Journal of Contaminant Hydrology 24 (1996) 117-143

JOURNAL OF
Contaminant
Hydrology

Nonideal transport of reactive solutes in heterogeneous porous media:
1. Numerical model development and moments analysis

R. Srivastava [a], M.L. Brusseau [b,*]

[a] Soil, Water and Environmental Science Department, University of Arizona, Tucson, AZ 85721, USA
[b] Soil, Water and Environmental Science Department and Hydrology and Water Resources Department, University of Arizona, Tucson, AZ 85721, USA

Received 12 October 1995; accepted 17 May 1996

Abstract

The transport of reactive solutes at the field scale is characteristically nonideal, and this nonideality is often caused by more than one factor. In these cases, mathematical models that explicitly account for multiple factors are necessary for proper simulation of transport and for accurate analysis of causative factors. The purpose of this paper is to present a mathematical model for simulating the transport of reactive solute in heterogeneous porous media. We have taken a multi-scale, multi-factor approach that explicitly accounts for such factors as hydraulic-conductivity variability, structured porous media, rate-limited diffusive mass transfer, and nonlinear, rate-limited, spatially variable sorption. The influence of these factors on the displacement and spreading of solute plumes and on mass flux is illustrated with a series of two-dimensional (vertical) simulations.

It is shown that rate-limited sorption/mass transfer and nonlinear sorption can significantly influence the first, second, and third spatial moments, whereas hydraulic-conductivity variability significantly influences only the second spatial moment. Plume skewness is especially sensitive to the specific factor controlling nonideal transport. For example, both rate-limited sorption/mass transfer and nonlinear sorption can create negatively skewed plumes during early stages of transport. However, the plume influenced by rate-limited sorption/mass transfer tends toward symmetry as global residence time increases. Conversely, the plume influenced by nonlinear

---

* Corresponding author.

PII S0169-7722(96)00039-3

sorption tends toward a constant degree of asymmetry as the spreading forces balance the concentration-dependent retardation behavior associated with nonlinear sorption. Furthermore, the results illustrate that unique behavior can result from the coupling of multiple processes. For example, when influenced by coupled heterogeneity and nonlinear sorption, the shape of a plume may change from positive to negative skewness during the course of transport.

Keywords: contamination; transport; groundwater quality; groundwater modeling

1. Introduction

The transport of reactive solutes in subsurface systems is a major focus of research in environmental science, especially with regard to the fate of contaminants in soils and aquifers. The development of mathematical models for simulating solute transport has been an important component of this research. Initial model-development efforts made use of two key assumptions, namely that the porous medium was homogeneous and that all reactions were linear and instantaneous. For purposes of discussion, transport that can be described by models based on these assumptions is considered ideal. Given the nature of subsurface systems, it is expected that models based on these two assumptions would not be valid for most field applications. This is supported by the results obtained from field-scale transport experiments for reactive solutes, recent analyses of which revealed that all such experiments exhibited behavior that to some degree deviated from ideal (Brusseau, 1992, 1994).

During the past 20 years, mathematical models have been developed to account for nonideal transport. For example, models that account for spatially variable hydraulic conductivity are now common and form the basis for most advanced modeling efforts. However, despite an awareness that transport of reactive solutes is influenced by many processes and factors, model development has until recently followed a reductionist approach wherein the influence of a single factor is studied in isolation. Considering the complexity of field-scale systems, it is clear that mathematical models incorporating multiple nonideality factors are needed to simulate transport of reactive solutes.

The recognition of the need for multi-factor models has led to the development of several models that account explicitly for two or more nonideality factors. A summary of previous "multi-factor" analyses of reactive-solute transport in heterogeneous porous media is provided in Table 1. It is clear that several authors have analyzed the case of combined physical (e.g., hydraulic-conductivity variability) and chemical (e.g., sorption variability) heterogeneity. Several analyses have also been reported that account for physical heterogeneity and rate-limited sorption. However, very few analyses have been reported that explicitly account for three or more nonideality factors. It is also evident that few analyses have incorporated nonlinear sorption. Furthermore, most analyses have focused on either solute spreading (second spatial moment) or mass flux (breakthrough curves), and have not integrated the two.

The purpose of this paper is to present a mathematical model for simulating the transport of reactive solutes in heterogeneous porous media. We take a multi-scale, multi-factor approach that explicitly accounts for such factors as hydraulic-conductivity

Table 1
Analyses involving multi-factor nonideal transport of reactive solutes in heterogeneous porous media

Author	Factors [a]	Form [b]
Smith and Schwartz (1981)	$\Delta K+\Delta K_d$	SM2
Jury (1983)	$\Delta K+\Delta K_d$	SM2
Bahr (1986)	$\Delta K+\Delta K_d$ +RLS	MF/BTC
van der Zee and van Riemsdijk (1987)	$\Delta K+\Delta K_d$ +NLS	SM2
Garabedian et al. (1988)	$\Delta K+\Delta K_d$	SM2
Valocchi (1988)	ΔK +RLS	SM0–2
Brusseau (1989)	ΔK +MT+RLS	SM2
Brusseau et al. (1989)	ΔK +MT+RLS	MF/BTC
Dagan (1989)	$\Delta K+\Delta K_d$	SM1,2
Valocchi (1989)	$\Delta K+\Delta K_d$ +RLS	SM0–2
Cvetkovic and Shapiro (1990)	$\Delta K+\Delta K_d$ +RLS	MF/BTC
Andricevic and Foufoula-Georgiou (1991)	$\Delta K+\Delta K_d$ +RLS	SM2
Brusseau (1991)	$\Delta K+\Delta K_d$ +MT+RLS	MF/BTC
Destouni and Cvetkovic (1991)	$\Delta K+\Delta K_d$ +RLS	MF/BTC
Kabala and Sposito (1991)	$\Delta K+\Delta K_d$	SM1,2
Brusseau (1992)	$\Delta K+\Delta K_d$ +MT+RLS	MF/BTC
Schäfer and Kinzelbach (1992)	$\Delta K+\Delta K_d$	MF/BTC
Selroos and Cvetkovic (1992)	ΔK +RLS	MF/BTC
Bosma et al. (1993)	$\Delta K+\Delta K_d$	SM2
Brusseau and Zachara (1993)	$\Delta K+\Delta K_d$ +MT+RLS	MF/BTC
Dagan and Cvetkovic (1993)	ΔK +RLS	SM0–3
Tompson (1993)	$\Delta K+\Delta K_d$ + NLS	MF/BTC+SM1–3
Quinodoz and Valocchi (1993)	ΔK +RLS	SM1,2
Bosma et al. (1994)	$\Delta K+\Delta K_d$ + NLS	SM1,2
Burr et al. (1994)	$\Delta K+\Delta K_d$ + MT/RLS [c]	SM1,2
Cvetkovic and Dagan (1994)	ΔK +NLS	SM1,2
Rabideau and Miller (1994)	ΔK +RLS+NLS [d]	MF/BTC
Srivastava and Brusseau (1994)	$\Delta K+\Delta K_d$	MF/BTC
Srivastava and Brusseau (present study)	$\Delta K+\Delta K_d$ +MT+RLS+NLS	MF/BTC+SM1–3

[a] ΔK = spatially variable hydraulic conductivity; ΔK_d = spatially variable sorption; RLS = rate-limited sorption; MT = smaller-scale heterogeneity and associated mass transfer; NLS = nonlinear sorption.
[b] Focus of analysis: MF/BTC = mass flux (e.g., breakthrough curves); SMn = spatial moments, where n = moment number.
[c] Simulations were presented for either rate-limited sorption *or* mass transfer.
[d] Spatially variable sorption (with spatially variable conductivity and linear, instantaneous sorption) considered separately.

variability, structured porous media, rate-limited diffusive mass transfer, and nonlinear, rate-limited, spatially variable sorption. We briefly describe the conceptual and mathematical framework of the model, as well as the numerical approaches used to implement the governing equations. The model is then used to illustrate, with selected examples, the impact of coupled physical–chemical processes on solute transport. Numerical simulations are used to examine both plume evolution (spatial moments) and mass flux (temporal moments).

2. Conceptual and mathematical framework

The model we present is based on the approach proposed by Brusseau (1989). This approach entails coupling a description of solute dynamics, influenced by multiple factors at the microscopic and macroscopic scales (Brusseau et al., 1989), to field-scale transport in heterogeneous porous media. The model presented by Brusseau (1989) was two-dimensional and did not include nonlinear sorption or a stochastic representation of spatially variable sorption, whereas the new model is fully three-dimensional and includes spatially variable, nonlinear sorption. The conceptual and mathematical framework of the model is discussed briefly in the following sections.

2.1. Conceptual basis

Local-scale dispersion is often neglected in the development of field-scale mathematical models. Although sometimes justified on a physical basis, the primary reason for excluding local-scale dispersion is mathematical and numerical expediency. In many cases local-scale dispersion can be significant, especially when molecular diffusion is involved (e.g., diffusion in clay lenses). It may also be important when concentration-dependent processes such as nonlinear sorption are involved. Therefore, local-scale dispersion (mechanical mixing and molecular diffusion) is included in our model.

The majority of field-scale transport models include the assumption that sorption is linear. However, the sorption of many contaminants of interest are slightly to strongly nonlinear. We employ the widely used Freundlich equation ($S = K_f C^N$) to represent nonlinear sorption.

Most solute transport models developed for field-scale applications include the local equilibrium assumption, which specifies that interactions between the solute and the sorbent are so rapid in comparison to hydrodynamic residence time that the interactions can be considered instantaneous. As indicated in Table 1, recent research has examined the influence of rate-limited sorption on field-scale solute transport. The majority of the models developed to simulate transport of rate-limited sorbing solutes in heterogeneous media make use of the simple "one-site" description of sorption kinetics. While the one-site model is mathematically expedient, it has been shown to be invalid for representing the sorption dynamics of many reactive solutes (cf. Davidson and McDougal, 1973; Schwarzenbach and Westall, 1981; Brusseau and Rao, 1989; Brusseau et al., 1989). Thus, while models that use one-site kinetics may be useful for roughly illustrating the potential effects of rate-limited sorption, they will be able to accurately predict the transport of rate-limited sorbing solutes in only limited situations.

Another widely used model, based on a two-domain description of rate-limited sorption, is the one used herein. With this model, sorption is assumed to be governed by two sets of rate coefficients, each representing a separate sorption domain. For our case, it is further assumed that the rate of sorption for one domain is so rapid that it can be considered instantaneous. The two-domain approach, developed by Giddings and Eyring (1955) for chromatographic systems, has been used successfully to simulate sorption/desorption and, when coupled to the advective–dispersive equation, the transport of both organic and inorganic solutes in soils, sediments, and aquifer materials [see Brusseau and Rao (1989) for review]. This approach is very flexible in that the equations can be used to represent rate-limited sorption/desorption caused by chemisorption (Jardine et al., 1985) or by intrasorbent diffusion (Brusseau et al., 1991).

