

MASS TRANSFER PROCESSES AND FIELD-SCALE TRANSPORT OF ORGANIC SOLUTES

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Abstract

The influence of mass transfer processes, such as sorption/desorption and mass transfer between immiscible liquid and water, on the transport of organic solutes is discussed. Rate-limited sorption of organic solutes, caused by a diffusion-constrained mechanism, is shown to be significant under laboratory conditions. The significance of the impact of nonequilibrium sorption on field-scale transport is scale dependent. The impact of organic liquids on mass transfer and transport of organic solutes depends upon the nature of the solute and the nature and form of the organic liquid. For example, while retardation of nonionic solutes is decreased in mixed-solvent systems (i.e., systems comprised of water and a miscible organic liquid or an immiscible liquid present in concentrations below phase separation), the retardation of organic acids may, in some cases, increase with addition of a cosolvent. While the presence of an immiscible liquid existing as a mobile phase will reduce retention of organic solutes, the presence of residual saturation of an immiscible liquid can significantly increase retention. A model is presented that incorporates the effects of retention resulting from residual saturation, as well as nonequilibrium sorption, on the transport of organic solutes.

Introduction

The transport and fate of organic contaminants in the subsurface has become a topic of great concern. Investigating the chemical profile and migration pattern of contaminant plumes emanating from landfills, hazardous waste sites, or sites of accidental spills, evaluating the potential of drinking-water supplies becoming contaminated, and assessing the efficacy of remediation schemes are examples of endeavors that require an understanding of the physical, chemical, and biological processes that influence the disposition of contaminants in the subsurface. Research on these processes has increased greatly in response to the desire to manage, remediate, and prevent soil and groundwater contamination. Mass transfer processes, such as sorption/desorption and mass transfer between immiscible liquid and water, have received a significant degree of attention because of their potential mediating impact on other transport and fate processes. The question of nonequilibrium is beginning to be addressed as the potential impact of rate-limited mass transfer is becoming recognized. The impact of mass transfer processes on field-scale transport of organic solutes will be discussed.

Sorption/Desorption in Aqueous Systems

Rate-limited sorption/desorption can have serious implications for modeling solute transport. A primary assumption employed for most solute transport models is the so-called local equilibrium assumption (LEA). With the LEA, interactions between a solute and the solid phase of the porous media (e.g., sorption) are assumed to be rapid in comparison to advective-dispersive transport (i.e., hydrodynamic residence time). The validity of the LEA has recently come into question, reflecting the results obtained from theoretical and experimental analyses (c.f., Rao and Jessup, 1983; Jennings and Kirkner, 1984; Valocchi, 1985; Bahr and Rubin, 1987; Brusseau and Rao, 1989a). Obviously, the validity of a model employing the LEA will be dependent upon the appropriateness of that assumption, which, in turn, is dependent in part upon whether or not sorption is rate limited. Rate-limited sorption/desorption can also impact the remediation of contaminated soils and aquifers by increasing the time required to attain cleanup (Brusseau and Rao, 1989a; Keely, 1989; Mackay and Cherry, 1989).

Rate-Limiting Mechanisms

Although a discourse on rate-limiting mechanisms is not the purpose of this presentation, some discussion in this regard is of interest. Processes proposed as causing nonequilibrium can be grouped into three categories (Brusseau and Rao, 1989a): 1) transport-related nonequilibrium, which results from heterogeneous soil/aquifer properties (e.g., hydraulic conductivity), 2) chemical nonequilibrium, which is caused by rate-limited sorbate-sorbent interactions, and 3) intrasorbent diffusion, which has been postulated to occur within sorbent organic matter (i.e., intraorganic matter diffusion) or microporous mineral particles (i.e., retarded intraparticle diffusion). The absence of transport-related nonequilibrium has been reported for laboratory experiments performed using columns uniformly packed with small particle-size materials (e.g., sandy soils and aquifer materials) (Bouchard et al., 1988; Lee et al., 1988; Brusseau, 1990; Brusseau and Rao, 1989a; Brusseau et al., 1989a; 1990a; 1990b; 1990c; Nkedi-Kizza et al., 1989). Thus, the nonequilibrium that is observed for organic solutes in such systems results from a sorption-related, rather than transport-related, mechanism.

The sorption of nonionic, low-polarity, hydrophobic organic chemicals (HOCs) is generally considered to be predominated by "solvophobic" interactions (c.f., Chiou et al., 1979; Karickhoff, 1984) and, as such, is unlikely to be constrained by a rate-limited chemical reaction (Brusseau and Rao, 1989a; 1989b). That such is the case was recently demonstrated by Brusseau et al. (1990b). Intrasorbent diffusion would, therefore, appear to be the most likely cause of the rate-limited sorption observed for HOCs. Diffusion-limited sorption has been proposed by several researchers as the probable cause of

nonequilibrium for organic solutes (Hamaker et al., 1966; Leenheer and Alrichs, 1971; Rao and Jessup, 1983; Karickhoff and Morris, 1985; Coates and Elzerman, 1986; Wu and Gschwend, 1986; Ball, 1989; Brusseau and Rao, 1989a). Until recently, however, it has not been possible to elucidate the particular mechanism causing nonequilibrium sorption. Results of experiments designed to identify the responsible mechanism were reported by Brusseau et al. (1990b). After demonstrating that the observed nonequilibrium was not caused by transport-related nonequilibrium or chemical nonequilibrium, they analyzed their data in terms of two mass-transfer-limited, intrasorbent diffusion models: intraorganic matter diffusion and retarded intraparticle diffusion. While the data could not be explained using the latter model, they could be explained using the former model. Hence, it was suggested that nonequilibrium sorption of HOCs is, in many cases, caused by intraorganic matter diffusion.

