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The effect of solute size on diffusive–dispersive transport in porous media

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Abstract

The purpose of this work was to investigate the effect of solute size on diffusive–dispersive transport in porous media. Miscible displacement experiments were performed with tracers of various sizes (i.e. tritiated water ($^3\text{H}_2\text{O}$), pentafluorobenzoate (PFBA), and 2,4-dichlorophenoxyacetic acid (2,4-D)) and a homogeneous, nonreactive sand for pore-water velocities varying by three orders of magnitude (70, 7, 0.66, and 0.06 cm h^{-1}). Hydrodynamic dispersion is the predominant source of dispersion for higher pore-water velocities (exceeding 1 cm h^{-1}), and dispersivity is, therefore, essentially independent of solute size. In this case, the practice of using a small-sized tracer, such as $^3\text{H}_2\text{O}$, to characterize the dispersive properties of a soil is valid. The contribution of axial diffusion becomes significant at pore-water velocities lower than 0.1 cm h^{-1} . At a given velocity below this value, the contribution of axial diffusion is larger for $^3\text{H}_2\text{O}$, with its larger coefficient of molecular diffusion, than it is for PFBA and 2,4-D. The apparent dispersivities are, therefore, a function of solute size. The use of a tracer-derived dispersivity for solutes of different sizes would not be valid in this case. For systems where diffusion is important, compounds such as PFBA are the preferred tracers for representing advective–dispersive transport of many organic contaminants of interest.

1. Introduction

An understanding of how solutes move in porous media is essential to the development of sound strategies for managing contaminants in the environment. Diffusive and dispersive flux is often an important component of solute transport. Dispersion is usually considered as the sum of hydrodynamic dispersion (mechanical mixing) and axial diffusion (movement in response to a longitudinal concentration gradient). The relative importance of hydrodynamic dispersion and axial diffusion in transport

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through porous media has been discussed by many workers (e.g. Biggar and Nielsen, 1962; Perkins and Johnston, 1963; Bear, 1969; Fetter, 1993). At low flow velocities, diffusive flux can be a major contributor to total solute transport. For these conditions, solute size (i.e. magnitude of the diffusion coefficient) may be expected to influence the relative importance of axial diffusion (Brusseau, 1993).

Handy (1959) first employed the double tracer method to evaluate the effect of solute size on advective–dispersive transport. He reported no significant difference in breakthrough curves for methanol and sucrose at flow velocities of 20 and 0.6 cm h⁻¹. Klotz and Moser (1974) investigated the dispersive transport of several tracers, including chloride, bromide and uranin, through sand. Similarly to Handy's study, no effect of solute size was observed. However, in both cases the pore-water velocities were higher than 0.5 cm h⁻¹, which generally precludes a significant contribution of axial diffusion. Thus, the negligible impact of solute size is expected. Nielsen and Biggar (1963) and Corey et al. (1963) investigated ³H₂O and chloride transport through sand and sandstone at pore-water velocities down to 0.122 cm h⁻¹. It was found that axial diffusion contributed a significant amount to total dispersion during displacement at the lowest pore-water velocities. However, little difference was observed between ³H₂O and chloride, which is to be expected as these two solutes have similar diffusion coefficients. Similar results were reported by Gerritse and Singh (1988). We have found no experiments that investigated the influence of solute size (e.g. where aqueous diffusion coefficients differed by more than a factor of two) on dispersive transport for conditions where axial diffusion was significant (e.g. pore-water velocity lower than 0.1 cm h⁻¹).

The effect of solute size on dispersive flux is of special concern for the sound interpretation of solute transport experiments. Miscible displacement experiments are usually performed with one or more nonsorbing, nonreactive solutes, such as ³H₂O or chloride, to characterize advective–dispersive transport. The dispersion-related parameter obtained with these tracers is thereafter used in the analysis of experimental results obtained for all other solutes, irrespective of solute characteristics such as size, shape, and chemical reactivity. A major assumption inherent in this approach is that dispersive flux will be the same for all solutes. For this to be true, hydrodynamic dispersion must be the only mechanism contributing to dispersive flux. As many reactive organic solutes of interest are larger than typical tracers (e.g. ³H₂O, and chloride), it is important to know if and when solute size has an effect on solute dispersion.

Clay liners and barriers are examples of field-scale systems for which diffusion may be important. Clay liners (such as soil–bentonite barriers) are frequently employed at waste disposal sites as a means of minimizing the potential for groundwater contamination. Design guidelines for clay liners commonly specify that they should have a hydraulic conductivity less than 10⁻⁷ cm s⁻¹, so that the rate of advective transport will be small. However, even when advection is minimal, contaminants can migrate at significant rates through clay barriers by diffusion (Johnson et al., 1989; Mott and Weber, 1991). Vadose-zone systems are another example of a case where flow rates are typically small enough such that axial diffusion can be important.

