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The effect of nonlinear sorption on transformation of contaminants during transport in porous media

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Abstract

The transport of contaminants through porous media is influenced by several processes, two of the most important being sorption and transformation. Several mathematical models have been developed to investigate the effects of sorption and transformation on contaminant transport. Almost all of these models are based on the assumption of linear sorption. However, it is well known that sorption of reactive contaminants is often nonlinear. A mathematical model that describes the transport of solute undergoing nonlinear, rate-limited sorption and first-order transformation is used to investigate the effect of coupled transformation and nonlinear sorption on contaminant transport. Results of the analyses show that a model based on linear sorption cannot provide an accurate simulation of the transformation and transport of nonlinearly sorbing solutes when n is less than ~ 0.9. In addition, the relative impact of nonlinear sorption on solute transport is mediated by the magnitude of transformation. The nondimensional time required for a specified fraction of solute mass to be transformed during transport is influenced by nonlinear sorption. These examples illustrate the intriguing effects that coupled processes can have on contaminant transport and which may be important for many contaminants of interest.

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1. Introduction

The transport and fate of many contaminants in subsurface systems is influenced by transformation processes such as biodegradation, hydrolysis and radioactive decay. A large number of mathematical models have been developed to simulate the effects of transformation on contaminant transport, as documented in a recent review (Brusseau et al., 1992a). The majority of these models are based on simplifying assumptions of linear, instantaneous sorption and homogeneous porous media. The

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invalidity of these assumptions is well known and models describing transport of transforming solutes have been developed that account for heterogeneity (cf. Molz and Widdowson, 1988; MacQuarrie and Sudicky, 1990; Miralles-Wilhelm et al., 1990), rate-limited sorption (cf. Eldor and Dagan, 1972; Lindstrom, 1976; Lassey, 1988; van Genuchten and Wagenet, 1989; Estrella et al., 1993), or both (Brusseau et al., 1992b). However, all of these models are based on linear sorption. It has been shown that the sorption isotherms for many contaminants are nonlinear (cf. Weber and Miller, 1989; Ball and Roberts, 1991; McGinley et al., 1993) and that it is important to account for this when simulating transport (cf. Rao and Davidson, 1979; Crittenden et al., 1986; Brusseau and Rao, 1989). Hence, there is a need to investigate the effect of nonlinear sorption on the transport of contaminants undergoing transformation reactions. Such is the purpose of this work.

2. Mathematical model

A solute transport model presented by Mansell et al. (1977) included nonlinear, rate-limited sorption and first-order irreversible reaction. However, sorption kinetics were described by the so-called one-site equation, which has been shown to be inadequate for many solutes. In addition, the irreversible sink term could apply to either the solution or sorbed phase, but not both simultaneously. Hoffman and Rolston (1980) presented a solute transport model that included nonlinear, rate-limited sorption and first-order transformation. However, transformation reactions were limited to the solution phase. A mathematical model that describes the transport of solute undergoing nonlinear, rate-limited sorption and first-order transformation in *all* domains was presented by Jessup et al. (1989). This model will be used for the analyses reported herein.

The widely used two-domain approach, wherein sorption is assumed to be essentially instantaneous for a fraction of the sorbent and is rate-limited for the remainder, is used to represent rate-limited sorption. One formulation of this approach is given by:

$$C \leftrightarrow S_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S_2 \tag{1}$$

where C is solution-phase concentration of solute [M L^{-3}]; S_1 is the concentration of instantaneously sorbed solute [M M^{-1}]; S_2 is the concentration of rate-limited sorbed solute [M M^{-1}]; k_1 is the first-order sorption rate coefficient [T^{-1}]; and k_2 is the first-order reverse sorption rate coefficient [T^{-1}]. The two-domain approach has been shown to be representative of the predominant mechanisms causing rate-limited sorption of contaminants by natural porous media (soil, sediment, aquifer material) (cf. Brusseau and Rao, 1989). For example, several researchers have shown that it can be used to simulate rate-limited sorption caused by intrasorbent diffusion as well as by chemical reactions. In the former case, S_1 can be viewed as the concentration of solute at the solution–sorbent interface and S_2 can be viewed as the average concentration of solute inside the sorbent.

The equation for sorption at equilibrium is:

$$S_\mathrm{T} = S_1 + S_2 = FK_\mathrm{f}C^n + (1 - F)K_\mathrm{f}C^n \tag{2}$$

where S_T is total sorbed-phase concentration [M M^{-1}]; K_f is the Freundlich sorption coefficient [L^{3n} M^{-1}]; n is the Freundlich exponent (power function); and F is the fraction of sorbent for which sorption is instantaneous. Note that the well-known Freundlich equation is used in Eq. 2 to represent a nonlinear sorption isotherm. The Freundlich equation is used because it is the most widely used isotherm function for many contaminants of interest (cf. Brusseau and Rao, 1989; Weber and Miller, 1989).