Relationship Between Kinetic and Equilibrium Parameters

The relationship between kinetic and equilibrium properties of a system is a question of great interest. To investigate the existence and nature of such relationships with regards to sorption, Brusseau and Rao (1989b) analyzed a large set of literature data using the linear free energy relationship technique. Their results revealed the existence of a log-log linear inverse relationship between the first-order desorption rate constant (k_2) and the equilibrium sorption constant (K_p). Such a relationship is consistent with a diffusion-limited nonequilibrium process (Brusseau and Rao, 1989b; Brusseau et al., 1990b). The k_2 - K_p relationship has since been substantiated through experiment (Brusseau, 1990; Brusseau et al., 1990a; 1990b; 1990c).

The regression equations relating k_2 to K_p should prove useful in providing a means to estimate parameter values for first-order bicontinuum models. Empirical equations of this type have been successfully used to provide estimates for the prediction of breakthrough curves influenced by nonequilibrium (Brusseau et al., 1989b). There is potential for applying these relationships in a manner similar to that in which the K_p - K_{ow} relationships are used.

Nonequilibrium Sorption in Low Organic Carbon Systems

Early research on rate-limited sorption and the influence of nonequilibrium on the transport of organic chemicals was performed by soil scientists (c.f., Hamaker et al., 1966; Hance, 1967; Kay and Elrich, 1967; Davidson et al., 1968; Leenheer and Alrichs, 1971; Davidson and Chang, 1972; Green et al., 1972). A significant amount of research on this subject has since been reported in both the soil science and environmental science literature (c.f., van Genuchten et al., 1977; Karickhoff, 1980; Schwarzenbach and

Westall, 1981; McCall and Agin, 1985; Karickhoff and Morris, 1985; Coates and Elzerman, 1986; Hutzler et al., 1986; Wu and Gschwend, 1986; Southworth et al., 1987; Bouchard et al., 1988; Miller and Weber, 1988; Brusseau et al., 1989a; 1989b; 1990a; 1990b; Nkedi-Kizza et al., 1989). The organic carbon contents of the sorbents employed in these studies ranged from 0.1% to 1.0% or greater. Research on the rate-limited sorption of organic chemicals by aquifer materials with organic carbon contents less than 0.1% has been reported by only a few authors (c.f., Curtis et al., 1986; Lee et al., 1988; Ball, 1989; Brusseau, 1990; Brusseau et al., 1990a; 1990b; 1990c).

The occurrence and significance of nonequilibrium sorption for HOCs in low organic carbon systems was evaluated in separate experiments by Brusseau (1990) and Brusseau et al. (1990c). Five aquifer materials collected from sites located in the U.S. and Canada were used in the former experiments, while three aquifer materials collected in Denmark were used in the latter experiments. Results from both sets of experiments were generally consistent with those obtained for systems comprised of higher organic carbon contents. For example, the relationships between k_2 and K_p reported for the low organic carbon systems were similar to those obtained for higher organic carbon systems.

An initial attempt at assessing the general applicability of the k_2 - K_p relationship for low organic carbon systems was made by Brusseau et al. (1990c) using data reported by Ball (1989), who employed long-term (100 days) batch rate studies to examine the sorption of tetrachloroethene by Borden aquifer material. The data point representing the k_2 and K_p values reported for Ball's experiment are plotted in Figure 1 along with the data reported by Brusseau et al. (1990c). The correspondence between the two data sets suggests that the k_2 - K_p relationship reported by Brusseau et al. (1990c) may be useful as a means to estimate rate constants for systems other than those used by Brusseau et al. (1990c). Although these results are promising, the general applicability of the k_2 - K_p relationships discussed herein is a question that requires further investigation.

It is interesting to note that the data reported by Ball (1989) was obtained using the batch-rate technique, while those of Brusseau et al. (1990c) were obtained using miscible displacement. The similarity between the data suggests that these two techniques provide comparable results. A similar observation was reported by Brusseau et al. (1990a), who compared the performance of the gas-purge and miscible-displacement techniques.

Impact of Time Scale on Rate Data

The potential impact of time-scale effects on the degree of nonequilibrium observed in, and the magnitude of resultant rate constants obtained from, sorption rate experiments is of great interest. To investigate this, Brusseau et al. (1990c) compared their data and that of Ball (1989) to data reported by Curtis et al. (1986) and Lee et al. (1988). Curtis et al. (1986) reported the results of relatively short term (i.e., 6 day) batch rate-study experiments performed with tetrachloroethene and Borden aquifer material, while Lee et al. (1988) reported results of miscible displacement experiments performed at relatively high pore-water velocities (i.e., 24 cm/hr) using trichloroethene and two aquifer materials, Borden and Lula. The time scales associated with the data of Brusseau et al. (1990c), which were obtained at pore-water velocities less than 1 cm/hr, and that of Ball are significantly greater than those associated with the data of Curtis et al. and Lee et al. Hence, comparison of these data sets should reveal the presence of time-scale effects, if any exist.