Nonideal transport, often referred to as physical nonequilibrium, can result from a structured flow domain for which the scale of heterogeneity ($> 10^{-3}$ to < 1 m) is smaller than that typically associated with measurements of "field-scale" heterogeneity. The existence of regions of small hydraulic conductivity within the flow domain creates a spatially variable velocity field at these smaller scales. In some cases, there is relatively minimal flow and advection in the low-conductivity domains. Due to the small advective flux, these domains act as sink/source components, with rate-limited diffusional mass transfer between the advective and nonadvective domains causing spreading of the solute front. These sink/source regions can take various forms, including the internal porosity of aggregates or porous particles, dead-end pores, the bulk matrix of fractured media, and the small hydraulic conductivity micro-layers or laminae typically found in aquifers of sedimentary origin. Many researchers have shown that these structures can cause asymmetrical and tailed breakthrough curves and enhanced dispersion [see Brusseau and Rao (1990) and Brusseau (1994) for recent reviews].

The dual-porosity approach has been used extensively in chemical engineering, petroleum engineering, and earth sciences to represent transport in small-scale heterogeneous media (Coats and Smith, 1964; van Genuchten and Wieringa, 1976; Rao et al., 1980). In this approach, the porous medium is conceptualized to consist of two domains, an "advective" domain, where advective–dispersive flux occurs, and a "nonadvective" domain wherein advection is negligible. Mass transfer of solute between the two domains can be represented with a diffusion equation based on Fick's law or by employing a first-order mass-transfer approximation. This latter approach will be used herein to describe the influence of structured or locally heterogeneous porous media on solute transport.

The influence of field-scale spatially variable hydraulic conductivity on water flow and contaminant transport in porous media has been a major research topic for many years, and its importance has been well established. The widely used stochastic approach will be employed herein to represent spatially variable hydraulic conductivity. Due to the heterogeneity of subsurface systems, it is logical to expect reaction-related properties to be spatially variable as well. Several field-scale investigations have shown that this is indeed the case for sorption (cf. Pickens et al., 1981; Elabd et al., 1986; Mackay et al., 1986; Rao et al., 1986; Robin et al., 1991). It has been shown through computational analysis by several investigators that spatially variable sorption can cause nonideal transport (see pertinent references in Table 1). The results of the few experimental-based investigations reported to date confirm that nonideal transport can be caused by spatially variable sorption (Brusseau, 1991; Brusseau and Zachara, 1993). The stochastic approach will also be used to represent spatial variability of the equilibrium sorption coefficient. Spatial variability of both sorption-rate coefficients and the mass-transfer coefficient can also be considered.

2.2. Governing equations

Sorption dynamics for the domains governed by rate-limited sorption are described by:

$$\frac{\partial S_{a2}}{\partial t} = k_{a2}\left[(1 - F_a) K_{fa} C_a^{N_a} - S_{a2}\right] \tag{1}$$

$$\frac{\partial S_{n2}}{\partial t} = k_{n2}\left[(1 - F_n) K_{fn} C_n^{N_n} - S_{n2}\right] \tag{2}$$

where C_a and C_n are aqueous-phase concentrations (M L^{-3}); S_{a2} and S_{n2} are the rate-limited sorbed-phase concentrations (M M^{-1}); k_{a2} and k_{n2} are the first-order reverse sorption rate coefficients (T^{-1}); F_a and F_n are the fractions of sorbent for which sorption is essentially instantaneous; K_{fa} and K_{fn} are the equilibrium sorption coefficients (L^{3N} M^{-N}) for the Freundlich isotherm; N_a and N_n are the exponents of the Freundlich isotherm; and a and n denote the advective and nonadvective regions, respectively.

Including the various nonidealities as described in the previous section, the equation governing the transport of a reactive solute through the advective zone can be written as:

$$\left(\theta_a + f\rho F_a N_a K_{fa} C_a^{N_a - 1}\right)\frac{\partial C_a}{\partial t} + f\rho\frac{\partial S_{a2}}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_a}{\partial x_j}\right) - q_i\frac{\partial C_a}{\partial x_i} - \alpha(C_a - C_n) \tag{3}$$

where q is specific discharge (L T^{-1}); D is the dispersion tensor (L^2 T^{-1}); θ_a is the fractional volumetric water content of the advective region; f is the mass fraction of sorbent constituting the advective region; ρ is the bulk density of the porous medium (M L^{-3}); t is time (T); α is the first-order coefficient (T^{-1}) for mass transfer between the advective and nonadvective regions; and x_i is a spatial coordinate.

The mass balance for the nonadvective zone can be described by the following equation:

$$\left(\theta_n + (1 - f)\rho F_n N_n K_{fn} C_n^{N_n - 1}\right)\frac{\partial C_n}{\partial t} + (1 - f)\rho\frac{\partial S_{n2}}{\partial t} = \alpha(C_a - C_n) \tag{4}$$

where the subscript n refers to the nonadvective region and the definitions of symbols is similar to that used for Eq. (3). Eqs. (3) and (4) together with the sorption dynamics equations (1) and (2) can be solved to obtain the concentrations C_a, C_n, S_{a2} and S_{n2} with given boundary and initial conditions.

2.3. Numerical approach

The complex governing equations comprising the model require numerical methods for solution. The flow equation is solved by using the Galerkin finite-element technique (cf. Istok, 1989) with linear shape functions used to describe the variation of head within an element. The saturated hydraulic conductivity is assumed to be piecewise constant over an element. The conductivity field is assumed to be log-normal and is generated from the mean, variance, and the covariance function by using the Turning Bands Method (Matheron, 1973; Mantoglou and Wilson, 1982). The set of linear simultaneous equations is solved using the Jacobi Conjugate Gradient iterative solver (Young and Kincaid, 1981; Ortega, 1988) which requires the storage of only the nonzero terms of the coefficient matrix and outperforms direct solvers by orders of magnitude in CPU time.

The transport equation is solved by using the modified method of characteristics for the advective part and the regular Galerkin technique for the dispersive part of the transport equation (cf. Chiang et al., 1989; Srivastava and Yeh, 1992). This scheme can handle advection-dominated flows with little or no numerical dispersion but the inherent Courant number limitation restricts the time step to a small value. The multi-scale approach used in the present model usually leads to very small local dispersivity values and therefore large Péclet numbers. Also, the inclusion of various rate constants limits the size of the time step that can be used for an accurate numerical solution. Therefore, the modified method of characteristics was considered to be an ideal choice for the numerical solution.

3. Illustrative simulations

In this section we describe the conditions for the simulations used to illustrate the effects of rate-limited sorption/mass transfer, nonlinear sorption, and spatially variable hydraulic conductivity on transport. Although the model is three-dimensional, we will conduct two-dimensional (vertical) simulations in interests of efficiency. The mean value of the natural log of hydraulic conductivity is set equal to 2, the correlation lengths in the horizontal (λ_x) and vertical (λ_z) directions are taken as 5 and 0.5 m, respectively, and simulations are generated for several variances ($\sigma_{\ln K}^2 = 0$ to 3; results are presented primarily for $\sigma_{\ln K}^2 = 0$ and 1). A cross-section of the simulation domain, which extends to 25 correlation lengths in each direction (length = 125 m, thickness = 12.5 m), is discretized by using rectangular finite elements with five elements per correlation length.

Various runs with one or more nonideality factors were conducted as described in Table 2. The parameters that were fixed for all the simulations are: K_a (linear sorption coefficient) = 0.15, $\rho_b = 2000$ kg/m^3, $\theta = 0.3$, $\alpha_L = 0.0005$ m, $\alpha_T = 0.00005$ m, $D_0 = 0.00004$ m^2/day. Almost all nonlinear isotherms reported for most solutes of interest have Freundlich power coefficients, N, that are < 1. Thus, we will use a representative value of 0.8 in our analyses.

The initial solute plume was spread over an area spanning one correlation length in both horizontal and vertical directions in such a way as to put the edges of this area at the center of the finite elements (cf. Srivastava and Yeh, 1992). The total solute mass and the plume size was the same for each case; this resulted in different initial aqueous concentrations for some cases. The initial distribution of solute mass was limited to the solution phase and the instantaneous sorbed phase in the advective domain. For cases where the rate constants were very large compared to the time step (an arbitrary value of $10\Delta t$ was chosen), the initial mass was also distributed to the corresponding rate-limited domains. The boundary conditions imposed for flow were no flow across the top and

Table 2
Individual simulation cases obtained by varying selected parameters

	θ_a	θ_n	f	F_a	F_n	K_a (l/kg)	K_n (l/kg)	α (day^{-1})	k_{a2} (day^{-1})	k_{n2} (day^{-1})
Case 1	0.3	0.0	1.0	1.0	–	0.15	–	–	–	–
Case 2	0.15	0.15	0.5	0.5	0.5	0.15	0.15	0.01	0.3	0.3
Case 3	0.15	0.15	0.5	0.5	0.5	0.15	0.15	10^5	10^5	10^5
Case 4	0.15	0.15	0.5	1.0	1.0	0.15	0.15	10^{-5}	–	–
Case 5	0.3	0.0	1.0	0.5	–	0.15	–	–	10^{-5}	–
Case 6	0.3	–	1.0	1.0	–	0.163 [a]	–	–	–	–
Case 7	0.15	0.15	0.5	0.5	0.5	0.163 [a]	0.163	0.01	0.3	0.3

[a] represents K_f for nonlinear sorption; $N = 0.8$. θ = water content; f = mass fraction of sorbent constituting the advective region; F = fraction of sorbent for which sorption is essentially instantaneous; K = equilibrium sorption coefficient; α = first-order coefficient for mass transfer between the advective and nonadvective regions; k_2 = first-order reverse sorption rate coefficient; and a and n denote the advective and nonadvective regions, respectively; – = process or factor represented by the pertinent parameter is not included in the specific case.

bottom boundaries, fixed head on the downgradient boundary, and specified flux (0.1 m/day) across the upgradient boundary. The boundary conditions for transport were those of zero concentration gradient normal to all four boundaries.

Results for each case that includes spatially variable hydraulic conductivity were based on 20 realizations, with the mean being presented. The results for each single realization varied from one realization to another, as is expected for a large variance of the conductivity field. However, in all cases, a majority of the realizations showed trends similar to those obtained for the means. Thus, while the mean behavior may not reflect the exact behavior exhibited by a specific realization, the means represent the general trends.

Our analyses are focused on the spatial (plume) and temporal (breakthrough curves) moments obtained for each case. The spatial moments were obtained by numerical integration of the concentration distribution at selected times. The first moment represents the normalized absolute moment (the travel distance from the center of the initial plume), and the second and third moments represent normalized central moments and are measures of the plume spread and skewness, respectively. In the cases involving use of the Monte Carlo technique, the spatial moments were obtained by first calculating the moments for each individual realization, and then determining the mean for all 20 realizations. This was done to eliminate the "artificial" spreading associated with direct moment analysis of the ensemble concentration data (e.g., Rajaram and Gelhar, 1993). The breakthrough-curve and temporal-moment data are based on single realizations.

