Chiou and Shoup, 1985; Rao et al., 1989; Smith et al., 1990; Ong and Lion, 1991]. Therefore the assumption of no vapor-phase sorption will be valid for most vadose zone systems.

Model Development

The multiprocess nonequilibrium transport by gas advection (MPNEG) model is presented in this section. The four equations governing one-dimensional transport under conditions of steady state gas flow and water content, and where water is immobile, are

$$\begin{aligned} & \theta_g \frac{\partial C_g}{\partial t} + \theta_{wg} \frac{\partial C_{wg}}{\partial t} + \theta_w \frac{\partial C_w}{\partial t} + f\rho \frac{\partial S_{m1}}{\partial t} + f\rho \frac{\partial S_{m2}}{\partial t} \\ & + (1-f)\rho \frac{\partial S_{im1}}{\partial t} + (1-f)\rho \frac{\partial S_{im2}}{\partial t} \\ & = \theta_g D \frac{\partial^2 C_g}{\partial x^2} - q \frac{\partial C_g}{\partial x} \end{aligned} \quad (1)$$

$$\begin{aligned} & \theta_w \frac{\partial C_w}{\partial t} + (1-f)\rho \frac{\partial S_{im1}}{\partial t} + (1-f)\rho \frac{\partial S_{im2}}{\partial t} \\ & = \alpha (C_g - K_H C_w) \end{aligned} \quad (2)$$

$$\frac{\partial S_{m2}}{\partial t} = k_{m2} [(1-F_m) K_m C_{wg} - S_{m2}] \quad (3)$$

$$\frac{\partial S_{im2}}{\partial t} = k_{im2} [(1-F_{im}) K_{im} C_w - S_{im2}] \quad (4)$$

All symbols are defined in the notation list unless defined by equation.

Inspection of (3) and (4) reveals that the sorption parameters (both equilibrium and rate constants) are described by a two-domain-type heterogeneity. That is, values for the equilibrium sorption constant and the sorption rate constant specified for the advective domain may be different from those specified for the nonadvective domain. This allows spatial heterogeneity of sorption parameters to be considered, albeit in a simple manner.

Equation (2) represents the mass balance on the nonadvective domain, where exchange of solute between the advective and nonadvective domains is governed by mass transfer. This mass transfer is composed of two steps: mass transfer between water residing in the nonadvective domain and water residing in the advective domain and mass transfer between advective domain water and the gas phase. Since both of these steps are incorporated into (2), the mass transfer coefficient (α) is a lumped parameter. However, as discussed above, gas-liquid mass transfer can often be considered as essentially instantaneous. In addition, gas-liquid mass transfer is likely to be more rapid than liquid-liquid micropore-macropore mass transfer. Since the slowest

step of a series of processes is rate limiting, gas-liquid mass transfer can usually be ignored, and α can be considered to represent liquid-liquid mass transfer.

Equations (1)-(4) can be transformed into the following nondimensional equations:

$$\begin{aligned} R_{m1} \frac{\partial C^*}{\partial T} + R_{m2} \frac{\partial S_m^*}{\partial T} + R_{im1} \frac{\partial C_w^*}{\partial T} + R_{im2} \frac{\partial S_{im}^*}{\partial T} \\ = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \end{aligned} \quad (5)$$

$$R_{im1} \frac{\partial C_w^*}{\partial T} + R_{im2} \frac{\partial S_{im}^*}{\partial T} = \omega (C^* - C_w^*) \quad (6)$$

$$R_{m2} \frac{\partial S_m^*}{\partial T} = k_m^0 (C^* - S_m^*) \quad (7)$$

$$R_{im2} \frac{\partial S_{im}^*}{\partial T} = k_{im}^0 (C_w^* - S_{im}^*) \quad (8)$$

by defining the following nondimensional parameters:

$$R = 1 + \frac{\theta_w T}{\theta_g K_H} + \frac{\rho}{\theta_g K_H} K_p \quad (9)$$

$$R_{m1} = 1 + \frac{\theta_{wg}}{\theta_g K_H} + \frac{f\rho}{\theta_g K_H} F_m K_m \quad (10)$$

$$R_{m2} = \frac{f\rho}{\theta_g K_H} (1 - F_m) K_m \quad (11)$$

$$R_{im1} = \frac{\theta_w}{\theta_g K_H} + \frac{(1-f)\rho}{\theta_g K_H} F_{im} K_{im} \quad (12)$$

$$R_{im2} = \frac{(1-f)\rho}{\theta_g K_H} (1 - F_{im}) K_{im} \quad (13)$$

$$T = tv/l \quad (14a)$$

$$P = vl/D \quad (14b)$$

$$X = x/l \quad (14c)$$

$$\omega = \alpha l / \theta_g v \quad (14d)$$

$$k_m^0 = \frac{k_{m2} l}{v} R_{m2} \quad (14e)$$

$$k_{im}^0 = \frac{k_{im2} l}{v} R_{im2} \quad (14f)$$

Relative or fractional retardation parameters may be defined as follows:

$$\beta_1 = R_{m1}/R \quad (15a)$$

$$\beta_2 = R_{m2}/R \quad (15b)$$

$$\beta_3 = R_{im1}/R \quad (15c)$$

$$\beta_4 = R_{im2}/R \quad (15d)$$

The total retardation factor (9) is the sum of R_{m1} , R_{m2} , R_{im1} , and R_{im2} . The four β parameters sum to unity.

A finite difference numerical method utilizing the Crank-Nicholson technique was programmed to solve the pertinent governing equations (5)–(8) under the following initial and boundary conditions [Brusseau *et al.*, 1989]:

$$C^*(X, 0) = C_{w0}^*(X, 0) = C_w^*(X, 0) = 0 \quad (16a)$$

$$S_m^*(X, 0) = S_{im}^*(X, 0) = 0 \quad (16b)$$

$$C_0^* = C^* - \frac{1}{P} \frac{\partial C^*}{\partial X} \Big|_{X=0} \quad (16c)$$

where

$$C_0^* = 1 \quad 0 \leq T \leq T_0 \quad (16d)$$

$$C_0^* = 0 \quad T > T_0 \quad (16e)$$

$$\frac{\partial C^*(X, T)}{\partial X} \Big|_{X=1} = 0 \quad T > 0 \quad (16f)$$

Note that the initial condition specified in (16a) and (16b) will be equal to 1, rather than 0, when gas stripping is simulated. Performance of the numerical solution was checked against an analytical solution [Brenner, 1962] for the simplified case of equilibrium sorption and homogeneous porous media ($f = 1$, $F = 1$, $\theta_w = 0$). The simulations produced with the numerical model closely matched those of the analytical solution.