This paper is specifically concerned with the effect of pore-water velocity and solute size on solute diffusion and dispersion in a homogeneous porous medium. Three tracers (tritiated water ($^3\text{H}_2\text{O}$), pentafluorobenzoate (PFBA), and 2,4-dichlorophenoxyacetic acid (2,4-D)) are used in miscible-displacement experiments to evaluate the impact of differences in aqueous diffusion coefficients on diffusion and dispersion over a wide range of pore-water velocities.

2. Materials and methods

2.1. Materials

Pure silica-glass beads (212–300 μm in diameter) were selected and used for all experiments to minimize fluid–solid and solute–solid interactions. The beads were soaked in 6 N HCl for 1 day and then washed with deionized water from a NANOpure ultrapure water system (Du Pont, Boston, MA) until acid free. $^3\text{H}_2\text{O}$ and ^{14}C -labeled 2,4-D were purchased from DuPont and Sigma Chemical Co. (St. Louis, MO), respectively. Analytical-grade PFBA and 2,4-D were purchased from Aldrich Chemical Co. (Milwaukee, WI).

Preparative chromatography columns made of precision-bore borosilicate glass (2.5 cm i.d., 5.0 cm in length, Kontes (Vineland, NJ)) or precision-bore stainless steel (2.1 cm i.d., 7.0 cm in length, Alltech Associates (Deerfield, IL)) were used in the experiments. The columns are designed to have a minimum void volume in the endplates. The measured dead volumes were used to determine the corrected pore volumes of the columns, i.e. the volume of water associated with the porous media.

2.2. Experimental procedures

The columns were packed in incremental steps with the dry glass beads to establish uniform bulk density. After packing, the columns were slowly wetted from the bottom with electrolyte solution (0.01 N CaCl_2). After saturation was achieved, about 100 pore volumes of solution were pumped through the columns to condition them to the electrolyte solution. Bulk densities for the glass and stainless-steel columns were 1.62 g cm^{-3} and 1.67 g cm^{-3} , respectively; the volumetric water contents were $0.38\text{--}0.39 \text{ cm}^3 \text{ cm}^{-3}$.

The apparatus and methods employed for the miscible displacement studies were similar to those used by Brusseau et al. (1990). One single-piston high-performance liquid chromatography (HPLC) pump (Gilson Medical Electronics, Model 305, Gilson, Middleton, WI) was connected to the column, with a three-way switching valve placed in-line to facilitate switching between solutions with and without the solute of interest. The system was designed so that the solute contacted only stainless steel, glass, or Teflon. Although Teflon tubing was found to sorb some organic solutes, no interaction was observed for PFBA and 2,4-D. The dual-tracer approach was used to facilitate direct comparison of results for PFBA and $^3\text{H}_2\text{O}$. A flow-through, variable-wavelength UV detector (Gilson, Model 115, Gilson, Middleton,

WI) was used to monitor continuously concentrations of PFBA or 2,4-D in the column effluent. Output was recorded on a strip-chart recorder (Fisher, Tustin, CA; Recordall Series 5000). A wavelength of 235 nm was used for PFBA and 2,4-D analysis. After passing through the UV detector, column effluent fractions were collected with an automated fraction collector (ISCO, Inc., Lincoln, NE, Foxy 200). The activities for $^3\text{H}_2\text{O}$ or ^{14}C -labeled 2,4-D in the effluent samples were analyzed by radioassay using liquid scintillation counting (Packard, Tri-Carb Liquid Scintillation Analyzer, Model 1600TR, Packard, Meriden, CT).

Specific activity of tritium and ^{14}C -labeled 2,4-D in the displacing solution was 5 nCi ml^{-1} and 2.5 nCi ml^{-1} , respectively. Four flow rates, 1.5, 0.15, 0.015, and 0.0015 ml min^{-1} , were used for the experiments. They correspond to pore-water velocities of 70, 7, 0.66 and 0.06 cm h^{-1} for the stainless-steel column for which breakthrough curves are reported. Almost all of the experiments were replicated in two columns.

2.3. Data analysis

The equation used to describe one-dimensional advective–dispersive transport of solute in a homogeneous porous medium under conditions of steady-state water flow is (see Freeze and Cherry, 1979)

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} \quad (1)$$

where C is concentration of solute in solution (M L^{-3}), x is distance, ν is average pore-water velocity ($\nu = q/\theta_T$, where q is Darcy flux and θ_T is volumetric water content) (L T^{-1}), t is time (T), $R(1 + (\rho/\theta_T K_p))$ is the retardation factor, K_p is the equilibrium sorption constant ($\text{L}^3 \text{M}^{-1}$) and D is the longitudinal dispersion coefficient ($\text{L}^2 \text{T}^{-1}$). The results of the miscible displacement experiments were analyzed by using a non-linear, least-squares optimization program (Van Genuchten, 1981) to solve the non-dimensional form of (1), giving values for Peclet number ($P = \nu L/D$) and retardation factor with 95% confidence intervals.

