ELSEVIER

Characterizing the contribution of diffusive mass transfer to solute transport in sedimentary aquifer systems at laboratory and field scales

N.T. Nelson[a], Q. Hu[b], M.L. Brusseau[c],*

[a]Daniel B. Stephens and Associates Inc., 6020 Academy NE, Albuquerque, NM 87109, USA
[b]Lawrence Livermore National Laboratory, 7000 East Ave., Livermore, CA 94550 , USA
[c]Department of Soil, Water and Environmental Science, and Department of Hydrology and Water Resources, University of Arizona, 429 Shantz Building, 38, Tucson, AZ 85721, USA

Abstract

The multi-tracer test method was used to investigate the impact of diffusion-mediated mass-transfer processes associated with physical heterogeneity on solute transport in sedimentary aquifer systems at different scales. Three systems were examined: (1) a column packed with homogenized aquifer material, (2) undisturbed aquifer cores, and (3) a section of a semi-confined alluvial aquifer encompassing approximately 2000 m^2. Tracer experiments were conducted using non-reactive tracers with different aqueous diffusion coefficients, based on the assumption that the impact of diffusion-mediated mass-transfer processes on solute transport will be dependent upon the magnitude of the diffusion coefficient. For the homogenized packed column, the breakthrough curves for the different tracers were very similar, and the attendant dispersivities were identical. These results indicate, as would be expected, that physical-heterogeneity related diffusive mass transfer did not measurably contribute to solute transport in the homogeneously packed column. Conversely, the results obtained for the undisturbed aquifer cores indicate that diffusive mass transfer, possibly associated with diffusion between zones of lower and higher advection, contributed to solute transport in this system. For the field test, the magnitudes of the dispersivity coefficients were different for the different tracers. Thus, solute transport at the field scale appeared to be influenced by diffusive mass transfer, most likely associated with mass transfer between regions of lower and higher permeability. These results illustrate that tracer tests using tracers with different diffusivities can be used to help elucidate the relative contribution of diffusion-mediated mass transfer to solute transport.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Diffusion-mediated mass transfer; Dispersivity coefficient; Heterogeneous aquifer material; Undisturbed core

1. Introduction

The occurrence and potential importance of diffusion-mediated processes for solute transport in subsurface systems has become well recognized. For example, rate-limited diffusion of contaminants out of low-permeability layers can lead to reduced performance and extended operational times for pump-and-treat based groundwater remediation systems. Examples of systems influenced by physical-heterogeneity-related diffusive mass transfer include

* Corresponding author. Fax: +1-520-626-6782.
  E-mail address: brusseau@ag.arizona.edu (M.L. Brusseau).

aggregated or macroporous soil, fractured media, and layered sedimentary aquifer systems. The impact of diffusive mass transfer on solute transport depends on the conditions and physical nature of the system, including the residence time, the characteristic time(s) of mass transfer, and the type and extent of physical heterogeneity. Unfortunately, it is often difficult to determine the relative significance of diffusive mass transfer processes versus that of other factors that may influence transport, especially for field-scale transport.

Various types of tests can be conducted to help determine the contribution of diffusion-mediated mass transfer processes to solute transport (e.g. Brusseau, 1998; Jardine et al., 1998). At the laboratory scale, the primary method used to date involves conducting tracer experiments at two or more pore-water velocities. Because diffusion is a rate-controlled process, changes in residence time (pore-water velocity) will influence the impact of a diffusion-mediated process on solute transport. Another method that can be used to examine the influence of rate-controlled processes on solute transport is the multi-tracer test method, which involves the use of a suite of non-reactive tracers with different aqueous diffusivities (Brusseau, 1993; Maloszewski and Zuber, 1993). For a system influenced by a diffusional mass-transfer process, it is expected that the solute with the larger diffusion coefficient would be closer to a condition of equilibrium at a given time than the solute with the smaller diffusion coefficient. Thus, the two tracers should exhibit different degrees of non-ideal transport

for a given set of conditions. The multi-tracer method may be especially useful for field systems, given that it does not require multiple tests to be conducted, as is required for the multiple-velocity method. This method has been used in several recent experiments conducted at both laboratory (e.g. Hu and Brusseau, 1994, 1995) and field (e.g. Brusseau et al., 1999; Jardine et al., 1999; Callahan et al., 2000) scales.

This work used the multi-tracer test method to investigate the impact of physical-heterogeneity-related diffusive mass transfer on solute transport in sedimentary aquifer systems at different scales. This was examined for three systems: (1) a column packed with homogenized aquifer material, (2) undisturbed aquifer cores, and (3) a section of a semi-confined alluvial aquifer approximately 2000 m^2 in area. Tracer experiments were conducted using non-reactive tracers with different aqueous diffusivities.

2. Materials and methods

2.1. Tracers

Combinations of tritiated water (^3H_2O), bromide (as $CaBr_2$), pentafluorobenzoate (PFBA), fluorescein, and hydroxypropl-beta-cyclodextrin (HPCD) were used in the experiments. Bromide, PFBA, and fluorescein were purchased from Aldrich Chemical Co, ^3H_2O was purchased from New England Nuclear, and HPCD was donated by Cerestar, Inc. Pertinent properties of the tracers are listed in Table 1.