Inspection of the data, provided in Figure 1, suggests that there is, indeed, a time-scale effect. It is possible that the longer times associated with the experiments of Ball (1989) and Brusseau et al. (1990c) may allow rate-limited processes characterized by large time constants (i.e., small rate constants) to proceed to a sufficient extent such that their impact is experimentally discernable. In contrast, the times associated with the experiments of Curtis et al. and Lee et al. may not be sufficient to capture the effects of highly rate-limited processes. The time-scale effect may also be related to the nature in which the first-order rate constant is defined. Although k_2 is assumed to be a constant, it can vary with time scale because of changes in "average" gradients with time. The time-averaged nature of first-order rate constants has been discussed by Rao et al. (1980) and Cussler (1984).

The velocity dependence of k_2 was investigated by Brusseau (1990), who reported that k_2 increased proportionately with pore-water velocity. However, K_p values were reported to be essentially independent of velocity. This latter observation suggests that additional sorption was not taking place at the slower velocity and, therefore, that the velocity dependence of k_2 was related to the nature of the first-order approximation.

These observations have significant import regarding the manner in which sorption-rate experiments are performed and the applicability of data so obtained. These results also suggest that a valid comparison of the performances of different experimental techniques will be obtained only when similar time scales are employed.

Implications For Field-Scale Transport

The question of whether the rate-limited sorption that has been observed for laboratory experiments would have a significant impact on transport at the field scale will depend on several factors, including the hydrodynamic residence time (i.e., pore-water velocity and system length) and the occurrence of other nonidealities such as soil/aquifer heterogeneity (Brusseau and Rao, 1989c; Brusseau et al., 1989b). This question was investigated by Brusseau and Rao (1989c) and Brusseau et al. (1990c) by comparing the magnitudes of the rate constants obtained for HOCs and low organic carbon systems from laboratory experiments to those obtained from analysis of a natural-gradient experiment performed at the Canadian Air Forces Base Borden. The data obtained from this field experiment were modeled by Goltz and Roberts (1986) and Brusseau and Rao (1989c) using single-process and multi-process nonequilibrium models, respectively. The rate constants reported by these researchers are approximately one order-of-magnitude smaller than the values estimated using the k_2 - K_p relationship reported by Brusseau et al. (1990c). Hence, it appears that rate-limited sorption was perhaps only a minor contributor to the nonideal behavior observed in the Borden field experiment. The impact of rate-limited sorption may be of greater significance, however, for induced-gradient systems, considering the increased velocities (and reduced residence times) obtained with pumping. The effect of induced gradients on the impact of rate-limited sorption is of special concern given that "pump and treat" is one of the most widely used means of remediating contaminated groundwater.

Miscible and Immiscible Organic Solvents

Much of the research on organic subsurface contaminants has focused on dissolved constituents in aqueous systems, as discussed above. However, the behavior of organic liquids (e.g., solvents, gasoline) is beginning to receive increased attention. The nature of this latter work has been defined by the characteristics of the two general classes of organic liquids: miscible and immiscible. Note that, although the term immiscible is used, such liquids are soluble to some degree in water. The following discussion will focus on the nature of mass transfer processes in the presence of organic liquids. The impact of organic liquids as cosolvents will be discussed first, while the impact of separate liquid phases will be discussed thereafter.

Cosolvency by Organic Liquids

Interest in miscible organic liquids has centered on their effect on the physicochemical properties of water and the resultant impacts on solute behavior in the mixed-solvent system. For example, addition of a miscible solvent such as methanol to an aqueous system results in enhanced solubility, reduced sorption, and enhanced transport of organic solutes (c.f., Yalkowsky et al., 1972; Rao et al., 1985; Nkedi-Kizza et al., 1985;

Fu and Luthy, 1986a; 1986b; Nkedi-Kizza et al., 1987; 1989; Brusseau et al., 1990a; Wood et al., 1990). The cosolvency of immiscible liquids present at concentrations below phase separation was investigated by Pinal et al. (1990) and Rao et al. (1990). They found that, while the impact of immiscible cosolvents on solubility and sorption of hydrophobic organic solutes depended upon the polarity of the cosolvent, the general trends were similar to those observed for miscible cosolvents.

The research discussed above has concentrated on the equilibrium behavior of nonionic, low-polarity organic solutes. In contrast, the equilibrium behavior of ionizable organic solutes in mixed-solvent systems has been addressed by few investigators. A dearth of research also exists for the impact of cosolvents on the kinetics of sorption/desorption. These two topics will be briefly discussed.

