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Evaluation of a Simple Method for Estimating Solute Transport Parameters Laboratory Studies

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Abstract

A two-domain, physical nonequilibrium solute transport model has been used to describe the transport and fate of solute in soil. The model contains the parameters θ_{im} (immobile water content) and α (mass transfer coefficient) which must be determined for a soil before applying the transport model. A simple field method that can estimate both θ_{im} and α without measuring extensive breakthrough curves (BTCs) has been presented. The purpose of this paper was to test in laboratory soil columns the simple method of estimating parameters by comparing to the conventional BTC analysis method of parameter estimation. The experiments involved 12-cm-long and 4-cm-diam. columns packed with five different soil materials. The BTCs were performed on each column using a sequential application of four fluorobenzoate tracers. Each tracer was applied for a different length of time. The soil columns were sectioned at the end of the BTC experiments. The simple method gave results of θ_{im} and α based upon the sectioned soil samples, and the BTC analysis gave results of θ_{im} and α based upon effluent concentrations. The estimates by the two different methods were from the same experiments. Most of the estimated α values using the simple method were within the 95% confidence interval (CI) of the BTC estimates. For 7 of 10 soil columns, the estimates of immobile water fraction, θ_{im}/θ , from the simple method were within the 95% CI of the estimates of θ_{im}/θ obtained from BTC data. Breakthrough curves calculated using the θ_{im} and α values estimated by the simple method were similar to observed BTCs. The simple method provides estimation of θ_{im} and α from easy to obtain soil samples in field and can be used as a first approximation to apply the analytical BTC method.

Disciplines

Agriculture | Hydrology | Soil Science | Statistical Models

Comments

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Evaluation of a Simple Method for Estimating Solute Transport Parameters: Laboratory Studies

Jaehoon Lee, Dan B. Jaynes, and Robert Horton*

ABSTRACT

A two-domain, physical nonequilibrium solute transport model has been used to describe the transport and fate of solute in soil. The model contains the parameters θ_{im} (immobile water content) and α (mass transfer coefficient) which must be determined for a soil before applying the transport model. A simple field method that can estimate both θ_{im} and α without measuring extensive breakthrough curves (BTCs) has been presented. The purpose of this paper was to test in laboratory soil columns the simple method of estimating parameters by comparing to the conventional BTC analysis method of parameter estimation. The experiments involved 12-cm-long and 4-cm-diam. columns packed with five different soil materials. The BTCs were performed on each column using a sequential application of four fluoro-benzoate tracers. Each tracer was applied for a different length of time. The soil columns were sectioned at the end of the BTC experiments. The simple method gave results of θ_{im} and α based upon the sectioned soil samples, and the BTC analysis gave results of θ_{im} and α based upon effluent concentrations. The estimates by the two different methods were from the same experiments. Most of the estimated α values using the simple method were within the 95% confidence interval (CI) of the BTC estimates. For 7 of 10 soil columns, the estimates of immobile water fraction, θ_{im}/θ , from the simple method were within the 95% CI of the estimates of θ_{im}/θ obtained from BTC data. Breakthrough curves calculated using the θ_{im} and α values estimated by the simple method were similar to observed BTCs. The simple method provides estimation of θ_{im} and α from easy to obtain soil samples in field and can be used as a first approximation to apply the analytical BTC method.

have shown that BTCs show early arrival and tailing with nonsymmetrical concentration distributions under certain conditions. To account for such results, a physical nonequilibrium model or two-region model, which is based on a dual-porosity concept, has been used as a means of investigating the transport and fate of solute in soil (Coats and Smith, 1964; van Genuchten and Wierenga, 1976). In this concept, water-filled pore space is divided into two regions based on flow velocities within the pores. One is a mobile region, where water is free to move and solute transport is by advection and dispersion, and the other is an immobile region, where water is stagnant and solute moves only by diffusion.

Based on the two-region approach, the transport of nonreactive solutes during steady, one-dimensional flow can be written

$$\theta = \theta_m + \theta_{im} \quad [1]$$

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \quad [2]$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad [3]$$

where θ is total volumetric water content, θ_m and θ_{im} are mobile and immobile water contents, C_m and C_{im} are concentrations in mobile and immobile domains, t is time, D_m is dispersion coefficient, q is water flux, x is depth, and α is chemical mass transfer coefficient between mobile and immobile domains.

This two-region model or mobile-immobile model (MIM) allows for preferential movement of nonsorbing solute in soil, since the effective transport volume (θ_m) is less than the total water-filled pore space (θ). However, a major difficulty in applying the two-domain

MANY STUDIES (van Genuchten and Wierenga, 1977; Rao et al., 1980; Nkedi-Kizza et al., 1983, 1984)

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Abbreviations: BTCs, breakthrough curves; CDE, convection-dispersion equation; CI, confidence interval; ME, mean error; MIM, mobile-immobile model; RMSE, root mean square error.

transport model is estimating the required model parameters: immobile water content (θ_{im}), mass transfer coefficient (α), and dispersion coefficient (D_m). Although one can determine the parameters by applying inverse methods to breakthrough data (Parker and van Genuchten, 1984; van Genuchten and Wagenet, 1989; Gamedainger et al., 1990), obtaining breakthrough data in the field is often not practical.