Table 1
Tracer properties

Tracer	MW[a]	D_0 (cm^2/h)	Homogenized column	Undisturbed core	Field site
^3H_2O	22	0.08[b]	NA[c]	2 nCi/ml	NA
Bromide	79.9	0.075[d]	200 mg/l	NA	76 mg/l
PFBA	212	0.03[e]	200 mg/l	100 mg/l	NA
Fluorescein	376	0.02[e]	NA	1 mg/l	NA
HPCD	1500	0.006[e]	1700 mg/l	NA	175 mg/l

[a] MW = molecular weight.
[b] Mills, 1973.
[c] NA = not applicable.
[d] Cussler, 1984.
[e] Estimated by use of Hayduk and Laudie approach (Tucker and Nelken, 1982).

2.2. Homogeneously packed column

The homogenized-column experiments were conducted using a glass column (2.5 cm inside diameter [i.d.] and 15 cm in length) packed homogeneously with aquifer material collected from a depth of 43–45 m below ground surface (bgs) during the drilling of a well at the field site. The <2 mm fraction was used for the experiments and consisted of 89.5% sand, 4.1% silt, 6.4% clay, 0.06% total carbon, and 0.03% organic carbon. The >2 mm fraction comprised less than 1% of the original sample.

The apparatus employed for the miscible displacement experiments consisted of an HPLC pump (SSI Acuflow series II) connected to the column by a three-way switching valve placed in line to facilitate switching between solutions, one of which contained the solute of interest and the other of which contained an electrolyte solution. The electrolyte solution, which comprised $Ca(NO_3)_2$ (9 mg/l), $CaCl_2$ (85 mg/l), $MgSO_4$ (124 mg/l), $NaHCO_3$ (171 mg/l), $NaCl$ (20 mg/l), was developed to represent the chemical composition of the groundwater at the field site. Several hundreds of pore volumes of the electrolyte solution was pumped through the column prior to the tracer tests to obtain complete water saturation and to acclimate the aquifer material to the electrolyte solution.

Two separate experiments were conducted with the packed column. For experiment 1, a solution containing 200 mg/l PFBA and 200 mg/l bromide was pumped into the column at a flow rate of 0.74 ml/min, corresponding to an average linear pore-water velocity of 25.2 cm/h. For experiment 2, a 1700 mg/l solution of HPCD was pumped through the column at a flow rate of 0.80 ml/min (corresponding to a pore-water velocity of 27.2 cm/h). These flow rates were used to achieve pore-water velocities similar to those measured at the field site under the induced-gradient conditions associated with the tracer tests and with a pump-and-treat system operating at the site. The small difference in velocities (8%) between the two experiments should not influence the magnitude of dispersion in homogeneously packed columns wherein dispersion is dominated by local-scale hydrodynamic dispersion. The bulk density and porosity of the columns were approximately 1.71 g cm^{-3} and 0.39, respectively.

2.3. Undisturbed column

Two undisturbed columns were obtained by pushing Plexiglas tubes (5.08 cm i.d., and 7.62 cm in length) through a section of undisturbed core collected from the field site (43–45 m bgs). This allowed the columns to be filled with 'undisturbed' porous media, maintaining the natural (resident) structural arrangement of the aquifer material within the columns. The columns were pressed through the core perpendicular to the vertical axis of the core so that flow generated during the experiments would be in the same direction as the in situ condition. The bulk density and porosity of the columns were approximately 1.64 g cm^{-3} and 0.4, respectively.

The apparatus and methods employed for the miscible displacement experiments were the same as used for the homogenized column experiments. Solutions containing 100 mg/l PFBA, 100 mg/l fluorescein, or ^3H_2O (specific activity of 2 nCi/ml) were pumped separately into the columns. Flow rates of 0.2 and 2.2 ml/min were used, corresponding to pore-water velocities of 1.5 and 15.0 cm/h. Pore-water velocities greater than 1 cm/h were used for these experiments, as well as for those conducted with the homogeneously packed column, to minimize the impact of axial (e.g. longitudinal) diffusion on transport. Flow interruption (Brusseau et al., 1989, 1997) was also employed to further examine the effect of diffusive mass transfer on solute transport. These latter experiments were also conducted in a manner to minimize the potential effects of axial diffusion on observed behavior, as discussed in Brusseau et al. (1989, 1997).

