Experimental Determination of Effective Diffusion Parameters in the Matrix of Fractured Till

Martin F. Helmke,* William W. Simpkins, and Robert Horton

ABSTRACT

Diffusion is often the dominant mode of solute transport in soils when advection is minimal. This paper describes the application of a radial diffusion cell method to estimate the effective diffusion coefficient (D_e) and effective diffusive porosity (θ_{De}) for use in solute transport models for fractured-porous media. Twenty-four experiments were conducted for 28 d using three conservative solutes (Br, PFBA, and PIPES) on eight late Wisconsinan and Pre-Illinoian till samples from Iowa. The mean value of the total porosity (θ_T) of the till samples was 30.0%. Concentrations of the three tracers in the reservoir decreased with time and eventually approached equilibrium concentrations. A model simulated the observed concentration data and the modified goodness-of-fit (d_1) values ranged from 0.878 to 0.950. Mean values of θ_{De} from the model were 28.3 (Br^-), 26.5 (PFBA), and 21.6% (PIPES) and there were significant differences in θ_{De} among the three tracers ($p = 0.05$). Mean values of D_e were 5.6×10^{-10} m^2 s^{-1} (Br^-), 2.9×10^{-10} m^2 s^{-1} (PFBA), and 1.3×10^{-10} m^2 s^{-1} (PIPES). Values of D_e differed significantly by compound and were significantly different ($p = 0.05$) from the aqueous diffusion coefficient (D_0). Calculated mean values of the first-order mass exchange coefficient (α) were 8.4×10^{-7} (Br^-), 4.1×10^{-7} (PFBA), and 1.6×10^{-7} s^{-1} (PIPES); they differed by compound ($p = 0.05$) and generally decreased with increasing molecular weight of the tracer. This study confirmed that the radial diffusion cell method is an efficient method to estimate effective diffusion parameters necessary to accurately model solute transport in fractured till and soil.

DIFFUSION IS THE predominant mode of solute transport in soils where advection is negligible (Sawatsky et al., 1997). Diffusion may also have a strong influence on solute concentration within mobile pores of a dual porosity medium or in soil of low permeability containing fractures or macropores. A small mass exchange by diffusion from the mobile to the immobile region (or vice versa) is likely to cause a large change in solute concentration within the mobile region (Coats and Smith, 1964). Although diffusion may take place at the pore scale, when diffusion controls the concentration of solutes in the mobile region (e.g., fractures), diffusion may influence concentration tens or hundreds of meters downgradient (McKay et al., 1993). Quantification of solute diffusion is therefore critical to our overall understanding of solute transport, most notably in fractured soils.

Diffusion is a function not only of the solute but also of characteristics of the fractured-porous medium. For example, the tortuosity of pore throats through which a solute diffuses may cause the observed, or *effective* diffusion coefficient (D_e) to be lower than the diffusion coefficient of a compound in water (D_0) (Rao et al., 1980). Moreover, exclusion of a solute from some pore classes may reduce the effective diffusive porosity (θ_{De}), or that portion of a porous medium that is accessible to diffusing molecules (van der Kamp et al., 1996). These effective parameters are likely to be specific to each soil–solute combination, and therefore require direct measurement for the solute and material of interest.

Mathematical solutions to the diffusion problem are well established (Crank, 1975). In addition, models are now capable of simulating solute diffusion coupled with advection through macroporous soil and fractured till (Therrien and Sudicky, 1996; Toride et al., 1999). These models require that effective diffusion parameters be provided as input. Laboratory methods, including the half-cell, the reservoir-cell, and radial diffusion cell, have been proposed for determination of D_e. The most widely used is the half-cell method, where two cells, one spiked with a solute, are pressed together, allowing diffusion to take place (Li and Gregory, 1974; Robin et al., 1987). Work by van Rees et al. (1991), however, demonstrated that the process of sectioning a soil column may cause errors in D_e estimates. As an alternative, they proposed a reservoir-cell method, where a reservoir of water spiked with a solute is allowed to diffuse into an adjacent soil column. This method was shown to be more accurate and less labor intensive than the half-cell method. A review of these and other similar methods is presented by Shackelford (1991) and Flury and Gimmi (2002). A more recent modification to these standard methods is the use of a radial diffusion cell (Novakowski and van der Kamp, 1996; van der Kamp et al., 1996), which consists of a small, cylindrical reservoir drilled into a saturated soil or till core along its axis. The sample reservoir is filled with a solution of known tracer concentration, which is then monitored at discrete times. Effective diffusion parameters (D_e and θ_{De}) are estimated by fitting a radial diffusion model to the time-concentration curve generated from the experiment (Novakowski and van der Kamp, 1996). Among the benefits of the method are (i) ease of sample collection and preparation, (ii) minimal sample disturbance, (iii) no sectioning of the soil sample, and (iv) that an estimate of θ_{De} may be obtained.

