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Dispersive–diffusive transport of non-sorbed solute in multicomponent solutions

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Abstract

The composition of fuels, mixed-solvent wastes and other contaminants that find their way into the subsurface are frequently chemically complex. The dispersion and diffusion characteristics of multicomponent solutions in soil have rarely been compared to equivalent single-solute systems. The purpose of this work was to examine the diffusive and dispersive transport of single- and multi-component solutions in homogeneous porous media. The miscible displacement technique was used to investigate the transport behavior of ^{14}C-labelled *2,4*-dichlorophenoxyacetic acid (*2,4*-D) in two materials for which sorption of *2,4*-D was minimal. Comparison of breakthrough curves collected for *2,4*-D in single- and multi-component solutions shows that there is little, if any, difference in transport behavior over a wide range of pore-water velocities (70, 7, 0.66 and 0.06 cm h^{-1}). Thus, dispersivities measured with a non-sorbing single-solute solution should be applicable to multicomponent systems.

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1. Introduction

The composition of fuels, mixed-solvent wastes, landfill leachate and other contaminants that find their way into the subsurface are frequently chemically complex. Thus, many contaminated sites have multiple contaminants in the aqueous phase. When multiple components are present in solution, a primary question to be addressed is the occurrence of antagonistic or synergistic interactions within the system (Brusseau, 1994). As such, it is important to understand the transport dynamics of multicomponent solutions. The behavior of multicomponent solutions has been widely investigated in chemical engineering. However, the dispersion and diffusion characteristics of multi-

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component solutions compared to equivalent single-solute solutions have rarely been addressed for soil systems. The purpose of this work is to investigate the effect of multicomponent solutions on solute dispersion and diffusion during transport in homogeneous porous media by comparing the transport behavior of a non-sorbed solute in single- and multi-component solutions.

2. Materials and methods

Pure silica-glass beads (212–300 μm in diameter, Sigma Chemical Co.) or Borden subsoil were used for all experiments. The glass beads were soaked in 6 *N* HCl for one day and then washed with deionized water until acid free. The Borden subsoil material was collected from the Canadian Air Forces Base in Borden, Ontario, Canada. The organic carbon content of the Borden subsoil is 0.29%, and the sand fraction comprises > 98% of the total mass (silt 1% and clay < 1%). The Borden subsoil was air dried and sieved (< 2 mm) prior to use.

The ^{14}C-labelled dichlorophenoxyacetic acid (*2,4*-D) was purchased from Sigma Chemical Co. The following analytical-grade chemicals (Aldrich Chemical Co.) were used in the experiments: pentafluorobenzoic acid (PFBA), *2,4*-D, benzene, naphthalene, *1,3,5*-triazine and atrazine.

A precision-bore stainless-steel column (2.1-cm i.d. and 7.0 cm in length, Alltech Associated Inc.) was used in the experiments. The column is designed to have a minimum void volume in the endplates. Column packing and the apparatus and methods used for the miscible displacement studies were similar to those used by Hu and Brusseau (1994).

The multicomponent mixture used for the glass beads column contained 85 mg L^{-1} ^{14}C-labelled *2,4*-D, 100 mg L^{-1} PFBA, 200 mg L^{-1} benzene, 12 mg L^{-1} naphthalene and 10 mg L^{-1} *1,3,5*-triazine. The multicomponent mixture for the Borden subsoil column contained 100 mg L^{-1} ^{14}C-labelled *2,4*-D, 100 mg L^{-1} PFBA, 30 mg L^{-1} atrazine and 10 mg L^{-1} *1,3,5*-triazine. $CaCl_2$ (0.01 *N*) was used as a background electrolyte for all solutions introduced to the columns. The density of the single- and multi-component solutions are not significantly different; hence, buoyancy effects should be minimal (Biggar and Nielsen, 1964; Krupp and Elrick, 1969; Paschke and Hoopes, 1984; Oostrom et al., 1992). Separate experiments showed little sorption of *2,4*-D by the glass beads and Borden subsoil.

