

The effect of local-scale physical heterogeneity and nonlinear, rate-limited sorption/desorption on contaminant transport in porous media

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Abstract

Nonideal transport of contaminants in porous media has often been observed in laboratory characterization studies. It has long been recognized that multiple processes associated with both physical and chemical factors can contribute to this nonideal transport behavior. To fully understand system behavior, it is important to determine the relative contributions of these multiple factors when conducting contaminant transport and fate studies. In this study, the relative contribution of physical-heterogeneity-related processes versus those of nonlinear, rate-limited sorption/desorption to the observed nonideal transport of trichloroethene in an undisturbed aquifer core was determined through a series of miscible-displacement experiments. The results of experiments conducted using the undisturbed core, collected from a Superfund site in Tucson, AZ, were compared to those obtained from experiments conducted using the same aquifer material packed homogeneously. The results indicate that both physical and chemical factors, specifically preferential flow and associated rate-limited diffusive mass-transfer and rate-limited sorption/desorption, respectively, contributed to the nonideal behavior observed for trichloroethene transport in the undisturbed core. A successful prediction of trichloroethene transport in the undisturbed core was made employing a mathematical model incorporating multiple sources of nonideal transport, using independently determined model parameters to account for the multiple factors contributing to the nonideal transport behavior. The simulation results indicate that local-scale physical heterogeneity controlled the nonideal transport

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behavior of trichloroethene in the undisturbed core, and that nonlinear, rate-limited sorption/desorption were of secondary importance.

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1. Introduction

Knowledge of contaminant interactions with subsurface porous material is crucial to accurately predict contaminant transport and fate. A natural porous medium can be described as having multiple retention domains, including soil-particle surfaces, inorganic coatings (e.g., metal oxides), microporosity associated with individual particles or aggregates of particles, and organic material. Sorption/desorption of organic contaminants, which can be influenced by all of these domains, has been shown to often be rate-limited and/or nonlinear (e.g., Karickhoff, 1984; Wu and Gschwend, 1986; Brusseau and Rao, 1989; Pignatello, 1990; Ball and Roberts, 1991; Brusseau et al., 1991a,b; Grathwohl and Reinhard, 1993; Pignatello and Xing, 1996). Nonideal transport behavior is often observed for such cases. Additionally, numerous miscible-displacement experiments have shown that local-scale physical heterogeneity of a porous medium (e.g., aggregation, stratification, and/or fracturing) can also result in nonideal transport behavior (e.g., Passioura, 1971; Passioura and Rose, 1971; Bouma and Anderson, 1977; van Genuchten and Wierenga, 1977; Rao et al., 1980; Nkedi-Kizza et al., 1982; Seyfried and Rao, 1987; Herr et al., 1989; Singh and Kanwar, 1991; Wildenschild et al., 1994; Reedy et al., 1996). Thus, it is reasonable to expect that nonideal transport behavior of organic contaminants may be associated with multiple physical and chemical factors, as shown by the results of several experiments (Brusseau et al., 1989a; Brusseau and Rao, 1990; Zurmühl et al., 1991; Brusseau, 1992; Bourg et al., 1993; Gaber et al., 1995). Accurate understanding of contaminant transport behavior would require knowledge of the relative contributions of these various factors.

The typical approach to laboratory characterization of contaminant transport behavior employs bulk samples of porous media collected from the field site. Laboratory studies usually involve the homogenization (i.e., mixing) of these bulk samples, followed by sieving to exclude the larger particles. These processed subsamples are then uniformly packed into columns for miscible-displacement experiments. It is common to employ parameters obtained from these laboratory experiments for field-scale transport and fate studies. Clearly, the typical homogenization approach is unable to capture the effect of local-scale porous-media structure on transport behavior.

One approach to investigate the transport behavior of contaminants in porous media that maintains the natural structure of the system is to collect and employ intact cores for miscible-displacement experiments. Many researchers have investigated transport of contaminants in such undisturbed systems. However, a review of the literature reveals that these experiments have been conducted primarily with cores collected from agricultural fields (Cassel et al., 1974; McMahon and Thomas, 1974; Anderson and Bouma,

1977; Tyler and Thomas, 1981; Smith et al., 1985; Seyfried and Rao, 1987; Zurmühl et al., 1991; Tindall et al., 1992; Wildenschild et al., 1994; Gaber et al., 1995; Starrett et al., 1996; Camobreco et al., 1996; Reedy et al., 1996; Cote et al., 1999). Conversely, few researchers have investigated the transport behavior of contaminants in undisturbed cores of aquifer material (Ptacek and Gillham, 1992; Bourg et al., 1993; Carmichael et al., 1999; Setarge et al., 1999). Furthermore, few of these transport studies include comparisons of results obtained for the undisturbed systems to those obtained for homogeneously packed systems comprised of the same porous media (Cassel et al., 1974; McMahon and Thomas, 1974; Smith et al., 1985; Starrett et al., 1996; Camobreco et al., 1996).

The objective of this study was to investigate the transport behavior of organic contaminants in an undisturbed core collected from a contaminated aquifer at a Superfund site in Tucson, AZ. The specific focus of this study was the relative contributions of physical-heterogeneity-related processes versus those of rate-limited and/or nonlinear sorption/desorption to the observed nonideal transport behavior. The investigation involved a series of miscible-displacement experiments conducted for the undisturbed core. Upon completion of these studies, the material was homogenized (i.e., well mixed) and the experiments were repeated. The contaminant transport behavior for the undisturbed system was compared to that for the homogeneously packed system, and the results were analyzed using a model that explicitly accounts for multiple sources of nonideal transport.

2. Materials and methods

2.1. Materials

Trichloroethene was chosen as the model contaminant as it is present at the field site and is one of the most ubiquitous groundwater contaminants. Pentafluorobenzoic acid (PFBA) was used as a nonreactive tracer to characterize the contribution of physical-related factors to solute transport. Additional nonreactive tracer experiments were conducted using fluorescein, bromide, and tritiated water. Trichloroethene (99.5+% purity), pentafluorobenzoic acid (99%), fluorescein (sodium salt), and bromide (calcium salt) were obtained from Aldrich Chemical. Tritiated water was purchased from DuPont.

Aquifer material was obtained from soil cores, 1.5 m long and 13 cm diameter, collected during well installation at a Superfund site in Tucson, AZ. Trichloroethene concentrations range from approximately 0.1 to 100 mg/l in the source zones at the site. To obtain undisturbed samples of the aquifer material, a portion of the core's sleeve was cut away and a Plexiglas column was gently forced into the exposed aquifer material. The column was inserted normal to the vertical axis of the core, thereby maintaining the same direction of flow in relation to structure orientation as that existing in the field. Analysis of subsamples of the aquifer material collected from the core yielded nondetectable trichloroethene concentrations ($<0.03 \mu\text{g g}^{-1}$).

Total carbon, organic carbon, and particle-size distribution were determined for subsamples of the aquifer material. Average gravel, sand, silt, and clay fractions are 0.1% (approximately), 89.4% ($\pm 0.6\%$), 4.1% ($\pm 0.6\%$), and 6.4% ($\pm 1.0\%$), respec-

tively. The average total and organic carbon are 0.06% ($\pm 0.01\%$) and 0.03% ($\pm 0.009\%$), respectively. A synthetic groundwater solution was used in all of the miscible-displacement experiments. This solution was created based on the identification and quantification of major ionic species in groundwater collected from the field site. The major cations in this synthetic groundwater (and average concentration, mg l^{-1}) were Na^+ (50), Ca^{2+} (36), Mg^{2+} (25), and major anions were NO_3^- (6), Cl^- (60), $\text{CO}_3^{2-}/\text{HCO}_3^-$ (133), and SO_4^{2-} (99).

2.2. Miscible-displacement experiments

Miscible-displacement experiments were conducted using Plexiglas columns, 7.6 cm in length and 5.7 cm in diameter. Preliminary experiments indicated negligible retention of trichloroethene by the apparatus. A series of experiments were conducted for the undisturbed core with aqueous solutions containing one of several nonreactive tracers or trichloroethene. The majority of these experiments were conducted in duplicate. Following these experiments, the column was opened and unpacked, the media was mixed (homogenizing the material), and re-packed into the same cleaned Plexiglas column. Similar miscible-displacement experiments were then conducted in this homogeneously packed system using a tracer and trichloroethene. Additionally, miscible-displacement experiments were conducted using a 15-cm-long, 2.1-cm-diameter glass chromatography column (Kontes) with homogeneously packed aquifer material to investigate the potential impact of the column apparatus on observed transport behavior and reproducibility of transport behavior in the system.