We describe a series of experiments on eight samples of unfractured late Wisconsinan and Pre-Illinoian till from Iowa where the radial diffusion cell method was applied to estimate diffusion properties. Diffusion parameters

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Published in Vadose Zone Journal 3:1050–1056 (2004).

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Abbreviations: BTC, breakthrough curve; DML, Des Moines Lobe; IES, Iowa Erosion Surface; MCL, maximum contaminant level; MSEA, Management Systems Evaluation Area; SIDP, Southern Iowa Drift Plain.

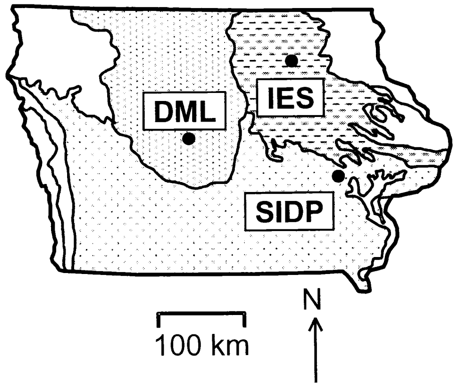

Fig. 1. Map showing the locations of the three study sites on the Des Moines Lobe (DML), Iowan Erosion Surface (IES), and Southern Iowa Drift Plain (SIDP) landform regions. Other mapped landform regions given in Prior (1991).

were used to simulate solute transport through fractured till as part of a larger study (Helmke, 2003; Helmke et al., 2004). The diffusion experiments were conducted under saturated conditions because most of the till sequence (1 to >30 m depth) remains saturated throughout the year in Iowa. By evaluating a variety of till units and tracers, we were able to determine a range for the diffusion parameters and identify their significant differences among the till samples and chemical tracers.

MATERIALS AND METHODS

Description of Sites

Till samples were collected from three separate landform regions of Iowa (Fig. 1). Sites were chosen because they represent some of Iowa's youngest and oldest till units, allowed access to a variety of depths, and because previous studies had established the till stratigraphy and hydrogeology at each site. The Des Moines Lobe (DML) site is located within the Walnut Creek watershed, 7 km south of Ames, IA on the DML landform region (Fig. 1). The Quaternary stratigraphy and hydrogeology of the watershed were previously investigated as part of the Management Systems Evaluation Area (MSEA) program (Seo, 1996; Eidem et al., 1999). The surficial deposit at the DML site (parent material) is the Alden Member till of the Dows Formation, deposited 14 000 to 12 500 yr ago during the late Wisconsinan (Prior, 1991; Eidem et al., 1999). The soil series at the DML site is the Clarion, a Typic Hapludoll and part of the Clarion-Nicollet-Webster soil association.

The Iowa Erosion Surface (IES) site is located 6 km southwest of Nashua, IA and within the Iowan Erosion Surface (Fig. 1). The site was part of the MSEA program to evaluate agricultural impacts on water quality. Previous studies established the till stratigraphy and hydrogeology at the site (Weis and Simpkins, 1996). The primary till unit is the Hickory Hills Member of the Wolf Creek Formation, which is Pre-Illinoian in age and approximately 500 000 yr old (Kemmis et al., 1992). Soil parent material is actually pedisediment derived from late Wisconsinan to Holocene erosion of till. The soil series at the IES site is the Kenyon, a Typic Hapludoll of the Kenyan-Floyd-Clyde soil association.

The Southern Iowa Drift Plain (SIDP) site is located in Coralville, Iowa (Fig. 1). At the SIDP site, the entire 30-m sequence of unconsolidated deposits had recently been removed to provide quarry access to limestone. Stratigraphic studies at the site (Kemmis et al., 1992) report the presence of tills belonging to the Hickory Hills, Aurora, and Winthrop Members of the Wolf Creek Formation (500 000–730 000 yr old), and till of the Alburnett Formation (>730 000 yr old). Peoria Formation loess caps Pre-Illinoian till units at the site. The Fayette–Downs soil association occurs in most of the uplands and the main soil series is the Fayette silt loam, a Typic Hapludalf.

Sample Preparation and Diffusion Cell Construction

Trenches were excavated at the DML and IES sites to depths of 4 and 2.3 m, respectively, to provide access for sample collection and fracture mapping. Only minimal excavation was required at the SIDP site to allow access to undisturbed till. Samples were collected in triplicate from depths between 1 and 27.5 m, and soil properties were characterized (Table 1). Fractures in the till were mapped on sheets of clear acetate at each site, which were used to determine the average fracture spacing (distance between adjacent fractures, $2B$) at each site and depth. To construct the diffusion cell, the till was carved by hand in-situ to produce vertical columns 6.7 cm (diameter) by 7 cm (height) and then encased in a 7-cm-long section of polyvinyl chloride (PVC) casing with an interior diameter of 7.65 cm. Although our prime objective in this study was to examine matrix diffusion in fractured till, we avoided collecting till samples with obvious fractures to observe diffusion in the matrix only. Paraffin wax was poured into the annulus between the sample and the casing. Upon removal from the excavation trench, each sample was sealed totally in paraffin wax and submerged in ambient groundwater to prevent disturbance and desaturation during transport to the laboratory.