Transformation reactions are described as a first-order process:

$$\frac{\partial C}{\partial t} = -\mu C \tag{3}$$

where μ is a first-order transformation rate constant [T^{-1}]. The first-order equation accurately describes transformation by radioactive decay and, under certain conditions (e.g., fixed pH), hydrolysis. First-order kinetics can also be used to represent biodegradation when substrate (i.e. solute) utilization is independent of microbial growth. This can occur when substrate concentrations are relatively low, when exposure time is minimal, or when, under certain conditions, degradation is occurring by co-metabolism (Alexander and Scow, 1989; Brusseau et al., 1992a).

The equations describing solute transport governed by steady-state, one-dimensional water flow, nonlinear, rate-limited sorption and first-order transformation are:

$$\theta\frac{\partial C}{\partial t} + \rho\frac{\partial S_1}{\partial t} + \rho\frac{\partial S_2}{\partial t} = -q\frac{\partial C}{\partial x} + \theta D\frac{\partial^2 C}{\partial x^2} - \mu_\ell\theta C - \mu_{\mathrm{s}_1}\rho S_1 - \mu_{\mathrm{s}_2}\rho S_2 \tag{4}$$

$$\frac{\partial S_2}{\partial t} = k_1S_1 - k_2S_2 - \mu_{\mathrm{s}_2}S_2 \tag{5}$$

where t is time [T]; x is distance [L]; ρ is bulk density of the soil [M L^{-3}]; θ is fractional volumetric water content [L^3 L^{-3}]; q is Darcy flux [L T^{-1}]; v is average linear pore-water velocity ($v = q/\theta$) [L T^{-1}]; D is the local dispersion coefficient (L^2 T^{-1}]; and μ_i is the first-order rate coefficient [T^{-1}] for transformation in solution (ℓ), equilibrium–sorbed (s_1) and rate-limited–sorbed (s2) phases, respectively. Note that transformation of solute may occur in all three domains, i.e. solution, instantaneous sorbed and rate-limited sorbed domains.

The governing equations may be written in the following nondimensional form:

$$\frac{\partial C^*}{\partial T} + (\beta R_n - 1)nC^{*n-1}\frac{\partial C^*}{\partial T} + \omega(C^{*n} - S^*) = \frac{1}{P}\frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} - \epsilon_\ell C^* - \epsilon_{\mathrm{s}_1}C^{*n} \tag{6}$$

$$(1 - \beta)R_n\frac{\partial S^*}{\partial T} = \omega(C^{*n} - S^*) - \epsilon_{\mathrm{s}_2}S^* \tag{7}$$

by defining the following dimensionless parameters:

$$S^* = S_2[(1-F)K_f C_0^n]^{-1} \tag{8a}$$

$$C^* = CC_0^{-1} \tag{8b}$$

$$P = vLD^{-1} \tag{8c}$$

$$X = xL^{-1} \tag{8d}$$

$$R_n = 1 + (\rho/\theta)K_f C_0^{n-1} \tag{8e}$$

$$T = tvL^{-1} \tag{8f}$$

$$\omega = k_2(1-\beta)RLv^{-1} \tag{8g}$$

$$\beta = [1 + (\rho/\theta)FK_f C_0^{n-1}]R_n^{-1} \tag{8h}$$

$$\epsilon_\ell = \mu_\ell Lv^{-1} \tag{8i}$$

$$\epsilon_{s_1} = (\beta R_n - 1)\mu_{s_1} Lv^{-1} \tag{8j}$$

$$\epsilon_{s_2} = (1-\beta)R_n \mu_{s_2} Lv^{-1} \tag{8k}$$

where C_0 is input concentration [M L^{-3}]; and L is system length [L]. When n is unity, this model reduces to one presented by van Genuchten and Wagenet (1989). When there is no transformation, the model reduces to one presented by Brusseau et al. (1989).

The governing equations are solved with a Crank–Nicholson finite-difference numerical approach under the following initial and flux-type boundary conditions:

$$C^*(X,0) = S^*(X,0) = 0 \tag{9a}$$

$$C_0^* = C^* - \frac{1}{P}\frac{\partial C^*}{\partial X}\Big|_{x=0} \tag{9b}$$

$$\frac{\partial C^*(1,T)}{\partial X} = 0 \tag{9c}$$

The numerical performance of the model was verified by comparing simulations produced with the model to breakthrough curves generated with analytical solutions to simplified problems.