Cosolvency of ionizable organic solutes

The sorptive behavior of ionizable organic solutes in aqueous systems, while having received less attention than nonionizable solutes, is beginning to be fairly well understood. The relative values of the dissociation constant (pK_a) of the solute and the pH of the system are of prime importance in mediating the magnitude and nature of sorption of ionizable solutes. For example, sorption of organic acids such as phenol is usually much greater when the system pH is lower than the pK_a value (i.e., when the molecule is neutral), than when pH is higher than the pK_a (i.e., when the molecule is anionic). The fact that sorption is essentially nonexistent (i.e., retardation factor = 1) for many organic acids under conditions typical to the subsurface has fomented the use of these organic acids as groundwater tracers.

The impact of organic cosolvents on the sorption of ionizable organic solutes has received very little attention to date. Decreases in sorption of ionizable solutes present in the neutral form with increasing fraction of cosolvent were similar to those observed for nonionizable solutes (Fu and Luthy, 1986b; Lee et al., 1990), as might be expected. In these cases, however, the system pH was fixed. The impact of cosolvents on sorption of ionizable solutes in systems where pH is not controlled is of great interest, considering the impact organic cosolvents can have on the pH of the system and on the pK_a of the solute. The pK_a of an ionizable solute changes with the composition of the solvent because of the so-called medium effect, which results from differences in solvent-solvent and solute-solvent interactions (c.f., Bates, 1969). The pK_a value of an organic acid will increase with increasing fraction of cosolvent (c.f., Parsons and Rochester, 1975; Rubino and Berryhill, 1986), while that of an organic base will decrease (c.f., Gowland and Schmid, 1969). Observe that for both cases, the shift in pK_a promotes formation of the

neutral species. This shift in speciation could significantly affect the nature and magnitude of sorption.

To illustrate the impact of cosolvent on transport of ionizable solutes, breakthrough curves obtained for pentafluorobenzoic acid in water and methanol systems are compared in Figure 2. Note that no sorption is observed for the aqueous system and that the retardation factor is, therefore, 1. In contrast, R is greater than 1 for the methanol system. This change in R would negate the use of pentafluorobenzoic acid as a tracer to delineate the velocity of water flow. The increase in retardation with addition of an organic cosolvent has also been observed for other acids such as dicamba and 2,4-dichlorophenoxyacetic acid (Hassett et al., 1981; Brusseau, 1989: unpublished data). The behavior discussed in this section may be important at waste-disposal sites, where ionogenic chemicals may co-exist with organic solvents.

The impact of cosolvents on nonequilibrium sorption

As discussed above, there has been little work reported on the impact of cosolvents on nonequilibrium sorption of organic solutes. A decrease in the symmetry of breakthrough curves with increasing volume fraction of cosolvent was reported by Nkedi-Kizza et al., (1987), who were investigating the transport of two herbicides (diuron and atrazine) in columns packed with a sandy soil. The decrease in breakthrough curve asymmetry, which was attributed by the authors to nonequilibrium sorption, with increasing cosolvent content suggests that the rate of sorption is greater in the presence of a cosolvent. The sorption of dioxins by soils from water/methanol mixtures was observed to be more rapid at higher methanol contents (Walters and Guiseppi-Elie, 1988). The desorption rate constant (k_2) has been observed to increase with increasing fraction of cosolvent (Brusseau et al., 1989c; Nkedi-Kizza et al., 1989; Elzerman, et al., 1989).

A quantitative investigation of the impact of organic cosolvents on nonequilibrium sorption of organic solutes was presented by Brusseau et al. (1989c; 1990d). They presented a model that predicts a log-linear relationship between k_2 and f_c , the volume fraction of cosolvent. The validity of this model was substantiated using experimental data. The mechanism responsible for the cosolvency effect on sorption kinetics was postulated to involve changes in conformation of the sorbent organic carbon matrix, which are induced by changes in solvent polarity that result from the addition of a cosolvent.

One question of interest is the applicability of the k_2 - K_p relationships discussed above, which were obtained for aqueous systems, to mixed-solvent systems. Brusseau et al. (1990d) have shown that k_2 - K_p relationships determined for systems comprised of mixtures of miscible cosolvents and water are no different from those determined for aqueous systems. Values of k_2 determined for systems where an immiscible liquid was the mobile phase have also been shown to be similar to those determined for aqueous systems, as will be discussed below. Thus, it appears that k_2 - K_p relationships developed from aqueous systems may be used for mixed-solvent systems.

Separate-Phase Organic Liquids

The disposition of immiscible organic liquids in the subsurface is of interest to environmental scientists, hydrologists, environmental/civil engineers, and petroleum engineers. The vast majority of research performed by these groups has focused on the movement, entrapment, and displacement of the liquid (c.f., Marle, 1981; Schwille, 1988). This reflects concerns associated with petroleum-reservoir engineering as well as remediation of solvent- and petroleum- contaminated sites. Another aspect that has begun to receive attention is the dissolution of residual immiscible phases, including the partitioning behavior of multi-component liquids and the rate of mass transfer to the aqueous phase. Consideration of the dissolution kinetics of residual phases is a departure from the majority of models developed for multi-phase systems, which have assumed instantaneous attainment of equilibrium. The results of earlier work, based on laboratory experiments, suggested that immiscible liquid-aqueous phase mass transfer is relatively rapid (van der Waarden et al., 1971; Fried et al., 1979; Schwille, 1988). More recent research, however, has shown that inter-phase mass transfer can be significantly rate-limited, especially under conditions that may be found in the field (Hunt et al., 1988a).