2.4. Field site

The field site is located within a Superfund site in Tucson, Arizona. The site is located in the Tucson Basin, which is underlain by about 1000 m of alluvial sediments interbedded locally with volcanic flows, agglomerates, and tuffaceous sediments. The upper, regional aquifer, which was the focus of our study, consists of sand and gravel lenses/layers separated in some areas by clayey sediment ranging in thickness from 1 to 7 m. The top of the saturated zone for this aquifer is about 42 m bgs. In the unsaturated zone, a 6–12 m thick laterally extensive but discontinuous
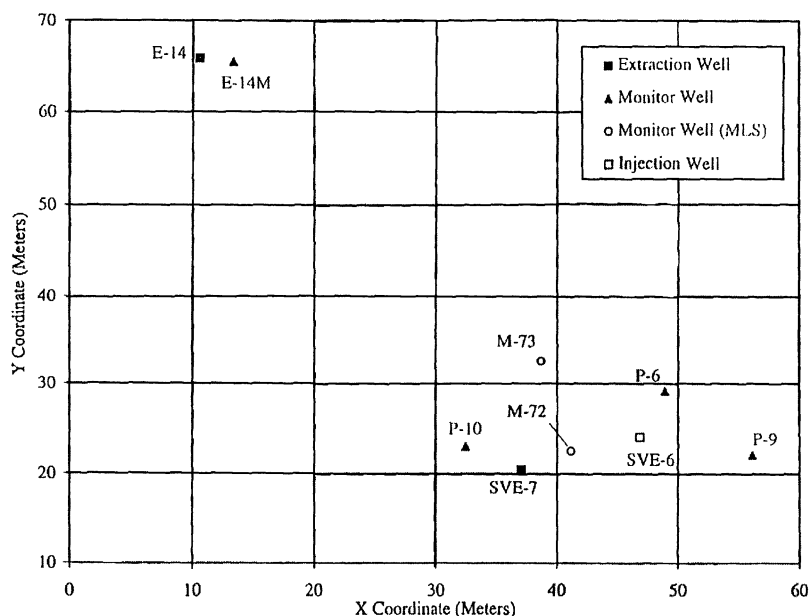
Fig. 1. Schematic showing location of wells for the field site.

clay or sandy clay unit overlies the upper aquifer. The horizontal hydraulic conductivity for the upper aquifer ranges between 0.1 and 82 m/d, with a mean value of approximately 24 m/d.

One fully screened injection well (SVE-6) and one fully screened extraction well (E-14), separated by 57 m, were used to create a steady-state flow field (see Fig. 1). Bromide and HPCD were used as tracers (Table 1). The tracer solution was injected at a rate of 170.3 l/min and extracted at a rate of 266.8 l/min. Mean pore-water velocities in the vicinity of the centerline monitoring well ranged from 1 to 40 cm/h based on the tracer travel times. The tracer solution was injected for 53 h, after which tracer-free ground-water was injected for 60 days. Depth-specific water samples were collected at a centerline monitor well (M-73, 11.7 m from injection well) using a four-port multi-level sampling device. Several fully screened monitor wells were bailed to collect depth-integrated samples.

2.5. Chemical analysis

For column experiments in which PFBA was used, a flow-through, variable-wavelength UV detector (Gilson, Model 115) was used to continuously monitor concentrations of PFBA in the column effluent (quantifiable detection limit approximately 0.5 mg/l). Output was recorded on a strip-chart recorder (Fisher, Recordall Series 5000). For column experiments in which bromide, fluorescein, HPCD, and ^3H_2O were used, effluent fractions were collected with an automated fraction collector (Pharmacia RediFrac). Bromide was analyzed using a bromide-specific electrode (Cole–Palmer) with a Fisher Scientific Accumet pH meter (quantifiable detection limit approximately 0.3 mg/l). HPCD was analyzed by measuring the fluorescence of HPCD complexed with TNS (2ptoluidinnaphthalene-6-sulfonate) using a Hitachi F-2000 fluorescence spectrophotometer (quantifiable detection limit approximately 1 mg/l). Fluorescein was also analyzed using the fluorescence spectrophotometer (quantifiable detection limit approximately 0.01 mg/l). The activity of ^3H_2O in the effluent samples was analyzed by radioassay using liquid scintillation counting (Packard Tri-Carb Liquid Scintillation Analyzer, Model 1600TR).

2.6. Data analysis

The data obtained from the tracer tests were plotted as relative concentration versus pore

volumes. The measured concentrations for each tracer were normalized by their respective injection concentrations to obtain relative concentration. For the laboratory data, the measured column effluent was normalized by the water-capacity volume of each column to obtain pore volumes. For the field data, pore volumes were determined by normalizing the measured times by the mean travel time obtained from the tracer test. The mean travel time was calculated using standard moment analysis procedures.

The breakthrough curves obtained from the experiments conducted using the homogeneously packed column and from the field-scale experiment were analyzed using the standard advection–dispersion transport equation. The values of the Peclet number were determined using a non-linear least-squares optimization program incorporating the advection–dispersion equation (Van Genuchten, 1981). Generally, the Peclet number is defined as $P = vL/D$, where v is the average linear pore-water velocity (LT^{-1}), L is representative system length (L), and D is the hydrodynamic dispersion coefficient (L^2T^{-1}). The dispersion coefficient is defined as $D = (D_0/\tau) + \alpha_L v$, where D_0 is the aqueous diffusion coefficient (L^2T^{-1}), τ is the tortuosity factor, and α_L is the longitudinal dispersivity (L). For larger velocities (e.g. $v > 1$ cm/h), the D_0/τ term is usually considered negligible and the dispersion coefficient reduces to $D = \alpha_L v$.

In some cases, the degree of non-ideal transport is such that the standard advection-dispersive transport equation cannot provide a satisfactory simulation of observed breakthrough curves. This was the case herein for the results obtained from the experiments conducted using the undisturbed cores. Thus, the breakthrough curves obtained for the cores were analyzed with the dual-porosity model, which has been widely used to simulate solute transport in structured and layered systems.