The dispersion coefficient is usually defined as

$$D = \frac{D_0}{T} + \alpha_L \nu^n \quad (2)$$

where D_0 is the diffusion coefficient of the solute in water ($\text{L}^2 \text{T}^{-1}$), T is the tortuosity factor (greater than unity), n typically varies from 1.0 to 1.3, and α_L is the longitudinal dispersivity (L), which is considered a characteristic of the porous medium. The $\alpha_L \nu^n$ term is the contribution of hydrodynamic dispersion and D_0/T is the contribution of axial diffusion. At higher pore-water velocities where diffusion effects are negligible, Eq. (2) reduces to

$$D = \alpha_L \nu^n \quad (3)$$

This form of the dispersion coefficient is often used even when axial diffusion or other diffusion-controlled mechanisms are significant. In these cases, the dispersivity becomes a lumped term that will be a function of pore-water velocity, solute size, and other factors (see Passioura, 1971; Brusseau, 1993).

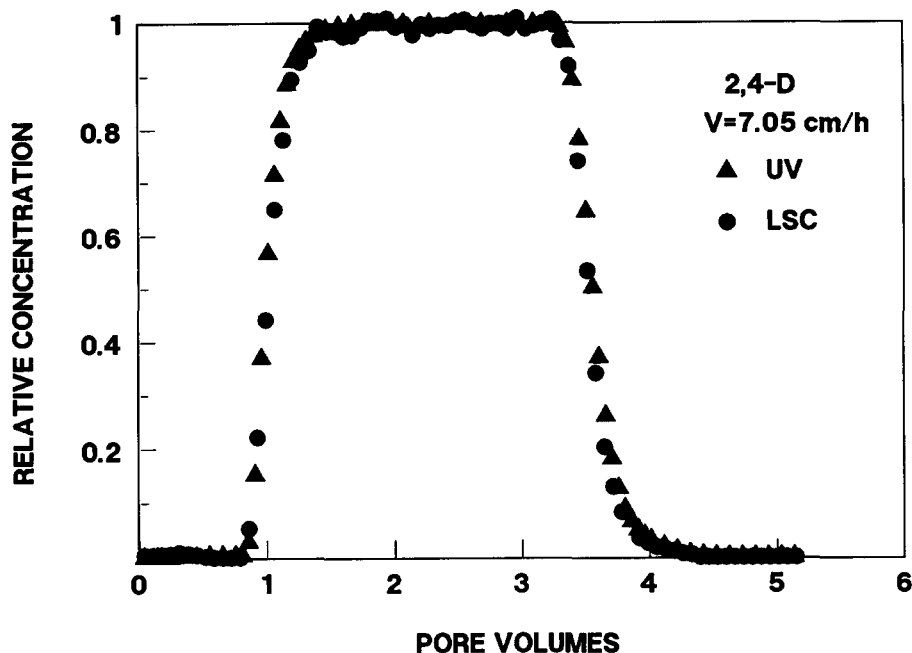


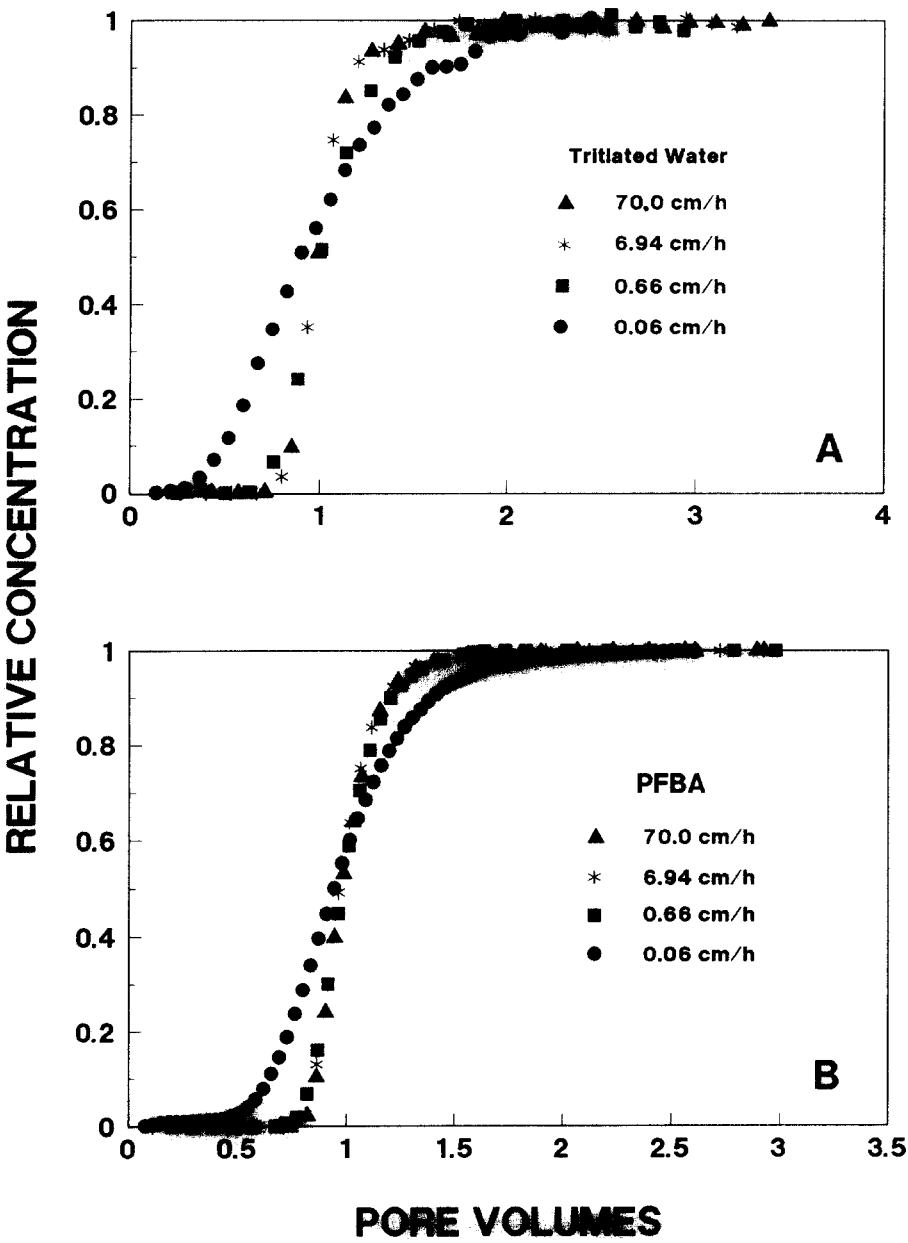
Fig. 1. Comparison of 2,4-D breakthrough curves measured by two detection methods at pore-water velocity of 7.05 cm h^{-1} . UV: UV flow-through detection; LSC: liquid scintillation counting measurement.