In the laboratory, the ends of each sample (≈1 cm) were removed, reducing the length to about 5 cm. We used the method of van der Kamp et al. (1996) to construct the radial diffusion cells (Fig. 2). The column ends were first sealed with a layer of paraffin wax about 0.5 cm thick. The base of each column was capped by an end plate of high-density polyethyl-

Table 1. Location, depth, stratigraphic classification, status of weathering (WTH), bulk density (ρ_b), and texture for eight till samples collected for this study.

Sample	Site†	Depth	Formation, member	WTH‡	ρ_b	Sand	Silt	Clay
		m			Mg m^{-3}		%	
ALG	DML	1.0	Dows, Alden	W	1.67	49.3	35.3	15.4
ALT	DML	2.0	Dows, Alden	W	1.84	52.1	33.5	14.4
BEM	DML	3.3	Dows, Alden	PW	1.83	50.7	34.5	14.8
H1	IES	1.3	Wolf Creek, Hickory Hills	W	1.82	41.2	31.3	27.5
H2	IES	1.5	Wolf Creek, Hickory Hills	W	1.86	46.6	30.7	22.7
AO	SIDP	10.5	Wolf Creek, Aurora	W	1.82	39.9	35.6	24.5
AT	SIDP	16.5	Wolf Creek, Aurora	PW	1.89	33.5	39.1	27.4
ALB	SIDP	27.5	Alburnett, N/A	U	2.01	33.5	43.1	23.4

† DML, Des Moines Lobe; IES, Iowan Erosion Surface; SIDP Southern Iowa Drift Plain landform regions.
‡ W, weathered; PW, partially weathered; U, unweathered.

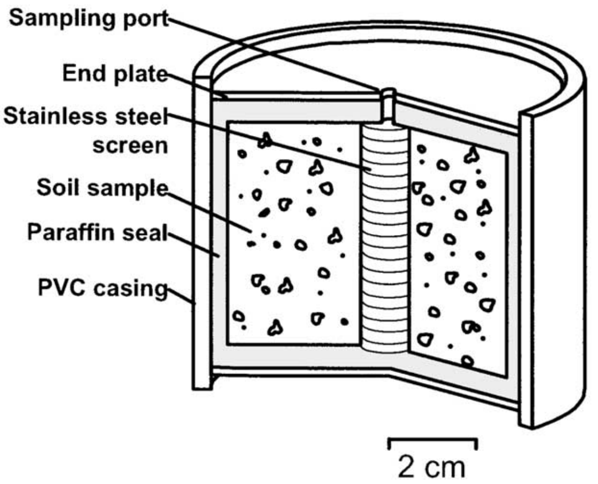

Fig. 2. Schematic diagram of the diffusion cell apparatus.

ene. A 1.2-cm-diameter reservoir was then drilled by hand into the center of each sample. Number 304 stainless-steel screens with a mesh opening of 1.1 mm were formed into 1.2-cm-diameter tubes and placed into the sample reservoirs to prevent sidewall collapse. The top of each sample was capped by an end plate with a hole in the center (2-mm diameter) to provide access to the sample reservoir. This access port was sealed with a removable rubber septum to minimize evaporation. The sample chambers were filled with ambient groundwater (the reservoir fluid) collected from each site and allowed to equilibrate for 1 mo before the experiment. Although the soil samples remained largely saturated after collection, small volumes of reservoir fluid (<0.1 mL per sample) were added during the equilibration period until the samples were fully saturated. The diffusion cells were partially submerged in a water bath to further reduce the chance of evaporation. The pH values of the ambient groundwater ranged from 7.5 to 7.7, which are typical of the HCO_3–rich (250–1 119 mg L^{-1}) groundwater in these tills.

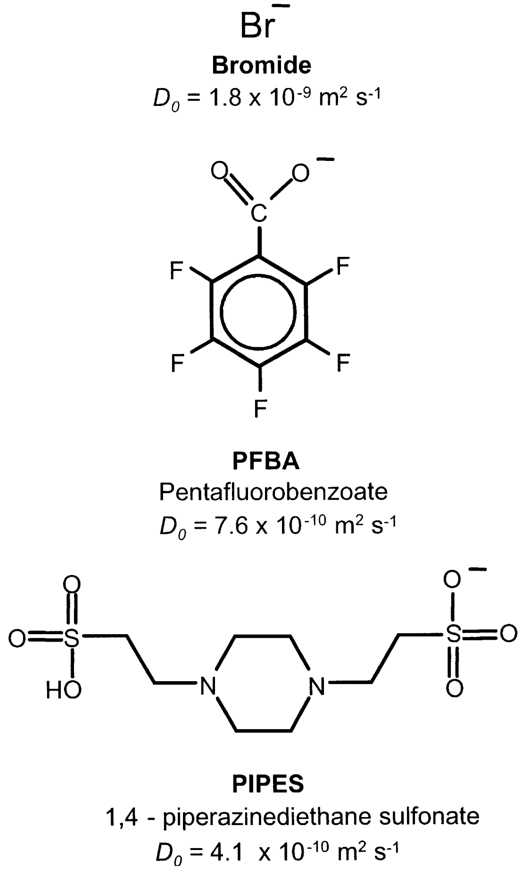

Fig. 3. Molecular structure and aqueous diffusion coefficient (D_0) for Br^-, PFBA, and PIPES.

