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Technical Note

Simulating solute transport in an aggregated soil with the dual-porosity model: measured and optimized parameter values

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Received 6 December 1993; revision accepted 19 March 1994

Abstract

The capability of the first-order, dual-porosity model, which explicitly accounts for non-ideal transport caused by the presence of 'immobile' water, to predict the non-ideal transport of non-sorbing solute in a constructed aggregated soil has been investigated. Miscible-displacement experiments performed with a well-characterized aggregated soil and a non-reactive tracer (pentafluorobenzoate) served as the source of the data. Values for the input parameters associated with physical non-equilibrium were determined independently and compared with values obtained by curve fitting of the experimental measurements. The calculated and optimized values compared well, suggesting that the non-equilibrium parameters represent actual physical phenomena.

1. Introduction

The impact of structured soils on the transport of dissolved chemicals has been studied by many researchers (see Brusseau and Rao, 1989, 1990, for recent reviews). These investigations have shown that the presence of macroscopic-scale low-permeability domains (e.g. aggregates, macropores) can cause non-ideal transport of solutes, as exemplified by asymmetrical breakthrough curves and 'preferential' transport. Several mathematical models have been developed to simulate solute transport in structured systems, the most widely used being the first-order, dual-porosity model developed by Deans (1963) and Coats and Smith (1964), and extended to sorbing solute by Van Genuchten and Wierenga (1976).

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The approach typically taken in using any mathematical model is to fit the model to a data set, whereby the values for one or more parameters are optimized. Given the uncertainties associated with solving the inverse problem, especially for multiple-parameter optimizations, there is concern that such optimized parameters may not represent actual physical phenomena. To address these concerns, a preferred method of evaluating a model's performance is to compare simulations produced with independently measured parameters to measured data. Despite its widespread use, the performance of the first-order, dual-porosity model has rarely been tested by use of the preferred method. One such test was reported by Rao et al. (1980), who used measured data to predict transport of non-sorbing solutes in columns packed with synthetic porous ceramic spheres. Such an evaluation has apparently not been done for solute transport in aggregated soil. The purpose of the present work was to evaluate the ability of the first-order, dual-porosity model to simulate solute transport in a well-characterized aggregated soil. Specifically, the optimized parameter values obtained by fitting the dual-porosity model to the breakthrough curves are compared with values measured independently.

2. Materials and methods

2.1. Materials

Spherical aggregates were prepared by placing a loam soil (Yolo loam), amended with a 0.5% polyacrylicamide solution, in plaster-of-paris moulds (see Rao et al., 1980). The moulded, moist aggregates were dried overnight at 50°C. This procedure produced well-characterized, stable soil aggregates having a large intraparticle porosity. These aggregates were packed into a column and dispersed in 125 μm glass beads. The use of the glass beads results in an interaggregate domain similar to that of a non-aggregated sandy medium. The properties of the aggregates and of the packed column are presented in Table 1. Pentafluorobenzoate (PFBA) was used as the non-sorbing tracer.

2.2. Miscible-displacement method

The approach and apparatus used in the miscible displacement experiments were

Table 1
Properties of aggregates and packed column

Aggregate diameter	1.1 cm
Total water content (θ)	0.42
Interaggregate water content (θ_m)	0.21
Intra-aggregate water content (θ_{im})	0.21
Bulk density (ρ)	1.66 g cm ⁻³
Column length	10 cm
Column diameter	2.5 cm
Peclet number (P)	40

identical to those described by Brusseau et al. (1990). Briefly, two single-piston HPLC pumps (Gilson Medical Electronics, Model 302) were connected to the glass column (packed with the soil) by a Rheodyne switching valve (Model 7060) placed in-line to facilitate switching between solutions which did or did not contain the solute of interest. After completion of packing, electrolyte solution (0.01 M CaCl_2) was pumped through the column to ensure complete water saturation and to condition the porous medium to the electrolyte. Solutions containing 100 mg l^{-1} of PFBA were then pumped into the column at three flow rates, equivalent to pore-water velocities of 1.4, 14.5, and 87.3 cm h^{-1} . A flow-through, variable-wavelength UV detector (Gilson Holochrome) was used to monitor continuously the concentration of PFBA in the column effluent, with output recorded on a strip chart recorder (Fisher, Recordall Series 5000).

2.3. Mathematical model

The results of the miscible displacement experiments were analysed with the dual-porosity model of Van Genuchten and Wierenga (1976):

$$\beta R \partial C_1^* / \partial T + (1 - \beta) R \partial C_2^* / \partial T = (1/P) \partial^2 C_1^* / \partial X^2 - \partial C_1^* / \partial X \quad (1)$$

$$(1 - \beta) R \partial C_2^* / \partial T = \omega (C_1^* - C_2^*) \quad (2)$$

where

$$C_1^* = C_m / C_0 \quad (3a)$$

$$P = qL / D\theta_m \quad (3b)$$

$$C_2^* = C_{im} / C_0 \quad (3c)$$

$$R = 1 + (\rho/\theta)K_p \quad (3d)$$

$$T = vt/L \quad (3e)$$

$$\beta = (\theta_m + f\rho K_p) / (\theta + \rho K_p) \quad (3f)$$

$$X = x/L \quad (3g)$$

$$\omega = \alpha L / v_m \theta_m \quad (3h)$$

where C_m and C_{im} are the aqueous-phase concentrations for the mobile and immobile domains, respectively [M L^{-3}], C_0 is the input concentration, v is the average pore-water velocity [L T^{-1}] (with $v_m = q/\theta_m$, the velocity in the mobile domain), q is Darcy flux [L T^{-1}], t is time, x is distance, L is column length, D is the local-scale dispersion coefficient for the mobile domain [$\text{L}^2 \text{T}^{-1}$], ρ is soil bulk density [M L^{-3}], θ is fractional volumetric water content (with subscripts m and im representing mobile and immobile domains, respectively), f is the fraction of sorbent associated with the mobile domain, K_p is the equilibrium sorption constant [$\text{L}^3 \text{M}^{-1}$], and α is the