3. Results and discussion

3.1. Effect of pore-water velocity

The analysis for the dual-tracer experiments involved two detection methods coupled in series. Therefore, the performance of the flow-through and effluent fraction detection methods was evaluated for equivalency. Breakthrough curves for 2,4-D collected with the two methods at a pore-water velocity of 7.05 cm h^{-1} are shown in Fig. 1 for illustration. There is virtually no difference between the two breakthrough curves, from which it is concluded that the two detection methods yield comparable results.

The breakthrough curves for $^3\text{H}_2\text{O}$, PFBA, and 2,4-D for all pore-water velocities are shown in Fig. 2. The retardation factors for $^3\text{H}_2\text{O}$, PFBA, and 2,4-D at the 70, 7, and 0.66 cm h^{-1} pore-water velocities are 1.0 (within 95% confidence limits). However, the retardation factors obtained at the 0.06 cm h^{-1} velocity are between 0.92 and 0.94. In this case, relative pore volume (pore volume/retardation factor) is used for the abscissa, to facilitate comparison of all breakthrough curves. The breakthrough curves for all solutes are indistinguishable at the two higher velocities. For PFBA and 2,4-D, the breakthrough curves are indistinguishable at the 0.66 cm h^{-1} velocity as well. At the 0.06 cm h^{-1} velocity, significantly greater dispersion is observed for $^3\text{H}_2\text{O}$, PFBA, and 2,4-D, consistent with a contribution from axial diffusion.



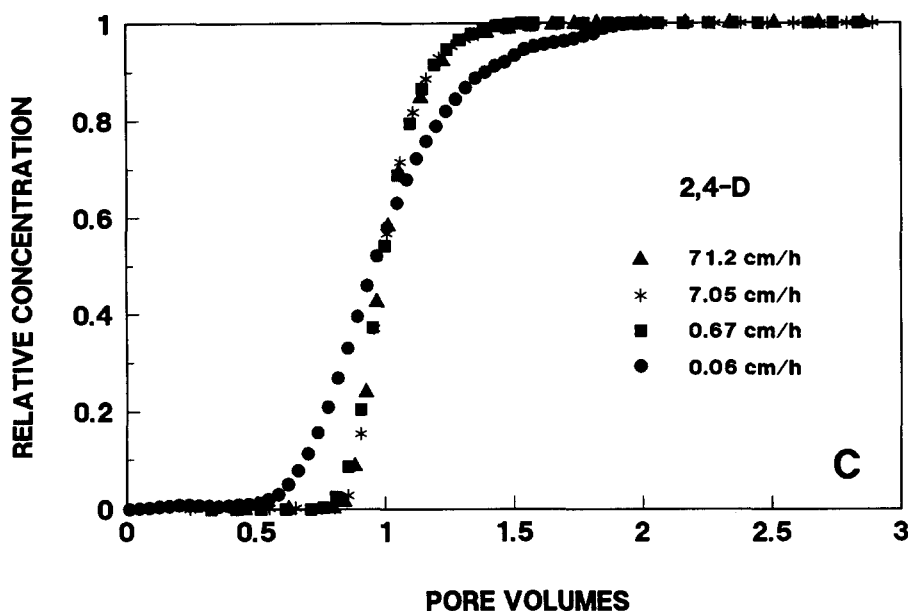


Fig. 2. Measured breakthrough curves for $^3\text{H}_2\text{O}$, PFBA, and 2,4-D transport at various pore-water velocities.