Most of the experiments were conducted using an average input trichloroethene concentration (C_0) of approximately 70 mg l^{-1} . Additional experiments were conducted in a homogeneously packed column to characterize nonlinear sorption/desorption of trichloroethene by the aquifer material using input concentrations equal to approximately 1, 9, 100, and 1000 mg l^{-1} . Pentafluorobenzoic acid (approximately 100 mg l^{-1}) was used as a nonreactive tracer for both the undisturbed and the homogeneously packed systems. Fluorescein, bromide, and tritiated water were used as additional tracers for the undisturbed system. The average input concentration for these tracers equaled 1 mg l^{-1} , 300 mg l^{-1} , and 2 nCi ml^{-1} , respectively. The bulk density and saturated water content equaled 1.64 g cm^{-3} and 0.40, respectively, for the undisturbed column and equaled 1.71 g cm^{-3} and 0.39, respectively, for the homogeneously packed columns.

For column experiments conducted using the undisturbed core, constant flow at one of two volumetric flow rates, 2.3 and 0.23 ml min^{-1} , equivalent to average pore-water velocities (v) of approximately 13 cm h^{-1} and 1.3 cm h^{-1} , was provided to the horizontally positioned columns by an Acuflo Series II LC pump. For column experiments conducted for the homogeneously packed columns, one of four average pore-water velocities, 13, 19, 25, and 30 cm h^{-1} , was used. Prior to each experiment, water was flushed through the apparatus (bypassing the column) and analyzed to ensure no trichloroethene or tracer was detected. A pulse of the solution, containing either a tracer or trichloroethene, was then injected into the column. Once the pulse was injected, the column was flushed with synthetic groundwater. Effluent samples for the trichloroethene experiments were collected manually using a glass gas-tight syringe to minimize

volatilization. Effluent samples for the tracer experiments were collected using an automated fraction collector.

To determine the potential contribution of diffusive mass-transfer to transport in the undisturbed system, a series of miscible-displacement experiments were conducted using several nonreactive tracers with different aqueous diffusion coefficients. Specifically, bromide, pentafluorobenzoic acid (PFBA), fluorescein, and tritiated water were employed with aqueous diffusion coefficients ($\text{cm}^2 \text{h}^{-1}$) equal to 0.0750 (Cussler, 1984), 0.03 (Hu and Brusseau, 1995), 0.02 (estimated by use of Hayduk and Laudie approach (Tucker and Nelken, 1982)), and 0.0805 (Mills, 1973), respectively. This approach is based on the premise that solutes with different diffusion coefficients will exhibit different degrees of nonideal behavior when diffusion-mediated mass-transfer processes affect transport (Brusseau, 1993). Additional investigation of diffusive mass-transfer and the potential existence of low-flow/no-flow domains for the undisturbed core was accomplished using the flow-interruption method (Brusseau et al., 1989b). Prior to dismantling the undisturbed core, a dye tracer experiment was conducted to characterize flow conditions in the undisturbed system.

2.3. Analytical methods

Trichloroethene was analyzed using one of two methods, either by headspace gas chromatography equipped with a flame ionization detector (FID) or by flow-through variable wavelength UV (Gilson, Model 115). The quantifiable detection limit for trichloroethene using headspace GC/FID equaled 0.1 mg l^{-1} and using flow-through UV equaled 0.6 mg l^{-1} . Pentafluorobenzoic acid was analyzed by spectrophotometry (Hitachi U-2000), with a lower detection limit equal to approximately 1 mg l^{-1} . Fluorescein was analyzed by fluorescence spectrophotometry (Hitachi F-2000), with a detection limit equal to $10 \mu\text{g l}^{-1}$. Bromide was analyzed using an ion-specific electrode with a detection limit equal to approximately 3 mg l^{-1} . The activities for tritiated water were analyzed by radioassay using liquid scintillation counting (Packard Tri-Carb Liquid Scintillation Analyzer, Model 1600TR).

2.4. Data analysis

The results of miscible-displacement experiments conducted in the homogeneously packed system were analyzed using the nonlinear, least-squared, optimization program CFITIM3 (van Genuchten, 1981), employing either the standard advection–dispersion equation (for the nonreactive tracers) or the two-domain-based transport equations (for trichloroethene). The two-domain model (e.g., Coats and Smith, 1964) simulates nonideal transport associated with either physical heterogeneity (e.g., mobile/immobile domains) or chemical heterogeneity (e.g., rate-limited sorption/desorption). The nondimensional forms of the two versions of the models are identical, with nondimensional parameters β and ω representing the partitioning of the porous media into equilibrium and nonequilibrium domains and a nondimensional rate coefficient, respectively. For the results of the trichloroethene experiments conducted for the homogeneously packed systems, nonideal transport may result at least in part from rate-limited sorption/desorption. In addition, these

data were analyzed using a mathematical model (NLNE) that accounts for both nonlinear and rate-limited sorption/desorption (Hu and Brusseau, 1998). Both of the models, the NLNE and the two-site, involved optimizing for three parameters: the Peclet number (P), β (the fraction of instantaneous retardation), and ω (the ratio of hydrodynamic residence time to characteristic time of sorption). The retardation factor, R , for trichloroethene was determined by standard moment analysis of the breakthrough curves.

For the undisturbed system, the nonreactive tracer results, assumed to exhibit non-ideality due to physical-heterogeneity-related processes, were also analyzed using CFI-TIM3, optimizing for three parameters: the Peclet number (P), β (in this case, representing the fraction of retention occurring in the mobile domain), and ω (in this case, related to the mass-transfer coefficient for solute exchange between mobile/immobile regions). Finally, using these independently determined model parameters describing both the physical-heterogeneity-related and the rate-limited sorption/desorption processes in the undisturbed system, the transport of trichloroethene in the undisturbed core was predicted using the multiprocess nonideality (MPNE) model presented by Brusseau et al. (1989a). A brief description of the two-domain and MPNE models is presented below.

2.4.1. Physical-heterogeneity-related processes

The “two-domain” nonideal transport model describing advective/dispersive transport and rate-limited mass-transfer in a porous medium comprised of “mobile” and “immobile” domains is defined by the following two equations:

$$\beta R \frac{\partial C_m^*}{\partial T} + (1 - \beta) R \frac{\partial C_{im}^*}{\partial T} = \frac{1}{P} \frac{\partial^2 C_m^*}{\partial X^2} - \frac{\partial C_m^*}{\partial X} \quad (1)$$

$$(1 - \beta) R \frac{\partial C_{im}^*}{\partial T} = \omega (C_m - C_{im}) \quad (2)$$

where C_m^* and C_{im}^* are the solute concentrations in the mobile and immobile domains, respectively, normalized by the input concentration (C_o). The remaining dimensionless parameters are defined as:

$$\beta = \frac{\theta_m + f\rho K_D}{\theta + \rho K_D}$$

$$\omega = \frac{\alpha L}{v\theta}$$

$$R = 1 + \frac{\rho K_D}{\theta}$$

$$T = \frac{tv}{L}$$

$$P = \frac{v_m L}{D}$$

where θ_m is the volumetric water content of the mobile domain, f is the fraction of sorbent associated with the mobile domain, D is the longitudinal dispersion coefficient, v_m is the

average pore-water velocity in the mobile domain, θ_m is the water content in the mobile domain, θ is the saturated water content, P is the Peclet number, ρ is the solid-phase bulk density, L is length, t is time, K_D is the equilibrium sorption coefficient, R is the retardation factor, and α is the first-order mass-transfer coefficient. In this model, sorption is assumed to be instantaneous and nonideal transport conditions are a result of preferential flow and rate-limited solute transfer between mobile and immobile regions in the porous medium. It is recognized that this conceptualization of the system as comprising advective and non-advective domains is a simplification, and may not accurately represent actual flow conditions in the undisturbed core. The applicability of employing this model to describe the undisturbed system will be evaluated upon application to the nonreactive tracer data.