Jaynes et al. (1995) presented a method to estimate both θ_{im} and α using a sequence of conservative, non-interacting tracers. The Jaynes et al. (1995) method uses a sequence of four different fluorobenzoate tracers applied through a tension infiltrometer for a step input. The method assumes that the initial tracer concentration in the soil is zero, tracer concentration in the mobile domain is constant and equal to the input concentration (C_0), and samples of soil solution for analysis are well behind the dispersive front of the tracers so that dispersion in the mobile domain is negligible at the time of sampling. To estimate θ_{im} and α , an expression, Eq. [4], was developed by separation of variables in Eq. [3] (Jaynes et al., 1995).

$$\ln\left(1 - \frac{C}{C_0}\right) = \ln\left(\frac{\theta_{im}}{\theta}\right) - \frac{\alpha}{\theta_{im}} t^* \quad [4]$$

where C is resident concentration, $t^* = t - x/v$ and is defined as the time required for the tracer front to reach the depth of sampling (x), t is time since the tracer was applied, and v is average pore water velocity.

Equation [4] describes a log-linear relationship between measured resident concentration and tracer application time. θ_{im} and α can be calculated from Eq. [4] by fitting the $\ln(1 - C/C_0)$ vs. t^* . The intercept and slope of the regression line give estimates of both θ_{im} and α . The Jaynes et al. (1995) method provides a means for determining estimates of θ_{im} and α in situ by using resident tracer concentrations. Although it is not as simple as the single tracer method of Clothier et al. (1992), it needs only a single soil sample, and total experimental time is relatively short, giving estimates of the additional parameter, α . The method is practical for field use in contrast with conventional curve-fitting methods that require extensive sampling and analysis. In its simplest form, only two tracers need to be applied for different lengths of time and measured concentration, although the use of multiple tracers allows for the confirmation of log-linear behavior predicted by Eq. [4].

Casey et al. (1997) used the Jaynes et al. (1995) method for field measurement of θ_{im} and α , and compared the field measured θ_{im} and α values with previous studies. Jaynes et al. (1995) and Casey et al. (1997) found good linearity when log-normalized resident concentration was plotted vs. time in applying Eq. [4]. This observed linear behavior is important, since it is required if Eq. [3] accurately explains the physical transport processes in the soil. The Jaynes et al. (1995) method for determining α and θ_{im} has not been fully tested against other inverse methods. Therefore, the main objective of this study is to compare the Jaynes et al. (1995) method with a conventional BTC analysis

Table 1. Physical properties of the soil columns and tracer experiments.

Column	Soil material	Soil texture (mass fractions)			Bulk density	Water content	Velocity
		Sand	Silt	Clay			
A1	Sand†	100			1.54	0.39	32.6
A2	Sand†	100			1.47	0.40	19.9
B1	Ap horizon, sicl‡	2.3	67.1	30.6	0.94	0.54	41.4
B2	Ap horizon, sicl‡	2.3	67.1	30.6	0.88	0.60	18.7
C1	C horizon, sicl‡	3.4	64.5	32.2	0.94	0.52	17.7
C2	C horizon, sicl‡	3.4	64.5	32.2	0.90	0.62	20.2
D1	Ap horizon, l§	48.0	30.6	21.4	0.96	0.56	45.9
D2	Ap horizon, l§	48.0	30.6	21.4	0.94	0.60	33.3
E1	C horizon, l§	49.5	34.5	16.0	0.96	0.49	35.3
E2	C horizon, l§	49.5	34.5	16.0	1.00	0.57	52.9

† 0.5–1 mm sieve fraction.

‡ Tama silty clay loam, 1–2 mm sieve fraction.

§ Clarion loam, 1–2 mm sieve fraction.

method. In this study, we tested the Jaynes et al. (1995) method using laboratory soil columns by comparing estimates based on Eq. [4] with estimates obtained by conventional inverse fitting of effluent breakthrough data.