For the dual-porosity model, the following two parameters were optimized in addition to P:

$$\omega = \alpha_{mt}L/q \tag{1}$$

$$\beta = \theta_a/\theta \tag{2}$$

where α_{mt} is the first-order mass transfer coefficient (T^{-1}), q is Darcy velocity (LT^{-1}), θ_a is the fraction

of porosity in which advection occurs, and θ is the porosity. For this model, the Peclet number represents the impact of local-scale dispersion processes on spreading, whereas the ω parameter, which is the ratio of the effective hydraulic residence time to the characteristic time of mass transfer, represents the impact of larger-scale physical heterogeneity (e.g. 'preferential flow', inter-region diffusive mass transfer) on transport. The larger the magnitude of ω, the closer the system is considered to be to a condition wherein transport behavior is similar to that expected for a homogeneous system. The β parameter indicates the relative 'size' of the 'non-advective' region (e.g. $\beta = 1$ indicates no non-advective region).

The first-order mass transfer coefficient, α_{mt}, can be related to diffusion-based parameters as follows (e.g. Parker and Valocchi, 1986):

$$\alpha_{mt} = \frac{aD_0\theta_n}{\tau l^2} \tag{3}$$

where a is a factor representing the shape of the non-advective domains, θ_n is the fraction of the porosity in which advection does not occur, and l is a characteristic length of the non-advective domains. The impact of solute diffusivity on the magnitude of ω is clear by substituting Eq. 3 into Eq. 1. Thus, we would expect a solute with a smaller D_0 to exhibit a greater degree of non-ideal transport (i.e. smaller ω) compared to a solute with a larger D_0 (larger ω) for a given system.

The parameter values obtained using the dual-porosity model (β, ω) cannot be compared directly to those obtained using the standard advection–dispersion equation (P). However, an 'apparent' dispersivity (α_a), which incorporates all contributions to spreading, can be calculated to allow approximate comparison on the basis of a single dispersivity term. To calculate an apparent dispersivity, an effective Peclet number (P_e) is calculated using the results obtained from application of the dual-porosity model as follows (Parker and Valocchi, 1986):

$$1/P_e = 1/P + (1 - \beta)^2/\omega \tag{4}$$

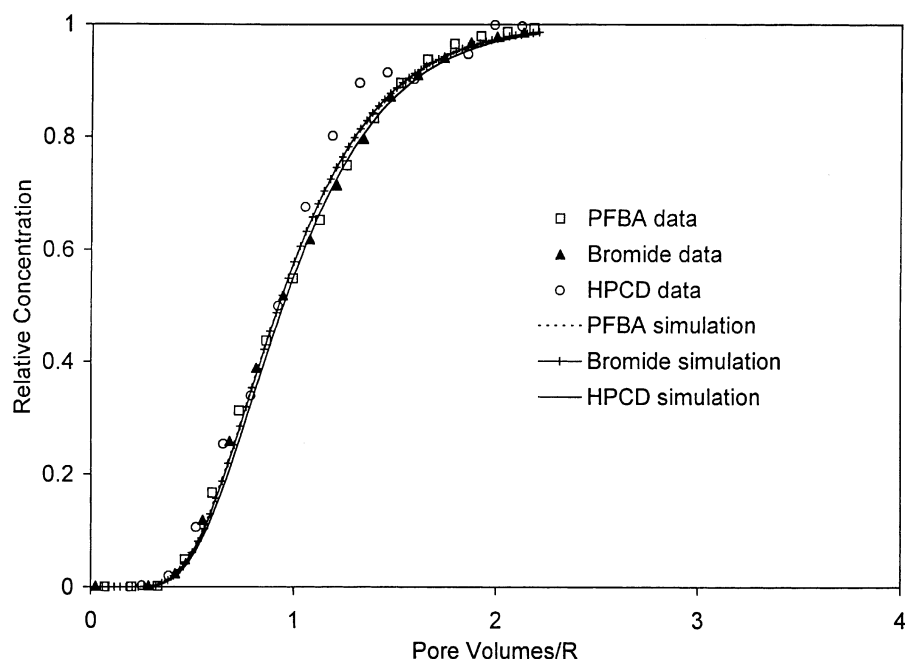where $\alpha_a = L/P_e$. It is important to recognize that this approach is an approximation and that

Fig. 2. Breakthrough curves for transport of three non-reactive tracers in the homogeneously packed column.

parameters so obtained may not provide a complete representation of transport behavior.

3. Results

3.1. Homogeneously packed column

Breakthrough curves for bromide, PFBA, and HPCD are relatively symmetric and similar in shape, indicating ideal transport (Fig. 2). In addition, all three curves are centered at one pore volume, indicating minimal sorption by the porous medium. The simulations produced with the standard advection–dispersion transport equation provide good fits to the measured data.

The breakthrough curves for all three tracers yielded the same dispersivity value (Table 2), indicating that, as would be expected, physical-heterogeneity related diffusive mass transfer did not measurably contribute to solute transport in the homogeneously packed column. This is supported by the results of experiments conducted using different pore-water velocities ($v = 20, \ 60$ cm/h),

for which the breakthrough curves were essentially identical (data not shown). The calculated α_L values (1.4 cm) 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 an α_L value of 0.06 cm for a column packed with glass beads comprising a very narrow distribution of diameters. Furthermore, Brusseau (1993) reported α_L values of 0.035, 0.05, and 0.11 cm (mean = 0.06 cm) for three sandy materials, all of which had silt + clay contents of approximately 4% or less.