To promote a comparative analysis of the results, the simulations are compared to those obtained for a base case (case 1). The base case represents transport with linear, instantaneous sorption and no smaller-scale heterogeneity and associated mass transfer. The travel distance ratio, which is defined as the distance travelled by a plume for a given case divided by the distance travelled by the case-1 plume, is used to illustrate the relative displacement behavior of the centers of mass of the plumes for selected cases.

Before investigating the influence of nonlinear, rate-limited sorption and mass transfer on transport in a heterogeneous porous medium, the impact of nonideal sorption on transport in a homogeneous porous medium will be discussed. This is done to evaluate the effects of coupling reaction processes with transport in a heterogeneous domain.

4. Results and discussion

4.1. Spatial first moments: homogeneous porous medium

The influence of rate-limited sorption/mass transfer on transport of solute plumes in the absence of hydraulic-conductivity variability is illustrated in Fig. 1a. Case 1 represents transport in a homogeneous porous medium with linear, instantaneous sorption and no smaller-scale heterogeneity and associated mass transfer. Case 2 represents conditions wherein transport is constrained by both rate-limited sorption/desorption and by diffusive transfer of solute between advective and nonadvective domains of a structured medium. In this case, the displacement of the center of mass is nonuniform with time during the early stages of transport. This behavior results in a temporally variable retardation factor, which has been observed in previous studies. At early times, the apparent retardation factor is < 2 for case 2, as indicated by the travel distance ratio (see Fig. 1b). This means that the plume is moving faster than the case-1 plume. As the residence time increases, the apparent retardation factor asymptotically approaches 2. At sufficiently long times, the transport of the center of mass will be equivalent to that of the ideal case, and the magnitude of the apparent R will coincide with that of the true R.

Case 3 represents conditions wherein the rates of mass transfer and sorption are rapid in comparison to advective transport. In this case, the displacement of the center of mass is identical to the ideal case (case 1), as expected. Given that the results obtained for this case are essentially identical to the ideal case, we will not further consider case 3.

For case 4, mass transfer is constrained only by diffusive exchange between advective and nonadvective domains. However, the magnitude of the exchange coefficient is so small that there is minimal transfer of solute to the nonadvective domain. The impact of negligible transfer results in a constant but greater (compared to case 1) rate of plume displacement (see Fig. 1a). In addition, the impact is indicated by examining the travel distance ratio, which remains constant at 2 (see Fig. 1b). This is equivalent to an apparent retardation factor, R_a, of 1 [$R_a = (\text{true } R)/(\text{travel distance ratio})$]. The apparent retardation factor for this limiting case can be defined as:

$$R_a = \frac{\theta_a}{\theta} + f\frac{\rho}{\theta}K_p \tag{5}$$

Given the values used for this simulation, R_a is calculated to be 1.0, which matches the results reported in Fig. 1. Solute transport could be simulated in this case by ignoring the nonadvective domain and using R_a in place of R. This approach would be valid only as long as the mass transferred to the nonadvective domain remains negligible.

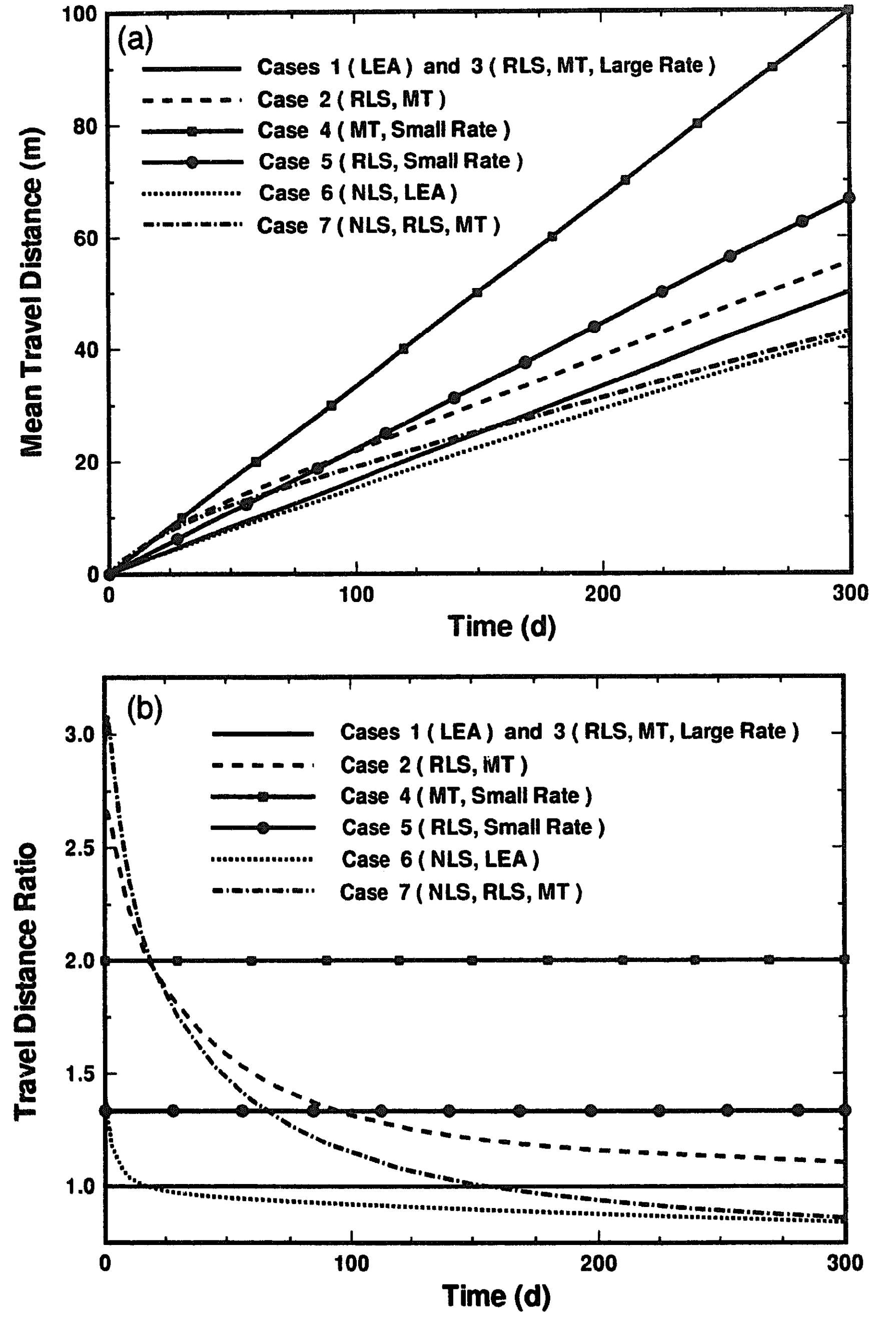

Fig. 1. Displacement of the plume center of mass in a homogeneous porous medium: (a) the influence of rate-limited sorption/mass transfer and nonlinear sorption on mean travel distance; and (b) the influence of rate-limited sorption/mass transfer and nonlinear sorption on travel distance ratio. The center of mass ratio is obtained by normalizing the measured center of mass for each case by the center of mass for the base case (homogeneous porous medium and linear, instantaneous sorption/mass transfer).

For case 5, mass transfer is constrained only by rate-limited sorption. However, the magnitude of the sorption rate coefficient is so small in comparison to the hydraulic residence time that there is minimal transfer of solute to the rate-limited domain. The impact of this condition is reflected by the essentially constant but greater (compared to case 1) rate of plume displacement (see Fig. 1a) and a constant travel distance ratio of 1.33 (see Fig. 1b), which translates to an apparent retardation factor of 1.5. An apparent retardation factor can be defined for this limiting case as:

$$R_a = 1 + F\frac{\rho}{\theta}K_p \tag{6}$$

Given the values used for this simulation, R_a is calculated to be 1.5, which matches the results reported in Fig. 1. With an assumption of local equilibrium, this apparent retardation factor could be used to simulate solute transport for times during which the quantity of solute transferred to the rate-limited domain is insignificant.

The displacement of the plume center of mass is nonuniform when sorption is nonlinear (see case 6, Fig. 1a). This behavior is caused by the dependence of sorption and retardation on solute concentration. As the plume evolves and spreads, concentrations decrease, thereby causing an increase in sorption and retardation (note that the Freundlich exponent in these simulations is < 1). The impact of this increase in sorption and retardation is illustrated in Fig. 1b, wherein the travel distance ratio is > 1 at very early times, and < 1 at later times. The degree to which, as well as the rate at which, the plume decelerates will depend on the magnitude of K_f, N, and C_0.

The degree of nonuniformity for the nonlinear-sorption case will also depend, in part, on the degree of spreading. This is illustrated by the results obtained for the case wherein sorption is nonlinear *and* rate limited (case 7, Fig. 1a and b). The degree of nonuniformity is greater for this case compared to case 6 for two reasons: (1) at early times the influence of rate-limited sorption/mass transfer causes an enhanced rate of displacement; and (2) at later times the enhanced spreading associated with rate-limited sorption/mass transfer, coupled with the nonlinear sorption, causes a greater increase in sorption and, therefore, a greater deceleration of the plume.

4.2. Spatial first moments: heterogeneous porous medium

The influence of hydraulic-conductivity variability on displacement of the plume center of mass is illustrated in Fig. 2a (case 1). The displacement of the center of mass is temporally nonuniform at early times, as clearly shown by the travel distance ratio presented in Fig. 2b. The magnitude of the deviation was larger for larger variances of $\ln K$ (data not shown). This nonideal behavior would be reflected in temporally variant apparent retardation factors. However, this effect is significant at only very early times. The influence of spatially variable sorption, and the impact of potential cross-correlations to hydraulic conductivity, on transport has been the focus of several investigators (see Table 1). Hence, we will not focus on this topic herein. In addition, we will not discuss the influence of spatially variable rate parameters on transport, which was recently examined by Xu and Brusseau (1996) for both reversible and irreversible reactions.