A regression between the dispersion coefficient and pore-water velocity was performed with the $\nu > 1 \text{ cm h}^{-1}$ data to determine the value of n in Eq. (3). The results showed a very good correlation ($r^2 = 0.98$), with n equal to 1.0. It should be noted that D is calculated from $\nu L/P$, where L is the column length and P is the Peclet number, values for which were optimized with the advective–dispersive transport model. A dispersivity (α_L) value of 0.06 cm was determined from the regression. Such small values are indicative of well-packed, homogeneous columns of sandy materials.

3.2. Contribution of axial diffusion

Data collected for $^3\text{H}_2\text{O}$, PFBA, and 2,4-D from two columns over a wide range of velocities are shown in Table 1. On the basis of these data, the relationship between D and pore-water velocity is presented in Fig. 3(A). For pore-water velocities lower than 1 cm h^{-1} , the curve for $^3\text{H}_2\text{O}$ diverges from that for PFBA and 2,4-D. This separation reflects the impact of diffusion on dispersive flux. The positions of the curves are determined by the aqueous diffusion coefficient and are consistent with the value for $^3\text{H}_2\text{O}$ being larger than that for PFBA and 2,4-D. At pore-water velocities higher than 1 cm h^{-1} , the two sets of data converge, signifying that dispersion coefficients for $^3\text{H}_2\text{O}$, PFBA, and 2,4-D are the same. This occurs when hydrodynamic dispersion predominates over dispersive flux.

Table 1

Measured Peclet numbers for transport of $^3\text{H}_2\text{O}$, PFBA, and 2,4-D

Column ^a	Tracer	ν (cm h ⁻¹)	P ^b
wq1	$^3\text{H}_2\text{O}$	46.9	122.1(114–130)
wq1	$^3\text{H}_2\text{O}$	46.8	122.8(116–130)
wq1	$^3\text{H}_2\text{O}$	4.91	96.8(88.5–105)
wq1	$^3\text{H}_2\text{O}$	0.42	41.0(38.4–43.5)
wq1	$^3\text{H}_2\text{O}$	0.42	32.2(29.7–34.7)
wq1	$^3\text{H}_2\text{O}$	0.42	19.9(18–21.3)
wq1	PFBA	46.9	125.7(116–135)
wq1	PFBA	46.8	119.8(117–123)
wq1	PFBA	4.91	119.7(109–135)
wq1	PFBA	0.42	95.9(92.1–99.7)
wq1	PFBA	0.42	73.2(67.2–79.1)
wq3	$^3\text{H}_2\text{O}$	70.0	125.8(104–147)
wq3	$^3\text{H}_2\text{O}$	6.94	94.8(84.0–106)
wq3	$^3\text{H}_2\text{O}$	0.66	48.2(44.0–52.4)
wq3	$^3\text{H}_2\text{O}$	0.06	8.76(8.33–9.19)
wq3	$^3\text{H}_2\text{O}$	0.05	12.5(11.3–13.8)
wq3	PFBA	70.0	105.8(93.7–118)
wq3	PFBA	6.94	103.8(90.5–117)
wq3	PFBA	0.66	88.0(82.0–94.0)
wq3	PFBA	0.06	21.1(20.7–21.6)
wq3	PFBA	0.05	31.1(30.4–31.8)
wq3	2,4-D ^c	71.2	88.8(79.2–98.4)
wq4	2,4-D	71.2	82.2(75.8–88.7)
wq3	2,4-D	68.2	85.6(75.6–95.6)
wq3	2,4-D	7.05	117.0(106–128)
wq3	2,4-D	6.99	111.3(102–121)
wq3	2,4-D	0.67	113.8(106–121)
wq3	2,4-D	0.65	98.7(92.2–105)
wq3	2,4-D	0.06	25.2(24.1–26.3)

^a wq1: Glass column; wq3: stainless-steel column.^b The 95% confidence limits are given in parentheses.^c All 2,4-D data represent the average value from two detection methods.

It is possible to quantify the relative contribution of hydrodynamic dispersion and axial diffusion to solute transport. Perkins and Johnston (1963) used a plot of D/D_0 versus the particle Peclet number (P_p) to delineate diffusion-controlled, transition, and advection-controlled regions. The relative contribution of axial diffusion to dispersion is a function of P_p (i.e. $\nu d/D_0$), where d is the particle diameter of the medium (in this case, $d = 250\mu\text{m}$). A D_0 value of $0.094\text{ cm}^2\text{ h}^{-1}$ was used for $^3\text{H}_2\text{O}$ and $0.026\text{ cm}^2\text{ h}^{-1}$ for PFBA (Brusseau, 1993). A D_0 value of $0.029\text{ cm}^2\text{ h}^{-1}$ was estimated for 2,4-D with the equation of Hayduk and Laudie (1974).