2.4.2. Chemical-heterogeneity-related processes

The “two-site” model describing transport of a solute undergoing rate-limited sorption/desorption is represented by the following two nondimensional equations:

$$\beta R \frac{\partial C^*}{\partial T} + (1 - \beta) R \frac{\partial S^*}{\partial T} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (3)$$

$$(1 - \beta) R \frac{\partial S^*}{\partial T} = \omega (C^* - S^*) \quad (4)$$

where C^* is the normalized concentration of solute in the aqueous phase and the remaining parameters are defined as:

$$S^* = \frac{S_2}{(1 - F)K_D C_o}$$

$$\omega = k_2(1 - \beta)R \frac{L}{v}$$

$$\beta = \frac{1 + F(R - 1)}{R}$$

where S_2 is the sorbed-phase concentration in the rate-limited domain, F is the fraction of sorbent for which sorption is instantaneous, and k_2 is the desorption rate coefficient.

2.4.3. Multiprocess nonideality

The multiprocess nonideality (MPNE) model accounts for multiple sources of non-ideality such as the presence of both physical-heterogeneity-related and chemical-heterogeneity-related processes. The governing equations for the model are as follows:

$$R_{m1} \frac{\partial C_m^*}{\partial T} + k_m^0 (C_m^* - S_m^*) + \omega (C_m^* - C_{im}^*) = \frac{1}{P} \frac{\partial^2 C_m^*}{\partial X^2} - \frac{\partial C_m^*}{\partial X} \quad (5)$$

$$R_{m2} \frac{\partial S_m^*}{\partial T} = k_m^0 (C_m^* - S_m^*) \quad (6)$$

$$R_{im1} \frac{\partial C_{im}^*}{\partial T} + k_{im}^0 (C_{im}^* - S_{im}^*) = \omega (C_m^* - C_{im}^*) \quad (7)$$

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

The dimensionless parameters employed in the model are defined as follows:

$$R = R_{m1} + R_{m2} + R_{im1} + R_{im2} = 1 + \frac{\rho K_D}{\theta}$$

$$\beta_1 = \frac{\phi + f\left(\frac{\rho}{\theta}\right)F_m K_m}{R} = \frac{R_{m1}}{R}$$

$$\beta_2 = \frac{f\left(\frac{\rho}{\theta}\right)(1 - F_m)K_m}{R} = \frac{R_{m2}}{R}$$

$$\beta_3 = \frac{(1 - \phi) + (1 - f)\left(\frac{\rho}{\theta}\right)F_{im} K_{im}}{R} = \frac{R_{im1}}{R}$$

$$\beta_4 = \frac{(1 - f)\left(\frac{\rho}{\theta}\right)(1 - F_{im})K_{im}}{R} = \frac{R_{im2}}{R}$$

$$k_m^0 = k_{m2} \left(\frac{L}{v} \right) \beta_2 R$$

$$k_{im}^0 = k_{im2} \left(\frac{L}{v} \right) \beta_4 R$$

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

$$S_{im}^* = \frac{S_{im2}}{(1 - F_{im})K_{im} C_o}$$

where $\phi = \theta_m/\theta$, f is defined as the mass fraction of sorbent associated with the mobile domain, and k_{m2} and k_{im2} are the first-order desorption rate coefficients for the mobile and immobile domains, respectively, and all other parameters are as described previously.

3. Results

3.1. Transport in the homogeneously packed systems

The breakthrough curves for transport of PFBA obtained from experiments conducted using homogeneously packed columns are essentially symmetrical (see Fig. 1), indicating ideal transport behavior. This suggests physical-heterogeneity-related nonideality is not a factor in this system. In contrast, the trichloroethene breakthrough curves obtained from the homogeneously packed columns exhibit a moderate amount of tailing, as illustrated in Fig. 1. Considering that the breakthrough curves obtained for PFBA are symmetrical, these results indicate rate-limited sorption/desorption may influence trichloroethene transport in this aquifer material. Similar results were obtained for trichloroethene versus PFBA for the glass column (results not shown).

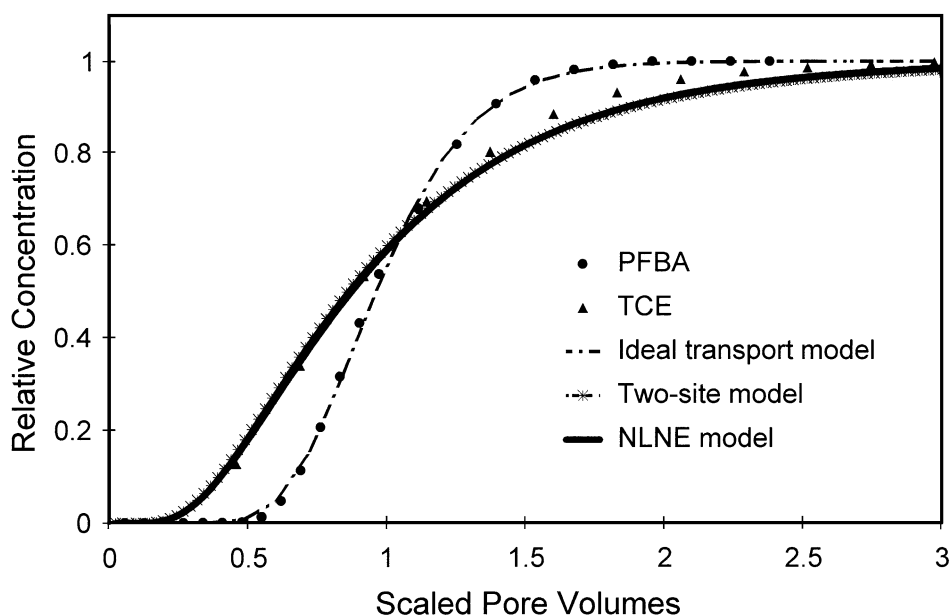


Fig. 1. Measured and simulated breakthrough curves for pentafluorobenzoic acid (PFBA) and trichloroethene transport in the homogeneously packed system. Experiments conducted at an average pore-water velocity equal to 13 cm h^{-1} . The standard advective–dispersive transport equation is used to simulate PFBA, whereas two models, one accounting for nonlinear, rate-limited sorption/desorption and the other for linear, rate-limited sorption/desorption, were used for trichloroethene. The abscissa has been scaled by the retardation factor, which allows for direct comparison of the transport behavior observed for the two compounds.

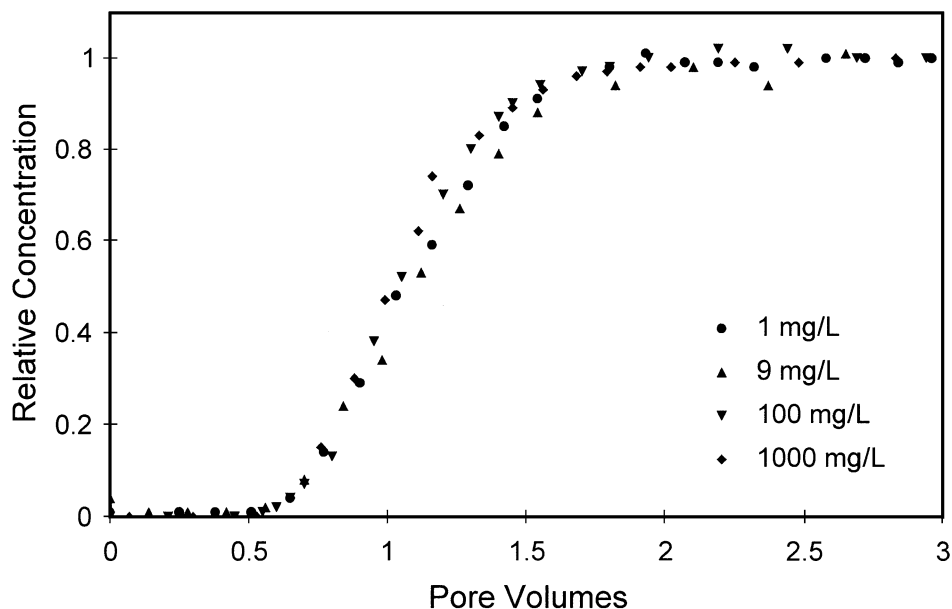


Fig. 2. Measured trichloroethene breakthrough curves obtained from miscible-displacement experiments conducted with various input concentrations in a homogeneously packed column (average pore-water velocity equaled 25 cm h^{-1}).