In contrast to the behavior of the immiscible liquid itself, very little work has been done on the impact of an immiscible liquid on the retention and transport of dissolved organic co-contaminants. This aspect is of interest since many sites of subsurface contamination are characterized by multiple contaminants. Enhanced transport of hydrophobic organic solutes may be expected when an immiscible organic liquid is the mobile fluid, based upon the differences in solubilities of hydrophobic organic solutes in organic liquids and water. The opposite effect is observed, however, when the immiscible liquid is present as a fixed residual phase. The residual phase serves as a sink for organic solutes, resulting in enhanced retention and retardation. While this effect is of great interest, considering the ubiquitous use of immiscible liquids and past disposal practices, very little research on this topic has been reported. The presence of a residual phase of aviation gas was observed to increase retention of petroleum constituents in column

experiments (Bouchard et al., 1989). A large increase in retardation of naphthalene was observed when a residual phase of tetrachloroethene was employed in a column packed with aquifer material (Brusseau, 1990).

Mobile-phase immiscible liquid

As mentioned above, enhanced transport of hydrophobic organic solutes may be expected when an immiscible organic liquid is the mobile fluid. This effect occurs because of the greater solubilities of hydrophobic organic solutes in organic liquids, compared to those in water. The enhanced transport effect is demonstrated by the data of Yousefi (1986), who qualitatively investigated the impact of various mobile phases (i.e., methanol/water, methanol, toluene, trichloroethene) on the transport of dioxin and benzene in packed-soil columns. While retardation was minimal in the toluene and trichloroethene systems, it was very large in the methanol and methanol/water systems.

A question of interest is whether or not nonequilibrium sorption in organic solvent systems is similar to that in aqueous systems. To investigate this, the data of Yousefi (1986) were quantitatively analyzed, using a first-order bicontinuum model, in a manner identical to the approach utilized by Brusseau and co-workers (Brusseau et al., 1990a; 1990b; 1990c). The values determined for k_2 for the immiscible-solvent systems of Yousefi (1986) are similar to those that would be predicted using the k_2 - K_p relationships reported by Brusseau and co-workers (Brusseau and Rao, 1989b; Brusseau et al., 1990b) for aqueous systems. It would appear, therefore, that the nature of nonequilibrium sorption in immiscible-solvent systems is similar to that in aqueous systems.

Residual-phase immiscible liquid

A mathematical model is presented below that allows for rate-limited uptake/release of solute by a residual phase of immiscible liquid. The model also includes rate-limited sorption/desorption of the solutes by the porous media solids, since such behavior is often observed for organic chemicals, as described above. An initial evaluation of the performance of the model is accomplished using data obtained from the literature.

The total sorbed concentration, S_T (mass sorbate/total sorbent mass), is the weighted-sum of the sorbed-phase concentrations in the two sorption domains and that of the residual phase:

$$S_T = f (S_{m1} + S_{m2}) + (1-f) C_r \quad (1)$$

where C_r and C_m are the concentrations of the solute in the residual and aqueous phases, respectively (M/M; M/L³); S_{m1} and S_{m2} are the sorbed-phase concentrations for the instantaneous and rate-limited sorption domains, respectively (M/M); K_r is the liquid-liquid partition coefficient (M/M); f is the mass fraction of sorbent comprising that portion of the porous medium that contains no residual liquid and $(1-f)$ is equivalent to the mass fraction of the residual organic liquid. At equilibrium,

$$S_T = f K_m C_m + (1-f) K_r C_m = K_p C_m ; \quad K_p = [f K_m + (1-f) K_r] \quad (2)$$

where K_p represents the weighted-average equilibrium sorption constant (L³/M) for the entire porous medium.

The one-dimensional, advective-dispersive, solute-transport equation, formulated in terms of the NANS model (non-aqueous phase-aqueous phase mass transfer with non-equilibrium sorption), is written:

$$\begin{aligned} & (\theta_m + f\rho F_m K_m) \frac{\partial C_m}{\partial t} + f\rho k_{m2} [(1-f_m) K_m C_m - S_{m2}] + (1-f)\rho k_r (K_r C_m - C_r) = \\ & \theta_m D \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \end{aligned} \quad (3)$$

where θ_m is the volumetric water content of the porous medium (L³ L⁻³); ρ is the bulk density (M L⁻³) of the entire porous medium (note $f\rho = \rho_m$ and $(1-f)\rho = \rho_r$); D is the hydrodynamic dispersion coefficient (L²/T); and q is Darcy flux (L/T).