As has been widely discussed in the literature, the flux-type boundary condition is more appropriate than a concentration-type condition for miscible displacement experiments and for representing samples taken from monitoring wells [cf. van Genuchten and Parker, 1984]. The boundary condition imposed in (16e) is used by Brenner [1962] and allows the determination of flux-averaged concentrations at $X = 1$. It has been shown that simulations produced with a solution employing this boundary condition are similar to those produced with a solution employing a semi-infinite column with no boundary effects accruing to the end plate, for P greater than approximately 5 [van Genuchten and Parker, 1984].

PARAMETER DETERMINATION

Mathematical models are often used to solve the inverse problem. The MPNEG model is coupled to a nonlinear, least squares, optimization program (UHAUS [Meeter and Wolfe, 1986]) to allow parameter determination by curve fitting of model simulations to experimental data. When curve fitting, it is wise to optimize as few parameters as possible. Thus determining values for input parameters by independent means (i.e., no curve fitting) is of interest. It is also of interest when using a model to predict solute transport. A general scheme for obtaining values for the parameters that are required to run the MPNEG model is presented below.

Peclet Number (P)

The Peclet number, in this case, represents the effect of gas-phase dispersion and diffusion on solute transport. The dispersion coefficient (D_a) represents the effect of nonuniform pore sizes and tortuous flow paths on advective flux.

Generally, all solutes will experience the same degree of dispersion (for one-dimensional transport). Hence the value for D_a determined from the breakthrough curve of an insoluble, nonsorbing solute may be used for soluble, sorbing solutes. The diffusion coefficient for a solute in a porous medium (D_d) is usually less than the free-gas diffusion coefficient (D_{g0}) because of tortuous paths (i.e., $D_d = D_{g0}/\tau_g$). Many correlation equations exist for estimating the tortuosity of the gas phase. These equations are typically based on the porosity of the gas phase. The performance of several of these equations have been evaluated [Sallam *et al.*, 1984; Collin and Rasmuson, 1988]. An equation of this type can be used to estimate τ_g , and D_d may then be calculated if D_{g0} is known.

Retardation Factor (R)

The retardation factor can be determined independently of curve fitting in two ways. The first method involves a mass balance analysis of the breakthrough curve (BTC). This can be done by measuring the area above the BTC for a frontal input [cf. Roberts *et al.*, 1980; van Genuchten and Parker, 1984; Nkedi-Kizza *et al.*, 1987] or by determining the first temporal moment for a pulse input [cf. Valocchi, 1985]. The second method involves calculating R values with (9). This approach obviously requires knowledge of all the parameters in (9). Values for K_H may be measured or taken from reference documents. Values for K_p may be measured (e.g., batch isotherm) or estimated by using correlation equations relating K_p to properties of the sorbent (e.g., organic carbon) and the solute (e.g., solubility, octanol-water partition coefficient).

Damkohler Number Representing Physical Heterogeneity (ω)

This parameter represents the effect of the heterogeneity or structure of the porous medium (i.e., mass transfer of solute between advective and nonadvective domains) on transport. We will assume that liquid-liquid mass transfer is the rate-controlling step and that the first-order mass transfer coefficient (α , see (14d)) can therefore be related to the free-liquid diffusion coefficient with an equation of the following form [cf. Parker and Valocchi, 1986; Brusseau and Rao, 1989a]:

$$\alpha = \frac{aD_{w0}\theta_w}{\tau_w\delta^2} \quad (17)$$

For a given porous medium the only solute-specific term in (17) is D_{w0} . The ω value for a sorbing solute (and for other nonsorbing solutes) can therefore be determined from that of a soluble, nonsorbing solute by use of the following equation:

$$\omega = \frac{\alpha_n\gamma l}{q} \quad (18)$$

where α_n is the first-order mass transfer coefficient calculated from the ω value determined for the soluble, nonsorbing solute and where

$$\gamma = D_{w0s}/D_{w0n} \quad (19)$$

(subscripts s and n represent the diffusion coefficients for the sorbing and nonsorbing solutes, respectively). Alternatively,

α can be calculated by using (17) if τ_w , δ , and D_{w0} are known. Values for α may be estimated by use of an empirical correlation equation. For example, α is a function of velocity [cf. van Genuchten and Wierenga, 1977; De Smedt and Wierenga, 1984] and a correlation equation of the form reported by De Smedt and Wierenga [1984] could be used to estimate α values for known velocities.

Damkohler Numbers Representing Rate-Limited Sorption (k^0)

The k_m^0 and k_{im}^0 parameters represent the contribution of rate-limited sorption to total nonideal transport. One approach for independent determination of sorption rate constants is a sorption rate experiment. Another approach is the use of an empirical correlation equation that relates the rate constant to the equilibrium sorption constant, as discussed by Brusseau and Rao [1989b].

Relative or Fractional Retardation Parameters (β_i)

These terms represent the contribution of each of the four mass distribution domains to total retardation. To independently determine values for all four β terms, knowledge of F_m , F_{im} , and f is required. Values for the F parameters could be determined by fitting a bicontinuum sorption model to the results obtained from a sorption rate experiment. F values may be estimated by using a correlation equation of the type reported by Brusseau et al. [1991]. Values for f may, in certain cases, be determined by direct measurement of physical properties of the porous medium. Various assumptions may be used to estimate f [Nkedi-Kizza et al., 1984]. For example, an assumption of $f = \theta_m/\theta$ has been used successfully [Nkedi-Kizza et al., 1984; Brusseau et al., 1989].