3. Results and discussion

3.1. The influence of nonlinear sorption on transport

The impact of nonlinear sorption on the transport of solute is illustrated in Fig. 1, where a breakthrough curve obtained for transport of solute undergoing nonlinear sorption is compared to that obtained for linear sorption. Note that the arrival wave of the breakthrough curve influenced by nonlinear sorption is sharper (less spread out) than the wave obtained when sorption is linear. Conversely, the elution wave of

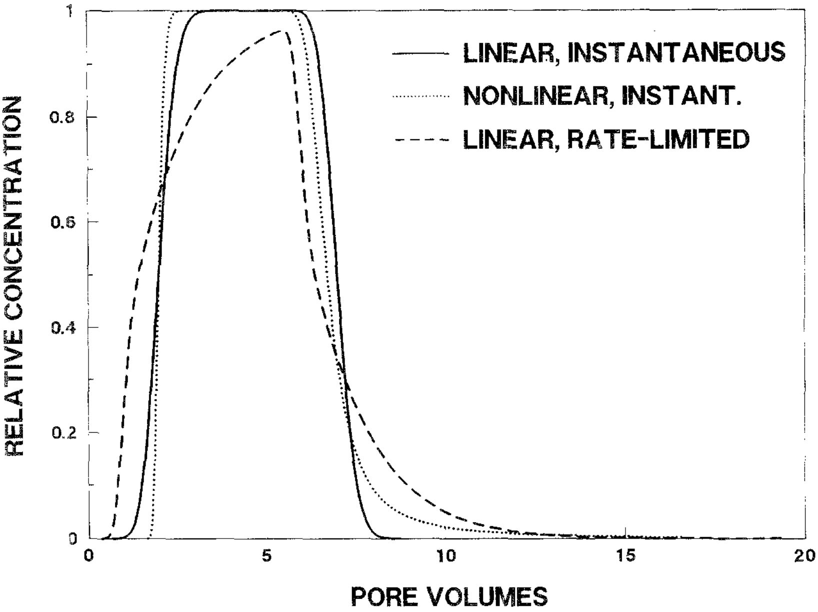


Fig. 1. Breakthrough curves for three cases: (1) linear, instantaneous sorption; (2) nonlinear, instantaneous sorption; and 3) linear, rate-limited sorption. Values used for all simulations: $P = 50$, $R = 2$, $\epsilon_\ell = \epsilon_{s_1} = \epsilon_{s_2} = 0$, $T_0 = 5$; values specific for each simulation: (1) $n = 1$, $\beta = 1$; (2) $n = 0.5$, $\beta = 1$; and (3) $n = 1$, $\beta = 0.5$, $\omega = 1$.

the breakthrough curve influenced by nonlinear sorption exhibits a significant amount of tailing, whereas that for the linear sorption case does not.

The impact of nonlinear sorption on the transport of contaminants undergoing transformation reactions is illustrated in Fig. 2. Inspection of Fig. 2 shows that there is a marked difference between the breakthrough curves obtained for nonlinearly and linearly sorbing solutes, just as there was for the case of no transformation. A major application of mathematical models is to use them to obtain values for transport parameters by solving the inverse problem. Incorrect values can be obtained when the model being used does not accurately represent the physical system. Since most coupled sorption–transformation models are based on linear sorption, it is important to investigate the impact of using such a model to analyze data influenced by nonlinear sorption. This was done by fitting a model based on linear sorption to breakthrough curves produced with the model that includes nonlinear sorption. The values for R and ϵ were optimized for each fitted breakthrough curve.

The values for R and ϵ obtained by optimization with the linear-sorption model are different from the true values for three of the four cases reported in Fig. 2. For example, $R = 18.8$ and $\epsilon = 1.2$ are obtained with the linear-sorption model for the $n = 0.5$ case. The true values for R and ϵ are 16.8 and 0.5, respectively. Conversely, the optimized values obtained with the linear-sorption model are identical to the true values for the $n = 0.95$ case (Fig. 2D). It is apparent that invalid estimates of