The results of several experiments (Fig. 2) indicate the overall trichloroethene transport behavior, including early breakthrough and tailing, was reproducible. In addition, there appears to be a slight impact of the input concentration on transport, indicating the existence of nonlinear sorption/desorption. Specifically, the magnitude of the retardation factor is slightly smaller for the higher input trichloroethene concentrations, wherein the retardation factors equal 1.2 and 1.07 for the lowest and highest input concentrations, respectively. The small retardation factors are expected for trichloroethene transport in low organic-carbon aquifer material such as used herein. The data were fit with the Freundlich nonlinear sorption isotherm ($r^2 = 0.93$) with a resultant Freundlich-sorption coefficient (K_F) equal to $0.05 \text{ mg}^{0.17} \text{ l}^{0.83} \text{ kg}^{-1}$ and Freundlich exponent equal to 0.83. Trichloroethene breakthrough curves obtained from homogeneously packed miscible-displacement experiments conducted in the glass column are nearly identical to those obtained from the Plexiglas column, indicating the transport behavior of trichloroethene was reproducible independent of the column employed.

3.2. Transport in the undisturbed core

Representative results of experiments conducted with pentafluorobenzoic acid (PFBA) in the undisturbed and the homogeneously packed systems are compared in Fig. 3. The breakthrough curves for the homogeneously packed system are symmetrical, as noted above. In contrast, the breakthrough curves for the undisturbed system are asymmetrical,

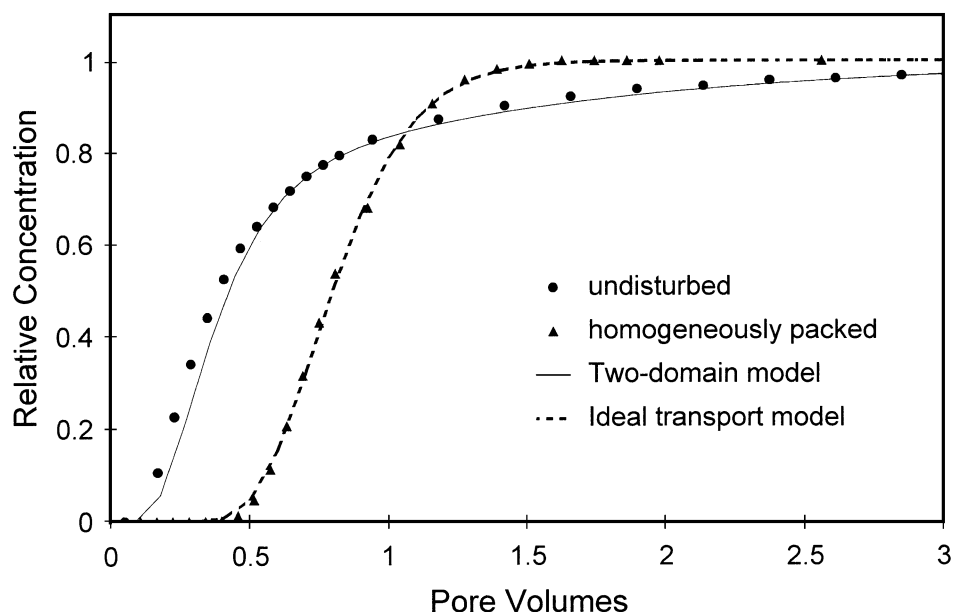


Fig. 3. Representative PFBA breakthrough curves for the undisturbed versus homogeneously packed systems including simulation results obtained using the two-domain versus the ideal transport models, respectively. Experiments conducted at an average pore-water velocity equal to 13 cm h^{-1} .

with earlier breakthrough and significantly greater tailing. The transport behavior of the tracer observed in the undisturbed system suggests the presence of nonideality associated with physical heterogeneity of the aquifer material.

A representative trichloroethene breakthrough curve obtained from miscible-displacement experiments conducted for the undisturbed system is shown in Fig. 4A. The breakthrough curve shows nonideal transport behavior as indicated by the asymmetrical shape of the curve, which exhibits early breakthrough and tailing for both the arrival and elution waves. Elution curves for trichloroethene from several experiments conducted at one of two average pore-water velocities, varying by an order of magnitude, are included in Fig. 4B. These results indicate the effect of flow velocity on the transport behavior of trichloroethene was not measurable in the range of pore-water velocities tested and that reproducibility was achieved in the undisturbed system.

Comparisons of representative arrival and elution waves obtained for trichloroethene in the undisturbed system versus those obtained for the same aquifer material packed homogeneously are shown in Fig. 5A and B, respectively. Trichloroethene transport in the undisturbed system exhibits greater nonideal behavior than that in the homogeneously packed system, with earlier breakthrough and significantly greater elution tailing. Sample concentrations in the column effluent reached C/C_0 of 0.01 after approximately three pore volumes of flushing in the homogeneously packed system versus greater than seven pore volumes in the undisturbed system. These results indicate that other factors in addition to

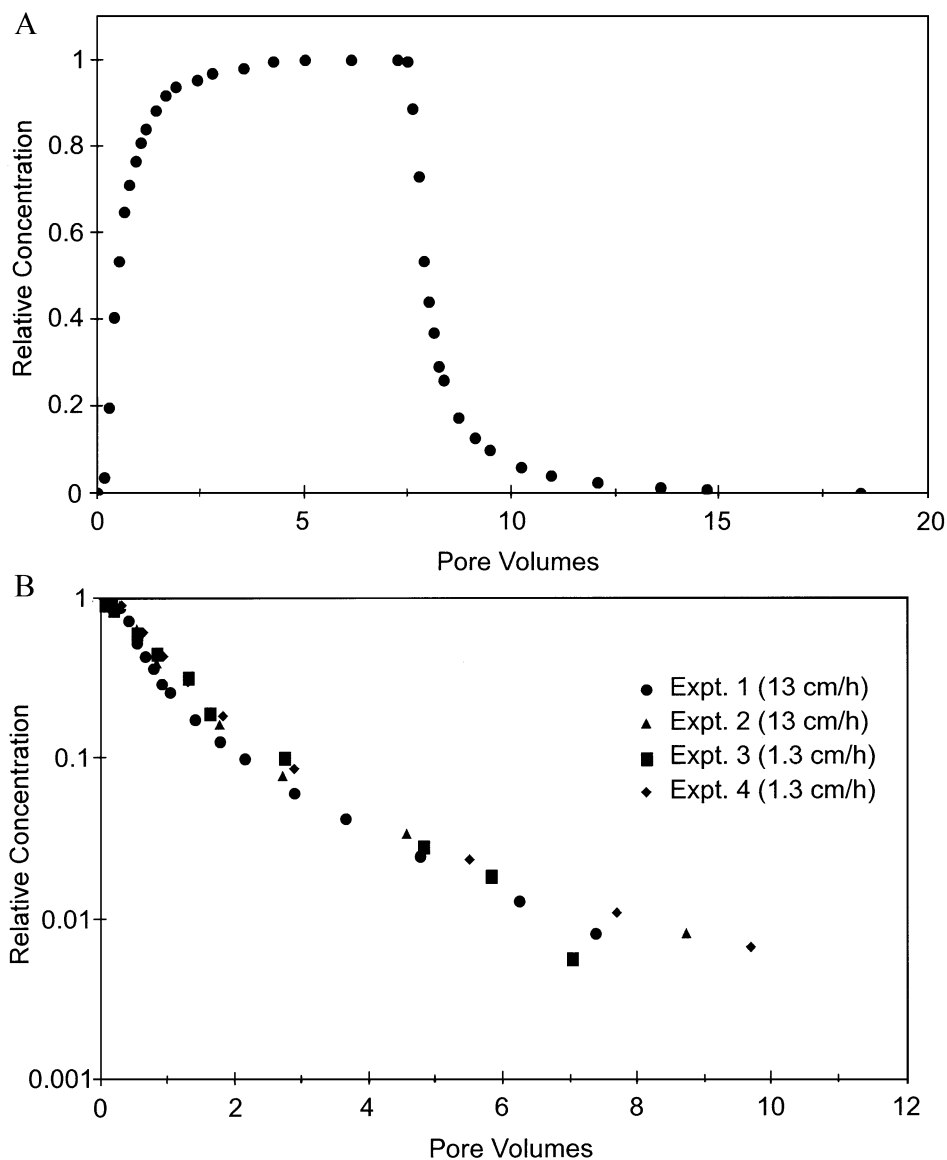


Fig. 4. Transport of trichloroethene in the undisturbed core: (A) representative full breakthrough curve (experiment conducted at 13 cm h^{-1}); (B) elution waves from several experiments conducted at one of two average pore-water velocities.

nonlinear and rate-limited sorption/desorption contribute to the nonideal transport behavior of trichloroethene in the undisturbed system.