first-order mass transfer coefficient [T^{-1}]. A non-linear, least-squares optimization program (Van Genuchten, 1981) was used under flux-type boundary conditions to determine values for the unknowns: P , R , β , and ω .

2.4. Predicting β and ω parameters

When R tends to 1, as was the case herein, the fraction of instantaneous retardation, β , is equivalent to θ_m/θ . Thus, values for β can be calculated from measured values of θ_m and θ . The values for θ_m and θ reported in Table 1 were measured by a gravimetric mass balance of the column (i.e. individual measurements for amount of water associated with each domain).

The Damkohler Number, ω , contains the first-order mass transfer coefficient (α) and represents the mass transfer of solute between the intra-aggregate and interaggregate domains. The coefficient associated with the first-order model can be related to a diffusion coefficient, based on a Ficks' Law approach, by employing an equation of the following form (cf. Parker and Valocchi, 1986; Brusseau et al., 1989)

$$\alpha = aD_0\theta_{im}/\tau l^2 \quad (4)$$

where a is a shape factor, D_0 is the aqueous diffusion coefficient [$L^2 T^{-1}$], τ is the tortuosity factor, and l is, for the present case, the radius of the aggregates. With measured values for θ_{im} and l (see Table 1), and known values for D_0 ($0.026 \text{ cm}^2 \text{ h}^{-1}$) and the shape factor (15 for the present case-spherical geometry), values for α can be calculated by using a value of 2 for τ , which is based on data reported in the literature (cf. Brusseau, 1993).

3. Results and discussion

Breakthrough curves for pentafluorobenzoate, obtained for three pore-water velocities (1.4, 14.5, and 87.3 cm h^{-1}), are presented in Fig. 1(A). These data exhibit behaviour typical of transport in structured soil systems, wherein the breakthrough curve is shifted leftward and the amount of tailing increases with increasing velocity. For all cases, the optimized simulations produced with the first-order, dual-porosity model provide very good fits to the data. The simulations produced with the independently determined values for β and ω reported in Table 1 provide good predictions of the experimental data (see Fig. 1(B)).

The optimized values for β and ω are reported in Table 2. The calculated values for these two parameters are also listed in Table 2. The 95% confidence intervals for two of the three optimized β values capture the calculated β value (0.5). This suggests that the optimized β term does, in fact, represent a real physical entity, i.e. the internal porosity of the aggregates. The β value obtained for the experiment performed at the fastest velocity is smaller than the measured value. Possibly, at relatively large velocities, the effective 'immobile' domain includes some interaggregate regions in addition to the intra-aggregate domain. A similar velocity dependence of β was reported by Nkedi-Kizza et al. (1983).

Fig. 1. Breakthrough curves for transport of pentafluorobenzoate in a column packed with 1.1 cm diameter aggregates: (A) experimental data and optimized simulations produced with the first-order, dual-porosity model; (B) experimental data and predicted simulations produced with the first-order, dual-porosity model. Pore-water velocities are in centimetres per hour.

Table 2
Calculated and optimized non-equilibrium parameter values

Experiment	β		ω	
	Calculated	Optimized	Calculated	Optimized
PFBA, $v = 1.4$	0.5	0.50 (0.49–0.52)	2.2	1.11 (1.04–1.18)
PFBA, $v = 14.5$	0.5	0.56 (0.49–0.64)	0.2	0.24 (0.18–0.31)
PFBA, $v = 87.3$	0.5	0.40 (0.39–0.41)	0.04	0.02 (0.01–0.03)

95% confidence intervals are in parentheses; pore-water velocities (v) are in centimetres per hour; PFBA = pentafluorobenzoate.

The optimized and calculated ω values differ by a factor of 2 or less. There is some uncertainty associated with the calculated values because of the use of an literature-based value for τ , the intra-aggregate tortuosity. However, the predicted ω values remain reasonably close to the optimized values for the range of tortuosity values typically reported in the literature (1.5–3).

4. Conclusion

The analyses presented above provide evidence that non-ideal transport caused by diffusive mass transfer between intra- and interaggregate pore-water domains is present in an aggregated-soil system. They also show that the first-order, dual-porosity model provides a valid and consistent description of the physical-non-equilibrium phenomenon. The non-equilibrium-associated parameters included in the model, values for which are typically obtained by fitting, appear to represent actual physical phenomena, at least for well-characterized systems. Thus, the dual-porosity model can be used to analyse experimental data with some degree of confidence. Of course, the use of this model and the physical meaning of the parameters should be evaluated carefully for each system to which the model is applied. The structure associated with soils found in the field will rarely be as well defined as that of our model system. Hence, it must be recognized that the application of the dual-porosity model to many field systems will be an approximation of reality, albeit a useful one.

Acknowledgement

A portion of this work was supported by a grant provided by the US Department of Agriculture CSRS Water Quality Program.

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