MATERIALS AND METHODS

Laboratory experiments were performed on 12 cm-long and 4-cm-i.d. soil columns. In each experiment, pre-sectioned Plexiglas columns were used to allow rapid sectioning of the columns after final tracer application. The outside of each column was paraffin-coated before the leaching experiment to avoid leaking. Each Plexiglas section was 1 cm high, and the Plexiglas was assembled to a height of 15 cm. The lower end of each column consisted of a detachable bottom plate enclosing a porous plate, and the upper end remained open. The soils used were beach sand from Florida, Tama Ap and C horizon soil (a fine-silty, mixed, mesic Typic Argiudolls), and Clarion Ap and C horizon soil (a fine-loamy, mixed-calcareous, mesic Typic Hapludolls) from Iowa. The soils were air dried. The sand was sieved through 0.5 to 1 mm (U.S. no. 35–18) standard sieve, and the other soils were sieved through 1 to 2 mm (U.S. no. 18–10) standard sieve. The organic C contents for Tama soils were 1.72 and 0.41 for Ap and C horizon, and 1.96 and 0.64 for Clarion soil, Ap and C horizon, respectively. Additional soil properties are shown in Table 1. The texture analysis for the soil was done using the hydrometer method described by Gee and Bauder (1986). All columns were uniformly packed with one of these five different soil materials to a height of 12 cm. The columns were then mounted vertically and saturated with a 4 mmol L⁻¹ solution of KCl to establish a constant molar concentration. After saturation, steady-flow miscible displacement experiments were conducted using sequences of four tracer solutions.

The columns were leached with the same solution (4 mmol L⁻¹ KCl) under slight positive head (1.5 cm at the surface and open to atmosphere at bottom) until steady flow conditions were achieved. The volume of outflow was measured as a function of time during each experiment to confirm the steady flow conditions. The outflow rate remained constant for all but two columns where the rate decreased 3% by the end of the experiments. The sequences of tracer solutions were then applied at the top of each column. The first solution was composed of 3 mmol L⁻¹ KCl and 1 mmol L⁻¹ of either 2,6 difluorobenzoate (DFBA), pentafluorobenzoate (PFBA), o-trifluoromethylbenzoate (TFMBA), or 2,3,6 trifluorobenzoate (TFBA) tracer. After leaching the column with about one pore volume of the first solution, a second solution

was applied containing 2 mmol L⁻¹ KCl, 1 mmol L⁻¹ of the first benzoate tracer, and 1 mmol L⁻¹ of a second benzoate tracer. The total electrolyte concentration of each tracer mixture was kept constant (4 mmol L⁻¹) by changing the amount of KCl in each solution. The process was repeated until the fourth solution was applied containing no KCl and the four benzoate tracers at a concentration of 1 mmol L⁻¹ each. The order in which the tracers were applied was varied so that any bias caused by nonidentical tracer transport, recovery, and analysis would be lessened. Three tracer application orders were made and randomized for the columns. Each 0.05 pore volume of outflow containing the tracers was collected from each column with a fraction collector, and effluent samples were stored at 4°C before analysis.

After infiltrating about one pore volume of the fourth solution, the application and outflow were stopped and the columns were quickly and carefully sectioned by each centimeter. The column sections were then weighed and extracted by adding 30 mL of a 0.002 M CaSO₄ solution. Each sample was shaken for 10 min and allowed to settle for 8 h. The extractions were then centrifuged at about 90 000 m s⁻² for 20 min and decanted for analysis. The remaining soil was oven dried at 105°C, and the dry weight of each sample was measured to calculate the water content and bulk density. Analysis for the fluorobenzoate tracers was done on a Dionex Series 4500i ion chromatograph (West Mont, IL) and UV detector by the method described by Bowman and Gibbens (1992) using a SAX column (Regis Chemical Co., Morton Grove, IL) with 30 mM KH₂PO₄, adjusted to a pH of 2.65 with H₃PO₄ and 20 mL L⁻¹ acetonitrile as the eluting solution. The flow rate was 1 mL min⁻¹, and the detection wavelength of the UV detector was set to 205 nm.

Parameter Estimation: Breakthrough Curve Method

The BTCs obtained from all four tracers were used to estimate transport parameters. Each BTC was normalized by the input concentration and adjusted so that $t = 0$ when the individual tracer was first applied to the column. The four BTCs were then combined to produce a single group BTC for analysis, and the values for the parameters D_m , α , and θ_{im} were estimated by BTC methods using the program CXTFIT (Parker and van Genuchten, 1984; Toride et al. 1995). The CXTFIT program was also used to determine D_m , α , and θ_{im} parameters from the resident concentrations of the last applied tracer.

Parameter Estimation: Jaynes et al. (1995) Method

Equation [4] was applied to the resident concentration data from each column to estimate θ_{im} and α . Only the values of

concentrations from the upper layers (2–5) were used because insufficient leaching of the last applied tracer would cause interference from dispersion processes.

Fitting Eq. [4] to resident concentrations of the four layers provides four sets of α and θ_{im} values from the slopes and intercepts. The intercept of the least square regression gives $\ln(\theta_{im}/\theta)$, and α can be obtained from the slope and θ_{im} . The four sets of estimates do not mean that the parameter values are different with soil depth. These are essentially repeated measurements of the same parameter values, and all that is really required in this method are data from any single layer. Because the soil depth varied for the layers, the time of tracer application was adjusted so that the effective application time would start when the tracer reached the center of each section layer.