Table 2
Results for homogeneously packed column

Tracer	P	α_L (cm)
PFBA	10.3 (9.5–11.1)	1.4 (1.3–1.6)
Bromide	10.7 (9.8–11.5)	1.4 (1.3–1.5)
HPCD	10.6 (7.8–13.4)	1.4 (1.1–1.9)

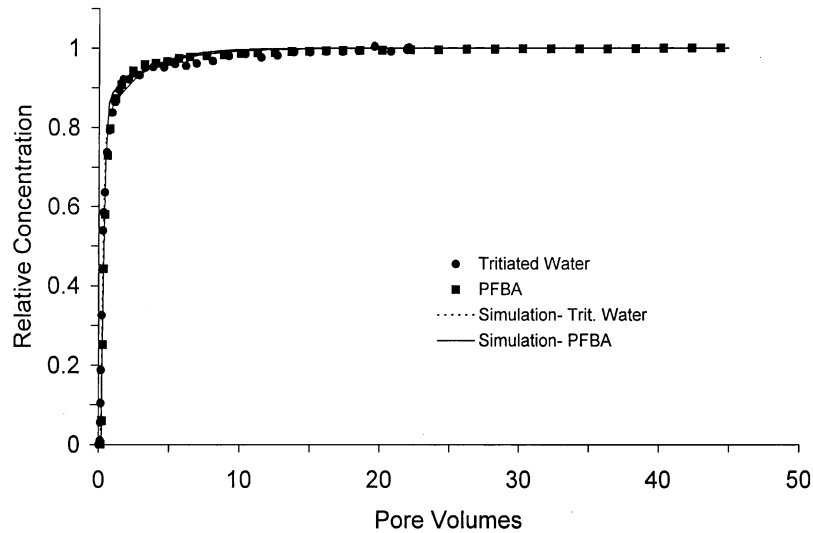Note: values in brackets represent 95% confidence intervals.

Fig. 3. Representative breakthrough curves for transport of non-reactive tracers in the undisturbed cores (Column 1).

3.2. Undisturbed cores

Breakthrough curves for transport of ^3H_2O and PFBA, in the undisturbed cores are shown in Fig. 3. The breakthrough curves are asymmetrical, exhibiting early breakthrough and extended approach to $C/C_0 = 1$ compared to the homogeneously packed columns. This non-ideal transport behavior, in contrast to the ideal behavior observed for the homogeneously packed column, reflects the impact of core-scale heterogeneity on solute transport.

To further investigate the potential impact of diffusion-mediated mass transfer on transport, flow interruption experiments were conducted using both ^3H_2O and PFBA. These experiments have an increased sensitivity in comparison to standard flow experiments for identifying the occurrence of diffusion-mediated mass transfer. During flow, a non-uniform concentration distribution may develop due to a non-uniform velocity distribution (e.g. the presence of dead-end pore zones or low permeability zones). For systems dominated by advection, in which residence time is short in comparison to the time necessary for diffusive mass transfer to occur, or where there is a relatively small fraction of 'non-advective' zones, the impact of diffusional mass transfer may not be clearly evident. However,

the occurrence of diffusion-mediated mass transfer may be more apparent during flow-interruption experiments.