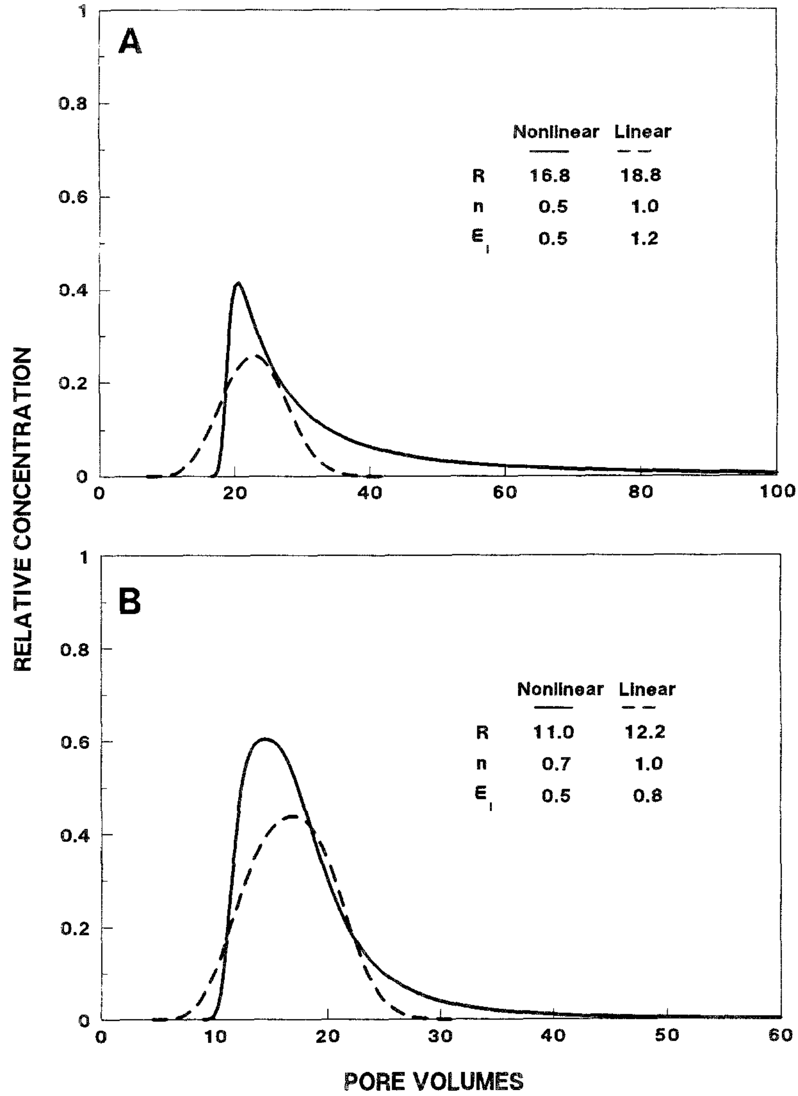


Fig. 2. Breakthrough curves simulated with transport models based on linear and nonlinear sorption, for different values of n. Values used for simulations: $P = 50$, $K_f = 1$, $\rho/\theta = 5$, $L/v = 10$, $\epsilon_l = 0.5$, $C_0 = 0.1$. For simplification, transformation is assumed to occur only in solution.

parameter values will be obtained if a linear-sorption model is used to analyze data influenced significantly by nonlinear sorption.

3.2. The influence of coupled transformation and nonlinear sorption on transport

For linearly sorbing solutes, advective transport is independent of the concentration of the solute in the aqueous phase. This is not the case, however, for transport

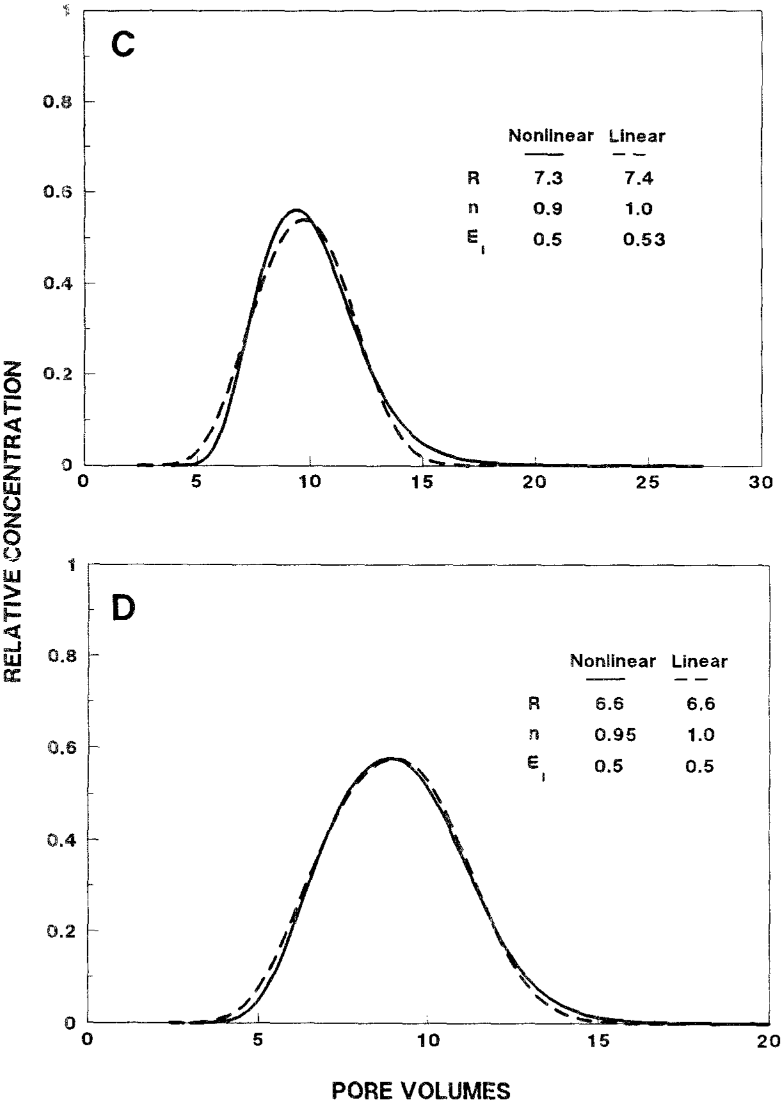
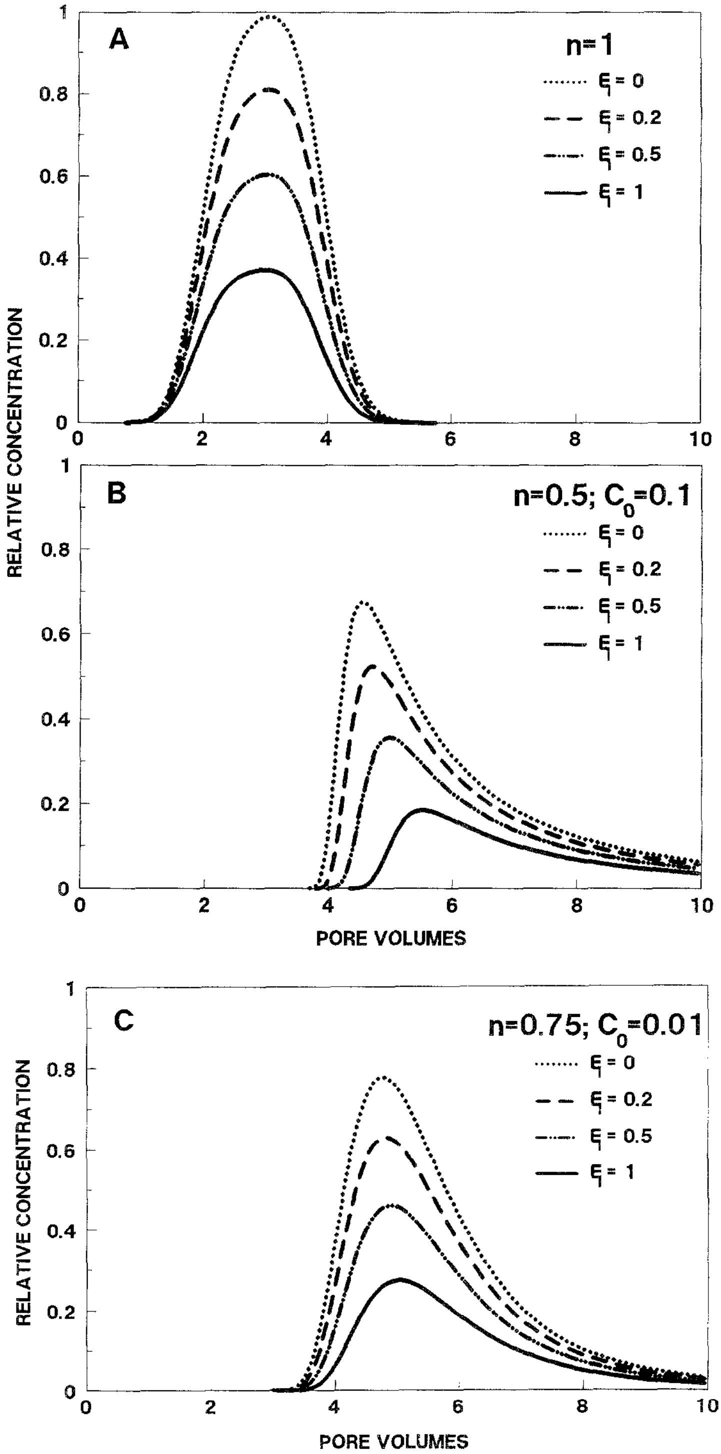