SENSITIVITY ANALYSIS

With the MPNEG model, considerable complexity is introduced into the solute transport equation in comparison to that imposed by models employing the assumptions of homogeneity and local equilibrium. It is important to identify the conditions under which the use of the MPNEG model is warranted and the conditions for which the simpler models are adequate. This endeavor is, in essence, one of identifying the conditions under which the local equilibrium assumption (LEA) is valid. To quantitatively evaluate LEA validity one must have a means to measure deviations from "ideal" behavior (i.e., behavior exhibited under conditions where the LEA is valid). A method based on comparison of temporal moments of solute breakthrough curves was presented by Valocchi [1985] and Parker and Valocchi [1986]. A quantitative error criterion was defined as

$$E_n = \frac{U_n^N - U_n^E}{U_n^E} \quad (20)$$

where U_n is the n th central temporal moment and the superscripts N and E refer to the nonequilibrium and LEA models, respectively. Inspection of (20) shows that E_n will increase as departure from conditions of local equilibrium increases and that $E_n = 0$ when LEA is valid.

The degree of "spreading" or dispersion, which is quan-

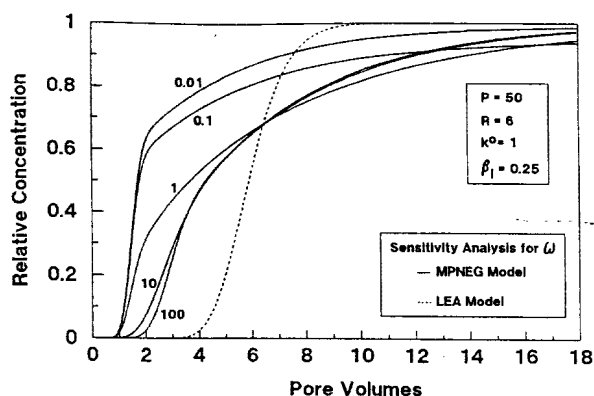


Fig. 2. Sensitivity analysis for ω , the nondimensional rate parameter (Damkohler number) specifying the degree of nonequilibrium between advective and nonadvective domains.

tified as the second central temporal moment, is often used to characterize nonideal solute transport. The second central temporal moment formula for the MPNEG model, for a square, finite pulse, is given by

$$U_2 = (2R^2/P) + (2R^2\beta_3^2/\omega) + (2R^2\beta_2^2/k_m^0) + (2R^2\beta_4^2/k_{im}^0) + (T_0^2/12) \quad (21)$$

The quantitative error criterion for the MPNEG model is

$$E_2 = P[\beta_3^2/\omega + \beta_2^2/k_m^0 + \beta_4^2/k_{im}^0] \quad (22)$$

when the influence of T_0 is neglected. Inspection of (22) shows that LEA validity, as measured by E_2 , is a function of P , the three β representing the three rate-limited mass transfer domains and the three Damkohler numbers. This concurs with the analyses presented by Valocchi [1985] and Parker and Valocchi [1986].

The influence of model parameters on the validity of the LEA can be assessed with (22). As evident from (22) and as discussed by Valocchi [1985], the magnitude of deviation from LEA is directly proportional to P . This functionality is a result of the manner in which the error criterion is defined. The criterion represented in (22) is an absolute measure. It can be shown that LEA validity is, in fact, independent of P if a relative approach is employed [Jennings and Kirkner, 1984; Brusseau et al., 1989]. Thus the two sets of parameters influencing relative LEA validity for the MPNEG model are the β terms representing the three rate-limited mass transfer domains and the three Damkohler numbers associated with these domains. The β terms are mass distribution parameters, whereas the Damkohler numbers are rate parameters. The sensitivity analyses will focus on the rate parameters.

A sensitivity analysis of the MPNEG model for ω is presented in Figure 2. Note that, for this discussion, it is assumed that $k_m^0 = k_{im}^0 = k^0$. When ω is greater than 10, the MPNEG simulation converges to that of a bicontinuum sorption model, becoming essentially identical at values greater than 100. The effect of mass transfer between water in the nonadvective domain and the mobile gas phase is relatively insignificant under conditions where ω is greater than 10 and becomes virtually nonexistent at values approaching 100. The dynamic range for ω is 0.01 to 100. Note the difference between the curve for $\omega = 100$ and the LEA curve. This results from rate-limited sorption (i.e., $k^0 = 1$).

TABLE 1. Values for Parameters

Data Set	v , cm/h	l , cm	ρ , g/cm ³	θ	θ_g	θ_{wg}	θ_w	D , cm ² /h	D_d , cm ² /h	K_p , cm ³ /g	K_H	F	f	k_2 , h ⁻¹	α , h ⁻¹
1	198	30	0.45	0.7	0.25	0.15	0.3	72	72	0	0.27	0	0	0	1.1
2	2290	30	1.63	0.41	0.31	0	0.1	723	53	0.42	0.286	0.35	0.76	10	100
3	57	10	1.3	0.609	0.483	0	0.126	220	220	3.18	3.63	0.2	0.79	3	4.6

The dynamic range for k^0 is also 0.01 to 100. When both ω and k^0 exceed 100, the simulation converges to that of the LEA model.

The magnitude of the Damkohler numbers is useful as a criterion for evaluating the validity of the LEA. The Damkohler number has been used by others as an LEA validity criterion. Results of their analyses showed the LEA to be valid when the limiting Damkohler number was approximately 100 or greater [Jennings and Kirkner, 1984; Valocchi, 1985; Bahr and Rubin, 1987]. These results are in agreement with those reported herein. Jennings and Kirkner [1984] reported a Damkohler number of 10 as being sufficient to produce a "reasonably good approximation" of LEA; this value is also in accord with the results presented above. It should be noted that, while the sensitivity analyses presented above were performed for one value of P and of R , the conclusions drawn from the analyses are applicable, in a relative sense, to all values of P and R .

MODEL EVALUATION

The performance of the MPNEG model will be evaluated by comparing predicted simulations to data obtained from the literature. These data represent some of the few column experiments that have been performed to investigate the transport of organic chemicals by gas-phase advective in soil.