Diffusion Cell Experiments

Twenty-four experiments were conducted, consisting of three replicates of eight soil samples. Three tracer compounds were added simultaneously during each experiment: KBr (potassium bromide), PFBA (pentafluorobenzoic acid), and PIPES (1, 4-piperazine-diethanesulfonic acid disodium salt) (Fig. 3). Bromide has traditionally been used as a tracer because it is conservative in most soils, is rarely present in natural soil water, and may be analyzed by ion chromatography or by ion-selective electrode. PFBA possesses similar conservative properties, yet can be distinguished from Br^- by ion chromatography (Bowman and Gibbens, 1992). In a study of solute transport through soil derived from DML till in Central Iowa, Jaynes (1993) concluded that PFBA behaved as a nonsorbing and nondegrading tracer, similar to Br^-. Although fluorobenzoates have been shown to sorb under acidic conditions (Boggs and Adams, 1992), it is unlikely that PFBA would sorb to the soils evaluated in this study because their pH values (7.5–7.7) are greater than the pK_a of PFBA (2.7; Bowman and Gibbens, 1992). PIPES is a biological buffer that was designed to minimize cation sorption and biological reactions under neutral pH (the pK_a of PIPES is 6.8 according to Good et al., 1966). Recent studies have demonstrated that PIPES behaves as a nonsorbing and conservative tracer in soils with neutral pH similar to this study (Jardine and Taylor, 1995; Moline et al., 2001; Mayes et al., 2003). Additional benefits of PIPES are that it is has an aqueous diffusion coefficient (D_0) approximately one-fifth that of Br^-, and it may be analyzed by ion chromatography. The tracers Br^- and PFBA show D_0 values of 1.8×10^{-9} and 7.6×10^{-10} m^2 s^{-1} (at 25°C), respectively (Bowman and Gibbens, 1992). A value for D_0 has not been determined for PIPES and was calculated by the Stokes–Einstein equation (Einstein, 1905):

$$D_0 = \frac{kT}{6\pi\mu r} \qquad [1]$$

where k is the Boltzman Constant, T is temperature, μ is viscosity, and r is the molecular radius (6.0×10^{-10} m for PIPES). Using Eq.[1], the D_0 for PIPES at 25°C was determined to be 4.1×10^{-10} m^2 s^{-1}.

Ambient site groundwater spiked with three tracers to an initial concentration of 0.5 mM (C_0) was used to replace the initial groundwater in the cell reservoir. This concentration is equivalent to 39.95 mg L^{-1} Br^-, 106.04 mg L^{-1} PFBA, and 167.69 mg L^{-1} PIPES. Because of the low hydraulic conductivity of the till matrix ($<10^{-10}$ m s^{-1}), the reservoir fluid could be removed using a syringe and quickly replaced without fear of desaturating the soil sample or causing advection within the matrix. Aliquots were withdrawn nine times during a period of 28 d during the experiment and were kept small (0.1 mL) to minimize changes in reservoir concentration. An equal volume of tracer-free groundwater (0.1 mL) was returned to the reservoir after sampling. After sampling, the reservoir fluid was gently stirred to homogenize the concentration within the reservoir. Samples were stored at 4°C and analyzed together at the end of the experiment. Concentrations of all tracers were determined by ion chromatography. Analytical precision was determined for Br^- (±0.63 mg L^{-1}), PFBA (±1.14 mg L^{-1}), and PIPES (±2.65 mg L^{-1}) by analyzing replicates of spiked samples with the Student's *t* distribution (Harris, 1991).

Estimates of Parameters

Effective diffusion parameters were estimated by fitting the radial diffusion model of Novakowski and van der Kamp (1996) to the experimental results. The model calculates solute concentration in the sample reservoir as a function of time, and includes diffusion, equilibrium adsorption, and first-order mass loss. The governing equation for radial diffusion is

$$\frac{\partial c}{\partial t} = \frac{D_e \partial^2 c}{R \partial r^2} + \frac{D_e \partial c}{R r \partial r} - \frac{\lambda}{R} c \qquad [2]$$

where *c* is solute concentration, *t* is time, *r* is distance from the cell center, *R* is the retardation factor, and is the first-order degradation coefficient (Novakowski and van der Kamp, 1996). The solution to Eq. [2] (Eq. [8] in Novakowski and van der Kamp, 1996) uses a Laplace transform method and assumes an equilibrium initial condition and a no-diffusion boundary at the outer edge of the diffusion cell. The boundary conditions of the radial diffusion cell necessitate a Laplace inversion algorithm to solve Eq. [2]; hence, the Stehfest (1970) algorithm was used for the inversion. The Novakowski–van der Kamp solution was fit to the experimental results using the Levenberg–Marquardt algorithm (Marquardt, 1963). In theory, this approach provides estimates of D_e, θ_{De}, R, and λ. In practice, however, the effect of sorption and degradation might be mistaken for diffusion, which would produce nonunique estimates of D_e and θ_{De} (Novakowski and Van der Kamp, 1996). Hence, only conservative compounds were evaluated in this study.