Fig 2. Continued.

of solutes that have nonlinear sorption. Any factor that modifies solute concentration might be expected to influence the transport of nonlinearly sorbing solutes because of the concentration dependency associated with nonlinear sorption. Since transformation reactions modify solute concentration, it is possible that transport is influenced by coupled nonlinear sorption and transformation.

The way in which transformation influences transport of sorbing solutes is clearly shown in Fig. 3, where breakthrough curves produced for different ϵ-values are reported. For the linear-sorption case, there is a slight delay of the breakthrough


A
n=1
ξ = 0
ξ = 0.2
ξ = 0.5
ξ = 1
B
n=0.5; C_0=0.1
ξ = 0
ξ = 0.2
ξ = 0.5
ξ = 1
C
n=0.75; C_0=0.01
ξ = 0
ξ = 0.2
ξ = 0.5
ξ = 1
RELATIVE CONCENTRATION
PORE VOLUMES
0
0.2
0.4
0.6
0.8
1
0
2
4
6
8
10

curve when transformation occurs (Fig. 3A). This results from the reduction in solute concentration caused by transformation (Angley et al., 1992). There is a much greater deviation between the transformation and no-transformation breakthrough curves for the nonlinear-sorption case (Fig. 3B and C). The additional delay is caused by the impact on transport of the coupled interactions between transformation and nonlinear sorption. The larger is the magnitude of transformation, the smaller is the aqueous-phase solute concentration. For a nonlinear isotherm, smaller concentrations result in larger sorption and retardation when n is < 1 (see Eq. 12). Thus, the concentration wave is delayed in comparison to the linear-sorption case.

An important consideration for systems influenced by transformation reactions is the location of the reactions. For example, available data suggest that in some cases biodegradation occurs primarily through the uptake of solution-phase substrate by sorbed and solution-phase bacteria (cf. Ogram et al., 1985; Robinson et al., 1990; Brusseau et al., 1992a). Thus, it is often assumed that biotransformation occurs only in the solution phase. In comparison, surface-catalyzed reactions occur primarily in the sorbed phase. Conversely, a transformation process such as radioactive decay occurs in both solution and sorbed phases. Given that the proportional distribution of solute between solution and sorbed phases is not constant for nonlinear sorption, it is important to consider the effect of the location of transformation on the transport of nonlinearly sorbing solute.