The relationship between D/D_0 and $\nu d/D_0$ for $^3\text{H}_2\text{O}$, PFBA, and 2,4-D is presented in Fig. 3(B). All data fall roughly within one line, as different aqueous diffusion coefficients are accounted for in the normalized terms (D/D_0 and $\nu d/D_0$). At very low velocities ($\nu d/D_0 < 0.01$ in Fig. 3(B)), the ratio of D/D_0 is

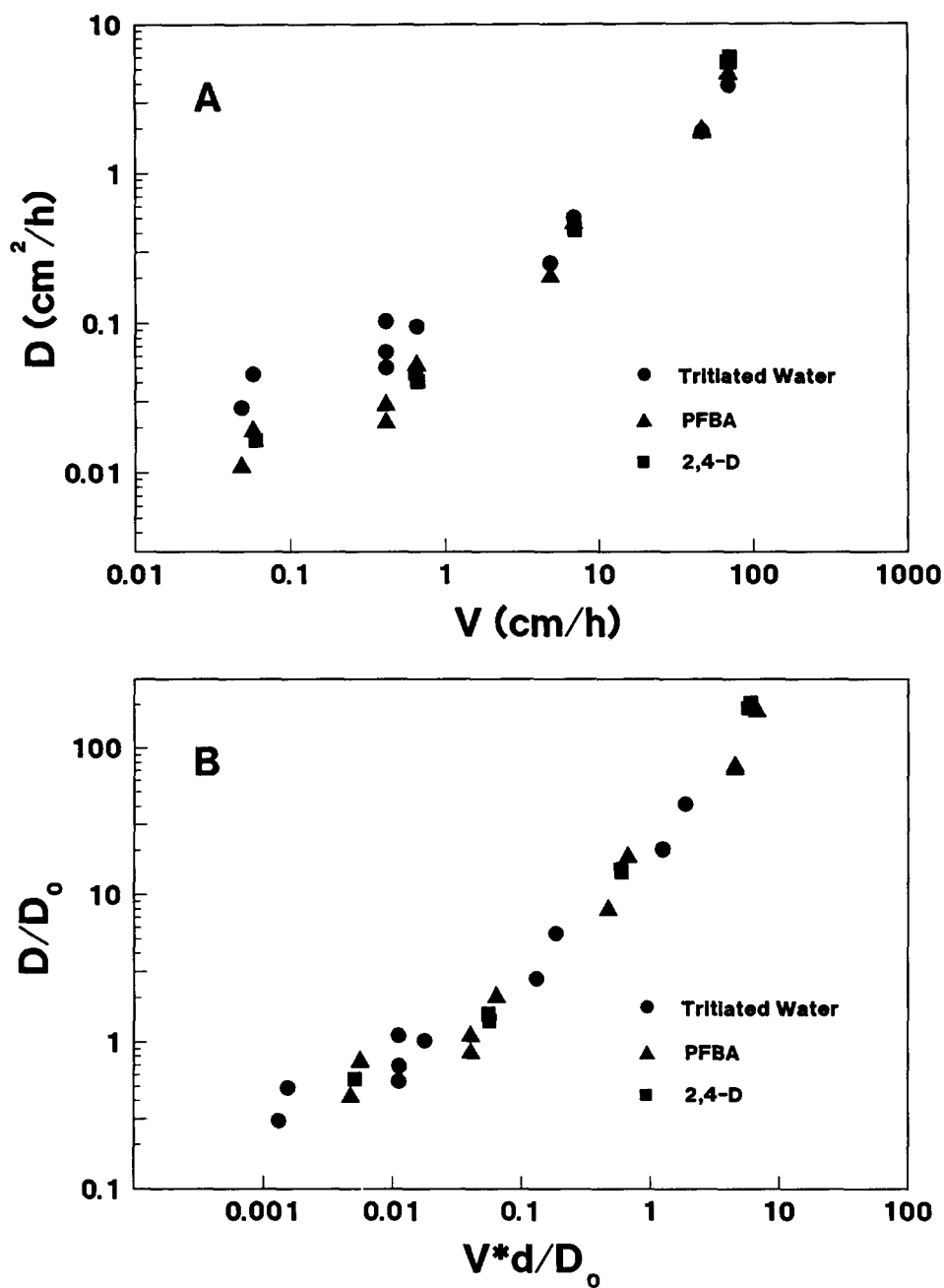


Fig. 3. (A) Relationship of dispersion coefficient (D) with pore-water velocity (v) for three solutes. (B) Plot of normalized dispersion coefficient (D/D_0) vs. particle Peclet number (vd/D_0) for three solutes.

nearly constant, and axial diffusion is the predominant source of dispersion. In this region, D/D_0 is approximately 0.6, which corresponds to a tortuosity factor of 1.67. This value is typical of those reported for sandy materials. With reliable measurement of the tortuosity factor, the contribution of axial diffusion can be calculated and evaluated from Eq. (2) for a specific solute at a specific pore-water velocity.