RESULTS AND DISCUSSION

General Results

Figure 1a shows the BTCs of four tracers in outflow from column D1. Since we applied four tracers sequentially at about one pore volume intervals, the result shows four distinct BTCs. The BTCs for all soil columns except sandy soil columns were similar. Sandy soil columns had steeper BTCs than the other soil columns, indicating less dispersion.

In Fig. 1b, the x -axis (pore volume) of the graph for each tracer was adjusted, so that $t = 0$ when the individual tracer was first applied to the soil column. The results show nearly identical flow characteristics of four fluorobenzoate tracers. Jaynes (1994) and Benson and Bowman (1994) have presented similar findings. Results from the other columns were similar. In general, the BTCs for all soil columns except for the sandy soil columns (A1 and A2) showed some early arrival of tracers and tailing, which is representative of preferential flow or physical nonequilibrium processes.

Figure 2 shows the resident concentrations of four tracers from column D1. The concentration profiles for the other soil columns were similar. The concentration of the last applied tracer decreases as depth increases, showing a zone where dispersion processes are important. Relative concentrations were all <1, ranging from 0.77 to 0.97, suggesting the presence of an immobile water domain in each column. At most depths, relative concentrations for tracers applied the longest were

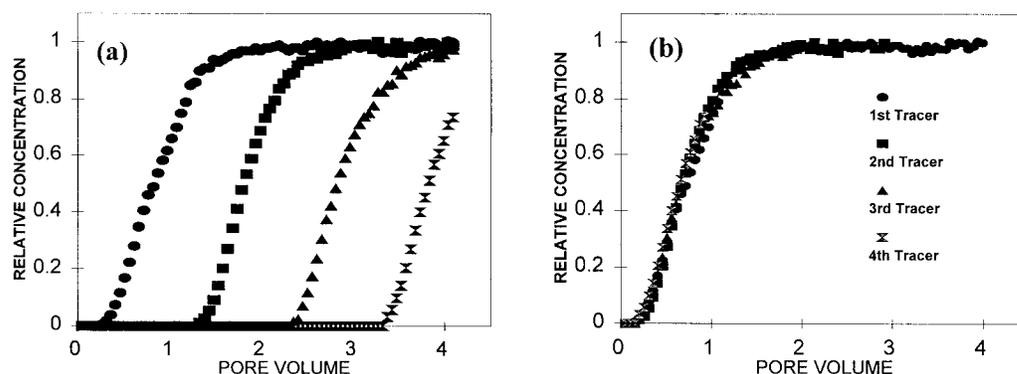


Fig. 1. (a) Breakthrough curves (BTCs) of the four different tracers for the column D1. (b) The BTCs adjusted so that $t = 0$ when each tracer was first applied to the column D1.

slightly greater than for other tracers. This result supports the assumption of mobile tracer diffusing over time into the immobile water-filled pore space.

Figure 3 shows resident concentrations in the upper four layers of column D1 plotted as $\ln(1 - C/C_0)$ vs. time (t^*) with regression lines fitted to the data. For the 10 columns, the overall average coefficient of determination (r^2) for the regression lines was 0.90, ranging from 0.61 to 0.99. This overall value of r^2 implies that Eq.[4] is a reasonable representation of physical non-equilibrium solute transport processes in the soil.

Comparison of the Jaynes et al. (1995) and the Breakthrough Curve Estimated Parameters

Table 2 is a summary of the estimated parameter values by the inverse method applied to BTC data and the Jaynes et al. (1995) method applied to resident concentrations for the 10 soil columns. The 95% CIs for the BTC method are also reported with the estimates. The estimated immobile water fraction, θ_{im}/θ , ranged from 0.04 (column A2) to 0.31 (column C1) for the BTC method, and from 0.07 (column A1) to 0.33 (column C1) for the Jaynes et al. (1995) method. The estimates of mass transfer coefficient, α , varied from $7.38 \times 10^{-3} \text{ h}^{-1}$ (column E1) to 0.27 h^{-1} (column B1) for BTC method and varied from $1.24 \times 10^{-3} \text{ h}^{-1}$ (column A1) to 0.30 h^{-1} (column D2) for the Jaynes et al. (1995) method. The estimated dispersion coefficient, D_m , from the BTC method is also provided for reference. In most columns, the 95% CIs for α and θ_{im} were notably smaller than that of D_m .

The values of α were proportional to the values of θ_{im} . Skopp et al. (1981) and Casey et al. (1997) reported similar findings. The consistency of the relationship may be derived by the mechanical diffusion model where the surface area increases as θ_{im} increases. Under this assumption, the contact area between the mobile and immobile domains expands, as immobile area (θ_{im}) increases then α will also increase, since the larger contact areas will allow for faster tracer exchange between the domains.