The combined effect of rate-limited sorption/mass transfer and hydraulic-conductivity variability on plume movement is shown in Fig. 2a and b. The impact of the mass-transfer processes is very similar to that reported for the case of the homogeneous

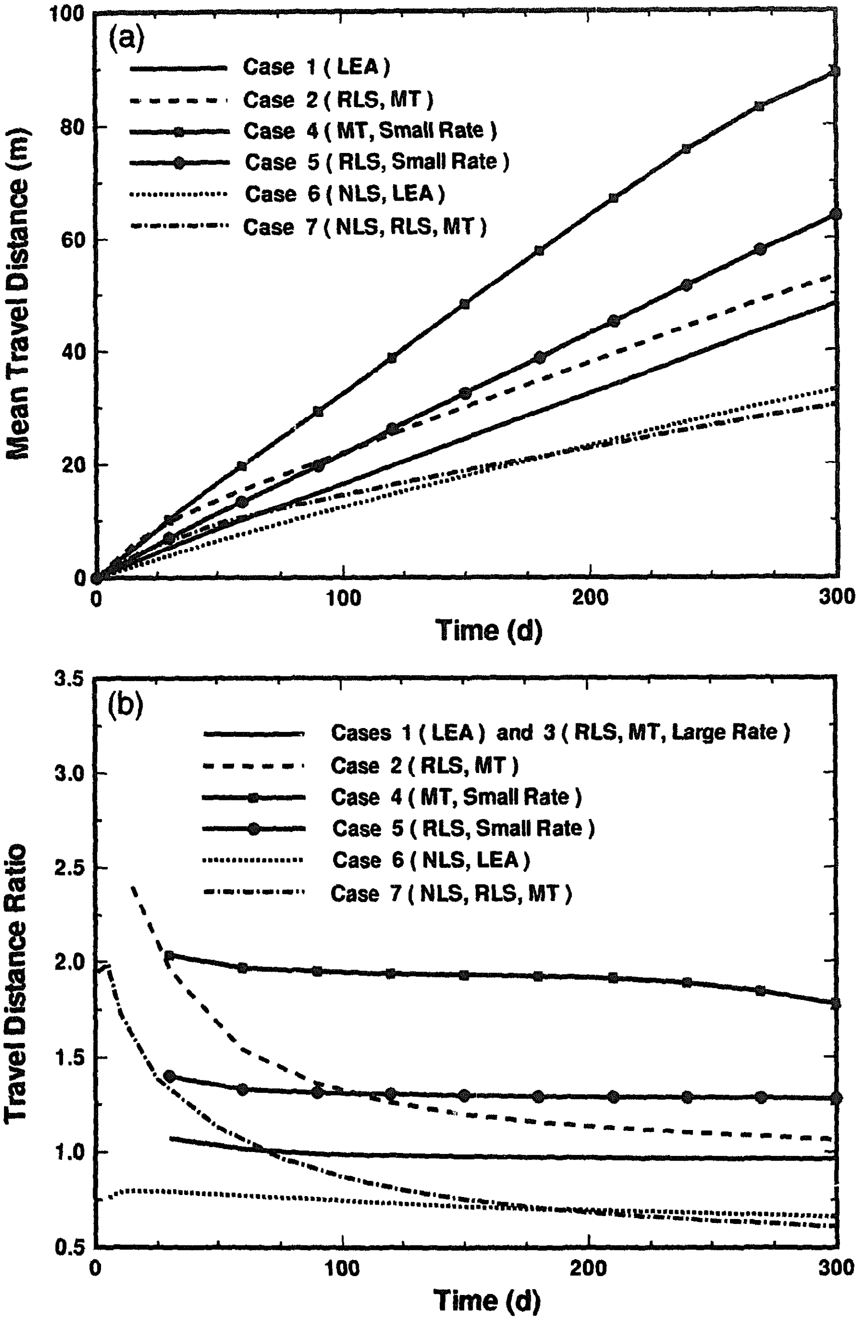

Fig. 2. Displacement of the plume center of mass in a heterogeneous porous medium: (a) the influence of rate-limited sorption/mass transfer and nonlinear sorption on mean travel distance; and (b) the influence of rate-limited sorption/mass transfer and nonlinear sorption on travel distance ratio. The variance of ln K was 1.

porous medium (Fig. 1). The magnitude of the impact of rate-limited sorption/mass transfer will, of course, depend on the magnitudes of the rate coefficients, the characteristic residence time (pore-water velocity, spatial scale of interest), and the degree of heterogeneity.

The influence of nonlinear sorption on plume displacement is enhanced for the heterogeneous porous medium (case 6, Fig. 2a and b). The additional spreading associated with transport in a heterogeneous domain increases the rate of concentration reduction, which enhances the rate at which sorption increases due to nonlinear sorption. Thus, the rate of plume deceleration is increased. Because the rate of deceleration is so great for the specific conditions used, the rate of plume displacement is less than that for case one at all times. Conversely, a wide range of displacement rates are observed for the case wherein transport is influenced by porous-medium heterogeneity, nonlinear sorption, and rate-limited sorption/mass transfer (see case 7, Fig. 2). At early times, plume displacement for case 7 is much faster than that for case 1; at later times it is much slower.

A comparison of the curves reported in Fig. 2 reveals that the impact of rate-limited sorption/mass transfer and of nonlinear sorption on the displacement behavior of the plume center of mass was much greater than the impact of hydraulic-conductivity variability. This result can be used to assist in elucidating the factors influencing field-scale solute transport. For example, the observation of a nonuniform rate of plume displacement indicates that factors other than, or in addition to, heterogeneity are influencing transport. In systems wherein hydraulic gradients are relatively uniform (both spatially and temporally), these additional factors could be nonlinear sorption, rate-limited sorption, rate-limited mass transfer, or some combination thereof.

4.3. Spatial second moments: homogeneous porous medium

The spreading behavior of solute plumes has been the primary focus of research on field-scale solute transport. In our analyses, the evolution of the second moment will be

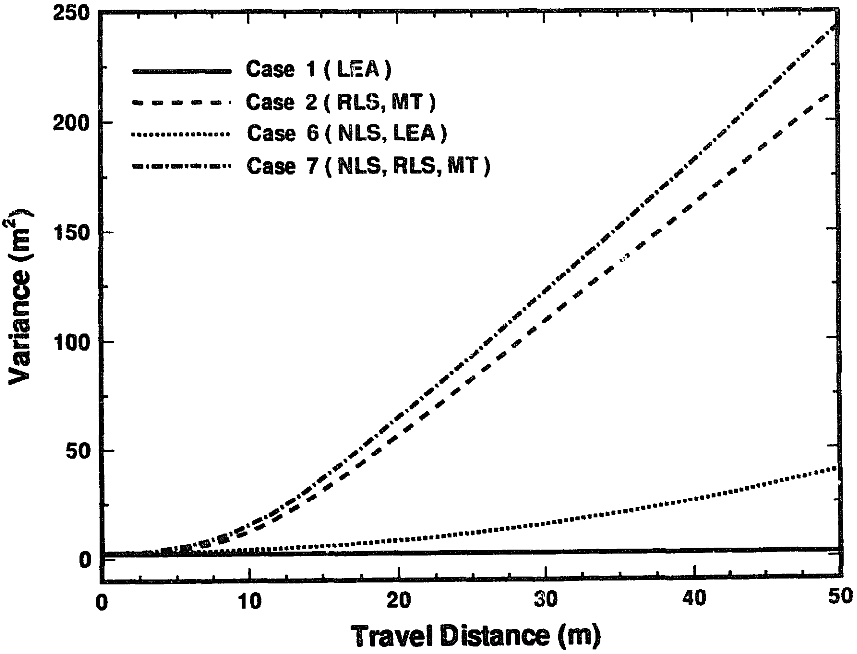

Fig. 3. The influence of nonlinear sorption and rate-limited sorption/mass transfer on the variance of a solute plume travelling through a homogeneous porous medium; travel distance is for the center of mass.

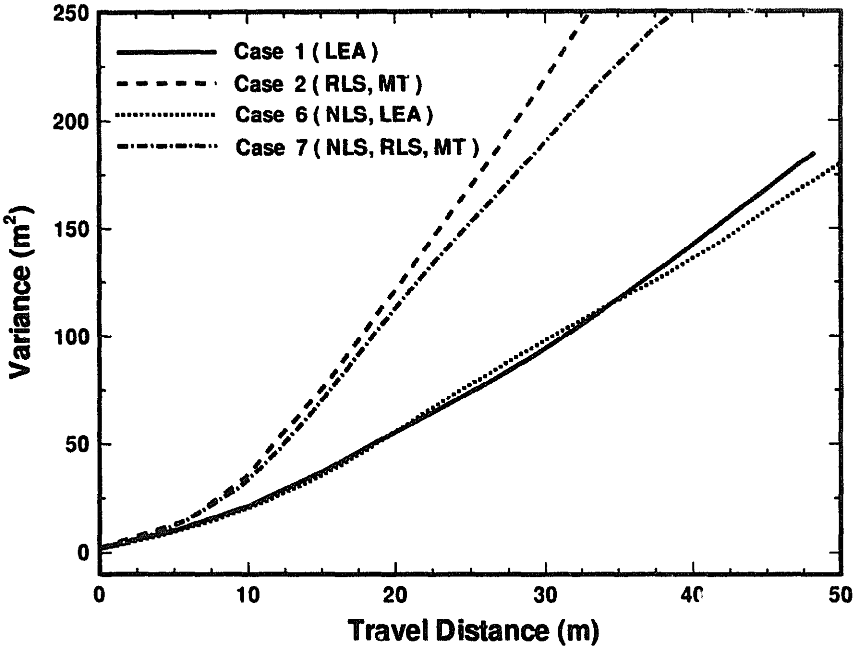

Fig. 4. The influence of nonlinear sorption and rate-limited sorption/mass transfer on the variance of a solute plume travelling through a heterogeneous porous medium (variance of ln $K = 1$); travel distance is for the center of mass.

evaluated as a function of travel distance of the center of mass. This is done to account for the impact of nonuniform plume velocities, thereby ensuring that the influence of each transport factor on spreading is compared for equivalent travel distances (i.e. equivalent spatial domains).

The influence of rate-limited sorption/mass transfer on spreading of the plume, as represented by the variance, is illustrated in Fig. 3 (case 2). Greatly enhanced spreading is observed only for the cases wherein rate-limited sorption/mass transfer was actively influencing transport. The degree of spreading for the two limiting cases, where the first-order mass-transfer coefficient (case 4) and the reverse sorption rate coefficient (case 5) are very small, was identical to the spreading observed for the ideal case (data not shown). This is consistent with the results obtained for the spatial first moments.

Nonlinear sorption caused enhanced spreading as a result of the nonuniform velocities existing throughout the plume (case 6, Fig. 3). The enhanced spreading becomes significant at later travel times. The degree of spreading for the case of nonlinear and rate-limited sorption/mass transfer (case 7, Fig. 3) was similar to that observed for the case of linear, rate-limited sorption/mass transfer.

4.4. Spatial second moments: heterogeneous porous medium

The influence of combined rate-limited sorption/mass transfer and hydraulic-conductivity variability on spreading of the plume is illustrated in Fig. 4. The existence of the variable hydraulic-conductivity field (case 1) resulted in enhanced spreading in comparison to the homogeneous case, as widely discussed in the literature. As expected, the behavior obtained for cases 3–5 is essentially identical to that of case 1 (data not shown). The existence of significant rate-limited sorption/mass transfer (case 2) caused additional spreading in comparison to case 1. This result is consistent with previous analyses of systems influenced by hydraulic-conductivity variability and rate-limited sorption/mass transfer (see pertinent references in Table 1).