3.3. Influence of solute size

Breakthrough curves for transport of $^3\text{H}_2\text{O}$, PFBA, and 2,4-D at all four velocities are compared in Figs. 4 and 5. The breakthrough curves are identical for all solutes at the two higher velocities. Such data indicate that transport is occurring under ideal hydrodynamic conditions, i.e. that hydrodynamic dispersion is the sole significant source of dispersion. In this case, D is not a function of D_0 and Eq. (3) is valid. Thus, for a given system, the same values of α_L , D , and P should apply to all solutes, irrespective of size. The use of D or P values determined with $^3\text{H}_2\text{O}$, chloride, bromide, or similar tracers for larger molecules is appropriate under these conditions.

The breakthrough curves for $^3\text{H}_2\text{O}$ diverge from those of PFBA and 2,4-D at the two lower velocities. In this situation, it is inappropriate to represent the dispersion of larger solutes with the D or P value obtained from the analysis of the transport of a small-sized tracer such as $^3\text{H}_2\text{O}$, chloride, or bromide. However, the PFBA and 2,4-D breakthrough curves are similar for all velocities. This reflects the fact that PFBA is similar in molecular structure and size to 2,4-D. In this case, a D value measured with PFBA or similar tracer is a better value to use for reactive organic chemicals.

4. Summary and conclusions

Pore-water velocity has an effect on the breakthrough curves for transport of $^3\text{H}_2\text{O}$, PFBA, and 2,4-D in a homogeneous sand. For pore-water velocities higher than approximately 1 cm h^{-1} , hydrodynamic dispersion predominates and the contribution of axial diffusion is negligible. In this case, the practice of using a nonreactive tracer such as $^3\text{H}_2\text{O}$ to characterize the dispersive properties of a soil column is valid, and it is appropriate to use a tracer-derived dispersivity to represent the dispersivity of other, dissimilar-sized solutes.

For pore-water velocities lower than 0.1 cm h^{-1} , axial diffusion contributes significantly to total dispersive flux. In this case, it is inappropriate to use a tracer-derived dispersivity for solutes of different sizes. The dispersion-related value obtained with a tracer such as PFBA will be a better representation than $^3\text{H}_2\text{O}$, as PFBA has a structure similar to many environmentally important organic compounds.