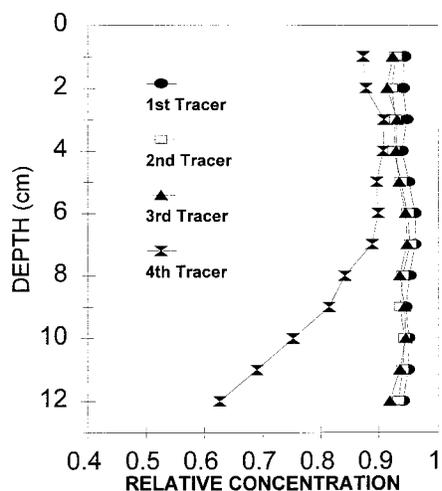


Fig. 2. Resident concentration of the four different tracers at end of leaching in the column D1.

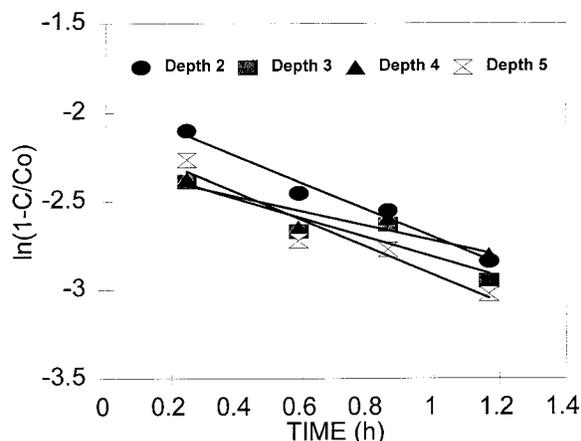


Fig. 3. The resident concentrations in the upper four layers for the column D1 plotted as $\ln(1 - C/C_0)$ vs. application time and regression lines fitted to the data using Eq. [4].

In Fig. 4, parameter estimates along with 95% CIs as calculated by CXTFIT are shown for the BTC method, and the parameter estimates from the top four soil layers are plotted for the Jaynes et al. (1995) method. The estimates from the Jaynes et al. (1995) method were within the 95% CI except for columns E1 and D2 where the Jaynes et al. (1995) method had values of θ_{im}/θ and α either larger or smaller than for the BTC method. In all cases, the parameter estimates from the four soil layers were similar to each other implying the consistency of the Jaynes et al. (1995) method. The BTC method generally produced large 95% CIs. The optimization seems not to converge to the correct solution for a couple of breakthrough data sets due to problems involving parameter uniqueness. This is especially true when three parameters (D_m , α and θ_{im}) are estimated at the same time (Parker and van Genuchten; 1984).

For both the Jaynes et al. (1995) method and the BTC method, the θ_{im}/θ values for silty clay loam (column B1, B2, C1, and C2) were always higher than any other soil columns. Soils with higher clay content usually have more complicated pore structure than sandy soil. This may cause larger immobile domain and more chemical exchange between two domains. It is believed that the immobile domain is also located inside aggregate pores (intra-aggregate). This implies that aggregate size is also

Table 2. Comparison of the estimated α and θ_{im} values from the two methods.

Column	BTC method†			Jaynes method	
	D ($\text{cm}^2 \text{ h}^{-1}$)	α (h^{-1})	θ_{im}/θ	α (h^{-1})	θ_{im}/θ
A1	2.4 ± 154.5	0.03 ± 0.05	0.05 ± 0.05	0.002	0.07
A2	9.3 ± 177.7	0.04 ± 0.09	0.04 ± 0.06	0.02	0.13
B1	44.6 ± 493.2	0.27 ± 0.29	0.25 ± 0.18	0.03	0.22
B2	18.6 ± 198.6	$0.001\ddagger \pm 0.06$	0.16 ± 0.06	0.01	0.17
C1	17.7 ± 543.5	0.10 ± 0.11	0.31 ± 0.19	0.03	0.33
C2	42.1 ± 122.1	0.001 ± 0.04	0.18 ± 0.04	0.01	0.15
D1	72.7 ± 431.7	0.18 ± 0.30	0.16 ± 0.16	0.04	0.12
D2	29.6 ± 119.9	0.02 ± 0.07	0.04 ± 0.04	0.30	0.28
E1	60.1 ± 134.1	0.001 ± 0.05	0.20 ± 0.04	0.01	0.09
E2	65.9 ± 178.8	$0.001\ddagger \pm 0.14$	0.10 ± 0.05	0.02	0.12

† BTC, breakthrough curve.

‡ Convergence failed.