Statistical Analysis

The goodness-of-fit of the diffusion model to observed data was evaluated using root mean square error (RMSE), coefficient of determination (R^2), and the modified index of agreement, d_1 (Willmott et al., 1985). The parameter d_1 is given by

$$d_1 = 1.0 - \frac{\sum_{i=1}^{n} |O_i - P_i|}{\sum_{i=1}^{n} \left(|P_i - \overline{O}| + |O_i - \overline{O}|\right)} \qquad [3]$$

where O and P are the observed and model-simulated data, $\overline{O}$ is the mean value of observations, and n is the number of observations. The value of d_1 varies from 0 to 1, with 1 indicating a perfect fit between the simulated and observed data. Therefore, d_1 may be interpreted similarly to R^2, although d_1 is considered superior to R^2 because it is less sensitive to outliers and is sensitive to additive and proportional differences (unlike R^2). The d_1 approach has been applied elsewhere to evaluate the goodness-of-fit of hydrologic models (Legates and McCabe, 1999) and has provided results superior to the other methods in a related study (Helmke et al., 2004); hence, d_1 alone is presented here.

Confidence intervals for D_e, θ_{De}, and α were calculated using a one-sample, two-tailed, *t* statistic, assuming a normal distribution (Helsel and Hirsch, 1992). For comparisons between samples, however, the nonparametric Mann–Whitney and Kruskal–Wallis tests were used to identify significant differences among samples and tracers (Conover, 1980). The Wilcoxon signed-rank test was also used to test for significance differences between D_e and D_o for each tracer (Helsel and Hirsch, 1992).

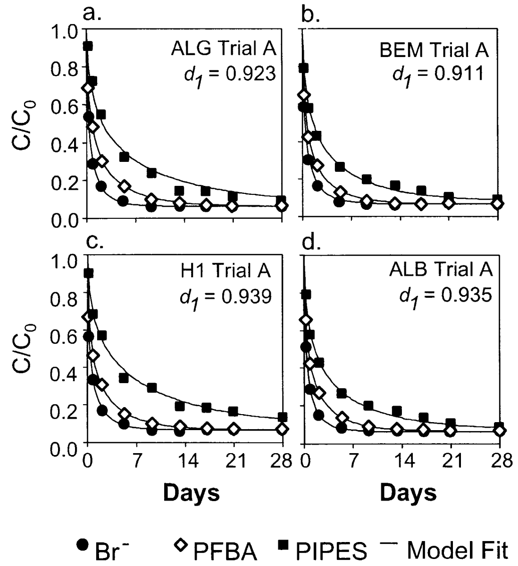

Fig. 4. Time-concentration plots for Br^-, PFBA, and PIPES taken from four representative radial diffusion cell experiments.

RESULTS AND DISCUSSION

Observed and Modeled Results

Concentrations of the three tracers decreased with time and approached equilibrium concentrations near the end of the 28-d experiment (Fig. 4). In all cases, the rate of concentration decline of Br^- was the most rapid, followed by PFBA, then PIPES. The rate of concentration decrease was inversely proportional to the D_0 of each compound. The tracers Br^-, PFBA, and PIPES reached a relative concentration of approximately 0.1 by the end of each experiment; however, the equilibrium concentrations of Br^- and PFBA at that point were slightly lower than that of PIPES, indicating that θ_{De} for PIPES is less than that for Br^- or PFBA. The radial diffusion model provided excellent fits to the observed data, and d_1 values ranged from 0.87 to 0.95 (Table 2). In short, diffusion occurred in the till, the experiments proceeded according to established theory, and the radial diffusion model was applied to provide estimates of effective diffusion parameters.