The influences of hydraulic-conductivity variability and of rate-limited sorption/mass transfer on spreading reflect the specific set of parameter values used for the simulations and are not meant to necessarily represent general conditions. In many field systems, it is probable that hydraulic-conductivity variability will affect spreading to a greater degree than will rate-limited mass-transfer processes. Such an evaluation, however, should be determined for each set of conditions (e.g., degree of heterogeneity, magnitudes of the characteristic times of the rate processes, and magnitudes of the temporal and spatial scales).

For transport in a homogeneous porous medium, nonlinear sorption caused additional spreading (case 6, Fig. 3). However, nonlinear sorption had negligible effect on spreading for transport in the heterogeneous system (case 6, Fig. 4). The degree of spreading associated with nonlinear sorption and rate-limited sorption/mass transfer is intermediate between the prior two cases (compare case 7 to cases 2 and 6). The results presented in Figs. 3 and 4 show that all the factors considered cause enhanced spreading to some degree (compared to the ideal, homogeneous case). Thus, the second moment cannot be used to identify which factor or factors may be controlling transport for a given system.

4.5. Spatial third moments: homogeneous porous medium

The majority of analyses of plume behavior have focused on the first and second moments. However, the degree of asymmetry of a plume (i.e. the third moment) is of great interest to analyses of solute transport. The higher-order moments are more difficult to measure robustly because of the enhanced weight given to the low-concentration tails of a distribution. However, detailed sampling can provide sufficient data to obtain third moments, as demonstrated by the data reported for the well-known natural-gradient experiment performed at Cape Cod, Massachusetts, U.S.A. (Garabedian et al., 1988). The plume measured for lithium is clearly asymmetrical in comparison to the bromide plume. In our analyses we report "skewness", which is defined as the third moment normalized by the 3/2 power of the second moment. This normalization is done to account for the impact of plume size on the magnitude of the third moment.

Rate-limited sorption/mass transfer creates a negatively skewed plume in the early stages of transport, wherein a "tail" of low concentration is formed at the trailing edge of the plume (case 2, Fig. 5). The degree of asymmetry gradually diminishes as residence time increases, allowing an approach to global equilibrium conditions. At later times, rate-limited sorption/mass transfer causes a very small degree of positive skewness, wherein a "tail" exists at the leading edge of the plume. This effect is related to the continual non-equilibrium condition, with respect to mass transfer, that exists at the leading edge of the plume, which leads to enhanced transport and a leading-edge tail. The two limiting cases for sorption/mass transfer do not cause asymmetry (cases 4 and 5, not shown).

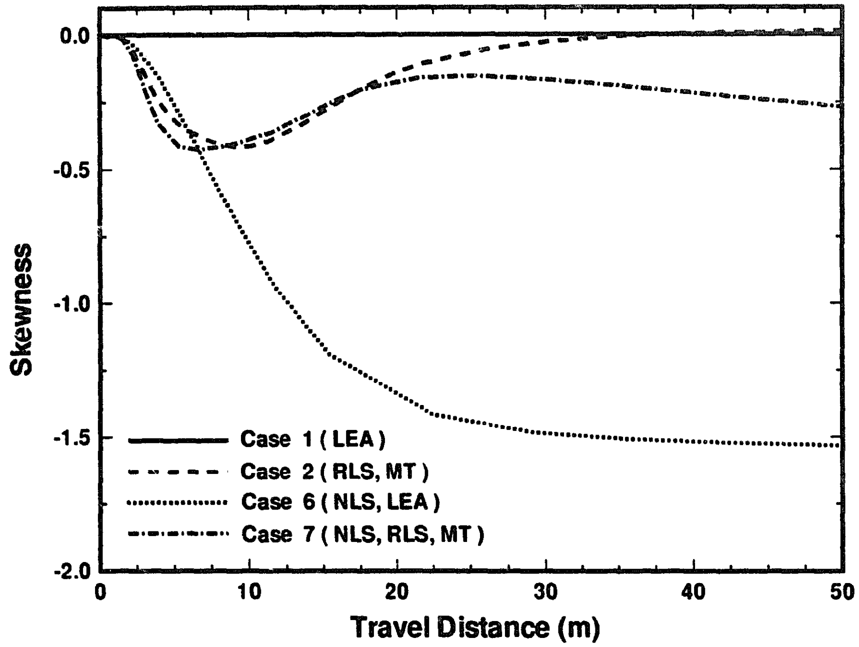

Fig. 5. The influence of nonlinear sorption and rate-limited sorption/mass transfer on the skewness of a solute plume travelling through a homogeneous porous medium; travel distance is for the center of mass.

Nonlinear sorption creates a negatively skewed plume, wherein a tail exists at the trailing edge of the plume (case 6, Fig. 5). The differential sorption behavior occurring at the two edges of the plume creates a self-sharpening front at the leading edge and a spreading front at the trailing edge. The degree of skewness asymptotically approaches a constant value, wherein the spatial distribution or shape of the plume remains constant. This constant shape would reflect the interaction of nonlinear sorption and the relevant spreading factors.

Inspection of Fig. 5 shows that both nonlinear sorption and rate-limited sorption/mass transfer cause negative skewness in the early stages of transport. This suggests that it would not be possible to differentiate between the two factors during the early stages of transport. However, a significant difference between the influence of the two processes exists at later stages; namely, the plume influenced by nonlinear sorption remains negatively skewed whereas the plume influenced by rate-limited sorption/mass transfer becomes nearly symmetrical. This suggests that the third moment can serve as a means to differentiate between systems controlled by rate-limited sorption/mass transfer and those controlled by nonlinear sorption after an early stage of transport.

Especially interesting results are obtained for the case wherein transport is influenced by nonlinear sorption and rate-limited sorption/mass transfer (case 7, Fig. 5). The impact of nonlinear sorption is counter-balanced by the impact of rate-limited sorption/mass transfer during the early stage of transport. Plume behavior similar to that observed for the plume influenced only by rate-limited sorption/mass transfer is maintained during this stage. Eventually, however, the influence of nonlinear sorption predominates, and the plume develops a constant degree of negative skewness.

4.6. Spatial third moments: heterogeneous porous medium

The influence of variable hydraulic conductivity on the skewness of the solute plume is illustrated in Fig. 6. Clearly, hydraulic-conductivity variability creates a positively skewed plume during the early stages of transport. The degree of asymmetry asymptotically decreases toward zero, as reported previously by Gelhar et al. (1979). The two limiting cases for rate-limited sorption/mass transfer have no effect on plume asymmetry (cases 4 and 5, not shown).

The impact of rate-limited sorption/mass transfer on plume skewness for the heterogeneous system (case 2, Fig. 6) is quite different from that observed for the homogeneous case (case 2, Fig. 5). The enhanced degree and rate of spreading associated with hydraulic-conductivity variability offsets the driving forces associated with rate-limited sorption/mass transfer that create negative asymmetry. Thus, the combined effect of hydraulic-conductivity variability and rate-limited sorption/mass transfer results in a positively skewed plume from the initiation of transport. However, the interaction between the two factors results in oscillations in the skewness during transport. At large travel distances, the plume skewness tends toward zero (data not shown).

The impact of nonlinear sorption on plume asymmetry for transport in the heterogeneous system differs from that observed for the homogeneous system (compare Figs. 5 and 6, case 6). The plume is positively skewed during the early stage of transport in the heterogeneous system as opposed to negatively skewed for transport in the homogeneous system. Eventually, however, the heterogeneous-system plume becomes nega-

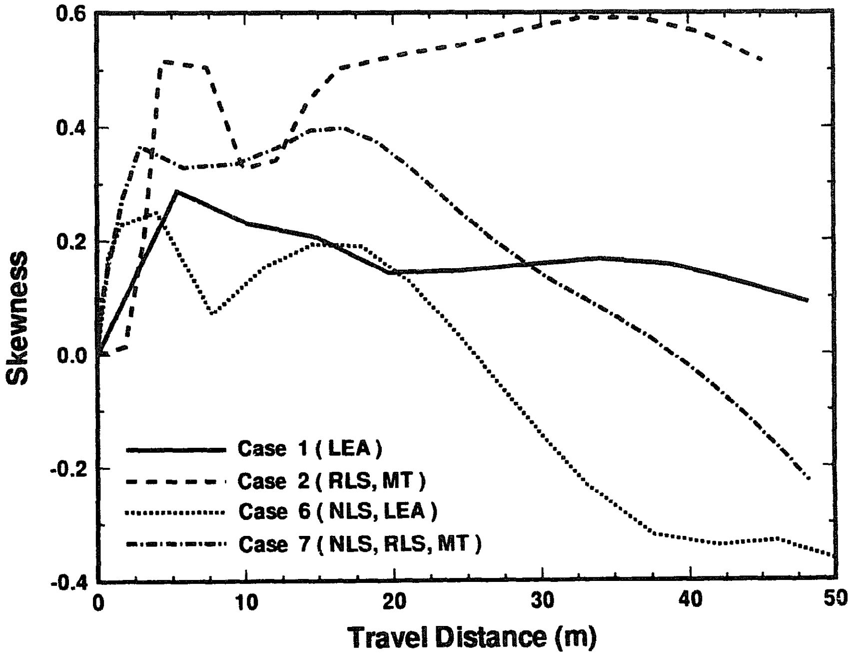

Fig. 6. The influence of nonlinear sorption and rate-limited sorption/mass transfer on the skewness of a solute travelling through a heterogeneous porous medium (variance of ln $K = 1$); travel distance is for the center of mass.

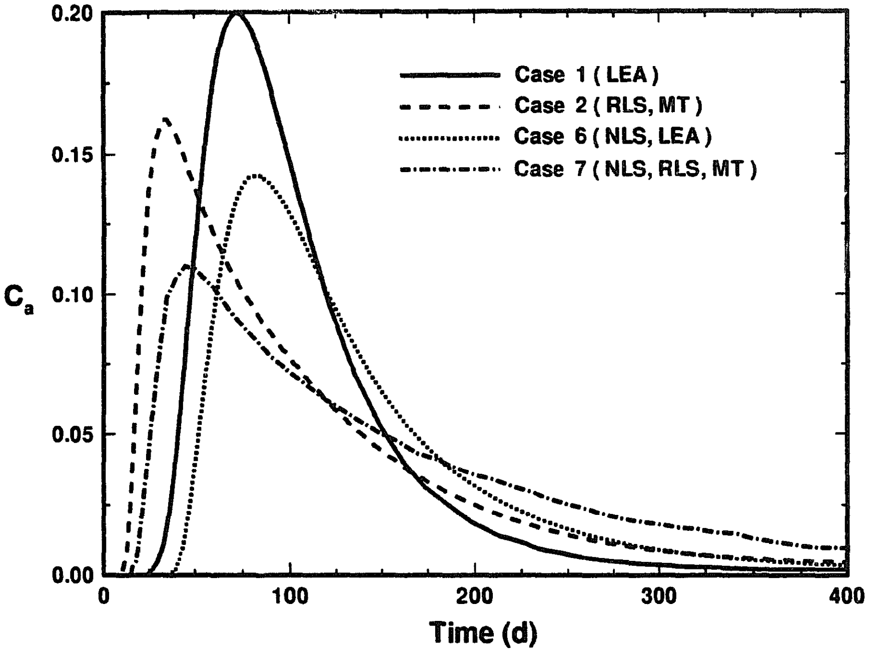

Fig. 7. Breakthrough curves for transport in a heterogeneous system; measured at $x = 15$ m from the center of the initial plume. Input parameters are identical to those used for the spatial analyses.

tively skewed, albeit to a lesser degree. The skewness profile for the case with nonlinear sorption and rate-limited sorption/mass transfer (case 7) is similar to the case-6 profile, with the exception of having somewhat larger positive skewness at early times and less negative skewness at later times. The behavior exhibited for cases 6 and 7, wherein the shape of a plume progresses from being positively skewed to symmetrical, and then to being negatively skewed is quite interesting and apparently has not been previously discussed.