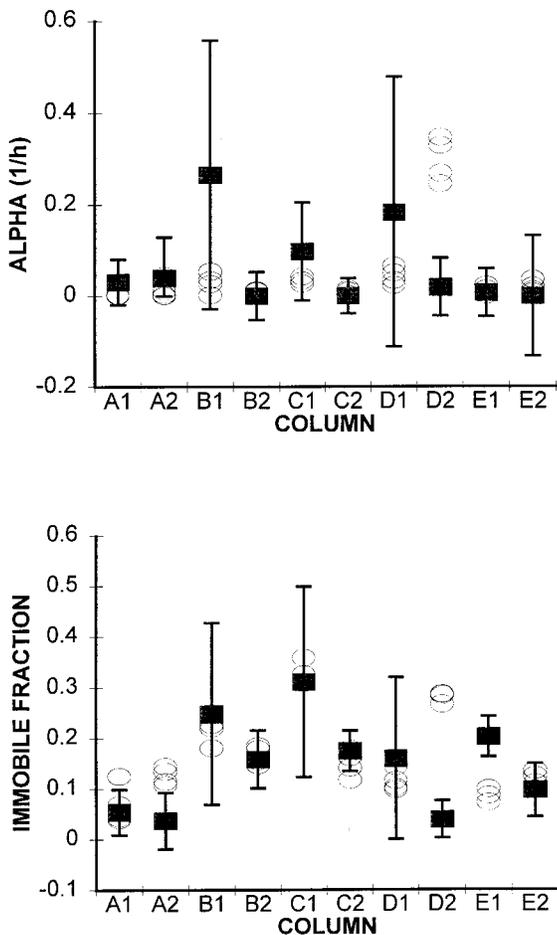


Fig. 4. Comparison of the estimated α and θ_{im} values of the breakthrough curve (BTC) method and the Jaynes et al. (1995) method. The best fit value and 95% confidence interval are plotted for the BTC method, and four independent estimates from two to five soil layers using the Jaynes et al. (1995) method are plotted.

an important factor that would affect immobile water content. Nkedi-Kizza et al. (1983, 1984) reported increasing immobile water content with an increase in aggregate size.

Disagreement between solute transport properties for the paired replicates could be due to dissimilar pore water velocities, water contents, and bulk densities between the replicates. Although we tried to produce exact replicates, there were differences in physical properties between the replicates, most significantly pore water velocities differed. It is well known that the three parameters (D_m , α , and θ_{im}) are functions of pore water velocity (Casey et al., 1997).

Finally, Jaynes and Shao (1998) evaluated the impacts of assuming negligible D_m , which is used for the Jaynes et al. (1995) method. They found that the estimates for $\omega = \alpha L/q$ (where L is depth of measurement, and q is Darcy flux density) and θ_{im} improve when ω is smaller than 0.1, and P (peclot number) is larger than 100. In this study, ω was smaller than 0.03 with an average of 0.002, and P was larger than 100 for almost all soil columns. Thus, it is believed that the Jaynes et al. (1995)

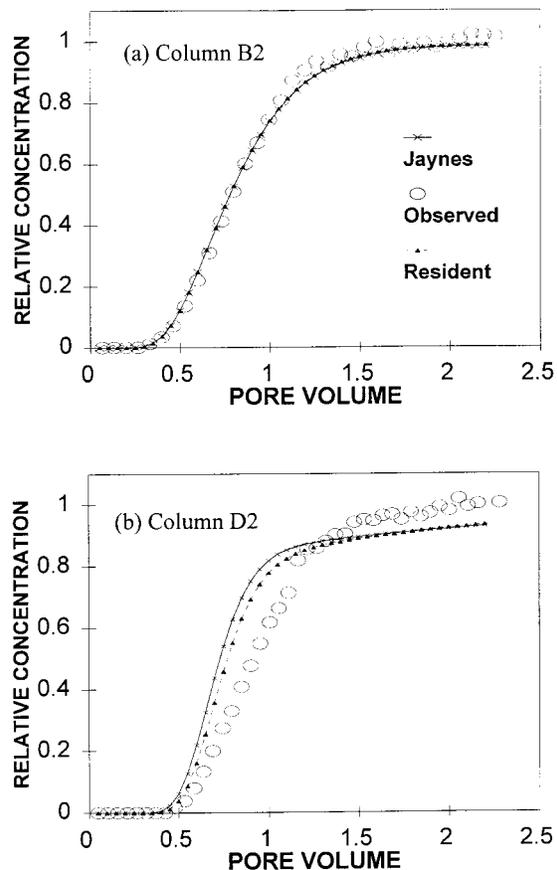


Fig. 5 (a), (b). Measured and predicted breakthrough curves (BTCs) for columns B2 and D2. The circles are the measured breakthrough data (first applied tracer), and the lines represent calculated BTCs. The predicted BTCs use the analytical solution and α and θ_{im} values estimated from resident concentrations.

approach is valid for this study and should make accurate parameter estimates.

Mobile-Immobile Model Consistency Estimated from Breakthrough Curves and Resident Concentrations

Some of the lack of fit found above may be due to the inadequacy of the MIM model's description of solute transport. The MIM model is very simplistic in partitioning the flow system into only two domains—a mobile and completely immobile domain. We can test the validity of this conceptual model by evaluating the model's success in predicting resident tracer concentrations from parameters fitted to BTC data and in predicting BTC data from parameters fitted to resident concentrations. The data collected here are uniquely suited for this purpose because we measured both resident and breakthrough concentrations during the same tracer experiments.