The results of miscible-displacement experiments conducted with trichloroethene for the homogeneously packed system clearly indicate nonideal transport behavior due to

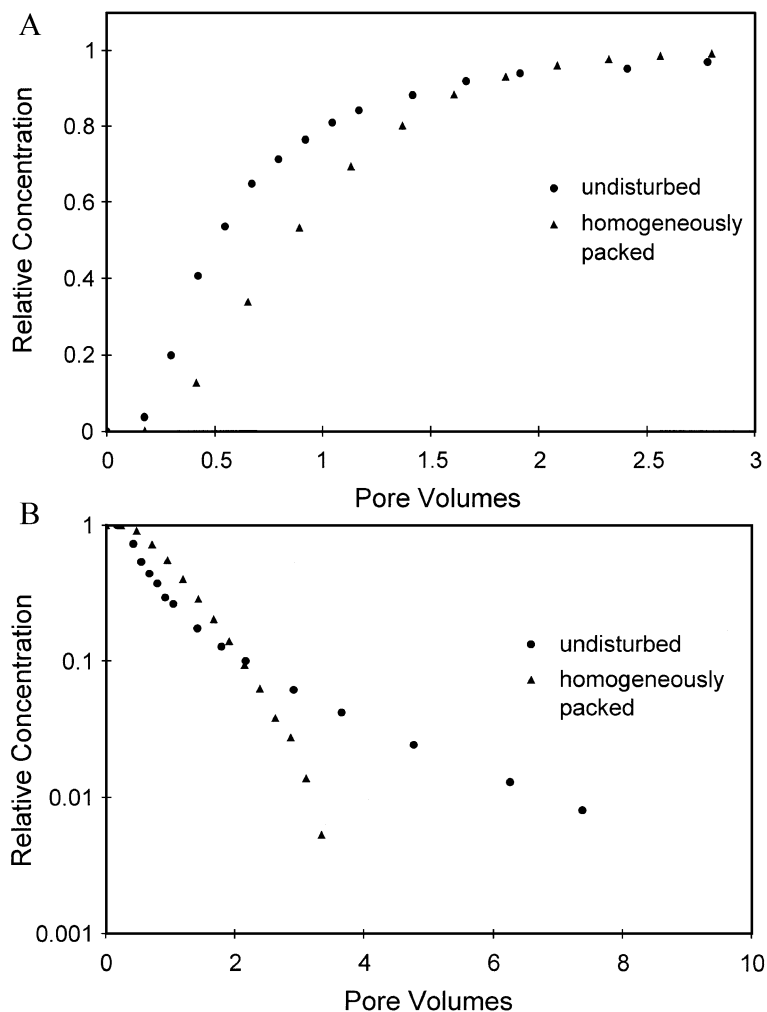


Fig. 5. Trichloroethene transport in the undisturbed versus homogeneously packed systems: (A) representative arrival waves; (B) representative elution waves (log-plot). Experiments conducted at an average pore-water velocity equal to 13 cm h^{-1} .

nonlinear and rate-limited sorption/desorption. Furthermore, the results obtained for PFBA in the undisturbed core indicate physical-heterogeneity-related factors are also contributing to nonideal transport. Thus, it is evident that the nonideal transport observed for trichloroethene in the undisturbed core was caused by both physical and chemical factors. The breakthrough curves obtained for trichloroethene from two miscible-displacement experiments conducted for the undisturbed system are compared to that obtained for PFBA in Fig. 6. The breakthrough curves are nearly identical, suggesting the degree of nonideal transport observed for the two solutes is similar. Given the small degree of sorption measured for trichloroethene (retardation factors ranging from 1.02 to 1.15), these results

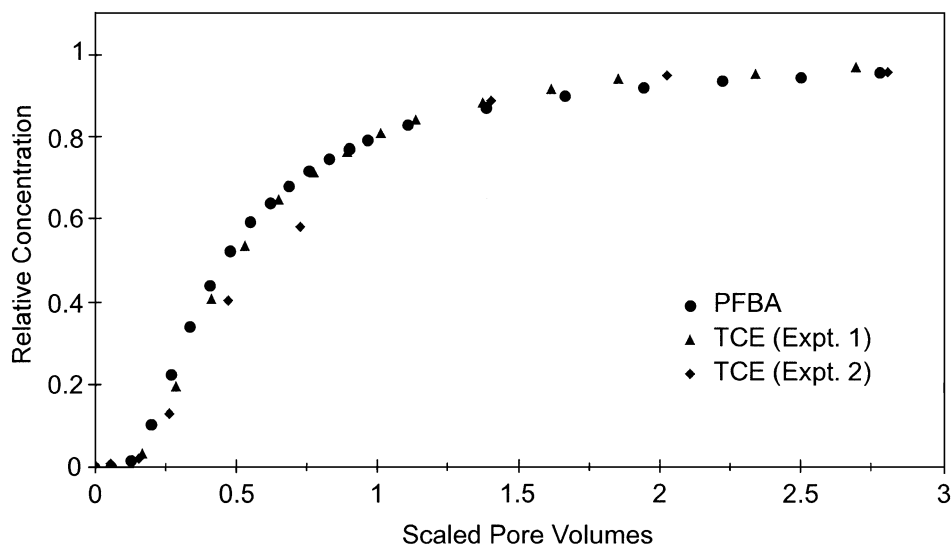


Fig. 6. Trichloroethene versus PFBA breakthrough curves (scaled for R) for the undisturbed system. Experiments conducted at an average pore-water velocity equal to 13 cm h^{-1} .

are not unexpected. Thus, while the contribution of nonlinear and rate-limited sorption/desorption to the nonideal transport of trichloroethene in this aquifer material is evident in the breakthrough curves obtained for the homogeneously packed systems, it appears that physical-heterogeneity-related processes are dominant in contributing to the nonideal transport of trichloroethene in the undisturbed system.

3.3. Impact of physical-heterogeneity-related processes on transport behavior

The results discussed above indicate that physical-heterogeneity-related factors contributed significantly to nonideal transport of both PFBA and trichloroethene in the undisturbed core. The mechanisms potentially responsible for this nonideal behavior include longitudinal, film (considered by many researchers to be insignificant as compared to other potential mechanisms), and intraparticle diffusion (associated with aggregated porous material potentially present in the core), as well as preferential flow and mass-transfer associated with variable-flow domains in the undisturbed aquifer material. Additional nonreactive tracer experiments were conducted to further investigate the physical-heterogeneity-related nonideal transport observed in the undisturbed system. Experiments were conducted using multiple tracers with different aqueous diffusion coefficients to specifically examine the contribution of diffusive mass-transfer to the nonideal transport. In theory, if diffusive mass-transfer is contributing to nonideal transport in the system, the degree of nonideality should vary for solutes with different magnitudes of aqueous diffusion coefficients (Brusseau, 1993; Maloszewski and Zuber, 1993). In addition, experiments were conducted at two pore-water velocities varying by an order of magnitude to evaluate the impact of hydraulic residence time on transport.

A comparison of the arrival waves for bromide, PFBA, and fluorescein is shown in Fig. 7. The extent of nonideal transport behavior indicated by early breakthrough and tailing is slightly greater for the solutes with smaller diffusion coefficients (i.e., bromide > PFBA > fluorescein), wherein approximately 4.7, 5.0, and 6.1 pore volumes, respectively, are required to reach a relative concentration of 1.0. These results suggest the possible presence of diffusive mass-transfer phenomena in the undisturbed system. It is of interest to note that similar experiments were conducted using bromide, PFBA, and a third tracer for the homogeneously packed aquifer material resulting in essentially identical breakthrough curves for all three solutes (Nelson et al., 2002).