The behavior illustrated in Fig. 6 indicates that during the early stage of transport, positively skewed plumes are associated with all three of the factors considered: hydraulic-conductivity variability, rate-limited sorption/mass transfer (combined with hydraulic-conductivity variability), and nonlinear sorption (combined with hydraulic-conductivity variability). At greater travel distances, the plumes influenced by nonlinear sorption tend toward a constant degree of negative asymmetry, whereas those influenced by hydraulic-conductivity variability and rate-limited sorption/mass transfer tend toward symmetry. This suggests that, even in heterogeneous systems, the third moment may be useful as a means to differentiate between cases wherein transport of reactive solutes is controlled by rate-limited sorption/mass transfer and those controlled by nonlinear sorption. However, this potential differentiation is made more difficult by the impact of hydraulic-conductivity variability on solute transport, which mediates the effects of sorption nonideality as well as creates greater uncertainty in concentration distributions.

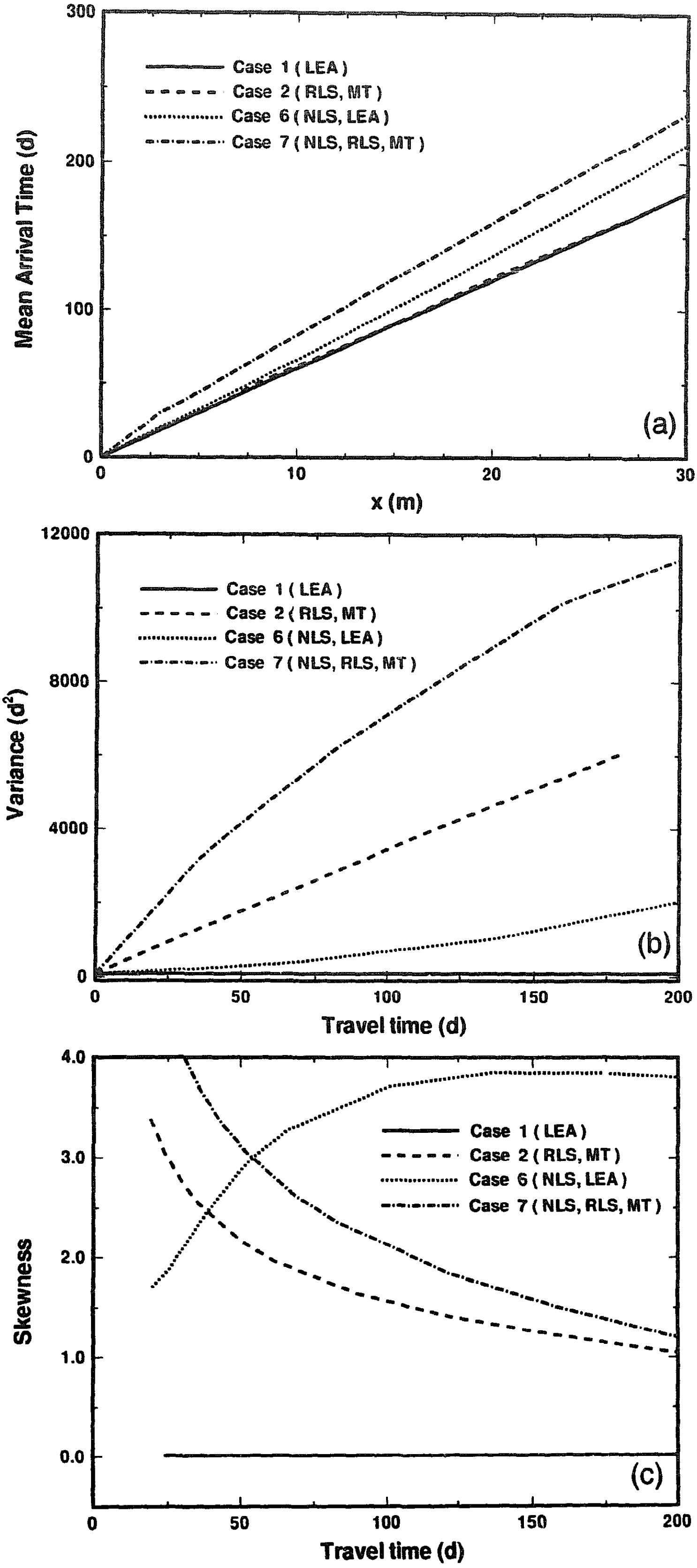

Fig. 8. Temporal moments for transport in a homogeneous system: (a) first; (b) second; and (c) third.

4.7. Breakthrough curves

The discussion presented above focused on the spatial behavior of solute plumes. Additional information concerning solute transport can be obtained by analysis of breakthrough curves. Breakthrough curves obtained at a selected location in the domain used for the simulations reported above are shown in Fig. 7. The curves represent integrated sampling over the entire vertical domain in which solute resides, such as associated with a fully screened monitoring well.

The breakthrough curve for the ideal case of homogeneity and linear, instantaneous mass transfer is sharp and rectangular, as expected (data not shown). In contrast, the breakthrough curves for the cases of rate-limited sorption/mass transfer and nonlinear sorption in a homogeneous porous medium are asymmetrical and exhibit "tailing" (data not shown), as widely discussed in previous work. The breakthrough curve obtained for the case of spatially variable hydraulic conductivity and linear, instantaneous sorption/mass transfer is shown in Fig. 7 (case 1). It is asymmetrical and exhibits "early arrival" and tailing, as has been reported previously (cf. Gelhar et al., 1979; Smith and Schwartz, 1980). The breakthrough curves for the transport of nonlinearly sorbing solute (case 6, Fig. 7) and rate-limited sorbing solute (case 2, Fig. 7) in a heterogeneous system are also asymmetrical. Clearly, the general shapes of the breakthrough curves shown in Fig. 7 are similar, which means that the factor or factors causing nonideal transport cannot be identified by analysis of breakthrough-curve shape.

4.8. Temporal moments: homogeneous porous medium

The influence of nonlinear and rate-limited sorption/mass transfer on the behavior of temporal moments for transport in a homogeneous system is shown in Fig. 8. Rate-limited sorption/mass transfer has no effect on the temporal first moment (case 2, Fig. 8a), as has been previously reported. Conversely, the mean arrival time is nonuniform when sorption is nonlinear (cases 6 and 7, Fig. 8a). For the selected condition (Freundlich N value < 1), the concentration-dependent retardation causes an increase in the mean arrival time as the pulse spreads and concentrations decrease with distanced travelled. This is consistent with the deceleration of the plume shown in Fig. 1.

Nonlinear sorption has minimal impact on the second temporal moment until later times. Conversely, rate-limited sorption/mass transfer has a significant effect on the second moment from the beginning of transport (Fig. 8b). This is the reverse of that observed for the first moment. Both nonlinear sorption and rate-limited sorption/mass transfer create positively skewed breakthrough curves, as indicated in Fig. 8c and shown in Fig. 7. However, the skewness associated with rate-limited sorption/mass transfer decreases with distance or time, whereas skewness increases for nonlinear sorption. This is consistent with the results obtained for the third spatial moments. In addition, the positive skewness of the temporal distributions is consistent with the negative skewness of the spatial distributions.

4.9. Temporal moments: heterogeneous porous medium

The influence of hydraulic-conductivity variability on solute transport causes a nonuniform temporal first moment at early times (case 1, Fig. 9a). In addition, the

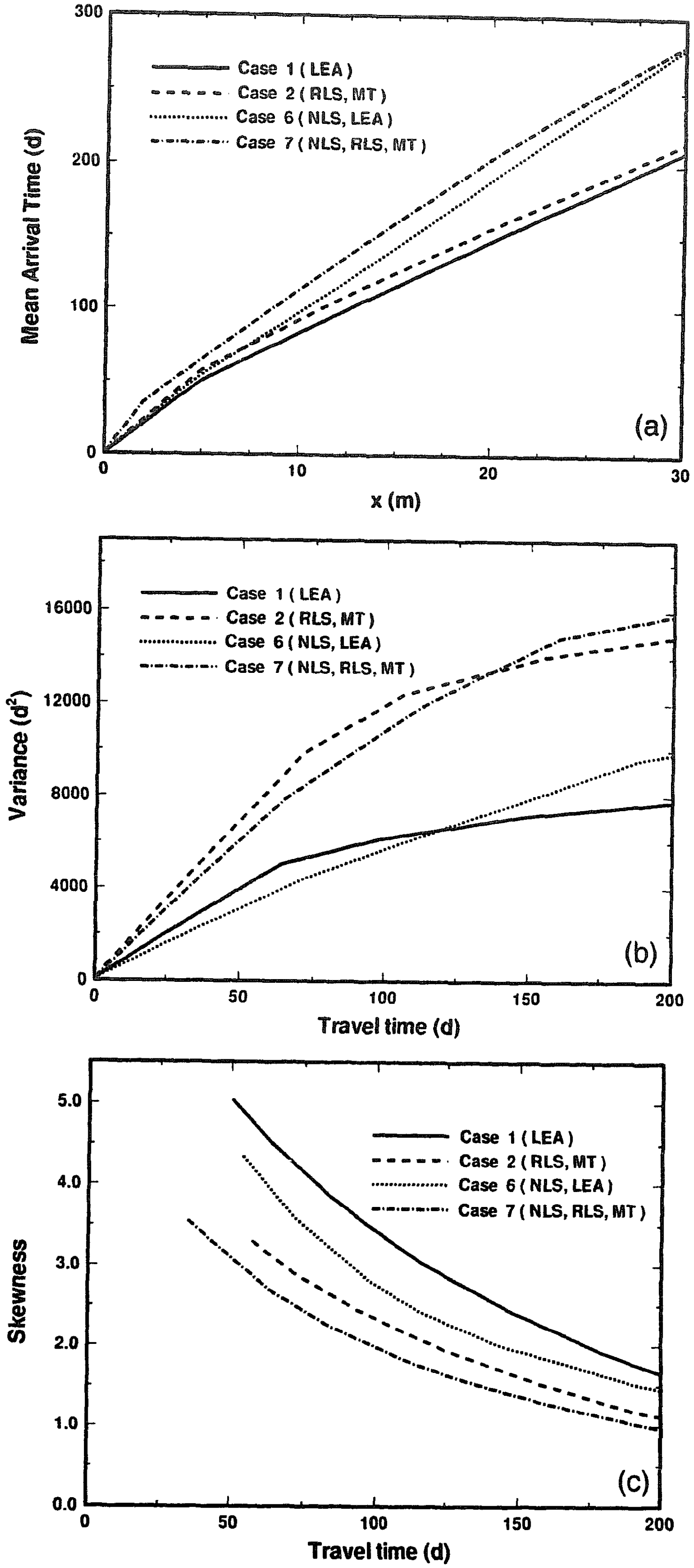

Fig. 9. Temporal moments for transport in a heterogeneous system: (a) first; (b) second; and (c) third.

magnitude of the first moment is greater than that for the homogeneous case for a given measurement location (case 1, Fig. 8a). This behavior is related to the spreading properties of a plume in a heterogeneous domain, which results in a skewed breakthrough curve. The combination of rate-limited sorption/mass transfer and hydraulic-conductivity variability causes an even greater increase in the first moment. While the general behavior of the first moment for nonlinear sorption in the heterogeneous case is similar to that for the homogeneous case, the degree of curvature is significantly less for the former case.