Total and Effective Diffusive Porosity

Values of θ_T varied between 28.7 and 31.2%, with an overall mean value of 30.0% (Table 3). These values are

Table 2. Goodness-of-fit of simulated to observed data as indicated by the value of d_1 (modified index of agreement) for each sample and tracer. The 95% confidence interval for each tracer is shown in parentheses.

	d_1		
Sample	**Br^-**	**PFBA**	**PIPES**
ALG	**0.949**	**0.945**	**0.878**
ALT	**0.947**	**0.946**	**0.932**
BEM	**0.912**	**0.918**	**0.935**
H1	**0.940**	**0.950**	**0.933**
H2	**0.930**	**0.942**	**0.931**
AO	**0.950**	**0.945**	**0.951**
AT	**0.934**	**0.938**	**0.941**
ALB	**0.944**	**0.950**	**0.915**
Overall (n = 24)	**0.943** **(0.932–0.945)**	**0.943** **(0.939–0.947)**	**0.932** **(0.915–0.936)**

Table 3. Mean and 95% confidence interval (parentheses) for total porosity (θ_T), effective diffusive (θ_{De}) porosity, effective diffusion coefficient (D_e), and first-order mass exchange coefficient (α) for Br, PFBA, and PIPES. Values represent three replicates. Fracture spacing ($2B$) is from field measurements at sample locations (Helmke et al., 2004).

			θ_{De} (%)			D_e			α		
Sample	θ_T	$2B$	Br^-	PFBA	PIPES	Br^-	PFBA	PIPES	Br^-	PFBA	PIPES
	%	cm	%			$\times 10^{-10}$ m² s⁻¹			$\times 10^{-7}$ s⁻¹		
ALG	29.9 (29.0–30.7)	4.3	30.0 (28.1–31.8)	28.5 (26.4–30.6)	24.6 (21.6–27.6)	5.4 (4.9–6.0)	3.1 (0.9–5.2)	1.5 (0.0–3.2)	10.5 (10.1–11.0)	5.6 (2.0–9.2)	2.4 (0.0–4.8)
ALT	30.6 (28.5–32.7)	4.6	29.1 (25.8–32.3)	29.2 (28.9–29.6)	22.9 (22.8–23.1)	5.0 (4.0–5.87)	1.9 (1.4–2.4)	0.79 (0.7–0.9)	8.2 (7.6–8.7)	3.1 (2.3–4.0)	1.0 (1.0–1.1)
BEM	29.6 (28.1–31.1)	4.3	26.9 (24.4–29.4)	25.2 (20.3–30.1)	21.5 (20.2–22.7)	5.8 (4.8–6.7)	3.5 (2.5–4.5)	1.7 (1.4–1.9)	10.0 (9.4–1.1)	5.6 (5.0–6.2)	2.3 (2.0–2.6)
H1	31.2 (30.2–32.2)	3.8	29.1 (28.3–30.0)	29.8 (24.9–34.7)	23.7 (17.7–29.7)	6.4 (5.6–7.1)	2.7 (2.0–3.5)	1.4 (0.9–1.9)	15.4 (13.1–17.6)	6.8 (5.7–7.8)	2.7 (2.4–3.0)
H2	30.8 (27.5–34.0)	6.8	27.1 (22.2–31.9)	24.1 (20.7–27.6)	18.6 (15.6–21.6)	5.7 (3.2–8.2)	3.0 (2.4–3.6)	1.7 (1.1–2.3)	4.0 (3.0–4.9)	1.9 (1.7–2.0)	0.82 (0.66–0.97)
AO	30.5 (27.6–33.4)	3.4	31.0 (27.9–34.1)	29.1 (26.4–31.9)	23.7 (20.5–26.9)	5.3 (4.3–6.3)	2.8 (1.6–3.9)	1.3 (0.2–2.3)	17.1 (15.6–18.5)	8.4 (4.3–12.4)	3.2 (0.2–6.1)
AT	28.9 (27.9–29.7)	17.8	24.7 (21.7–27.7)	21.0 (19.1–23.0)	18.6 (17.1–20.1)	6.3 (4.2–8.4)	3.2 (2.8–3.7)	1.1 (1.0–1.1)	0.59 (0.46–0.72)	0.26 (0.24–0.27)	0.075 (0.070–0.079)
ALB	28.7 (28.2–29.0)	10.4	28.7 (25.5–31.9)	25.3 (20.2–30.4)	19.5 (16.0–23.1)	5.1 (4.3–5.9)	3.0 (1.8–4.2)	1.1 (0.6–1.6)	1.6 (1.4–1.8)	0.82 (0.67–0.98)	0.23 (0.16–0.30)
Overall	30.0 (29.6–30.5)	6.9 (2.8–11.1)	28.3 (27.4–29.2)	26.5 (25.2–27.9)	21.6 (20.5–22.7)	5.6 (5.3–5.9)	2.9 (2.6–3.1)	1.3 (1.1–1.5)	8.4 (6.0–10.9)	4.1 (2.8–5.3)	1.6 (1.1–2.1)