The use of a ^{14}C-labelled compound made it possible to characterize the transport of *2,4*-D in a multicomponent solution. Specific activity of ^{14}C-labelled *2,4*-D in the displacing solution was 2.5 nCi mL^{-1} for both single- and multiple-component solutions. Effluent fractions containing ^{14}C-labelled *2,4*-D were collected with an automated fraction collector (ISCO, Inc., Foxy *200*®) and the activities were analyzed by radioassay using liquid scintillation counting (Packard®, Tri-Carb Liquid Scintillation Analyzer, Model *1600*TR). Four flow rates, namely 1.5, 0.15, 0.015 and 0.0015 mL min^{-1}, were used for the glass beads column. They correspond to pore-water velocities of 70, 7, 0.66 and 0.06 cm h^{-1}. Two flow rates (0.15 and 0.0015 mL min^{-1}) were used for the Borden subsoil column.

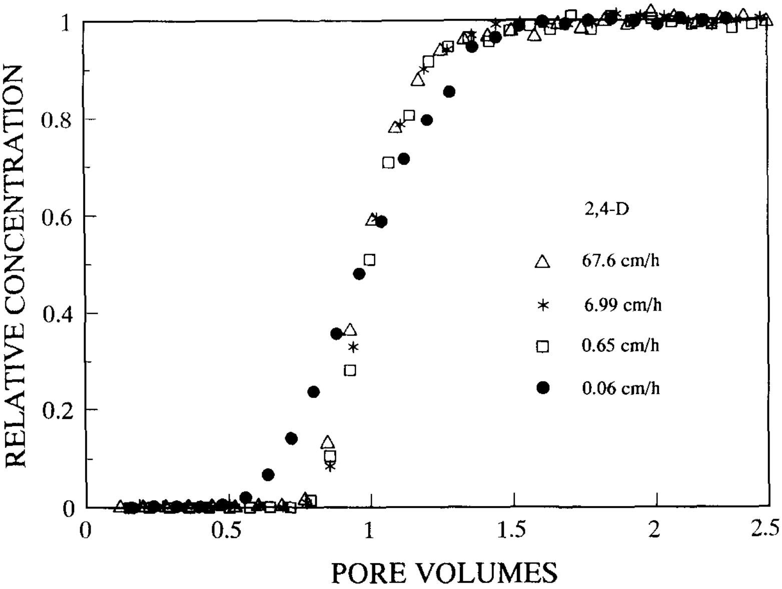

Fig. 1. Measured breakthrough curves for transport of 2,4-D (multicomponent solution) in the column packed with glass beads.

The results of the miscible displacement experiments were analyzed by using a nonlinear, least-squares optimization program (van Genuchten, 1981) to solve the nondimensional advective–dispersive local equilibrium transport model. Optimized val-

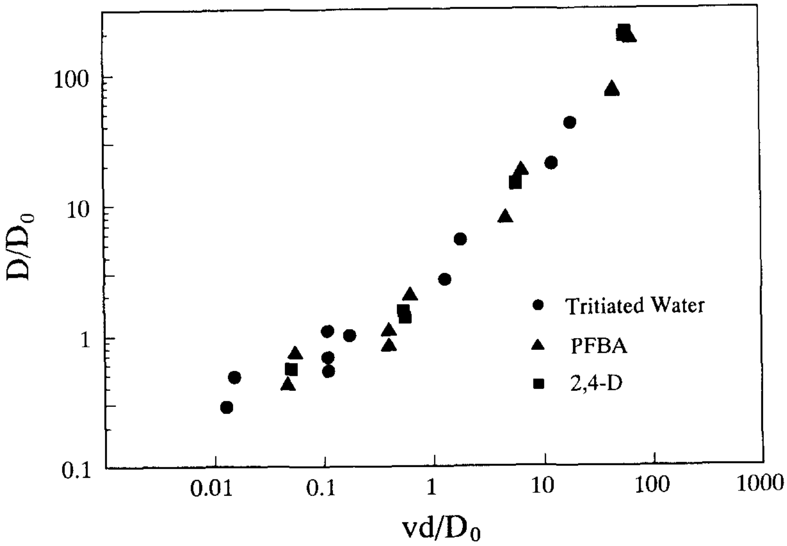

Fig. 2. Relationship of normalized dispersion coefficient (D/D_0) vs. particle Péclet number (vd/D_0) for ^3H_2O, PFBA and 2,4-D in the column packed with glass beads (reproduced from Hu and Brusseau, 1994).

ues are obtained for the Péclet number ($P = vL/D$, where v is the pore-water velocity, L is the column length and D the longitudinal dispersion coefficient) and retardation factor with 95% confidence intervals.