The breakthrough curves for three nonreactive tracers obtained at two pore-water velocities (13 and 1.3 cm h⁻¹) are shown in Fig. 8. All of the tracers exhibit nonideal transport behavior. Given that diffusive mass-transfer is a rate-limited process, the degree of transport nonideality might be expected to increase as hydraulic residence time decreases. However, for all of the tracers employed, there was no measurable difference in the breakthrough curves obtained at the two pore-water velocities, which is similar to the results obtained for trichloroethene (Fig. 4B). These results suggest that diffusive mass-transfer is not measurably influencing transport, which appears inconsistent with the results discussed above. This apparent inconsistency may reflect a relative insensitivity of the system to an order-of-magnitude change in pore-water velocity. Recognizing these potential limitations, the flow-interruption method, which has been shown to have a greater sensitivity for characterizing mass-transfer processes (Brusseau et al., 1989b, 1997; Hu and Brusseau, 1995; Reedy et al., 1996), was used to further examine mass-transfer in the undisturbed system.

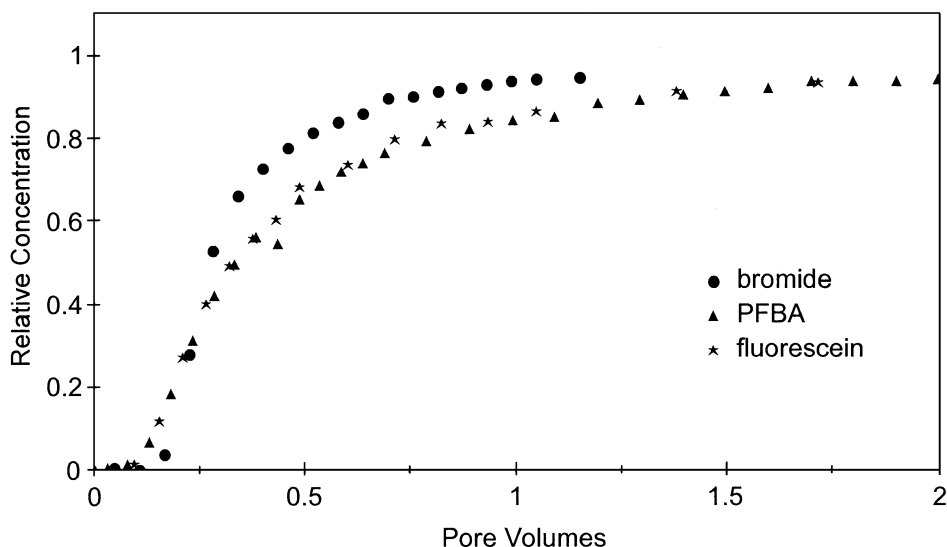


Fig. 7. Representative breakthrough curves for nonreactive tracer transport in the undisturbed core. Experiments conducted at an average pore-water velocity equal to 13 cm h⁻¹.

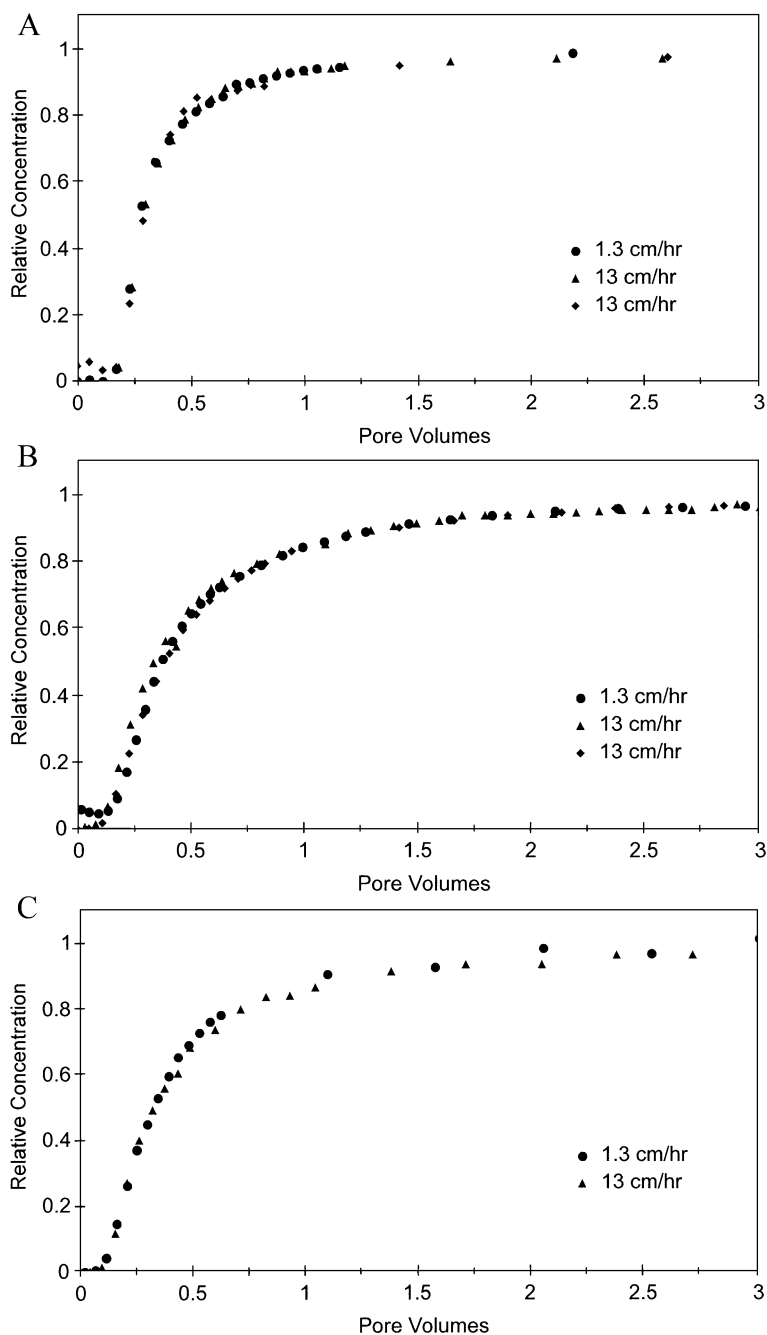


Fig. 8. Breakthrough curves obtained for nonreactive tracer transport in the undisturbed core at two average pore-water velocities. (A) Bromide. (B) PFBA. (C) Fluorescein.

The experiments, conducted using two tracers (PFBA and tritiated water), involved 4-h periods of flow interruption during the elution phase of transport. The effluent concentrations increased after flow was resumed (Fig. 9). This indicates the existence of nonuniform concentration distributions and associated rate-limited mass-transfer in the system. As the solutes employed in these experiments are nonreactive, these results suggest the existence of “no-flow” domains in the undisturbed core, consistent with the results of the red-acid dye experiment conducted for the undisturbed core. The results of