The three, nondimensional, governing equations:

$$\begin{aligned} & R_{m1} \frac{\partial C_m^*}{\partial p} + k_m^0 (C_m^* - S_m^*) + k_r^0 (C_m^* - C_r^*) = \\ & \frac{1}{\bar{P}} \frac{\partial^2 C_m^*}{\partial X^2} - \frac{\partial C_m^*}{\partial X} \end{aligned} \quad (4)$$

$$\frac{\partial S_m^*}{\partial p} = k_{m2} (L\theta/q) (C_m^* - S_m^*) \quad (5)$$

$$\frac{\partial C_r^*}{\partial p} = k_r (L\theta/q) (C_m^* - C_r^*) \quad (6)$$

are developed by defining the following dimensionless parameters:

$$X = \frac{x}{L} \quad (7a)$$

$$P = \frac{qt}{\theta L} \quad (7b)$$

$$k_m^0 = \frac{k_{m2} L\theta}{q} R_{m2} \quad (7j)$$

$$\phi = \frac{\theta_m}{\theta} \quad (7c)$$

$$k_r^0 = \frac{k_r L\theta}{q} R_r \quad (7k)$$

$$P = \frac{qL}{\theta_m D} \quad (7d)$$

$$S_m^* = \frac{S_{m2}}{(1-F_m) K_m C_o} \quad (7l)$$

$$C_m^* = \frac{C_m}{C_o} \quad (7e)$$

$$C_r^* = \frac{C_r}{K_r C_o} \quad (7f)$$

$$R_{m1} = \phi + \frac{f\rho}{\theta} F_m K_m \quad (7g)$$

$$R_{m2} = \frac{f\rho}{\theta} (1-F_m) K_m \quad (7h)$$

$$R_r = \frac{(1-f)\rho}{\theta} K_r \quad (7i)$$

where L is the length of interest; θ is total porosity ($L^3 L^{-3}$); and C_0 is input concentration (M/L^3). Note that the total retardation factor, R , is given by:

$$R = R_{m1} + R_{m2} + R_r = [1 + (\rho/\theta) K_p] \quad (8)$$

Relative or fractional retardation parameters may be defined as follows:

$$\beta_{m1} = \frac{R_{m1}}{R} \quad (9a) \quad \beta_r = \frac{R_r}{R} \quad (9c)$$

$$\beta_{m2} = \frac{R_{m2}}{R} \quad (9b)$$

Note that the three β values sum to unity, and that β_i represents the fraction of retardation that is attributed to sorption in domain i .

A finite-difference numerical program (Brusseau et al., 1989b) utilizing the Crank-Nicholson technique is used to solve the pertinent governing equations (4-6) under the following initial and boundary conditions:

$$C_m^*(X,0) = C_r^*(X,0) = 0 \quad (10a)$$

$$S_m^*(X,0) = 0 \quad (10b)$$

$$C_o^* = C_m^* - \frac{1}{\bar{P}} \frac{\partial C_m^*}{\partial X} \quad x=0 \quad (10c)$$

where

$$C_o^* = 1; \quad 0 \leq p \leq T_0 \quad (10d)$$

$$C_o^* = 0; \quad p > T_0$$

and T_0 = pulse width

$$\frac{\partial C_m^*(X,p)}{\partial X} \quad x=1 = 0; \quad p > 0 \quad (10e)$$

It must be stressed that we are concerned with the interaction of an organic solute with a residual-phase organic liquid and not the movement of the immiscible liquid itself. As such, the residual phase will be assumed to be immobile in constructing the model. This is not a particularly limiting condition, however, since it has been shown that very large pore-water velocities (i.e., hydraulic gradients) are required to displace residual saturation (Wilson and Conrad, 1984; Willhite, 1986; Hunt et al., 1988b). In addition, the size of the residual phase is assumed to be constant. This means that dissolution of the residual is not accounted for in the model. While this constraint may limit the applicability of the model, it is probably not severe given the nature of residual saturation. In cases where dissolution is significantly rate limited or where the mass of residual is relatively large, the rate of change in residual saturation may be slow enough relative to the time scale of solute-residual phase interaction that dissolution is insignificant. For example, Hunt et al. (1988a) have shown that residual saturation can persist for years under conditions representative of field sites. In these cases, constraining residual saturation to a constant value should not affect the performance of the model.

The Damkohler Number k_r^0 represents the contribution of nonequilibrium associated with liquid-liquid mass transfer to the total nonequilibrium influencing solute transport. Inspection of (7k) reveals that knowledge of the liquid-liquid mass transfer constant (k_r) is required to determine k_r^0 . Such knowledge can be obtained through measurement or estimation. However, heterogeneity in the size, shape, and position of residual phase, as well as the large impact associated with small quantities of residual, makes the independent determination of k_r difficult. For example, the rate of liquid-liquid mass transfer could be measured using a batch-type experiment. The applicability of the rate constant so obtained to a dynamic column system is questionable, however, given the significant difference between the two systems in the nature of the interface. Many correlation equations have been developed for the estimation of mass transfer coefficients. Application of these to our system of interest may also be problematic, given our inability to obtain many of the required parameter values. In many cases we may, therefore, have to resort to the use of "effective" mass transfer constants.

These effective rate parameters would be obtained by fitting a model that includes a term for liquid-liquid mass transfer to a data set obtained from a system influenced by liquid-liquid mass transfer. To make sure that the mass transfer constant obtained in this fashion represents only liquid-liquid mass transfer, the system would ideally be influenced only by liquid-liquid mass transfer. In such cases, a simpler, two-compartment model (i.e., pore water and residual phase) could be used. Data reported by Brusseau (1990) will be used to briefly illustrate this approach.