3. Results and discussion

The optimized retardation factors for 2,4-D are 1.0 (within 95% confidence limits) for the glass beads ($v = 70$, 7 and 0.66 cm h^{-1}) and Borden subsoil ($v = 7$ cm h^{-1}) systems. However, the optimized retardation factors for the 0.06-cm-h^{-1} velocity are ~ 0.94 for both the glass beads and Borden systems. Since there is no chemical interaction between 2,4-D and the porous medium used, this reduced retardation factor reflects a reduction in the effective pore volume. This indicates that the solution does not displace the entire volume of water retained by the porous medium at this small velocity. Similar data have been reported by Nielsen and Biggar (1961). In this case, relative pore

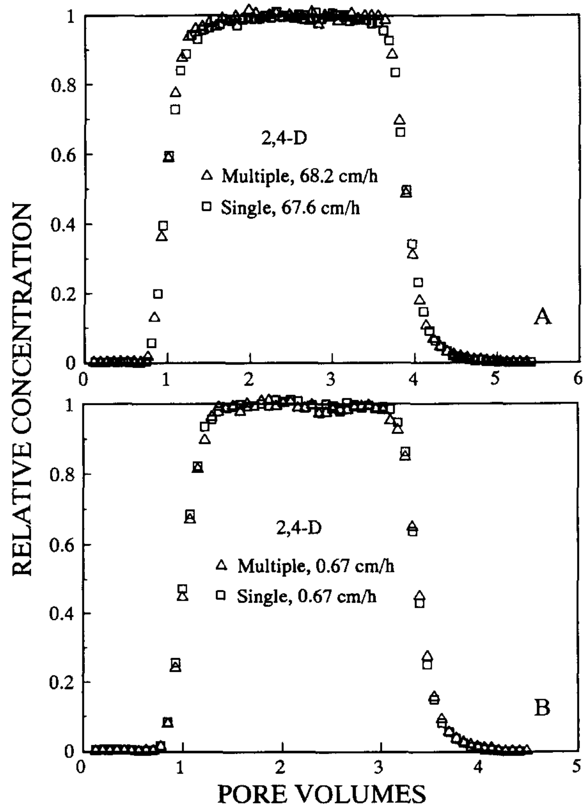

Fig. 3. Comparison of breakthrough curves for transport of single- and multi-component 2,4-D solutions in the column packed with glass beads.

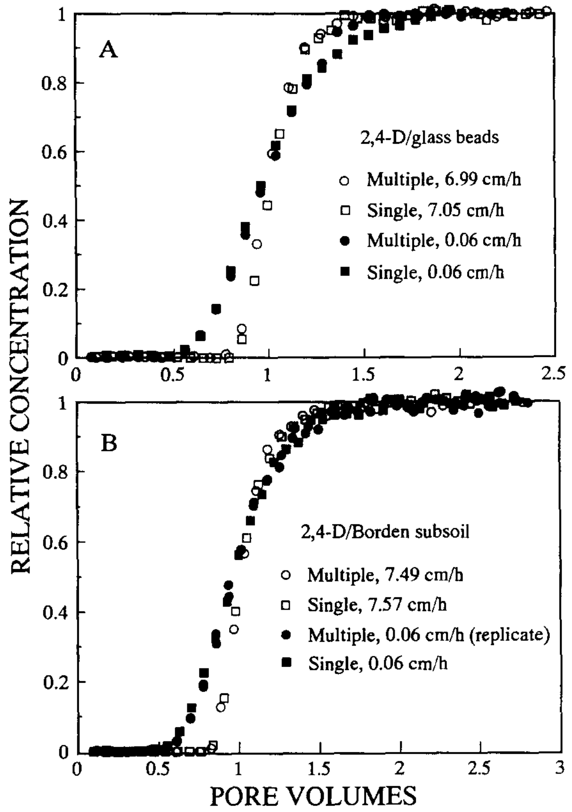

Fig. 4. Comparison of breakthrough curves for single- and multi-component *2,4*-D transport at two pore-water velocities in: (A) glass beads; and (B) Borden subsoil.