Data Set 1

Gierke *et al.* [1991] investigated the influence of moisture content on the removal of toluene by vapor extraction from laboratory columns packed with a uniform sand and with an aggregated porous material (fired clay). For the aggregated material, removal was constrained by intraaggregate diffusion when the aggregates were saturated with water. This constraint resulted in a relatively long "tail", or delayed approach to $C^* = 0$. The investigators used a one-dimensional advective-diffusive transport model that included an intraaggregate diffusion term to simulate the data collected from the water-saturated aggregate column. Intraaggregate diffusion was described with an equation based on Fick's law. Toluene was not sorbed by the aggregated material under moist conditions. Hence this data set represents a system that is affected by physical nonideality but not by rate-limited sorption. This data set will be used to evaluate the ability of the MPNEG model to accurately simulate advective-diffusive transport affected by mass transfer between immobile water residing in micropores and a flowing gas phase.

For the evaluation, values for all parameters were obtained independent of curve fitting. This allows the MPNEG model to be used in a predictive mode. Values for v , l , θ , θ_g , θ_{wg} , θ_w , K_H , and D , were obtained from Gierke *et al.* [1991] and are reported in Table 1. All values except K_H

represent quantities measured by Gierke *et al.*; the value for K_H was taken from measurements reported by Ashworth *et al.* [1988]. Note that the value for D was calculated from $D = D_{g0}/\tau_g$, where D_{g0} was estimated with the method of Wilke and Lee [1955] and τ_g was estimated with the correlation equation of Millington [1959]. The remaining parameters were determined following the approach discussed in the parameter determination section.

A value for R was calculated with (9), and the Peclet number was calculated with (14b). The mass transfer coefficient (α) was calculated with (17) and the values for r and D_{w0}/τ_w reported by Gierke *et al.*, and ω was determined with (14d). Since toluene was not sorbed by the aggregated material, β_2 , β_4 , k_m^0 , and k_{im}^0 are zero. Values for β_1 and β_3 were calculated with (10), (12), (15a), and (15c). Values for the parameters required to run the MPNEG model are listed in Figure 3. The prediction obtained with the MPNEG model will be compared to one obtained with the LEA model, where mass transfer is assumed to be instantaneous.

The prediction obtained with the MPNEG model simulated the data much better than the prediction obtained with the LEA model, especially the early breakthrough and the extensive tailing (see Figure 3). The similarity between the MPNEG prediction and the data is especially encouraging, given that values for all of the parameters were calculated with measured properties. On the basis of this result it appears that the MPNEG model accurately represents the effect of micropore-macropore mass transfer on the advective-diffusive transport of organic solutes in the gas phase.

Data Set 2

Roberts [1990] investigated the effect of system variables on the removal of benzene and *p*-xylene by vapor extraction

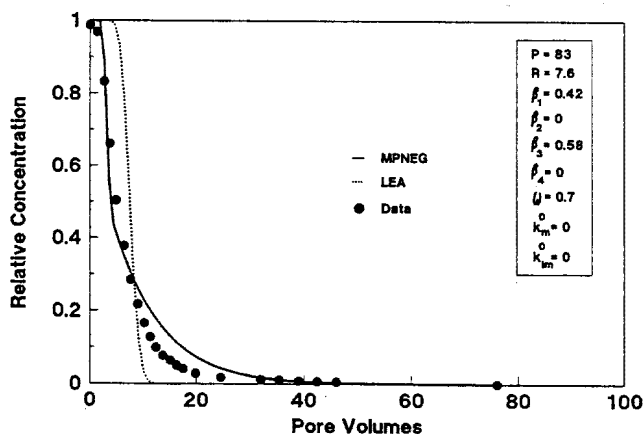


Fig. 3. Comparisons of predictions obtained with the MPNEG and LEA (local equilibrium assumption) models to data reported by Gierke *et al.* [1991].

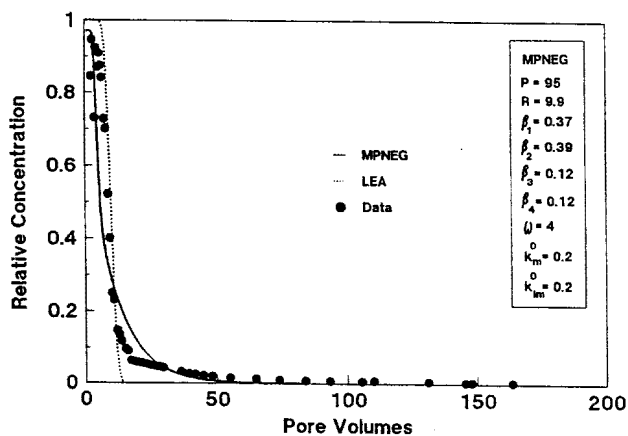


Fig. 4. Comparisons of predictions obtained with the MPNEG and LEA models to data reported by Roberts [1990].

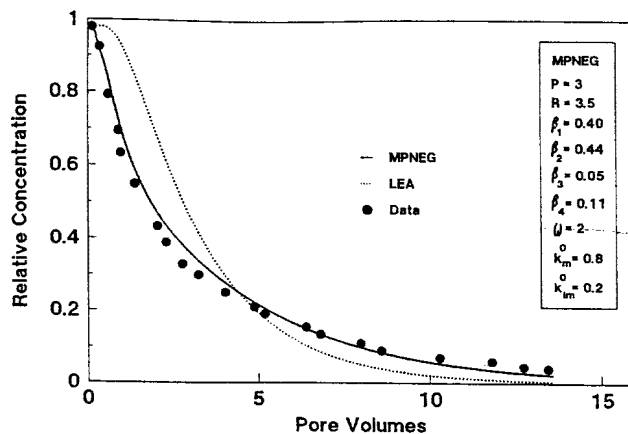


Fig. 5. Comparisons of predictions obtained with the MPNEG and LEA models to data reported by Brown and Rolston [1980].

from a laboratory column packed with a desert soil. The efficiency of removal increased with decreasing flow rate. Some of the data exhibited tailing that could not be simulated with either an LEA-based model or a rate-limited sorption model. A data set for *p*-xylene will be used to evaluate the performance of the MPNEG model in a case where both rate-limited sorption and physical nonideality may be operative.