As expected, the magnitude of the second moment is much greater for the case wherein rate-limited sorption/mass transfer and hydraulic-conductivity variability are combined (case 2, Fig. 9b), compared to the homogeneous case (case 2, Fig. 8b). However, the qualitative behavior is similar. When nonlinear sorption and hydraulic-conductivity variability are combined, breakthrough curve spreading during the early stages of transport is less than that for the case with hydraulic-conductivity variability and linear sorption. Conversely, the addition of nonlinear sorption had minimal impact at early times for the homogeneous case.

All cases exhibit a positive skewness, that decreases with time (Fig. 9c). The existence of hydraulic-conductivity variability does not change the qualitative behavior for the cases with rate-limited sorption/mass transfer, but it does change the behavior for transport with nonlinear sorption. For the homogeneous system, the skewness increases with time (case 6, Fig. 8c), whereas it decreases with time for the heterogeneous system (case 6, Fig. 9c).

The temporal third moment for transport in a heterogeneous porous medium (e.g., case 1 — spatially variable hydraulic conductivity) is positively skewed, as shown in Fig. 7b and 9c. The spatial distributions of concentrations are also positively skewed, although to a much lesser extent (case 1, Fig. 6). This dichotomous behavior suggests that the two asymmetrical distributions are caused by different processes. The skewed temporal distribution is related to the continuous growth (i.e. spreading) of the plume as it passes by a fixed monitoring point. The skewed spatial distribution is related to differential advection occurring at the leading edge of the plume. For both cases, however, the degree of asymmetry decreases with time.

4.10. Comparison to field data

The analyses presented above illustrate the complex behavior associated with the transport of reactive solutes in heterogeneous porous media. This complex behavior can only be simulated by use of mathematical models that incorporate the multiple factors and processes influencing transport. When developing and using complex transport models, it is important to evaluate their performance by comparing resultant simulations to measured field data. We have evaluated our model by using it to predict the results of the well known Borden (Ontario, Canada) natural-gradient field experiment. This detailed analysis is too lengthy to report herein. However, at the request of the reviewers of this paper, for purposes of illustrating the application of our model to measured field data, we will report one example of the results of our Borden data analysis.

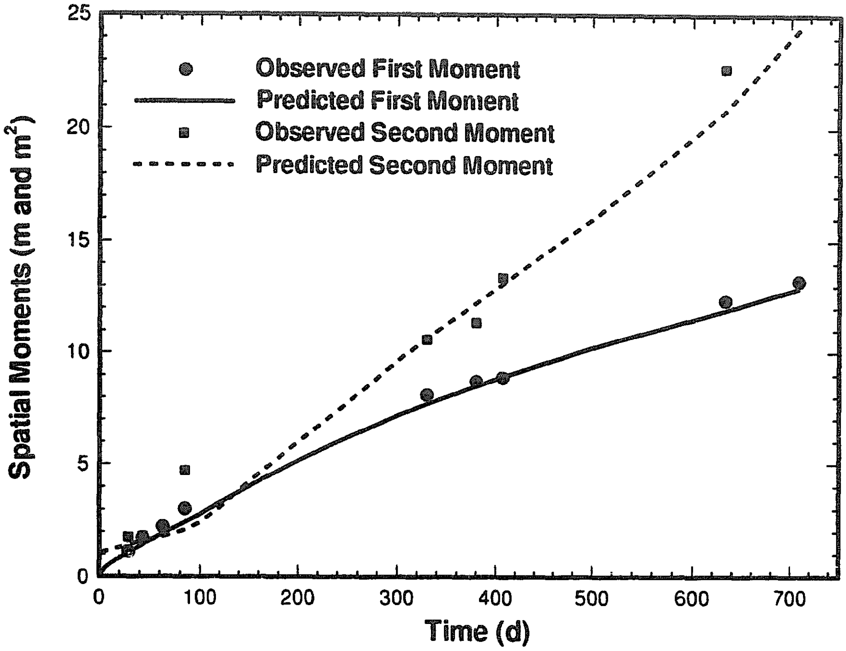

Fig. 10. Measured and predicted first and second spatial moments representing tetrachloroethene transport during the Borden natural-gradient field experiment. The measured data are from Roberts and Mackay (1986), and the simulations are from Brusseau and Srivastava (1996). The simulations represent a single realization obtained from a two-dimensional (vertical) analysis using the Monte Carlo approach.

The measured and predicted first and second spatial moments obtained for the tetrachloroethene plume are presented in Fig. 10. Based on our analyses, we concluded that a measured trend of increasing sorption in the direction of transport was a primary cause of the deceleration of the centers of mass of the organic-solute plumes. In addition, the coupled effects of nonlinear sorption and enhanced spreading caused by spatially variable aquifer properties also influenced the first moment. These conclusions are in contrast to those of most previous analyses, which have considered a rate-limited sorption/mass-transfer process as being responsible for the plume deceleration. The combined spatial variability of hydraulic conductivity and of sorption, and a potential negative cross correlation between them, appears to have been the major cause of the enhanced spreading observed for the organic-solute plumes in comparison to the nonreactive-solute plumes. However, nonlinear sorption, the spatial trend of increasing sorption, and rate-limited sorption/mass transfer also influenced spreading behavior. It is evident that the predictions produced with the mathematical model matched the measured field data well, providing support for the basis of the model. Full details of these analyses are reported by Brusseau and Srivastava (1996).

5. Conclusions

With a series of numerical simulations, we have shown that rate-limited sorption/mass transfer and nonlinear sorption can significantly influence the first, second, and third spatial moments associated with the transport of solute plumes. Conversely, the influence of spatial heterogeneity (e.g., hydraulic-conductivity variability) on transport significantly impacts only the second spatial moment. While most previous investigations have focused on the first and second moments (see Table 1), we have shown that plume skewness is sensitive to the specific factor controlling nonideal transport and, therefore, deserves attention. For example, both rate-limited sorption/mass transfer and nonlinear sorption can create negatively skewed plumes during early stages of transport in a homogeneous porous medium. However, the plume influenced by rate-limited sorption/mass transfer tends toward symmetry as global residence time increases. Conversely, the plume influenced by nonlinear sorption tends toward a constant degree of asymmetry, as the spreading forces balance the concentration-dependent retardation behavior associated with nonlinear sorption. The influence of hydraulic-conductivity heterogeneity modified the impact of nonideal sorption/mass transfer on plume skewness during the early stage of transport, causing positive skewness. Finally, while the majority of previous investigations have focused on either spatial or temporal moments (see Table 1), we have illustrated the usefulness of considering them together.

The results of the analyses showed that the impact of heterogeneity on plume spreading (second moment) was qualitatively similar in effect to that of rate-limited sorption/mass transfer and nonlinear sorption. The influence of heterogeneity and of nonideal sorption/mass transfer on the shapes and moments of breakthrough curves was also similar. These results indicate that the identification of factors controlling nonideal transport in a specific system can be very difficult and uncertain when based on analysis of plume spreading or breakthrough curves alone. Conversely, rate-limited sorption/mass transfer and nonlinear sorption had a much greater effect on the displacement of the plume center of mass (first moment) and on plume skewness (third moment) than did heterogeneity. Thus, the first and third spatial moments may be useful to help distinguish between systems wherein transport of reactive solutes is controlled only by heterogeneity and those wherein nonideal sorption/mass transfer is also important. However, this potential differentiation is made more difficult by the impact of hydraulic-conductivity variability on solute transport, which mediates the effects of sorption nonideality as well as creates greater uncertainty in concentration distributions.

It is important to stress that our results were obtained for a single set of parameter values. It is expected that the trends we have shown will generally be consistent for a range of parameter values. However, the degree of the observed behavior will, of course, depend on the magnitude of the parameter values used, as well as system properties (initial conditions, temporal and spatial scales, etc.). Spatial variability of the reaction-related parameters, and possible correlations among them and between them and hydraulic conductivity, will also influence the behavior.

To date, there have been few analyses of the combined effects of nonlinear and rate-limited sorption/mass transfer on solute transport, especially for heterogeneous systems. The results of our analyses illustrate that transport of reactive solutes in heterogeneous systems can be quite complex, and that unique behavior can result from the coupling of multiple processes. For example, we demonstrated that, when influenced by coupled heterogeneity and nonlinear sorption, the shape of a plume may change from positive to negative skewness during the course of transport. This complex behavior can only be simulated by use of mathematical models that explicitly account for each important transport factor. Thus, there is continued need to develop such models. However, as transport models become more and more complex, it becomes evermore critical to test these models against measured field data.

Acknowledgements

We thank the reviewers for their comments. This research was supported, in part, by grants provided by the U.S. Environmental Protection Agency and the Superfund Basic Research Program of the National Institute of Environmental Health Sciences.

References

Andricevic, R. and Foufoula-Georgiou, E., 1991. Modeling kinetic non-equilibrium using the first two moments of the residence time distribution. Stochast. Hydrol. Hydraul., 5: 155–171.

Bahr, J.M., 1986. Applicability of the local equilibrium assumption in mathematical models for groundwater transport of reacting solutes. Ph.D. Dissertation, Stanford University, Palo Alto, CA.

Bosma, W.J.P., Bellin, A., van der Zee, S. and Rinaldo, A., 1993. Linear equilibrium adsorbing transport in physically and chemically heterogeneous porous formations, 2. Numerical results. Water Resour. Res., 29(12): 4031–4043.