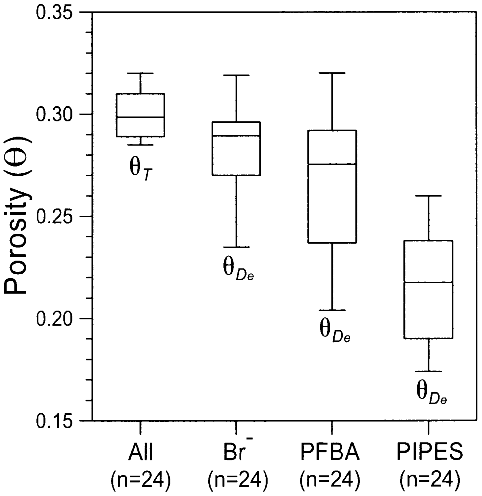

Fig. 5. Standard boxplots (Helsel and Hirsch, 1992) of total porosity (θ_T) and effective diffusive porosity (θ_{De}) for Br^-, PFBA, and PIPES. Median values of θ_{De} are significantly different from each other and from θ_T ($\alpha = 0.05$) and decrease with increasing molecular weight of the tracer.

typical for the till and comparable to those determined from the large till columns (Helmke et al., 2004). In contrast, θ_{De} ranged from 24.7 to 31.0, 25.3 to 29.8, and 18.6 to 24.6% for Br^-, PFBA, and PIPES, respectively (Table 3), with overall means of 28.3 (Br^-), 26.5 (PFBA), and 21.6% (PIPES). Significant differences were noted in values of θ_{De} ($p = 0.05$) among the till samples as shown by the Kruskal–Wallis test; however, comparison of paired samples with the Mann–Whitney test failed to show those differences. For all till samples ($n = 24$), values of θ_{De} were significantly different among the tracers and all were significantly less than values of θ_T ($p = 0.05$). The deviation of θ_{De} from θ_T increased with the increase in tracer weight, with PIPES showing the smallest θ_{De} values (Fig. 5), suggesting a compound-specific influence on diffusion. Meegoda and Gunasekera (1992) reported that θ_{De} was smaller for heavier compounds (propanol and glycerol) than lighter compounds (acetone), similar to what was observed for the heavier PIPES compound in our experiments. Van der Kamp et al. (1996) reported values of θ_{De} for chloride and sulfate ions were less than θ_T values. Although θ_{De} was significantly less (statistically) than θ_T values in most cases, this difference was smaller than the 50% difference between θ_{De} and θ_T reported by Meegoda and Gunasekera (1992) and van der Kamp et al. (1996). Those authors attributed differences between θ_{De} and θ_T to isolated pores, bound water, and ion exclusion that are perhaps more typical of the clayey materials they investigated than the loamy till investigated here.

Effective Diffusion Coefficient

Values of D_e ranged from 5.0 to 6.4 $\times 10^{-10}$, 1.9 to 3.5 $\times 10^{-10}$, and 0.79 to 1.7 $\times 10^{-10}$ m² s⁻¹ for Br^-, PFBA, and PIPES, respectively (Table 3, Fig. 6). Overall mean values were 5.6 $\times 10^{-10}$ m² s⁻¹ (Br^-), 2.9 $\times 10^{-10}$ m² s⁻¹ (PFBA), and 1.3 $\times 10^{-10}$ m² s⁻¹ (PIPES). The Kruskal–Wallis test indicated that there were no significant dif-

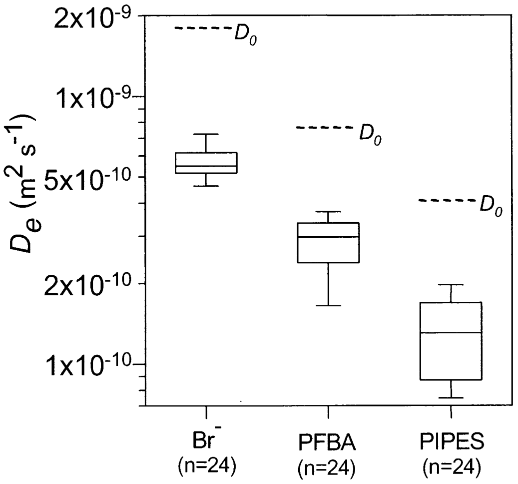

Fig. 6. Standard boxplots showing the effective diffusion coefficient (D_e) for Br$^-$, PFBA, and PIPES. Median values are significantly different ($\alpha = 0.05$) and decrease with increasing molecular weight of the tracer. Dotted lines indicate values of the aqueous diffusion coefficient (D_0) for the tracers.

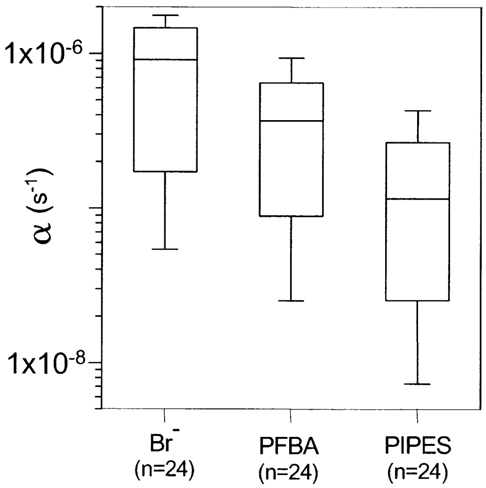

Fig. 7. Standard boxplots showing the mass exchange coefficient (α) for Br$^-$, PFBA, and PIPES. Median values are significantly different ($\alpha = 0.05$) and decrease with increasing molecular weight of the tracer.