For the evaluation, values for all parameters were again obtained independent of curve fitting. Values for v , l , ρ , θ , θ_g , θ_w , K_H , D , K_p , R , and P were obtained from Roberts [1990] and are reported in Table 1 and Figure 4. All values except K_H represent quantities measured by Roberts; the value for K_H was taken from data reported by Mackay and Shiu [1981]. Note that R was determined by mass balance analysis of the column data and that the Peclet number was calculated using a value of D determined from $D = D_a + D_{g0}/\tau_g$, where D_a was obtained from a helium tracer experiment and τ_g was estimated with the correlation equation of Millington [1959]. The remaining parameters were determined following the approach discussed in the parameter determination section.

The mass transfer coefficient (α) was estimated with the correlation equation of De Smedt and Wierenga [1984], and ω was determined by using (14d). A value for F was estimated by using the correlation equation reported by Brusseau et al. [1991]. The f parameter, which represents the fraction of sorbent associated with the advective domain, was approximated by the ratio of gas-filled porosity to total porosity. Inspection of (10)–(13) reveals that all parameters needed to calculate the retardation terms are now known (see Table 1). It was assumed that $k_{m2} = k_{im2} = k_2$; a value for k_2 was estimated with the correlation equation reported by Brusseau et al. [1991]. Values for k_m^0 and k_{im}^0 were calculated with (14e) and (14f). Values for the parameters required to run the MPNEG model are listed in Figure 4.

The prediction obtained with the MPNEG model provides a good representation of the data reported by Roberts [1990] (see Figure 4). The prediction obtained with the LEA model, wherein homogeneity and equilibrium sorption is assumed, is also shown in Figure 4. The MPNEG model provides a much better simulation of the data, especially of the tailing.

Data Set 3

Brown and Rolston [1980] investigated the gas-phase advective transport of methyl bromide through packed soil columns. The results of experiments conducted with Yolo loam at four velocities revealed the influence of rate-limited mass transfer. The investigators found that a model that included a "one-site" description of rate-limited sorption could not adequately simulate the data. The data set for the fastest velocity will be used to evaluate the performance of the MPNEG model in a case where both rate-limited sorption and physical nonideality may be operative.

Values for all parameters were obtained independent of curve fitting. Values for v , l , ρ , θ , θ_g , θ_w , and D were obtained from Brown and Rolston [1980] and are reported in Table 1. Note that D was determined from $D = D_{g0}/\tau_g$, where τ_g was obtained by approximation. A value for R was determined by mass balance analysis of the column data, and the Peclet number was calculated by using (14b). Values for α , ω , F , f , R_{m1} , R_{m2} , R_{im1} , R_{im2} , k_{m2} , k_m^0 , and k_{im}^0 were calculated in the same way as they were for data set 2. The value for K_H was approximated as the ratio of vapor pressure to aqueous solubility, values for which were obtained from Verschueren [1983]. Values for the parameters required to run the MPNEG model are listed in Figure 5.

The prediction obtained with the MPNEG model provides a very good representation of the data reported by Brown and Rolston [1980] (see Figure 5). The prediction obtained with the LEA model, wherein homogeneity and equilibrium sorption is assumed, is also shown in Figure 5. The MPNEG model provides a much better simulation of the data. On the basis of the results obtained from data sets 2 and 3, it appears that the MPNEG model can accurately simulate the effect of rate-limited sorption, as well as physical nonideality, on gas-phase transport of solute.

CONCLUSION

A model was presented that was designed to simulate gas-phase advective transport of organic chemicals in heterogeneous or structured porous media wherein sorption is rate limited. On the basis of comparisons of predictions obtained with the model to laboratory column data, it appears that the model provides an accurate description of solute transport under at least some conditions of nonideal-

ity. While further validation is required, the model should be useful in analyzing data obtained from laboratory column experiments. Given the conditions under which most soil venting systems are operated, the model may also be useful in analyzing the effect of soil venting on the transport of organic contaminants in the field. Of course, a complete analysis of soil venting would require a transient flow model of two or three dimensions.

NOTATION

- a geometric shape factor; spherical is 15 and planar is 3.
- C_g concentration of solute in gas phase $[M/L^3]$.
- C_0 concentration of solute in influent gas $[M/L^3]$.
- C_w concentration of solute in water located in nonadvective domain, that is, in disequilibrium with gas phase $[M/L^3]$.
- C_{wg} concentration of solute in water located in advective domain, that is, in equilibrium with gas phase $[M/L^3]$.
- C^* normalized gas-phase concentration (C_g/C_0).
- C_0^* normalized concentration of solute in influent gas (C_g/C_0).
- C_w^* normalized liquid-phase concentration in nonadvective domain ($C_w K_H/C_0$).
- D global dispersion coefficient ($D = D_a + D_d$) $[L^2/T]$.
- D_a "mechanical" dispersion coefficient $[L^2/T]$.
- D_d diffusion coefficient in gas-filled pores ($D_d = D_{g0}/\tau_g$) $[L^2/T]$.
- D_{g0} diffusion coefficient in gas $[L^2/T]$.
- D_{w0} diffusion coefficient in water $[L^2/T]$.
- f fraction of sorbent associated with advective domain.
- F_{im} fraction of sorbent in the nonadvective domain for which sorption is instantaneous.
- F_m fraction of sorbent in the advective domain for which sorption is instantaneous.
- k_{im2} first-order reverse sorption rate constant for nonadvective domain $[T^{-1}]$.
- k_{m2} first-order reverse sorption rate constant for advective domain $[T^{-1}]$.
- K_H Henry's law constant ($C_g = K_H C_{wg,w}$).
- K_{im} equilibrium sorption constant for the nonadvective domain $[L^3/M]$.
- K_m equilibrium sorption constant for the advective domain $[L^3/M]$.
- K_p weighted equilibrium sorption constant for entire porous medium ($K_p = fK_m + (1-f)K_{im}$) $[L^3/M]$.
- l length of porous medium $[L]$.
- q Darcy flux $[L/T]$.
- r radius of aggregate $[L]$.
- S_{m1} concentration of sorbate in "instantaneous" sorbent associated with advective domain ($S_{m1} = F_m K_m C_{wg}$) $[M/M]$.
- S_{m2} concentration of sorbate in "rate-limited" sorbent associated with advective domain (at equilibrium, $S_{m2} = (1 - F_m) K_m C_{wg}$) $[M/M]$.
- S_{im1} concentration of sorbate in "instantaneous" sorbent associated with nonadvective domain ($S_{im1} = F_{im} K_{im} C_w$) $[M/M]$.
- S_{im2} concentration of sorbate in "rate-limited" sorbent