To evaluate the effect of transformation location, a set of four simulations is produced for each case (linear vs. nonlinear sorption). Each set consists of one simulation representing no transformation and three simulations representing three possible scenarios for the location of transformation. The first scenario represents a system wherein transformation occurs only in solution. For this scenario the nondimensional transformation parameters are set as follows: $\epsilon_\ell = 1$ and $\epsilon_{s_1} = 0$. Note that $\epsilon_{s_2} = 0$ for all simulations discussed in this section because sorption is considered to be instantaneous. The second scenario represents a system wherein transformation occurs at equal nondimensional rates in both solution and sorbed phases (i.e. $\epsilon_\ell = \epsilon_{s_1} = 0.5$). The third scenario represents systems wherein transformation occurs only in the sorbed phase (i.e. $\epsilon_\ell = 0$ and $\epsilon_{s_1} = 1$). The results of these simulations are shown in Fig. 4.

For the case of linear, instantaneous sorption, the proportional distribution of solute between the solution and sorbed phases is constant. Hence, the location of the transformation reaction has no effect on transport (see Fig. 4A). Conversely, the location of transformation does affect transport of nonlinearly sorbing solute (see Fig. 4B). This results from the fact that the proportional distribution between the solution and sorbed phases is not constant for sorption governed by nonlinear isotherms. Inspection of Fig. 4B reveals that breakthrough is delayed and the mass of solute transformed is greater when transformation takes place in the sorbed phase. When the Freundlich exponent (n) is < 1, as it is for these simulations, the pro-

Fig. 3. The effect of transformation on transport of: (A) linearly; and (B and C) nonlinearly sorbing solutes. Values used for simulations: $P = 50$, $K_f = 0.2$, $\rho/\theta = 5$, $L/v = 10$. For simplification, transformation is assumed to occur only in solution.

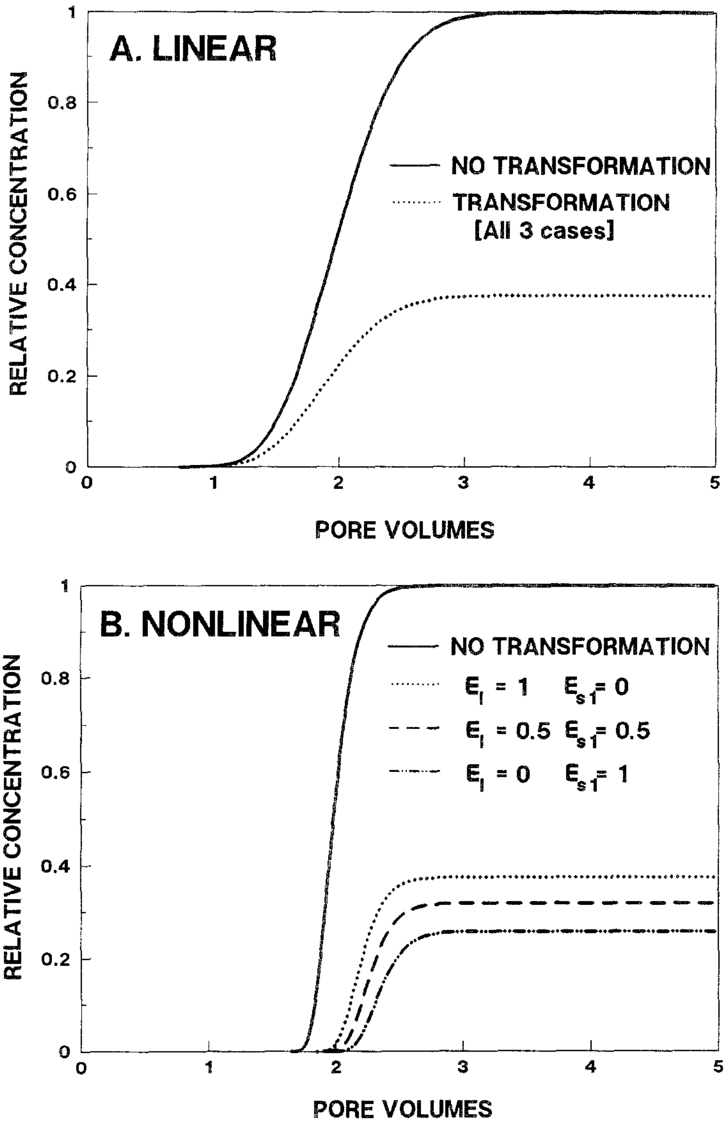


Fig. 4. Breakthrough curves illustrating the effect of transformation location on transport: (A) linear sorption; and (B) nonlinear sorption. Values used for all simulations: $P = 50$, $R = 2$; values specific for each simulation: (A) $n = 1$; and (B) $n = 0.5$.

portional distribution of solute favors the sorbed phase. In other words, the fraction of solute residing in the sorbed phase is proportionally greater for the nonlinear-sorption case than it is for the case of linear sorption. Hence for the case of nonlinear sorption, a larger mass of solute is transformed when the transformation reaction takes place in the sorbed phase than when it occurs in solution. As expected, the situation is reversed when n is > 1. In this case, the breakthrough is delayed and a larger mass of solute is transformed when the transformation occurs in solution (data not shown).