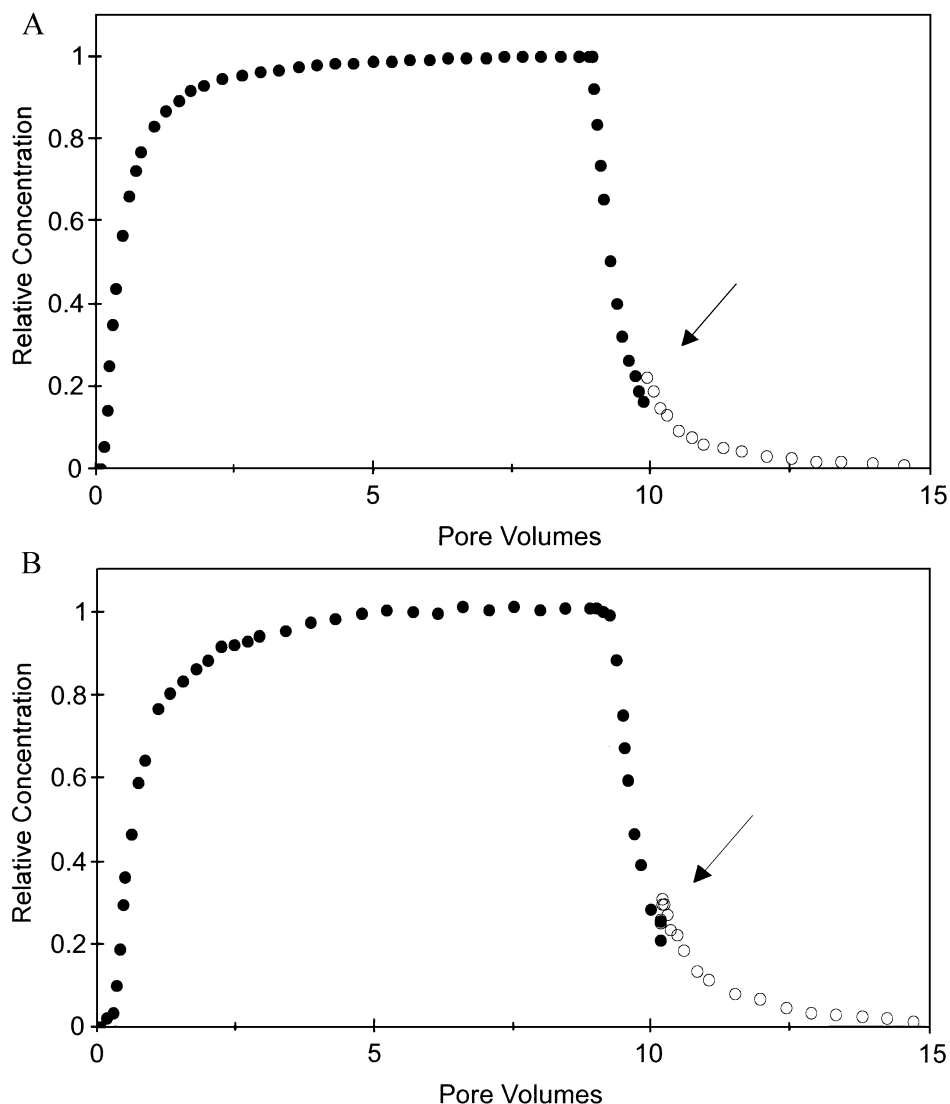


Fig. 9. Breakthrough curves for the flow-interruption experiments conducted at an average pore-water velocity equal to 13 cm h^{-1} with PFBA (A) and tritiated water (B). Flow was interrupted during the elution front for 4 h.

the latter experiment (shown in Fig. 10) indicate nonuniform flow conditions in the column. Obvious preferential flow-paths were observed along the length of the column. Heterogeneously distributed gravel and silt/clay lenses were apparent upon dissection and visual inspection of the cores. However, obvious fractures and/or macropores in the core material were not apparent. Furthermore, the material is composed primarily of single particles (predominately sand), with no evidence of aggregated material. Based on these results, the undisturbed system likely has a wide range of flow domains, with some of such relatively low flow that they behave essentially as “no-flow” regions, for which solute access is primarily by diffusive mass-transfer.

In summary, tracer experiments conducted with solutes having different aqueous diffusivities yielded a slight increase in nonideality with a solute-size increase, suggesting the presence of a diffusive mass-transfer process. The nonuniform flow conditions of the system (clearly indicated by the results of the dye experiment) and associated rate-limited diffusive mass-transfer appears to be the primary physical-heterogeneity-related process contributing to the nonideal transport behavior associated with the undisturbed core. These results were further supported by results of the flow-interruption experiments, wherein the presence of nonequilibrium conditions (e.g., diffusive mass-transfer between nonuniform flow domains) were clearly indicated. The following section will discuss the application of various mathematical models to the data, using parameters describing the nonideal sorption/desorption processes, determined through the analysis of the trichloroethene data measured in the homogeneously packed core, along with parameters describing the physical-heterogeneity-related nonideality in the undisturbed core, determined through the analysis of the nonreactive tracer data. This analysis will be used to determine the relative contribution of each factor to the nonideal transport behavior of trichloroethene in the undisturbed system.

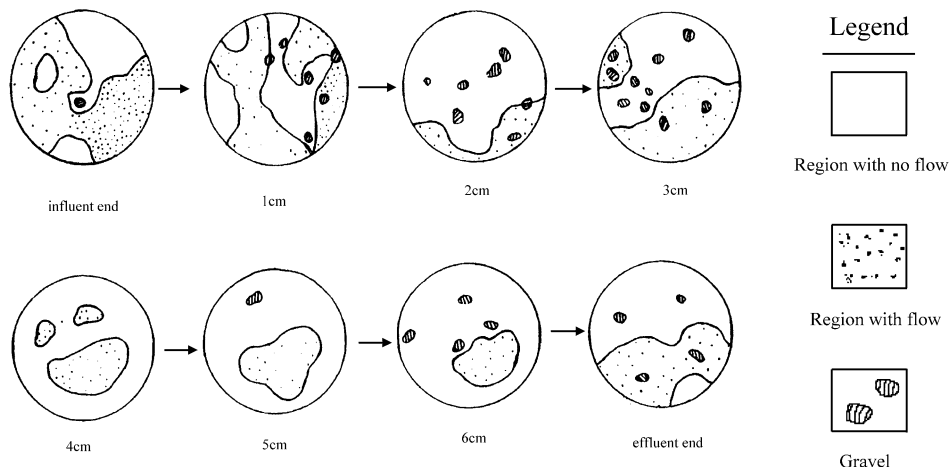


Fig. 10. Results of red-acid dye experiment conducted for the undisturbed system (cross-sections shown at 1-cm intervals, perpendicular to the direction of flow).

3.4. Simulation results

The nonreactive tracer data obtained for the homogeneously packed system were analyzed using the ideal-transport-based model (i.e., β equals 1 for Eqs. (1) and (2)). The ideal model provides a good fit to the measured data (see Fig. 1). The optimized dispersivity values range from 0.3 to 0.9 cm. These dispersivity values are larger than typical values reported for sand-packed columns. This is most likely due to the larger grain-size distribution of the aquifer material used in our experiments (silt + clay > 10%) compared to others. For example, Hu and Brusseau (1994) measured a dispersivity value of 0.06 cm for a column packed with glass beads comprising a very narrow distribution of diameters. Furthermore, Brusseau (1993) reported dispersivity values of 0.035, 0.05, and 0.11 cm (mean = 0.06 cm) for three sandy materials, all of which had silt plus clay contents of approximately 4% or less.

The results of the trichloroethene experiments conducted using the homogeneously packed columns were analyzed with the nonlinear, rate-limited sorption/desorption model and the two-domain model accounting only for rate-limited sorption/desorption (Eqs. (3) and (4)). An example of the simulation results obtained from the two models is included in Fig. 1. The two simulations, one accounting for both nonlinear and rate-limited sorption/desorption versus the other accounting only for rate-limited sorption/desorption, are nearly identical. Both models provide a good fit to the measured data, simulating the early breakthrough and tailing. These results indicate that nonlinear sorption has minimal impact on transport for this system. Thus, it appears that rate-limited sorption/desorption is the dominant cause of the nonideal transport behavior for trichloroethene in the homogeneously packed systems. Optimized desorption rate coefficients (k_2) for experiments conducted in the Plexiglas and glass columns using the “two-site” model are similar, equaling 3 and 2 h^{-1} , respectively. It is of interest to note that these mass-transfer rate coefficients, associated with rate-limited sorption/desorption, are an order of magnitude larger than the optimized mass-transfer coefficients, α , representing the characteristic time of solute (PFBA) exchange between the variable flow domains of the undisturbed system (for experiments conducted at the same pore-water velocity, see Table 1).