volume (pore volume/retardation factor) is used for the abscissa to facilitate comparison of breakthrough curves.

The breakthrough curves for ^{14}C-labelled *2,4*-D in the multicomponent solutions for four pore-water velocities are shown in Fig. 1. The breakthrough curves are essentially indistinguishable at the three higher velocities. At the 0.06-cm-h^{-1} velocity, additional spreading is observed. The same phenomenon was reported for ^3H_2O, PFBA and *2,4*-D in comparable single-solute transport experiments (Hu and Brusseau, 1994). At the slowest velocity (0.06 cm h^{-1}), axial diffusion contributes significantly to total dispersive flux.

The relationship between D/D_0 and the particle Péclet number ($P_e = vd/D_0$, where D_0 is aqueous diffusivity and d is particle diameter) has been widely used to examine the relative contributions of axial diffusion and hydrodynamic dispersion. Such an analysis for single-solute transport of ^3H_2O, PFBA and *2,4*-D in the glass beads is shown in Fig. 2 which is reproduced from Hu and Brusseau (1994). At very low velocities ($vd/D_0 < 0.01$ in Fig. 2), the ratio of D/D_0 is nearly constant, and axial diffusion is the predominant source of dispersion. The value for P_e for the $v = 0.06$ cm

Table 1
Péclet numbers for single- and multi-component 2,4-D transport in glass beads

Component	v (cm h^{-1})	P [(a)]
Single	71.2	79.3 (73.8–84.8)
Single	71.2	82.2 (75.8–88.7)
Single	68.2	74.5 (68.7–80.2)
Multi	69.0	84.0 (77.1–91.0)
Multi	67.6	82.2 (75.9–88.6)
Single	7.05	115.1 (107–124)
Single	6.99	106.2 (98.5–114)
Multi	6.99	104.3 (95.6–113)
Multi	6.94	100.7 (91.5–110)
Single	0.67	111.0 (104–118)
Single	0.65	98.7 (92.2–105)
Multi	0.67	102.2 (94.9–110)
Multi	0.65	105.1 (96.1–114)
Single	0.061	24.8 (23.5–26.1)
Multi	0.062	30.0 (27.6–32.4)

[a] 95% confidence limits in parentheses.

h^{-1} experiments is 0.052, which falls within the region wherein axial diffusion is significant.

Selected breakthrough curves for single- and multi-component 2,4-D solutions at different pore-water velocities in glass beads and Borden subsoil columns are presented in Figs. 3 and 4. It is evident that the breakthrough curves of 2,4-D in single- and multi-component solutions are essentially indistinguishable for all pore-water velocities for both porous media. Accordingly, values for the Péclet number are similar (Tables 1 and 2). Péclet numbers are comparable for corresponding pore-water velocities between the glass beads and Borden subsoil columns, which is reasonable considering that both are sandy materials. Based on these results, dispersivities measured with a non-sorbing single-solute solution should be applicable to multicomponent systems. This result should be tested for structured and heterogeneous media.

Table 2
Péclet numbers for single- and multi-component 2,4-D transport in Borden subsoil

Component	v (cm h^{-1})	P [(a)]
Single	7.57	96.6 (86.5–107)
Multi	7.49	115.8 (104–127)
Single	0.057	25.3 (23.5–27.2)
Multi	0.060	26.0 (23.7–28.2)
Multi	0.062	30.8 (28.3–33.4)

[a] 95% confidence limits in parentheses.

Acknowledgements

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