- associated with nonadvective domain (at equilibrium, $S_{im2} = (1 - F_{im}) K_{im} C_w$) $[M/M]$.
- S_m^* normalized solid-phase concentration for "rate-limited" sorbent associated with the advective domain ($S_{m2} K_H / (1 - F_m) K_m C_0$).
- S_{im}^* normalized solid-phase concentration for "rate-limited" sorbent associated with the nonadvective domain ($S_{im2} K_H / (1 - F_{im}) K_{im} C_0$).
- t time $[T]$.
- T_0 size of input pulse in pore volumes.
- v average linear velocity ($v = q/\theta_g$) $[L/T]$.
- x distance $[L]$.
- α first-order mass transfer coefficient for mass transfer between water in nonadvective domain and mobile gas phase $[T^{-1}]$.
- δ characteristic diffusion length; r for spherical geometry $[L]$.
- θ total porosity ($\theta = \theta_g + \theta_{wg} + \theta_w$).
- θ_g gas-filled porosity.
- θ_m porosity of advective domain.
- θ_w water-filled porosity of nonadvective domain.
- θ_{wg} water-filled porosity of advective domain.
- θ_{wT} total water-filled porosity ($\theta_{wT} = \theta_{wg} + \theta_w$).
- ρ bulk density of porous medium $[M/L^3]$.
- τ_g tortuosity factor for gas-filled porous media.
- τ_w tortuosity factor for water-saturated porous media.

REFERENCES

- Alzaydi, A. A., C. A. Moore, and I. S. Rai, Combined pressure and diffusional transition region flow of gases in porous media, *AIChE J.*, 24(1), 35-43, 1978.
- Ashworth, R. A., G. B. Howe, M. E. Mullins, and T. N. Rogers, Air-water partitioning coefficients or organics in dilute aqueous solutions, *J. Hazard. Mater.*, 18, 25-36, 1988.
- Baehr, A. L., and C. J. Bruell, Application of the Stefan-Maxwell equations to determine limitations of Fick's law when modeling organic vapor transport in sand columns, *Water Resour. Res.*, 26(6), 1155-1163, 1990.
- Baehr, A. L., G. E. Hoag, and M. C. Marley, Removing volatile contaminants from the unsaturated zone by inducing advective air-phase transport, *J. Contam. Hydrol.*, 4(1), 1-26, 1989.
- Bahr, J. M., and J. Rubin, Direct comparison of kinetic and local equilibrium formulations for solute transport affected by surface reactions, *Water Resour. Res.*, 23(3), 438, 1987.
- Ball, W. P., and P. V. Roberts, Long-term sorption of halogenated organic chemicals by aquifer material, 2, Intraparticle diffusion, *Environ. Sci. Technol.*, 25(7), 1237-1249, 1991.
- Brenner, H., The diffusion model of longitudinal mixing in beds of finite length, *Chem. Eng. Sci.*, 17, 229-243, 1962.
- Brown, B. D., and D. E. Rolston, Transport and transformation of methyl bromide in soils, *Soil Sci.*, 130(2), 68-75, 1980.
- Brusseau, M. L., Application of multiprocess nonequilibrium-sorption model to solute transport in a stratified porous medium, *Water Resour. Res.*, 27(4), 589-595, 1991.
- Brusseau, M. L., and P. S. C. Rao, Sorption nonideality during organic contaminant transport in porous media, *CRC Crit. Rev. Environ. Control*, 19(1), 33-39, 1989a.
- Brusseau, M. L., and P. S. C. Rao, The influence of sorbate-organic matter interactions on sorption nonequilibrium, *Chemosphere*, 18(9/10), 1691-1706, 1989b.
- Brusseau, M. L., R. E. Jessup, and P. S. C. Rao, Modeling the transport of solutes influenced by multiprocess nonequilibrium, *Water Resour. Res.*, 25(9), 1971-1988, 1989.
- Brusseau, M. L., R. E. Jessup, and P. S. C. Rao, Sorption kinetics of organic chemicals: Evaluation of gas-purge and miscible-displacement techniques, *Environ. Sci. Technol.*, 24(5), 727-735, 1990.
- Brusseau, M. L., R. E. Jessup, and P. S. C. Rao, Nonequilibrium sorption of organic chemicals. Elucidation of rate-limiting processes, *Environ. Sci. Technol.*, 25(1), 134-142, 1991.