The impact of a residual phase of tetrachloroethene (@ 10% saturation) on the retention and transport of naphthalene in a column packed with a low organic-carbon-content (0.02%) aquifer material was investigated by Brusseau (1990). The retention associated with the residual phase comprised 99.9% of total retardation. Sorption by the porous media solids was therefore ignored and the data were simulated with a first-order two-compartment model. The mass transfer constant so obtained was an effective constant representing system-wide liquid-liquid mass transfer. Interestingly, the value of the mass transfer constant was similar to the value that would be predicted using the k_2 - K_p relationship presented by Brusseau and Rao (1989b).

To evaluate the validity of the model's conceptual basis, as well as to illustrate its use, the model will be applied to the data set reported by Bouchard et al. (1989). They reported the results of column experiments employing aquifer material contaminated with a residual saturation (@ 1%) of aviation gas. The retardation of toluene and three other gasoline constituents was shown to be greater in the presence of the residual phase, compared to systems containing no residual. No quantitative analysis, however, was presented. The performance of the NANS model will be tested by attempting to predict this data, with all parameter values being obtained independent of curve fitting.

A value for R (total retardation) was obtained using moment analysis of the pertinent breakthrough curve (BTC). The contribution of sorption by the porous media solids was determined by analyzing a BTC obtained by Bouchard et al. (1989) for a system identical to that used to obtain the BTC being analyzed herein, except that no residual was present. An optimization program (van Genuchten, 1981), employing a first-order bicontinuum model, was used to determine values for k_{m2} and F_m . Values for the β terms and for k_m^0 were calculated using this information. The remaining two unknown parameters are P and k_r^0 . A value for P was estimated based on experiments reported for non-sorbing tracers and similar column systems (Bouchard et al., 1988; Lee et al., 1988; Brusseau et al., 1990b; 1990c). A value for k_r was estimated using the relationship reported by Brusseau and Rao (1989b), which was used to calculate k_r^0 . All parameter values are now specified.

The prediction obtained with the NANS model is compared to the data in Figure 3. The model provides a very good description of the data, especially considering that all parameter values were obtained independently. The success of the NANS model in predicting the data of Bouchard et al. (1989) suggests that the conceptual basis of the model is sound. Further tests are required, however, to substantiate these initial results.

A question of special interest is the relative impact of nonequilibrium liquid-liquid mass transfer in relation to other nonideality factors, such as aquifer heterogeneity (e.g., hydraulic-conductivity- or sorption-capacity- heterogeneity), on solute transport at the field scale. The relative impact of rate-limited sorption is scale dependent and appears to be of lesser significance, in comparison to heterogeneity, for field-scale solute transport, as discussed above. Based on the analysis of the Bouchard et al. (1989) data presented above and the results reported by Brusseau (1990), it appears that mass transfer between the residual phase and water may not be significantly rate-limited under natural-gradient conditions typical to the field. This may not be the case, however, for induced-gradient conditions, such as those reflective of pump-and-treat groundwater remediation systems. The hydraulic residence time may be short enough under these conditions that mass transfer between the residual saturation and water is in a state of nonequilibrium. If this nonequilibrium were not accounted for, the time required to remediate the site would be significantly underpredicted.

Summary and Conclusions

Rate-limited sorption of organic solutes, caused by a diffusion-constrained mechanism, was shown to be significant under laboratory conditions. The significance of the impact of nonequilibrium sorption on field-scale transport is scale dependent. The impact of organic liquids on mass transfer and transport of organic solutes depends upon the nature of the solute and the nature and form of the organic liquid. For example, while retardation of nonionic solutes is decreased in mixed-solvent systems (i.e., systems comprised of water and a miscible organic liquid or an immiscible liquid present in concentrations below phase separation), the retardation of organic acids may, in some cases, increase with addition of a cosolvent. While the presence of an immiscible liquid existing as a mobile phase will reduce retention of organic solutes, the presence of residual saturation of an immiscible liquid can significantly increase retention. A model that incorporates the effect of a residual organic liquid on the transport of dissolved organic contaminants was presented. The impact of residual saturation on increasing retardation was shown to be great, even at relatively low levels of saturation. The validity of the conceptual basis of the model was tested through application to data reported in the literature. Successful prediction of the data, where all parameter values were obtained independent of curve-fitting, suggested that the conceptual basis is valid. The model should prove useful in further investigations of the effect of residual organic liquids on the retention and transport of organic solutes.