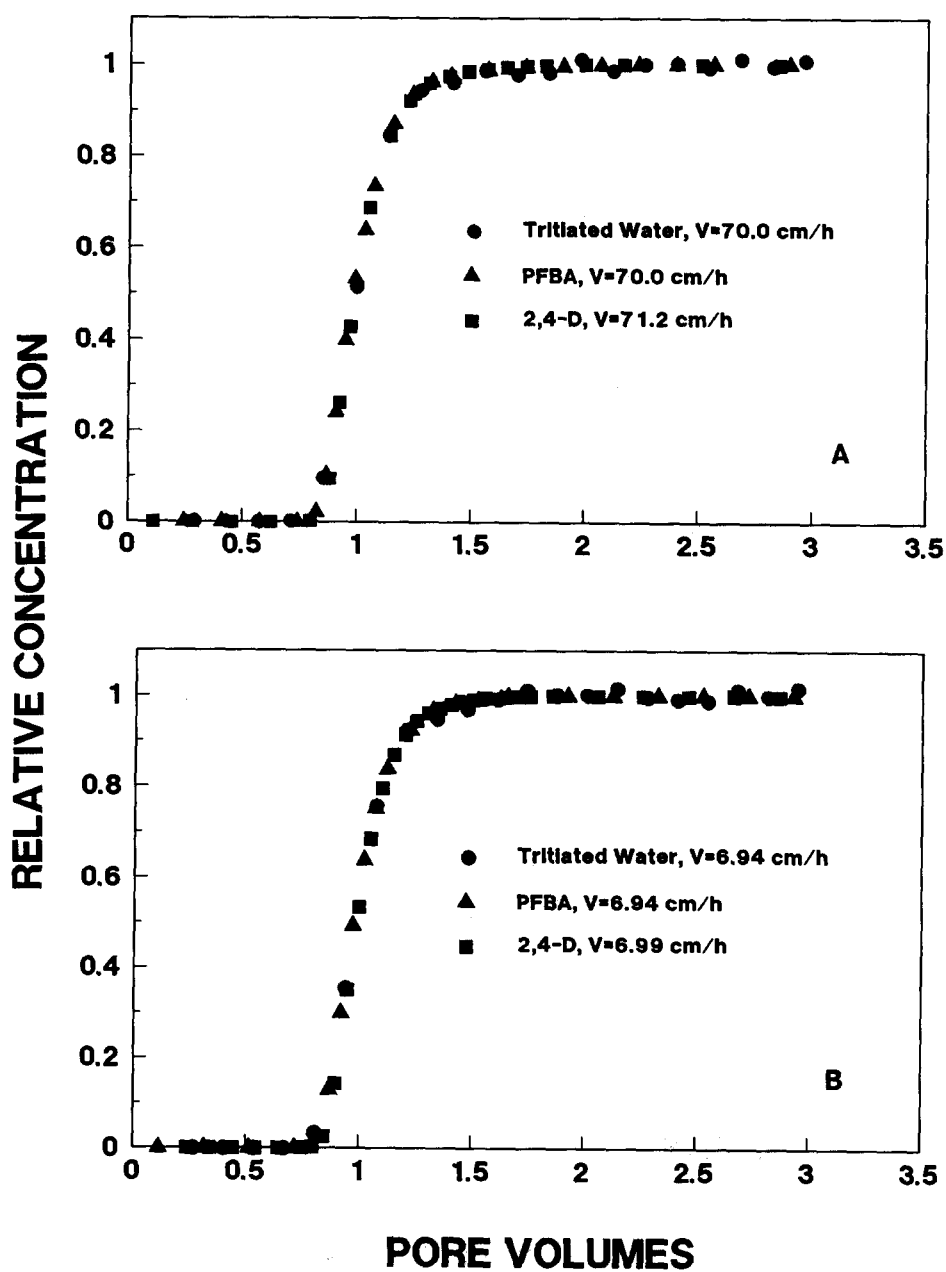


Fig. 4. Comparison of breakthrough curves for solutes at higher pore-water velocities.

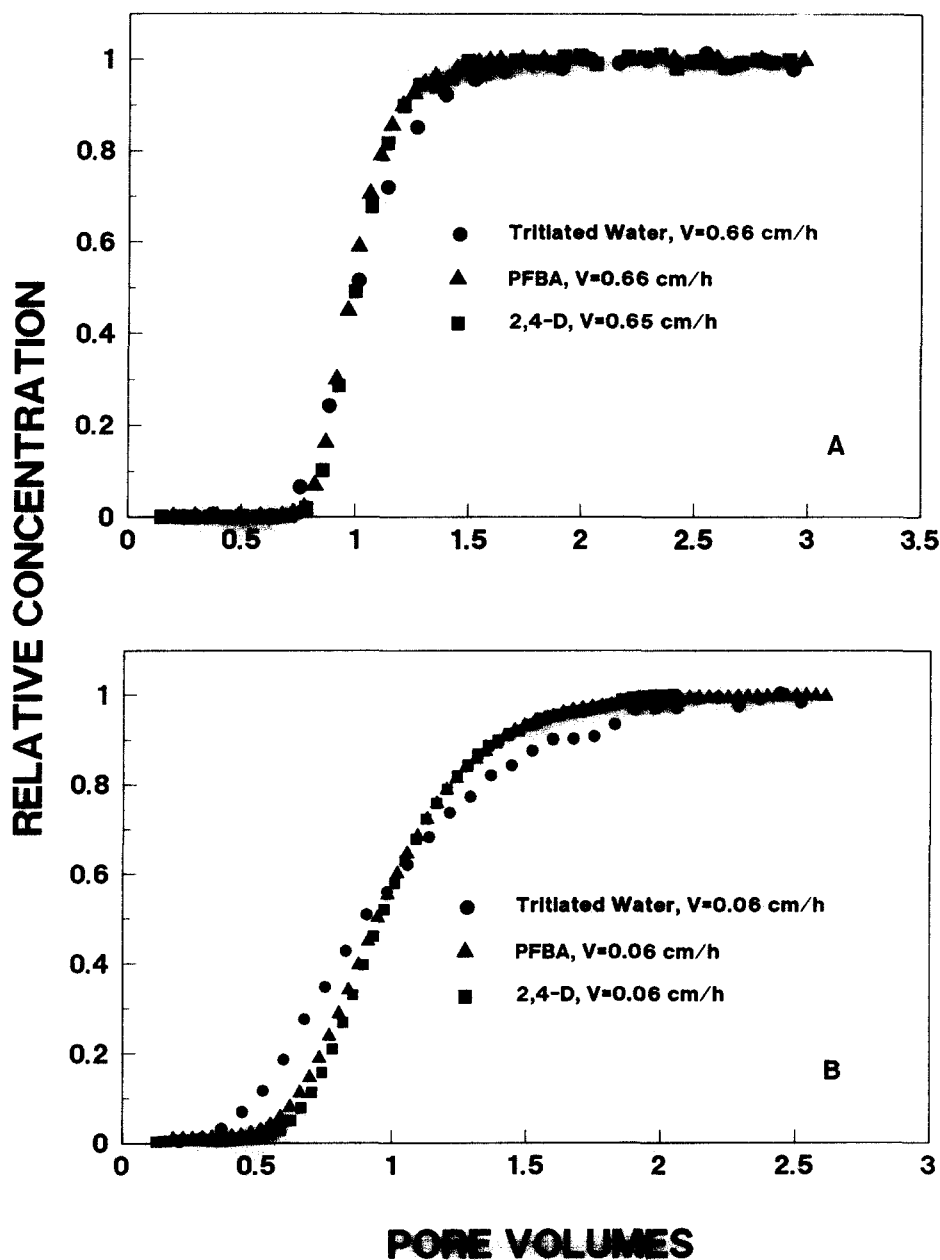


Fig. 5. Comparison of breakthrough curves for solutes at lower pore-water velocities.

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