Inspection of Fig. 4(A) and (B) reveals that PFBA exhibited a greater relative amount of concentration rebound after the flow interruption, wherein the relative concentration rebounded from 0.1 to 0.3 (a factor of 3) for PFBA, compared to a rebound from 0.22 to 0.44 (factor of 2) for ^3H_2O. This suggests that PFBA was farther from a condition of equilibrium solute distribution at the point of flow interruption compared to ^3H_2O, despite the fact that flow was interrupted later in the PFBA experiment. For a system influenced by a diffusional mass transfer process, it is expected that the solute with the larger diffusion coefficient (^3H_2O) would be closer to equilibrium at a given time than the solute with the smaller diffusion coefficient (PFBA). Thus, PFBA may be expected to exhibit a greater degree of non-equilibrium behavior (e.g. greater rebound) for flow-interruption tests. Flow interruptions were also implemented for two PFBA experiments conducted at different pore-water velocities. The rebound is greater for the experiment conducted with the larger velocity (Fig. 4(B)) than it is for the smaller-velocity experiment (Fig. 4(C)). This is consistent with the increase in the contribution of diffusion-mediated
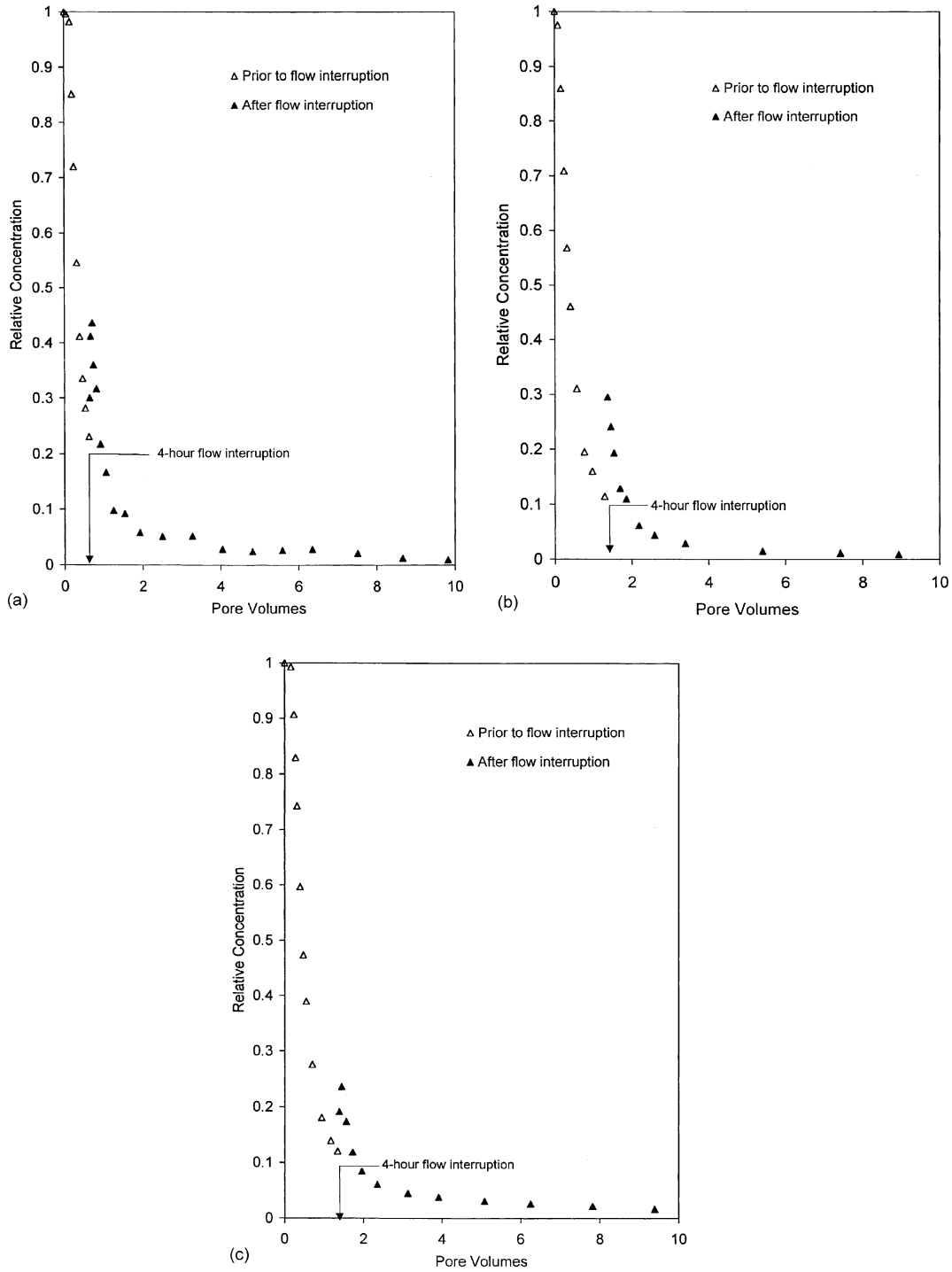
Fig. 4. Results of flow-interruption tests conducted for undisturbed core #1: (A) tritiated water; $v = 15$ cm/h; (B) PFBA, $v = 15$ cm/h,; (C) PFBA, $v = 1.5$ cm/h.

mass transfer to non-ideal transport associated with increased velocity and shorter residence time.

The flow-interruption results presented above indicate the existence of non-uniform concentration distributions and associated rate-limited mass-transfer in the columns. As the solutes employed in these experiments are non-reactive, these results suggest the existence of some combination of preferential and 'no-flow' domains in the undisturbed cores (data not shown). This is consistent with the results of a red-acid dye experiment conducted for one of the undisturbed cores(data not shown). The results of this experiment indicate non-uniform flow conditions existed in the column wherein 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 core. 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 cores likely have 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.

The simulations produced with the dual-porosity model provide good fits to the measured breakthrough curves (see Fig. 3). Inspection of Table 3 reveals that the α_{mt} values are statistically different for the three tracers, wherein fluorescein has the smallest value and

^3H_2O has the largest. These results are consistent with the differences in aqueous diffusivities among the three tracers (H_2O > PFBA > fluroescein), and further suggest that diffusion-mediated mass-transfer processes are contributing to solute transport in the undisturbed core.

The α_a values calculated for the undisturbed cores are approximately ten times larger than the α_L values measured for the homogeneously packed column. Similar results have been reported in previous research. For example, the dispersivities obtained for undisturbed cores collected from the Chalk River experimental site (Champ et al., 1985) are an order of magnitude larger than dispersivity values reported for tracer transport in columns homogeneously packed with the Chalk River aquifer material (Pickens and Grisak, 1981). The dispersivities measured for undisturbed cores collected from the Twin Lake field experiment site (Moltyaner and Killey, 1988) are about five times larger than typical longitudinal dispersivities reported for homogeneous sandy porous media (Pickens and Grisak, 1981).