3.3. The impact of nonlinear sorption on the magnitude and rate of transformation

The fraction of contaminant mass that will be transformed or degraded during a transport event is an important factor in applications such as in situ remediation. For example, the larger the fraction of mass degraded in situ, the smaller is the mass of contaminant brought to the surface requiring treatment. The mass fraction of contaminant transformed during transport is mediated by the relative magnitudes of the characteristic time of transformation and the hydraulic residence time. This relationship is quantified by the Damköhler numbers for transformation (the ϵ terms). The effect of pore-water velocity on the magnitude of transformation occurring during transport is an example of this relationship. Angley et al. (1992) evaluated the influence of velocity on the biodegradation of gasoline constituents during their transport in an aquifer material and observed a greater magnitude of biodegradation at a smaller velocity.

The time required for the transformation or degradation of a specified fraction of contaminant mass to be completed (i.e. "maximum" transformation) is also an important factor, especially in remediation applications. The nondimensional time, which is equivalent to real time or number of pore volumes for a given pore-water velocity, required for maximum transformation to occur can be influenced by nonlinear sorption. For example, the tailing associated with the elution waves of nonlinearly sorbing solutes can negatively influence transformation when transformation occurs primarily in solution. As mentioned previously, it appears that biodegradation of many organic compounds takes place only in solution. Thus, the impact of nonlinear sorption on biodegradation may constrain the effectiveness of in situ bioremediation.

This possibility is examined by comparing the results obtained from two sets of simulations where each set consists of a range of Freundlich exponent values ($n = 1$, 0.75 and 0.5). The two sets differ by the value selected for the influent solute concentration ($C_0 = 0.1$ or 10). The results of the simulations are presented in Table 1, where the total percent of solute mass transformed and the nondimensional times required for 96% and maximum transformation to occur are reported.

For the $C_0 = 0.1$ case, the nondimensional time required for maximum transformation increases as the value for n decreases (i.e. as sorption becomes more nonlinear). In addition, the nondimensional time required to complete 96% of the maximum transformation increases as n decreases. This increase in nondimensional time is due to two factors: the increase in R_n as n decreases (see Eq. 8e and Table 1) and the tailing associated with the elution wave of nonlinearly sorbing solutes.

For the $C_0 = 10$ case, the nondimensional time required for maximum transformation increases as the value for n decreases. In contrast, the nondimensional time required to complete the majority (96%) of the maximum transformation decreases

Table 1
The impact of nonlinear sorption on transformation

	$C_0 = 0.1$			$C_0 = 10$		
	$n = 1$	$n = 0.75$	$n = 0.5$	$n = 1$	$n = 0.75$	$n = 0.5$
% transformed	62.5	62.5	62.4[a]	62.5	62.5	62.5
T_{96}	8.5	17.1	189	8.5	7.3	6.7
T_t	14	90	5000[a]	14	104	450
R_n	6.0	9.9	16.8	6.0	3.8	2.6

T_{96} is the nondimensional time required to complete 96% of maximum transformation. T_t is the nondimensional time required to complete maximum transformation. In this example, maximum transformation is 62.5% (i.e. 62.5% of the total mass was transformed and 37.5% was eluted). Values used for simulations: $P = 50$, $K_f = 1$, $\rho/\theta = 5$, $L/v = 10$, $\epsilon_f = 1$.

[a] Transformation not complete.

as n decreases. This latter effect results from the decrease in R_n associated with a decreasing n (see Eq. 8e and Table 1). The significant effect of elution tailing on transformation is exemplified by comparing the nondimensional times required for completion of maximum transformation for the $C_0 = 10$ case. For $n = 0.5$, the nondimensional time required is 450, which is > 30 times as large as that required for the linear case. This is despite the fact that R_n is smaller for the $n = 0.5$ case.

It is clear from the preceding analyses that whereas the total fraction of contaminant mass transformed is independent of nonlinear-sorption effects, the time required for this fraction to be transformed is not. This phenomena has implications for several aspects of contaminant transport. For example, the time and pore volumes required to remediate an aquifer by in situ bioremediation may be significantly greater when sorption is nonlinear than when it is linear. It must be remembered, however, that these results apply to the case where transformation occurs only in solution.