- Buxton, D. S., and R. E. Green, Desorption and leachability of DBCP residues in soils, in *Agronomy Abstracts*, p. 167, American Society of Agronomy, Madison, Wis., 1987.
- Cameron, D. R., and A. Klute, Convective-dispersive solute transport with a combined equilibrium and kinetic adsorption model, *Water Resour. Res.*, 13(1), 183-188, 1977.
- Chiou, C. T., and T. D. Shoup, Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity, *Environ. Sci. Technol.*, 19(12), 1196-1200, 1985.
- Coats, K. H., and B. D. Smith, Dead-end volume and dispersion in porous media, *Soc. Pet. Eng. J.*, 4, 73-84, 1964.
- Collin, M., and A. Rasmuson, A comparison of gas diffusivity models for unsaturated porous media, *Soil Sci. Soc. Am. J.*, 52(6), 1559-1565, 1988.
- Croise, J., W. Kinzelbach, and J. Schmolke, Computation of air flows induced in the zone of aeration during in situ remediation of volatile hydrocarbon spills, in *Contaminant Transport in Groundwater*, edited by H. E. Kobus and W. Kinzelbach, pp. 437-444, Balkema, Rotterdam, Netherlands, 1989.
- Davidson, J. M., and R. K. Chang, Transport of picloram in relation to soil physical conditions and pore water velocity, *Soil Sci. Soc. Am. Proc.*, 36, 257-261, 1972.
- De Smedt, F., and P. J. Wierenga, Solute transfer through columns of glass beads, *Water Resour. Res.*, 20(2), 225-232, 1984.
- Falta, R. W., I. Javandel, K. Pruess, and P. A. Witherspoon, Density-driven flow of gas in the unsaturated zone due to the evaporation of volatile organic compounds, *Water Resour. Res.*, 25(10), 2159-2169, 1989.
- Gaudet, J. P., H. Jegat, G. Vachaud, and P. J. Wierenga, Solute transfer, with exchange between mobile and stagnant water, through unsaturated sand, *Soil Sci. Soc. Am. J.*, 41(4), 665-671, 1977.
- Gierke, J. S., N. J. Hutzler, and J. C. Crittenden, Modeling the movement of volatile organic chemicals in columns of unsaturated soil, *Water Resour. Res.*, 26(7), 1529-1547, 1990.
- Gierke, J. S., N. J. Hutzler, and D. B. McKenzie, Vapor transport in unsaturated soil columns: Implications for vapor extraction, *Water Resour. Res.*, in press, 1991.
- Gillham, R. W., E. A. Sudicky, J. A. Cherry, and E. O. Frind, An advection-diffusion concept for solute transport in heterogeneous unconsolidated geological deposits, *Water Resour. Res.*, 20(3), 369-378, 1984.
- Goltz, M. N., and P. V. Roberts, Simulations of physical nonequilibrium solute transport models: Application to a large-scale field experiment, *J. Contam. Hydrol.*, 3(1), 37-63, 1988.
- Grisak, G. E., and J. F. Pickens, Solute transport through fractured media, 1, The effect of matrix diffusion, *Water Resour. Res.*, 16(4), 719-730, 1980.
- Hamaker, J. W., and J. M. Thompson, Adsorption, in *Organic Chemicals in the Soil Environment*, edited by C. A. I. Goring and J. W. Hamaker, pp. 49-143, Marcel Dekker, New York, 1972.
- Hutzler, N. C., J. C. Crittenden, J. S. Gierke, and A. S. Johnson, Transport of organic compounds with saturated groundwater flows: Experimental results, *Water Resour. Res.*, 22(3), 285-295, 1986.
- Hutzler, N. J., B. E. Murphy, and J. S. Gierke, State of technology review: Soil vapor extraction systems, *Rep. EPA 600/2-89-024*, 87 pp., Environ. Prot. Agency, Washington, D. C., 1989.
- Jennings, A. A., and D. J. Kirkner, Instantaneous equilibrium approximation analysis, *J. Hydraul. Eng.*, 110(12), 1700-1716, 1984.
- Johnson, P. C., M. W. Kemblowski, and J. D. Colthart, Quantitative analysis for the cleanup of hydrocarbon-contaminated soils by in-situ venting, *Ground Water*, 28(3), 413-429, 1990.
- Johnson, R. L., C. D. Palmer, and J. F. Keely, Mass transfer of organics between soil, water and vapor phases: Implication for monitoring, biodegradation and remediation, in *Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater-Prevention, Detection and Restoration*, pp. 493-507, National Water Well Association, Dublin, Ohio, 1987.
- Karickhoff, S. W., and K. R. Morris, Sorption dynamics of hydrophobic pollutants in sediment suspensions, *Environ. Toxicol. Chem.*, 4(5), 469-479, 1985.
- Krishnayya, A. V., M. J. O'Connor, J. G. Agar, and R. D. King, Vapour extraction systems factors affecting their design and performance, in *Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater-Prevention, Detection and Restoration*, pp. 547-568, National Water Well Association, Dublin, Ohio, 1988.
- Mackay, D., and W. Y. Shiu, Critical review of Henry's law constants for chemicals of environmental interest, *J. Phys. Chem. Ref. Data*, 10(4), 1175-1199, 1981.
- Massmann, J. W., Applying groundwater flow models in vapor extraction system design, *J. Environ. Eng.*, 115(1), 129-149, 1989.
- McWhorter, D. B., Unsteady radial flow of gas in the vadose zone, *J. Contam. Hydrol.*, 5(3), 297-314, 1990.
- Meeter, D. A., and P. J. Wolfe, UHAUS, *Suppl. Program Ser. 50*, Univ. of Wisc. Computing Cent., Madison, 1968.
- Mendoza, C. A., and E. O. Frind, Advective-dispersive transport of dense organic vapors in the unsaturated zone, 2, Sensitivity analysis, *Water Resour. Res.*, 26(3), 388-398, 1990.
- Metcalfe, D. E., and G. J. Farquhar, Modeling gas migration through unsaturated soils from waste disposal sites, *Water Air Soil Pollut.*, 32, 247-259, 1987.
- Millington, R. J., Gas diffusion in porous media, *Science*, 130, 100-102, 1959.
- Miyamoto, S., A. W. Warrick, and H. L. Bohn, Land disposal of waste gases, 1, Flow analysis of gas injection systems, *J. Environ. Qual.*, 3(1), 49-55, 1974.
- Nkedi-Kizza, P., J. W. Biggar, H. M. Selim, M. T. van Genuchten, P. J. Wierenga, J. M. Davidson, and D. R. Nielsen, On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated Oxisol, *Water Resour. Res.*, 20(8), 1123-1130, 1984.
- Nkedi-Kizza, P., P. S. C. Rao, and A. G. Hornsby, The influence of organic cosolvents on leaching of hydrophobic organic chemicals through soils, *Environ. Sci. Technol.*, 21(11), 1107-1111, 1987.
- Ong, S. K., and L. W. Lion, Effects of soil properties and moisture on the sorption of trichloroethylene vapor, *Water Res.*, 25(1), 29-36, 1991.
- Parker, J. C., and A. J. Valocchi, Constraints on validity of equilibrium and first-order kinetic transport models in structural soils, *Water Resour. Res.*, 22(3), 399-407, 1986.
- Payne, F. C., C. P. Cabbage, G. L. Kilmer, and L. H. Fish, In-situ removal of purgeable organic compounds from vadose zone soils, pp. 365-369 in *Proceedings of the 41st Industrial Waste Conference*, Purdue University, Lewis Publishers, Ann Arbor, Mich., 1987.
- Rao, P. S. C., D. E. Rolston, R. E. Jessup, and J. M. Davidson, Solute transport in aggregated porous media: Theoretical and experimental evaluation, *Soil Sci. Soc. Am. J.*, 44(6), 1139-1146, 1980.
- Rao, P. S. C., R. A. Ogwada, and R. D. Rhue, Adsorption of volatile organic compounds on anhydrous and hydrated sorbents: Equilibrium adsorption and energetics, *Chemosphere*, 18(11/12), 2177-2191, 1989.
- Rasmuson, A., T. Gimmi, and H. Fluhler, Modeling reactive gas uptake, transport, and transformation in aggregated soils, *Soil Sci. Soc. Am. J.*, 54(5), 1206-1213, 1990.
- Roberts, P. A., The effects of system variables on soil-vapor extraction of benzene and p-xylene in an unsaturated desert soil, M.S. thesis, Univ. of Ariz., Tucson, 1990.
- Roberts, P. V., P. L. McCarty, M. Reinhard, and J. Schreiner, Organic contaminant behavior during groundwater recharge, *J. Water Pollut. Control. Fed.*, 52(1), 161-171, 1980.
- Roberts, P. V., M. N. Goltz, R. S. Summers, J. C. Crittenden, and P. Nkedi-Kizza, The influence of mass transfer on solute transport in column experiments with an aggregated soil, *J. Contam. Hydrol.*, 1(4), 375-393, 1987.
- Rolston, D. E., D. Kirkham, and D. R. Nielsen, Miscible displacement of gases through soil columns, *Soil Sci. Soc. Am. Proc.*, 33(4), 488-492, 1969.
- Sallam, A., W. A. Jury, and J. Letey, Measurement of gas diffusion coefficient under relatively low air-filled porosity, *Soil Sci. Soc. Am. J.*, 48(1), 3-6, 1984.
- Scotter, D. R., Preferential solute movement through larger soil voids, I, Some computations using simple theory, *Aust. J. Soil Res.*, 16, 257-267, 1978.
- Selim, H. M., J. M. Davidson, and R. S. Mansell, Evaluation of a two-site adsorption-desorption model for describing solute transport in soils, in *Proceedings of the Summer Computer Simulation*