3.3. Field site

The breakthrough curves for bromide and HPCD obtained for the field experiment exhibit the typical shape observed for pulse-input field tests, as illustrated in Fig. 5. As was observed for the laboratory experiments, there is no evidence of sorption. The simulations produced with the standard advection–dispersion transport equation provide reasonable fits to the measured

Table 3
Results for undisturbed cores

Tracer	P	β	ω	α_{mt} (hr^{-1})	P_e	α_a (cm)
Column 1						
^3H_2O	15.5 (7.5–23.5)	0.39 (0.35–0.43)	0.54 (0.42–0.66)	0.46 (0.36–0.56)	1.3 (0.9–1.9)	5.9 (4.0–8.5)
PFBA	10.8 (6.9–14.7)	0.47 (0.43–0.52)	0.28 (0.20–0.36)	0.24 (0.17–0.31)	0.9 (0.6–1.4)	8.5 (5.4–12.7)
Column 2						
PFBA-1	7.3 (6.5–8.1)	0.64 (0.62–0.66)	0.26 (0.22–0.30)	0.19 (0.16–0.22)	1.6 (1.2–2.0)	4.8 (3.8–6.4)
PFBA-2	6.4 (3.9–9.0)	0.54 (0.50–0.58)	0.27 (0.15–0.40)	0.20 (0.11–0.29)	1.1 (0.5–1.8)	7.2 (4.2–15)
Fluro[a]	2.9 (2.2–3.6)	0.46 (0.43–0.48)	0.12 (0.09–0.16)	0.08 (0.04–0.12)	0.36 (0.25–0.51)	21 (15–30)

Note: values in brackets represent 95% confidence intervals; results are for the faster-velocity experiments.
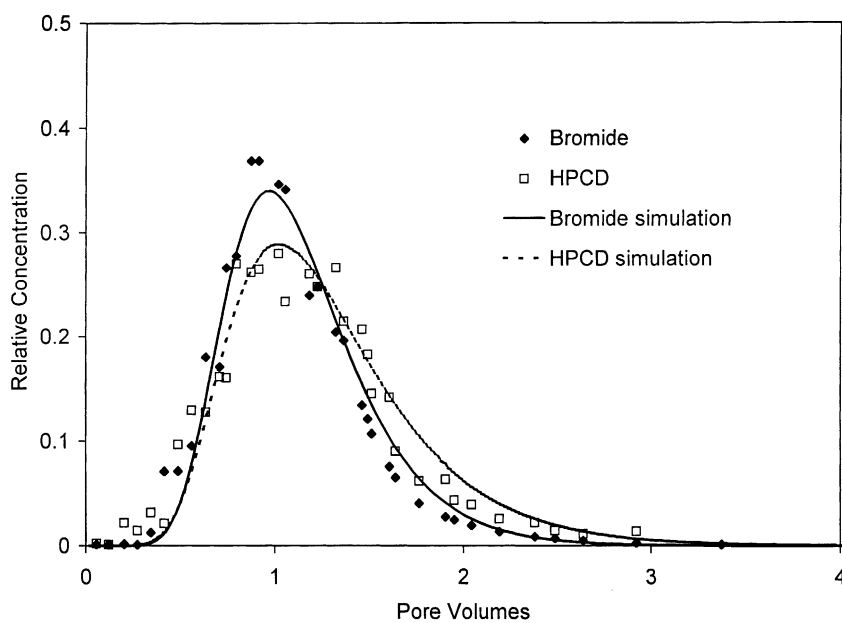[a] Fluorescein.

Fig. 5. Representative breakthrough curves for tracer test conducted at field site (location P10).

data. This is in contrast to the undisturbed-core system, for which it was necessary to use the dual-porosity model to describe transport. This situation illustrates the impact of scale on observed transport behavior, wherein the much larger spatial scale and associated residence times characteristic of the field system moderate the impact of physical heterogeneity and associated diffusion-mediated mass-transfer on transport.

Breakthrough curves for HPCD appear to exhibit a slightly greater degree of spreading than does bromide for all locations (e.g. Fig. 5). This

observation is supported by the smaller Peclet numbers obtained for HPCD (Table 4) and suggests that a diffusion-mediated mass transfer process, most likely diffusive mass transfer between zones of lower and higher permeability, influenced solute transport during the tracer experiment.

The apparent dispersivity values calculated for the centerline well are in the range of 2.5 m for bromide. These relatively large values may be due in part to the large degree of heterogeneity present at the site. The grain sizes observed at this field site

Table 4
Results for field test

Sample location	P-Bromide	P-HPCD	α_a-Bromide	α_a-HPCD
Centerline well[a] Level 1	5.1 [3.9–6.4]	2.4 [2.0–2.8]	2.3 m [1.8–3.1]	4.9 m [4.2–5.8]
Centerline well Level 2	6.4 [6.1–6.8]	3.9 [3.7–4.2]	1.8 m [1.7–1.9]	3.0 m [2.8–3.2]
Centerline well Level 3	2.9 [2.4–3.3]	2.4 [2.2–2.6]	4.1 m [3.5–4.8]	4.9 m [4.5–5.3]
Centerline well Level 4	3.1 [2.8–3.4]	2.1 [1.9–2.3]	3.8 m [3.5–4.2]	5.7 m [5.2–6.3]
M72[b]	13.4[10.5–16.4]	10.5 [7.1–13.9]		
P10[b]	13.2[11.9–14.5]	9.2 [7.8–10.7]		

Note: values in brackets represent 95% confidence intervals.
[a] Data collected at a centerline well equipped with a four-port multi-level sampling device.
[b] Data collected at a fully screened monitoring well.

range between clay and large cobbles. Laminations at the centimeter scale and textural variations (layers) between 0.3 and 5 m in thickness have been observed from borehole cores. These values are much larger than those obtained for the laboratory systems, illustrating the scale effect typical to the lumped dispersivities obtained with the application of the standard advection–dispersion equation.