3.4. *Linear, rate-limited sorption vs. nonlinear, instantaneous sorption*

To focus directly on the effects of nonlinear sorption, rate-limited sorption was excluded from the analyses reported above. However, it is known that the sorption of many contaminants of interest is rate-limited. The influence of rate-limited sorption on transformation during transport has been discussed by a few authors (Gamerdinger et al., 1991; Angley et al., 1992; Brusseau et al., 1992a, b; Estrella et al., 1993). When transformation occurs primarily in solution, rate-limited sorption/desorption can reduce the rate at which mass is transformed thereby requiring greater time and pore volumes to reach maximum transformation. The effects of rate-limited sorption are identical to those discussed above for the case of nonlinear, instantaneous sorption.

The fact that similar results can be produced by two different processes suggests that it may not always be possible to identify the controlling process by examination of transport data alone. This is illustrated in Fig. 5, where a breakthrough curve for

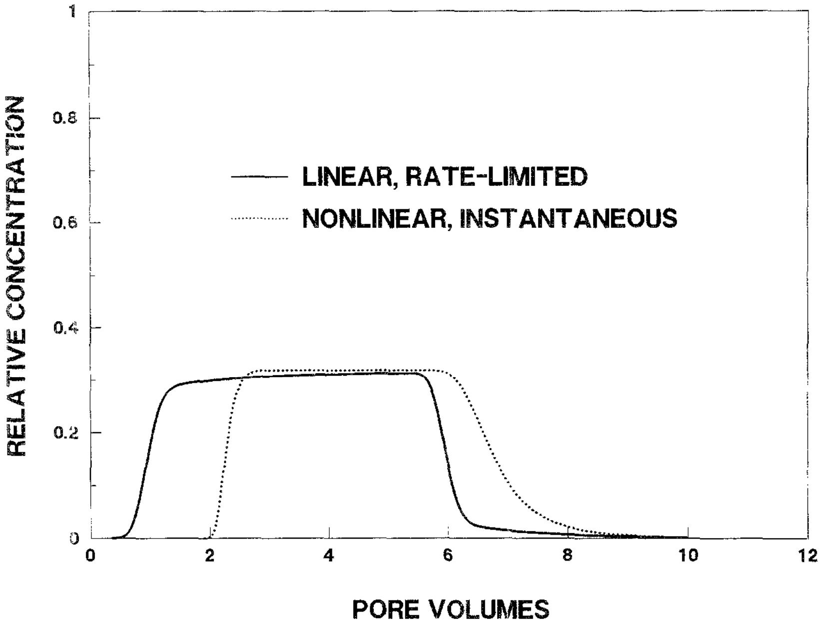


Fig. 5. Comparison of transport influenced by: (1) linear, rate-limited sorption; and (2) nonlinear, instantaneous sorption. Values used for all simulations: $P = 50$, $R = 2$, $T_0 = 5$; values specific for each simulation: (1) $n = 1$, $\beta = 0.5$, $\omega = 0.3$, $\epsilon_\ell = \epsilon_{s_1} = \epsilon_{s_2} = 0.5$; and (2) $n = 0.5$, $\beta = 1$, $\epsilon_\ell = \epsilon_{s_1} = 0.5$, $\epsilon_{s_2} = 0$.

solute influenced by linear, rate-limited sorption is compared to one influenced by nonlinear, instantaneous sorption. Inspection reveals that both curves exhibit sharp arrival waves, tailing elution waves, and plateau regions where the effluent concentration is constant. The only significant difference between the two curves is that the curve for rate-limited sorption exhibits earlier arrival. However, this difference can not be used as a demarkation criterion without an external frame of reference (i.e. independent measure of sorption).

Breakthrough curves for nonlinear, instantaneous sorption and for linear, rate-limited sorption are compared in Fig. 1 for the case of no transformation. In this case, the differences between the two curves are clear. The curve influenced by rate-limited sorption is self-similar in that it exhibits tailing for both the arrival and elution waves (asymptotic approach to $C/C_0 = 1$ and $C/C_0 = 0$, respectively). Conversely, the curve influenced by nonlinear sorption exhibits tailing only for the elution wave. Thus, the problem of differentiating between the two curves reported in Fig. 5 is directly caused by the action of transformation.

4. Conclusions

A mathematical model that describes the transport of solute undergoing nonlinear, rate-limited sorption and first-order transformation was used to investigate the effect of coupled transformation and nonlinear sorption on contaminant transport. Results of the analyses showed that a model based on linear sorption cannot provide an accurate simulation of the transformation and transport of nonlinearly sorbing solutes when n is less than ~ 0.9. In addition, the relative impact of nonlinear sorption on solute transport is mediated by the magnitude of transformation. The nondimensional time required for a specified fraction of solute mass to be transformation during transport is influenced by nonlinear sorption. When transformation occurs primarily in solution (as may be the case for biodegradation), the time and pore volumes required to reach maximum transformation can be much greater when sorption is nonlinear. Thus, nonlinear sorption can constrain the effectiveness of in situ bioremediation. This is also true for rate-limited sorption. These examples illustrate the intriguing effects that coupled processes can have on contaminant transport and which may be important for many contaminants of interest. They also support further consideration of nonlinear sorption in the development of mathematical models designed to simulate contaminant transport.

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