- Conference, Washington, D. C., July 12-14, 1976, pp. 444-448, Simulation Councils, La Jolla, Calif., 1976.
- Skopp, J., and A. W. Warrick, A two-phase model for the miscible displacement of reactive solutes in soil, *Soil Sci. Soc. Am. Proc.*, 38(4), 545-550, 1974.
- Sleep, B. E., and J. F. Sykes, Modeling the transport of volatile organics in variably saturated media, *Water Resour. Res.*, 25(1), 81-92, 1989.
- Smith, J. A., C. T. Chiou, J. A. Kammer, and D. E. Kile, Effect of soil moisture on the sorption of trichloroethene vapor to vadose-zone soil at Picatinny arsenal, New Jersey, *Environ. Sci. Technol.*, 24(5), 676-683, 1990.
- Steinberg, S. M., J. J. Pignatello, and B. L. Sawhney, Persistence of 1,2-dibromomethane in soils: Entrapment in intraparticle micropores, *Environ. Sci. Technol.*, 21, 1201-1208, 1987.
- Thorstenson, D. C., and D. W. Pollock, Gas transport in unsaturated porous media: The adequacy of Fick's Law, *Rev. Geophys.*, 27(1), 61-78, 1989.
- Valocchi, A. J., Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils, *Water Resour. Res.*, 22(4), 693-820, 1985.
- van de Water, J. G., Physical and chemical processes affecting forced ventilation of benzene and p-xylene in a desert soil, M.S. thesis, Univ. of Ariz., Tucson, 1989.
- van Genuchten, M. T., and J. C. Parker, Boundary conditions for displacement experiments through short laboratory soil columns, *Soil Sci. Soc. Am. J.*, 48(3), 703-708, 1984.
- van Genuchten, M. T., and P. J. Wierenga, Mass transfer studies in sorbing porous media: Analytical solutions, *Soil Sci. Soc. Am. J.*, 40(3), 473-479, 1976.
- van Genuchten, M. T., and P. J. Wierenga, Mass transfer studies in sorbing porous media: Experimental evaluation with tritium, *Soil Sci. Soc. Am. J.*, 41(2), 272-278, 1977.
- Verschuere, K., *Handbook of Environmental Data on Organic Chemicals*, Van Nostrand Reinhold, New York, 1983.
- Wilke, C. R., and C. Y. Lee, Estimation of diffusion coefficients for gases and vapors, *Ind. Eng. Chem. Res.*, 47(6), 1253-1257, 1955.
- Wilson, D. E., R. E. Montgomery, and M. R. Sheller, A mathematical model for removing volatile subsurface hydrocarbons by miscible displacement, *Water Air Soil Pollut.*, 33, 231-255, 1987.
- Wilson, D. J., A. N. Clarke, and J. H. Clarke, Soil clean up by in-situ aeration, I, Mathematical modeling, *Sep. Sci. Technol.*, 23(10-11), 991-1037, 1988.
- Wu, S., and P. M. Gschwend, Sorption kinetics of hydrophobic organic compounds to natural sediments and soils, *Environ. Sci. Technol.*, 20(7), 717-725, 1986.
- Youngquist, G. R., Diffusion and flow of gases in porous solids, in *Flow Through Porous Media*, pp. 58-69, American Chemical Society, Washington, D. C., 1970.

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