The results of predicting BTCs from resident concentration data are shown in Fig. 5 along with measured BTCs. The calculated BTCs use the analytical solution of MIM model. The BTC marked "Resident" uses α , θ_{im} , and D_m values obtained from an inverse method using CXTFIT to fit the resident concentration profile

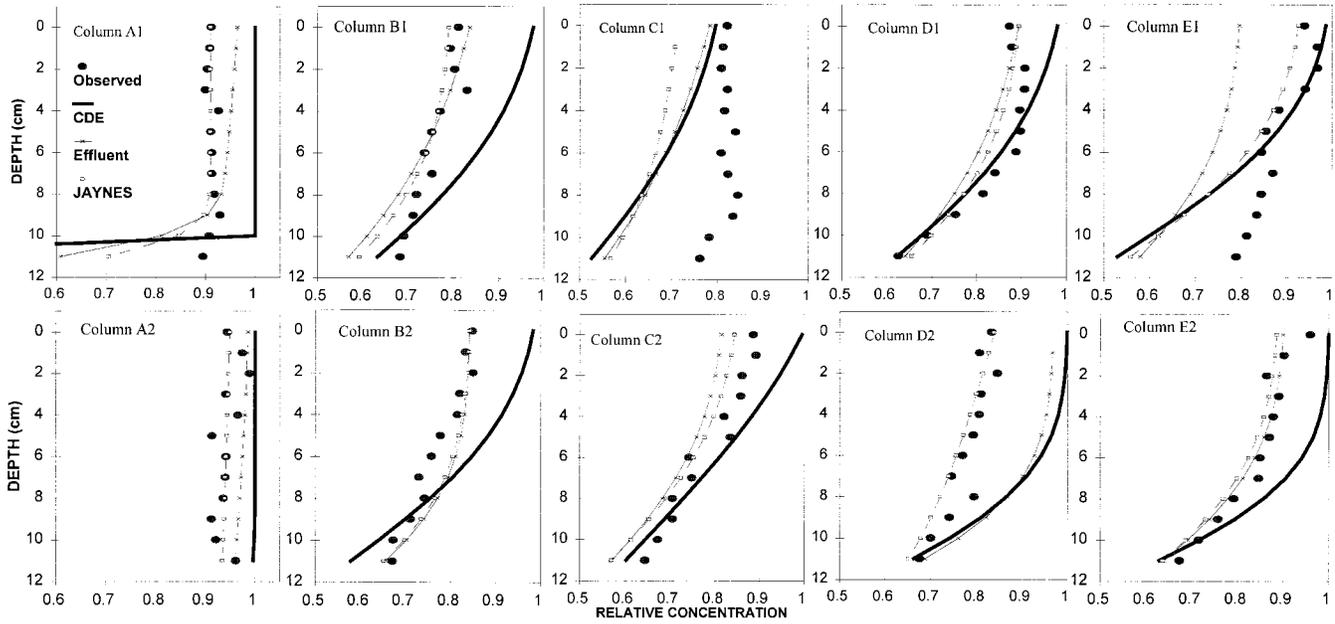


Fig. 6. Measured and calculated resident concentrations. The calculated curves are obtained using parameters estimated from measured out-flow data.

of the last applied tracer. The BTC marked “Jaynes” uses α and θ_{im} estimates obtained from the Jaynes et al. (1995) method and the same D_m obtained from inverse method using CXTFIT, since the Jaynes et al. (1995) method does not estimate D_m . Note that both calculated BTCs used estimated parameters only from resident concentration data. In general, both calculated BTCs reasonably describe the shape of the curves for almost all columns, although some of the calculated curves show early or lagged BTCs compared with measured BTCs.

Column B2 is the best result of 10 columns (Fig. 5a). For column B2, Jaynes and Resident calculated BTCs agree very well with measured BTCs. Column D2 is the worst result of 10 columns (Fig. 5b). The two calculated curves do not match the measured BTCs well. Remember that the parameters from the BTC method were considerably smaller than those of the Jaynes et al. (1995) method for this column. However, the Resident method gives α and θ_{im} very close to the Jaynes et al. (1995) estimates. The Resident calculated BTC were very similar to the Jaynes calculated BTC, although the calculated BTCs do not match well with the measured BTCs. This was true for all soil columns. The Jaynes and Resident calculated BTCs were always very similar. This result implies that the discrepancies of estimated parameters from the BTC method and Jaynes et al. (1995) method for some columns might be somewhat normal because the estimated parameters presented in Table 2 are obtained from two different concentration modes (effluent and resident).

As mentioned before, simultaneous estimation of three parameters may increase deviations from the correct solution. D_m is an important factor influencing the shape of BTCs, and small changes in the D_m value may affect the shape of BTCs. Since both calculated BTCs

use D_m values from a method that estimates three parameters at the same time, it could be another reason that both calculated curves do not match with measured BTCs for some columns. However, again, both calculated BTCs were well in agreement with measured BTCs for most of the soil columns.