Bosma, W.J.P., van der Zee, S., Bellin, A. and Rinaldo, A., 1994. Instantaneous injection of a nonlinearly adsorbing solute in a heterogeneous aquifer. In: T.H. Dracos and F. Stauffer (Editors), Transport and Reactive Processes in Aquifers, Proc. IAHR/AIRH Symp., Zürich, Switzerland, 11–15 April, 1994. A.A. Balkema, Rotterdam, pp. 411-417.

Brusseau, M.L., 1989. Nonequilibrium sorption: Investigation at microscopic to megascopic scales. Ph.D. Dissertation, University of Florida, Gainesville, FL.

Brusseau, M.L., 1991. Application of a multiprocess nonequilibrium sorption model to solute transport in a stratified porous medium. Water Resour. Res., 27(4): 589–595.

Brusseau, M.L., 1992. Transport of rate-limited sorbing solutes in heterogeneous porous media: Application of a one-dimensional multi-factor nonideality model to field data. Water Resour. Res., 28(9): 2485–2497.

Brusseau, M.L., 1994. Transport of reactive contaminants in heterogeneous porous media. Rev. Geophys., 32(3): 285–314.

Brusseau, M.L. and Rao, P.S.C, 1989. Sorption nonideality during organic contaminant transport in porous media. CRC Crit. Rev. Environ. Control, 19: 33–99.

Brusseau, M.L. and Rao, P.S.C., 1990. Modeling solute transport in structured soils: A review. Geoderma, 46(1-3): 169–192.

Brusseau, M.L. and Srivastava, R., 1996. Nonideal transport of reactive solutes in heterogeneous porous media: 2. Analysis of the Borden natural-gradient field experiment (in review).

Brusseau, M.L. and Zachara, J., 1993. Transport of Co^{2+} in a physically and chemically heterogeneous porous medium. Environ. Sci. Technol., 27(9): 1937–1939.

Brusseau, M.L., Jessup, R.E. and Rao, P.S.C., 1989. Modeling the transport of solutes influenced by multi-process nonequilibrium. Water Resour. Res., 25(9): 1971–1988.

Brusseau, M.L., Jessup, R.E. and Rao, P.S.C., 1991. Nonequilibrium sorption of organic chemicals: Elucidation of rate-limiting processes. Environ. Sci. Technol., 25(1): 134–142.

Burr, D.T., Sudicky, E.A. and Naff, R.L., 1994. Nonreactive and reactive solute transport in three-dimensional heterogeneous porous media: Mean displacement, plume spreading, and uncertainty. Water Resour. Res., 30(3): 791–815.

Chiang, C.Y., Wheeler, M.F. and Bedient, P.B., 1989. A modified method of characteristics technique and mixed finite elements method for simulation of ground water solute transport. Water Resour. Res., 25: 1541–1549.

Coats, K.H. and Smith, B.D., 1964. Dead-end pore volume and dispersion in porous media. J. Soc. Pet. Eng., 4: 73-81.

Cvetkovic, V.D. and Dagan, G., 1994. Effect of nonlinear sorption on contamination/remediation of heterogeneous aquifers. In: T.H. Dracos and F. Stauffer (Editors), Transport and Reactive Processes in Aquifers, Proc. IAHR/AIRH Symp., Zürich, Switzerland, 11-15 April, 1994. A.A. Balkema, Rotterdam, pp. 411-417.

Cvetkovic, V.D. and Shapiro, A.M., 1990. Mass arrival of sorptive solute in heterogeneous porous media. Water Resour. Res., 26(9): 2057-2067.

Dagan, G., 1989. Flow and Transport in Porous Formations. Springer, Berlin.

Dagan, G. and Cvetkovic, V., 1993. Spatial moments of a kinetically sorbing solute plume in a heterogeneous aquifer. Water Resour. Res., 29(12): 4053-4061.

Davidson, J.M. and McDougal, J.R., 1973. Experimental and predicted movement of three herbicides in water-saturated soil. J. Environ. Qual., 2: 428-433.

Destouni, G. and Cvetkovic, V., 1991. Field scale mass arrival of sorptive solute into the groundwater. Water Resour. Res., 27(6): 1315-1325.

Elabd, H., Jury, W.A. and Cliath, M.M., 1986. Spatial variability of pesticide adsorption parameters. Environ. Sci. Technol., 20(3): 256-260.

Garabedian, S.P., Gelhar, L.W. and Celia, M.A., 1988. Large-scale dispersive transport in aquifers: field experiments and reactive transport theory. Dep. Civ. Eng., Mass. Inst. Technol., Cambridge, MA, Rep. No. 315.

Gelhar, L.W., Gutjahr, A.L. and Naff, R.L., 1979. Stochastic analysis of macrodispersion in a stratified aquifer. Water Resour. Res., 15(6): 1387-1397.

Giddings, J.C. and Eyring, H., 1955. A molecular dynamic theory of chromatography. J. Phys. Chem., 59: 416-421.

Istok, J., 1989. Groundwater modeling by the finite element method. Am. Geophys. Union, Washington, DC, Water Resour. Monogr. No. 13, 495 pp..

Jardine, P.M., Parker, J.C. and Zelazny, L.W., 1985. Kinetics and mechanisms of aluminum adsorption on kaolinite using a two-site nonequilibrium transport model. Soil Sci. Soc. Am. J., 49: 867-873.

Jury, W.A., 1983. Chemical transport modeling: Current approaches and unresolved problems. In: Chemical Mobility and Reactivity in Soil Systems, Ch. 4. Soil Sci. Soc. Am., Madison, WI, SSSA Spec. Publ. No. 11.

Kabala, Z.J. and Sposito, G., 1991. A stochastic model of reactive solute transport with time-varying velocity in a heterogeneous aquifer. Water Resour Res., 27(3): 341-350.

Mackay, D.M., Ball, W.P. and Durant, M.G., 1986. Variability of aquifer sorption properties in a field experiment on groundwater transport of organic solutes: methods and preliminary results. J. Contam. Hydrol., 1(1/2): 119-132.

Mantoglou, A. and Wilson, J.L., 1982. The turning bands method for simulation of random fields using line generation by a spectral method. Water Resour. Res., 18(5): 1379-1394.

Matheron, G., 1973. Intrinsic random functions and their applications. Adv. Appl. Prob., 5: 439-468.

Ortega, J.M., 1988. Introduction to Parallel and Vector Solution of Linear Systems. Plenum, New York, NY, 305 pp. , 1988.

Pickens, J.F., Jackson, R.E., Inch, K.J. and Merritt, W.F., 1981. Measurements of distribution coefficients using a radial injection dual-tracer test. Water Resour. Res., 17(3): 529-544.

Quinodoz, H.A.M. and Valocchi, A.J., 1993. Stochastic analysis of the transport of kinetically sorbing solutes in aquifers with randomly heterogeneous hydraulic conductivity. Water Resour. Res., 29(9): 3227-3240.

Rabideau, A.J. and Miller, C.T., 1994. Two-dimensional modeling of aquifer remediation influenced by sorption nonequilibrium and hydraulic conductivity heterogeneity. Water Resour. Res., 30(5): 1457-1470.

Rajaram, H. and Gelhar, L.W., 1993. Plume-scale dependent dispersion in heterogeneous aquifers, 1. Lagrangian analysis in a stratified aquifer. Water Resour. Res., 29(9): 3249-3260.

Rao, P.S.C., Rolston, D.E., Jessup, R.E. and Davidson, J.M., 1980. Solute transport in aggregated porous media: Theoretical and experimental evaluation. Soil Sci. Soc. Am. J., 44: 1139-1146.

Rao, P.S.C., Evardsson, K., Ou, L.T., Jessup, R.E., Nkedi-Kizza, P. and Hornsby, A.G., 1986. Spatial variability of pesticide sorption and degradation. In: Evaluation of Pesticides in Ground Water. Am. Chem. Soc., Washington, DC, ACS Symp. Ser., 315: 100-115.

Roberts, P.V. and Mackay, D.M., 1986. A natural gradient experiment on solute transport in a sand aquifer. Dep. Civ. Eng., Stanford Univ., Stanford, CA, Tech. Rep. No. 292.

Robin, M.J.L., Sudicky, E.A., Gillham, R.W. and Kachanoski, R.G., 1991. Spatial variability of strontium distribution coefficients and their correlation with hydraulic conductivity in the Canadian forces base Borden aquifer. Water Resour. Res., 27(10): 2619–2632.

Schäfer, W. and Kinzelbach, W., 1992. Stochastic modeling of in situ bioremediation in heterogeneous aquifers. J. Contam. Hydrol., 10(1): 47–73.

Schwarzenbach, R.P. and Westall, J., 1981. Transport of nonpolar organic compounds from surface water to groundwater. Environ. Sci. Technol., 15: 1360–1368.

Selroos, J. and Cvetkovic, V., 1992. Modeling solute advection coupled with sorption kinetics in heterogeneous formations. Water Resour. Res., 28(5): 1271–1278.

Smith, L. and Schwartz, F.W., 1980. Mass transport, 1. A stochastic analysis of macroscopic dispersion. Water Resour. Res., 16(2): 303–313.

Smith, L. and Schwartz, F.W., 1981. Mass transport, 2. Analysis of uncertainty in prediction. Water Resour. Res., 17(2): 351–369.

Srivastava, R. and Brusseau, M.L., 1994. Effect of physical and chemical heterogeneities on aquifer remediation by pump and treat. In: Proceedings of the American Chemical Society National Meetings, Vol. 34(1), Environmental Chemistry Division, San Diego, CA, March 13–18, 1994. Am. Chem. Soc., Washington, DC, pp. 262–265.

Srivastava, R. and Yeh, T.-C.J., 1992. A three-dimensional numerical model for water flow and transport of chemically reactive solute through porous media under variably saturated conditions. Adv. Water Res., 15: 275–287.

Tompson, A.F.B., 1993. Numerical simulation of chemical migration in physically and chemically heterogeneous porous media. Water Resour. Res., 29(11): 3709–3726.

Valocchi, A.J., 1988. Theoretical analysis of deviations from local equilibrium during sorbing solute transport through idealized stratified aquifers. J. Contam. Hydrol., 2(3): 191–207.

Valocchi, A.J., 1989. Spatial moment analysis of the transport of kinetically adsorbing solutes through stratified aquifers. Water Resour. Res., 25(2): 273–279.

van der Zee, S. and van Riemsdijk, W.H., 1987. Transport of reactive solute in spatially variable soil systems. Water Resour. Res., 23(11): 2059–2069.

van Genuchten, M.Th. and Wierenga, P.J., 1976. Mass transfer studies in sorbing porous media: Analytical solutions. Soil Sci. Soc. Am. J., 40(3): 473–479.

Xu, L. and Brusseau, M.L., 1996. Semi-analytical solution for solute transport in porous media with multiple spatially variable reaction processes. Water Resour. Res. (in press).

Young, D. and Kincaid, D., 1981. The ITPACK package for large sparse linear systems. In: M. Schultz (Editor), Elliptic Problem Solvers. Academic Press, New York, NY, pp. 163–185.