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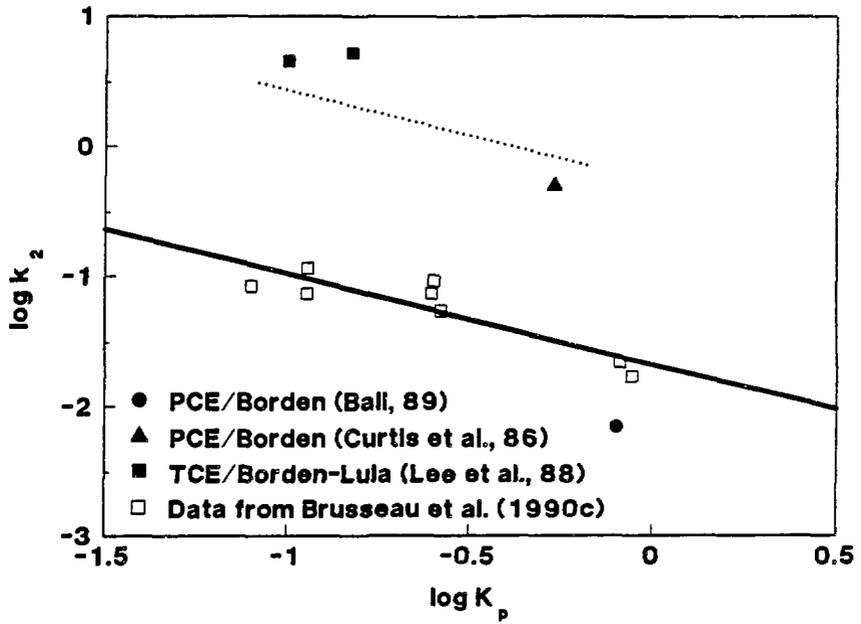


Figure 1. Sorption-kinetics data for organic solutes and aquifer materials.

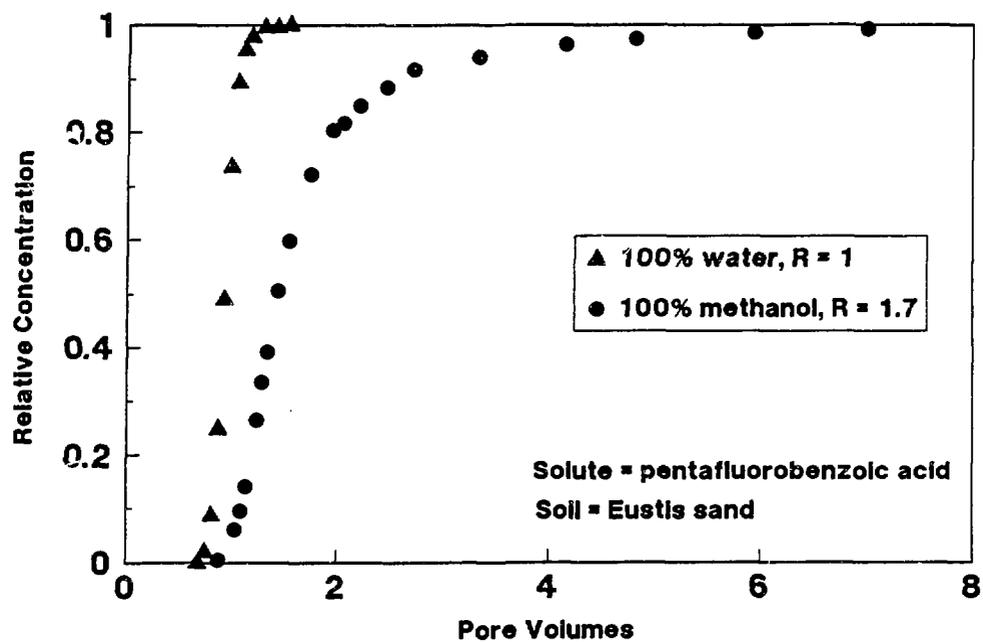


Figure 2. Impact of cosolvent on transport of an organic acid.

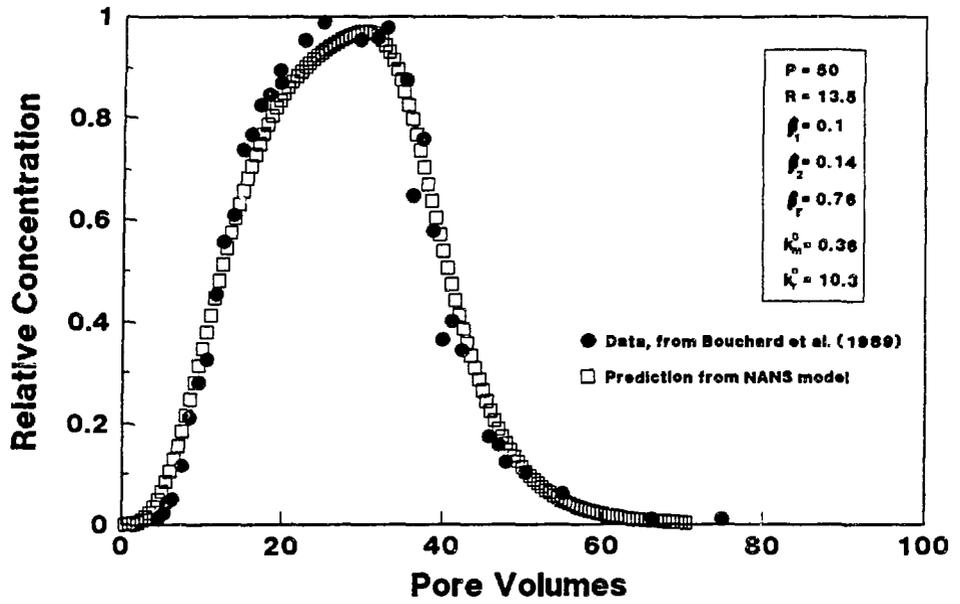


Figure 3. Application of the NANS model