Figure 6 shows measured and calculated resident concentrations. The circles are the measured resident concentrations (last applied tracer), and the curves represent calculated resident concentrations obtained from the analytical solution of the CDE (a one-domain convection–dispersion equation) and the MIM model. To generate CDE-marked resident concentration curves, we used parameter values obtained from measured out-flow data. As expected, the CDE model provided poor estimation of the resident concentration profiles.

The calculated curves marked “Effluent” are obtained from parameters (α , θ_{im} , and D_m) estimated with the BTC method from measured outflow concentrations, shown in Table 2. The calculated curves marked

Table 3. Mean error (ME) and root mean square error (RMSE) for the calculated resident concentration.

Column	CDE†		BTC‡		JAYNES	
	ME	RMSE	ME	RMSE	ME	RMSE
A1	0.0051	0.2716	-0.0051	0.0947	-0.0250	0.0588
A2	0.0545	0.0592	0.301	0.0365	-0.0025	0.0214
B1	0.0887	0.1121	-0.0267	0.0507	-0.0290	0.0398
B2	0.0628	0.0953	0.0216	0.0326	0.0177	0.0287
C1	-0.1287	0.1511	-0.1282	0.1436	-0.1557	0.1605
C2	0.0358	0.0583	-0.0541	0.0586	-0.0391	0.0451
D1	0.0125	0.0475	-0.0352	0.0490	-0.0203	0.0358
D2	0.1281	0.1434	0.1168	0.1258	-0.0201	0.0302
E1	-0.0613	0.1174	-0.1566	0.1601	-0.0850	0.1114
E2	0.0649	0.0804	-0.0162	0.0260	-0.0280	0.0338
Avg.	0.0262	0.1136	-0.0254	0.0778	-0.0387	0.0566

† CDE represents a one-domain convection–dispersion model.
‡ BTC, breakthrough curve.

JAYNES use α and θ_{im} obtained from the Jaynes et al. (1995) method and the same D_m as used for Effluent curves. In general, the calculated resident concentrations using the MIM model and the estimated parameters match well with observed data, except columns C1, E1, and D2. In column C1 and E1, both calculated curves made poor predictions showing overestimates of D_m and θ_{im} . In column D2, the Effluent curves does not match well with measured data, while the JAYNES calculated curve agrees with measured data.

Two quantitative measures, mean error (ME) and root mean square error (RMSE) (Willmott et al., 1985), are used to evaluate the accuracy of the predictions. Table 3 shows the ME and RMSE for the calculated resident concentrations. The average ME for CDE, BTC, and JAYNES calculated values were 0.026 (from -0.129 to 0.128), -0.025 (from -0.157 to 0.117) and -0.039 (from -0.156 to 0.018), respectively. The CDE calculated values tended to overestimate and BTC and JAYNES calculated values tended to underestimate resident concentrations. The average RMSE for CDE, BTC, and JAYNES calculated values were 0.114, 0.078, and 0.057, respectively. This implies that the JAYNES parameter estimates made better predictions of resident concentrations than CDE and BTC estimates. It is somewhat reasonable because the Jaynes et al. (1995) method uses resident concentrations to estimate parameters and the CDE and BTC methods use effluent data.

The use of the MIM model improved descriptions of all measured resident concentration profiles over the classical one-region CDE model. The CDE model did not match well with measured data for any soil column. This implies that physical nonequilibrium for solute transport must be modeled, especially when soil aggregates are present. However, the MIM solution does not give accurate estimates of resident concentrations using effluent data nor vice versa for some of the soil columns, implying that the MIM model is not an accurate representation of the transport processes in these soil columns.

CONCLUSIONS

The method described by Jaynes et al. (1995) for estimating both θ_{im}/θ and α without measuring extensive breakthrough curves was evaluated by using carefully controlled laboratory experiments. Most of the estimated α values using the Jaynes et al. (1995) method were within the 95% CI of the BTC estimates. In seven of 10 columns, estimated θ_{im}/θ values were within the 95% CI of the BTC estimates. Overall, the Jaynes et al. (1995) method gave reasonable agreement with a conventional curve fitting method for several different soils, and there were no significant trends among the different flow velocities with θ_{im}/θ and α . This method requires only a surface soil sample with minimum disturbance of soil, while the BTC method needs many samples and analysis. The Jaynes et al. (1995) method is a relatively simple method that determines both θ_{im} and α and can be used to test the mobile-immobile assump-

tions for field soil where it is not easy to collect BTC data. The Jaynes et al. (1995) method, therefore, can be used as a first approximation to apply the analytical BTC method. We believe that this method is a promising in situ method to delineate solute transport if it is used under conditions where the Jaynes et al. (1995) method provides valid θ_{im} and α estimates.

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