The nonreactive tracer data obtained for the undisturbed system were analyzed using the two-domain model (Eqs. (1) and (2)) to account for the nonideality due to physical heterogeneity as suggested by the results discussed above. This model provided very good simulations of the measured data, as illustrated in Fig. 3. The optimized parameters obtained from the two-domain model for several nonreactive tracer experiments conducted at two pore-water velocities for the undisturbed system are listed in Table 1. For the larger pore-water velocity, the average first-order mass-transfer coefficient, α , equaled 0.2 and 0.08 h^{-1} for PFBA and fluorescein, respectively. For the smaller pore-water velocity, α equaled 0.02 h^{-1} and 0.01 h^{-1} for PFBA and fluorescein, respectively. The mass-transfer coefficients are smaller for fluorescein than for PFBA as would be expected given the smaller aqueous-diffusion coefficient of fluorescein. As stated previously, the two-domain model is based on a conceptualization of the system as comprising mobile and immobile domains. Based on the results of the dye experiment, the undisturbed system is probably best described as having a wide range of flow domains rather than strict mobile and immobile domains. However, given that the two-domain model successfully simulates the

Table 1

Parameter values determined through analysis of measured nonreactive tracer data using the two-domain model for the undisturbed core

Solute	Experiment	ν (cm h ⁻¹)	R^a	P	β	ω	Mass-transfer coefficient, α (h ⁻¹)	Apparent dispersivity (cm) ^b
PFBA	5	12	0.65	12	0.45	0.30	0.2	8 [6–11]
				[8.2–16]	[0.43–0.48]	[0.25–0.36]	[0.2–0.2]	
PFBA	6	14	0.70	6.4	0.54	0.27	0.2	7 [4–15]
				[3.9–9.0]	[0.50–0.58]	[0.15–0.40]	[0.1–0.3]	
PFBA	7	1.3	0.65	6.4	0.50	0.28	0.02	8 [6–10]
				[5.1–7.7]	[0.48–0.52]	[0.23–0.34]	[0.02–0.02]	
Fluorescein	8	13	0.67	2.9	0.46	0.12	0.08	21 [15–32]
				[2.2–3.6]	[0.43–0.48]	[0.09–0.16]	[0.06–0.1]	
Fluorescein	9	1.1	0.58	3.0	0.52	0.11	0.006	18 [11–36]
				[2.2–3.7]	[0.49–0.55]	[0.06–0.17]	[0.003–0.009]	

^a Retardation factor (R) determined from temporal analysis of the measured data.

^b Calculated from the two-domain modeling results, accounting for hydrodynamic dispersion (as measured by P) and the effects of core-scale physical heterogeneity (as measured by β and ω) using $1/P_{app} = 1/P + (1 - \beta)^2/\omega$ (e.g., Lee et al., 1988).

nonideal behavior of the tracer in the undisturbed system, we will use this approach for simplicity.

The transport of trichloroethene in the undisturbed core was simulated using the MPNE model. The model parameters were independently determined through analysis of the experiments discussed previously. For example, analysis of results obtained for the homogeneously packed system yielded parameters related to rate-limited sorption/desorption (i.e., F and k_2). Analysis of the nonreactive tracer results obtained for the undisturbed system yielded parameters representing the physical-heterogeneity-related nonideality associated with the system (i.e., the Peclet number, β , the fraction of sorbent associated with the “mobile” domain, and α , the characteristic time of solute exchange between the variable flow domains of the aquifer material). Using these parameters to describe the processes contributing to the nonideal transport behavior, a prediction of trichloroethene transport in the undisturbed system was obtained with the multiprocess nonideality model.

Comparison of the predicted simulation to the measured data for trichloroethene shows the MPNE model successfully represents the nonideal transport behavior for the undisturbed system (see Fig. 11). The values for each β term (representing the fraction of retardation occurring within each of the four domains as described for the MPNE model) are included in Table 2. The average values equaled $\beta_1 = 0.49$ (± 0.03), $\beta_2 = 0.03$ (± 0.02), $\beta_3 = 0.45$ (± 0.03), and $\beta_4 = 0.03$ (± 0.02). It is apparent when comparing the β terms that the contribution of rate-limited sorption to the nonideal transport observed in the undisturbed system is expected to be relatively insignificant compared to the contribution of physical-heterogeneity-related processes. Specifically, β_2 and β_4 , representing the fraction of retardation associated with rate-limited sorption, are significantly smaller than β_1 and β_3 , which represent the fraction of retardation associated with retention in the mobile and immobile pore-water domains (and associated instantaneous sorption). As stated previously, this conclusion is not unexpected based on the minimal sorption

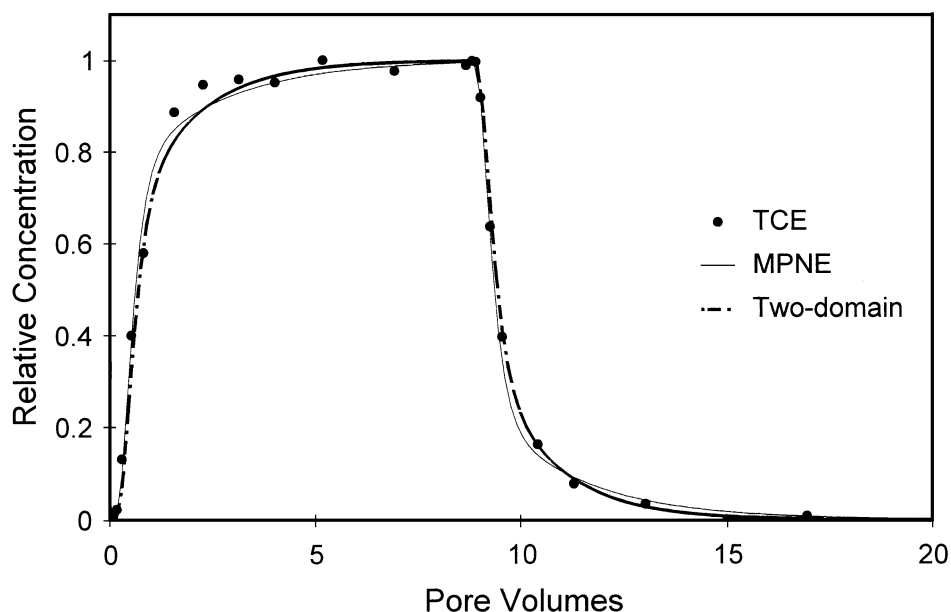


Fig. 11. Results of trichloroethene transport in the undisturbed system: comparison of predicted simulations and measured data. Experiments conducted at an average pore-water velocity equal to 13 cm h^{-1} . The predictions were obtained using the multiprocess nonideality (MPNE) model (accounting for both physical-heterogeneity-related factors and rate-limited sorption/desorption) and the two-domain model (accounting for only physical-heterogeneity-related factors).

measured for trichloroethene with this aquifer material. These results are further supported by the outcome of a simulation conducted for trichloroethene transport in the undisturbed system using the two-domain-based model. Employing only the parameters related to the physical-heterogeneity-related processes, the prediction using the two-domain approach (included in Fig. 11) is nearly identical to the prediction made using the MPNE model.

Table 2

Parameter values used with the MPNE model to predict the transport of trichloroethene for the undisturbed core

Solute	Experiment	v (cm h^{-1})	R^a	β_1	β_2	β_3	β_4
TCE	1	13	1.08	0.50 [0.46–0.54]	0.040 [0.037–0.043]	0.43 [0.46–0.39]	0.034 [0.037–0.031]
TCE	2	13	1.03	0.53 [0.49–0.57]	0.016 [0.015–0.018]	0.44 [0.48–0.40]	0.014 [0.015–0.013]
TCE	3	1.3	1.15	0.44 [0.42–0.45]	0.063 [0.061–0.066]	0.44 [0.45–0.42]	0.063 [0.066–0.061]
TCE	4	1.3	1.02	0.49 [0.47–0.51]	0.008 [0.007–0.008]	0.49 [0.51–0.47]	0.008 [0.008–0.007]

^a Retardation factor (R) determined from temporal analysis of the measured data.

4. Summary

The results of miscible-displacement experiments conducted using undisturbed aquifer cores compared to homogeneously packed columns clearly indicate that the transport of trichloroethene in the aquifer material is affected by both physical and chemical non-idealities. Using independently determined parameters describing these processes, the transport of trichloroethene in the undisturbed core was successfully predicted using the multiprocess nonideality model. While successful, however, analysis of the magnitudes of the retention parameters indicated the fraction of retardation associated with rate-limited sorption are significantly smaller than the fraction of retardation associated with retention in the mobile and immobile pore-water domains (and associated instantaneous sorption). These results are further supported by simulation results for the transport of trichloroethene in the undisturbed core using the two-domain model, accounting only for physical-heterogeneity-related factors. The simulation results indicate that local-scale physical heterogeneity controlled the nonideal transport behavior of trichloroethene in the undisturbed core, and that nonlinear, rate-limited sorption/desorption were of secondary importance.

This research has shown the typical homogenization approach employed in laboratory characterization studies of contaminant transport in porous media is unable to capture the effect of core-scale porous-media structure on transport behavior. In this case, the transport behavior of trichloroethene was controlled by physical-heterogeneity-related processes. The possible existence of multiple sources of nonideal behavior clearly must be considered for each site when conducting characterization studies of contaminant transport. This becomes especially important when parameters obtained from these laboratory experiments are applied for field-scale transport and fate studies.

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