ferences in D_e (Table 3) among the till samples within a single tracer ($p = 0.05$). This was not unexpected because D_e is most influenced by a significant difference in pore structure (Mehta et al., 1995) and all the tills evaluated in this study were similar in texture (loam) and porosity (Tables 1 and 3). However, when all samples ($n = 24$) were grouped by tracer, D_e values for the three tracers were significantly different from each other and appear to decrease with increasing molecular weight of the tracer. The D_e values were also significantly less ($p = 0.05$) than their respective D_0 values of 1.8×10^{-9} m^2 s^{-1} (Br$^-$), 7.6×10^{-10} m^2 s^{-1} (PFBA), and 4.1×10^{-10} m^2 s^{-1} (PIPES). The mean tortuosity factors (τ, calculated as mean D_e/D_0) for these compounds are 0.311, 0.382, and 0.317, respectively. These values indicate that tortuosity plays an important role in diminishing D_e and emphasize the need for compound- and site-specific experiments to accurately estimate this diffusion parameter.

Mass-Exchange Coefficient

Whereas diffusion parameters D_e and θ_{De} are required for models that simulate diffusion as a second-order process (Helmke et al., 2004), mobile–immobile models, such as those proposed by Coats and Smith (1964), Sudicky (1989), van Genuchten and Wagenet (1989), and Toride et al. (1999), require a first-order mass exchange coefficient (α) and the porosity of the immobile region (θ_{im}). Our experiments allow direct estimates of α from D_e and θ_{De} through the equation:

$$\alpha = \frac{aD_e\theta_{im}}{l^2} \qquad [4]$$

where a is a shape factor, θ_{im} is the immobile porosity (represented here by θ_{De}), and l is a characteristic length (van Genuchten, 1985; Parker and Valocchi, 1986; Sudicky, 1990). Equation [4] can be applied to a system of equally spaced, parallel fractures (Sudicky, 1990) and to spherical soil aggregates (Rao et al., 1980). Due to the efficiency of models that use a first-order diffusion approach, these models are particularly well suited for field-scale simulations of advection and diffusion through fractured till. For this study, the matrix blocks were assumed to be prismatic slabs (requiring a shape factor of 3 as proposed by van Genuchten, 1985) of width equal to the fracture spacing ($2B$). Therefore, parameters a and l were set equal to 3 and B, respectively, in Eq. [4].

Values of α ranged from 5.9×10^{-8} to 1.5×10^{-6} s^{-1} (Br$^-$), 2.6×10^{-8} to 8.4×10^{-7} s^{-1} (PFBA), and 7.5×10^{-9} to 2.7×10^{-7} s^{-1} (PIPES), with mean values of 8.4×10^{-7}, 4.1×10^{-7}, and 1.6×10^{-7}s^{-1} for the three tracers, respectively (Table 3). Again, some significant differences in α occurred among the samples for a single tracer ($p = 0.05$), as indicated by the Kruskal–Wallis test. However, differences between paired samples were not apparent in the Mann–Whitney test. Values of α were significantly different from each other ($p = 0.05$) when grouped by tracer, and a similar trend of decreasing α with greater molecular weight of the tracer is also shown (Fig. 7).

CONCLUSIONS

Experiments conducted with tracers in eight till samples indicated that diffusion was the primary process of solute transport in the radial diffusion cells. Agreement between observed and modeled tracer concentration during a 28-d period shows that the radial diffusion model provides an accurate and efficient method for obtaining effective diffusion parameters, D_e and θ_{De}, in till. In all cases, effective diffusion parameters D_e and θ_{De} decreased in value with the molecular weight of the compound. Estimates of D_e from the experiments were significantly less than D_0, suggesting that D_e is worth estimating to increase model accuracy. This reduction of D_e is most likely the result of tortuosity in the till, assuming that the conservative tracers used in this study were nonsorbing. The first-order mass exchange coefficient, α, was calculated directly from D_e, θ_{De}, and field parameters (i.e., fracture spacing). Not surprisingly, α decreased as tracer weight increased. However, α is also sensitive to the internal geometry of the material, which can only be ascertained through a field investigation. Whether diffusion is a controlling process in till or soil depends on the presence of other solute transport mechanisms (e.g., advection and dispersion) that may overwhelm it.

ACKNOWLEDGMENTS

This research was funded by grants from the American Geophysical Union (Horton Grant), Association of Ground Water Scientists and Engineers, Geological Society of America, Sigma Xi, USDA, and USEPA through an Interagency Agreement DW12036252 to the Agricultural Research Service. We thank Phil Jardine and Gerilynn Moline for the suggestion of using PIPES as a tracer and Garth van der Kamp for suggesting the use of the radial diffusion cell method. The authors appreciate the constructive comments of Boris Faybishenko and two anonymous reviewers.

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