4. Conclusion

For the homogeneously packed column, the breakthrough curves for the different tracers were very similar, and the attendant dispersivities were identical. These results indicate, as would be expected, that diffusive mass transfer did not measurably contribute to solute transport in the homogeneously packed column. Conversely, the results obtained for the undisturbed aquifer cores indicate that diffusive mass transfer, possibly associated with diffusion between zones of lower and higher advection, contributed to solute transport in this system. For the field test, the magnitudes of the dispersivity coefficients were different for the different tracers. Thus, solute transport at the field scale appeared to be influenced by diffusive mass transfer, most likely associated with mass transfer between layers of lower and higher permeability. In summary, the results illustrate that the multi-tracer test method can be used to examine the contribution of diffusion-mediated mass-transfer processes to solute transport at both the laboratory and field scales. This information can be used to help elucidate the relative significance of diffusion-mediated mass transfer for solute transport.

References

Brusseau, M.L., 1993. The influence of solute size, pore-water velocity, and intraparticle porosity on solute dispersion and transport in soil. Water Resour. Res. 29, 1071–1080.

Brusseau, M.L., 1998. Multiprocess nonequilibrium and nonideal transport of solutes in porous media. In: Selim, H.M., Ma, L. (Eds.), Physical Nonequilibrium in Soils: Modeling and Application, Ann Arbor Press, Chelsea, MI, Chapter 3.

Brusseau, M.L., Rao, P.S.C., Jessup, R.E., Davidson, J.M., 1989. Flow interruption: a method for investigating sorption nonequilibrium. J. Contam. Hydrol. 4, 233–240.

Brusseau, M.L., Hu, Q., Srivastava, R., 1997. Using flow interruption to identify factors causing nonideal contaminant transport. J. Contam. Hydrol. 24, 205–219.

Brusseau, M.L., Hu, Q., Nelson, N.T., Cain, R.B., 1999. A diffusive tracer-test method for investigating the influence of mass transfer processes on field-scale solute transport. In: Brusseau, M.L., Sabatini, D.A., Gierke, J.S., Annable, M.D. (Eds.), Innovative Subsurface Remediation, American Chemical Society, Washington, DC, Chapter 18.

Callahan, T.J., Reimus, P.W., Bowman, R.S., Haga, M.J., 2000. Using multiple experimental methods to determine fracture/matrix interactions and dispersion of nonreactive solutes in a saturated volcanic tuff. Water Resour. Res. 36, 3547–3558.

Champ, D.R., Moltyaner, G.L., Lapcevic, P.A., Young, J.L., 1985. A downhole column technique for field measurements of transport parameters. Rep. AECL-(8905), At. Energy of Can. Ltd, Chalk River Nucl. Lab., Chalk River, Ont.

Cussler, C.L., 1984. Diffusion: Mass Transfer in Fluid Systems, Cambridge University Press, New York, NY.

Hu, Q., Brusseau, M.L., 1994. The effect of solute size on diffusive–dispersive transport in porous media. J. Hydrol. 158, 305–317.

Hu, Q., Brusseau, M.L., 1995. Effect of solute size on transport in structured porous media. Water Resour. Res. 31, 1637–1646.

Jardine, P.M., O'Brien, R., Wilson, G.V., Gwo, J.P., 1998. Experimental techniques for confirming and quantifying physical nonequilibrium processes in soils. In: Selim, H.M., Ma, L. (Eds.), Physical Nonequilibrium in Soils: Modeling and Application, Ann Arbor Press, Chelsea, MI, Chapter 9.

Jardine, P.M., Sanford, W.E., Gwo, J.P., Reedy, O.C., Hicks, D.S., Riggs, J.S., Bailey, W.B., 1999. Quantifying diffusive mass transfer in fractured shale bedrock. Water Resour. Res. 35, 2015–2030.

Maloszewski, P., Zuber, A., 1993. Tracer experiments in fractured rocks: matrix diffusion and the validity of models. Water Resour. Res. 29, 2723–2735.

Mills, R., 1973. Self-diffusion in normal and heavy water in the range 1–450. J. Phys. Chem. 77 (5), 685–688.

Moltyaner, G.L., Killey, R.W.D., 1988. Twin lake tracer tests: longitudinal dispersion. Water Resour. Res. 24, 1613–1620.

Parker, J.C., Valocchi, A.J., 1986. Constraints on the validity of equilibrium and first-order kinetic transport models in structured soils. Water Resour. Res. 22, 399–407.

Pickens, J.F., Grisak, G.E., 1981. Dispersion in a stratified granular aquifer. Water Resour. Res. 17, 1191–1211.

Tucker, W.A., Nelken, L.H., 1982. Diffusion coefficients in air and water. In: Lyman, W.J., Reehl, W.F., Rosenblatt, D.H. (Eds.), Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds, McGraw-Hill, New York, pp. 17.1–17.25.

Van Genuchten, M.Th., 1981. Nonequilibrium transport parameters from miscible displacement experiments. Research Report No. 119, US Department of Agriculture, US Salinity Lab., Riverside, CA.