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Comparing Field Methods that Estimate Mobile–Immobile Model Parameters

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Abstract

Recent studies have used field techniques that estimate soil hydraulic and solute transport parameters. These methods utilize a tension infiltrometer to infiltrate either a single tracer or a series of tracers in order to estimate immobile water content (θ_{im}) and mass exchange coefficient (α) of the mobile–immobile solute transport model. The objective of this study was to compare two single tracer methods (basic and variance) with one multiple tracer method for estimating θ_{im} and α from data obtained on the same field soil location. Hydraulic conductivity ($K(h_0)$) was also estimated using these methods. Research was done at five interrow sites in a ridge-tilled corn (*Zea mays* L.) field, and the soil was mapped as a Nicollet series (fine-loamy, mixed, superactive, mesic, Aquic Hapludoll). The values of θ_{im} and α estimated by the multiple tracer method compared well with previously measured values using the same technique on the same field. The θ_{im} values for the multiple tracer technique were larger than values derived from the basic single tracer technique. The basic single tracer technique did not take into consideration a mass exchange between θ_{im} and the mobile water domain (θ_m). The α values were less variable for the multiple tracer method than for the single tracer-variance method. Values of immobile water fraction (θ_{im}/θ) for the multiple and basic single tracer techniques ranged from 0.30 to 0.52 and from 0.24 to 0.35, respectively. The values of α for the multiple and single tracer-variance techniques ranged from 0.06 to 0.9 d^{-1} and from 0.03 to 60 d^{-1}, respectively. The volumetric water content (θ) changed considerably over the course of the experiment for the estimation of α using the single tracer-variance method; thus, the assumptions of this technique were compromised. The measured values of $K(h_0)$ at the five sites ranged from 0.47 to 1.66 μm s^{-1} There was evidence that the basic single tracer method underestimated θ_{im} and overestimated θ_m, because this method considers $\alpha = 0$ during the tracer application.

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Comparing Field Methods that Estimate Mobile–Immobile Model Parameters

F. X. M. Casey,* D. B. Jaynes, R. Horton, and S. D. Logsdon

ABSTRACT

Recent studies have used field techniques that estimate soil hydraulic and solute transport parameters. These methods utilize a tension infiltrometer to infiltrate either a single tracer or a series of tracers in order to estimate immobile water content (θ_{im}) and mass exchange coefficient (α) of the mobile–immobile solute transport model. The objective of this study was to compare two single tracer methods (basic and variance) with one multiple tracer method for estimating θ_{im} and α from data obtained on the same field soil location. Hydraulic conductivity ($K(h_0)$) was also estimated using these methods. Research was done at five interrow sites in a ridge-tilled corn (*Zea mays* L.) field, and the soil was mapped as a Nicollet series (fine-loamy, mixed, superactive, mesic, Aquic Hapludoll). The values of θ_{im} and α estimated by the multiple tracer method compared well with previously measured values using the same technique on the same field. The θ_{im} values for the multiple tracer technique were larger than values derived from the basic single tracer technique. The basic single tracer technique did not take into consideration a mass exchange between θ_{im} and the mobile water domain (θ_m). The α values were less variable for the multiple tracer method than for the single tracer-variance method. Values of immobile water fraction (θ_{im}/θ) for the multiple and basic single tracer techniques ranged from 0.30 to 0.52 and from 0.24 to 0.35, respectively. The values of α for the multiple and single tracer-variance techniques ranged from 0.06 to 0.9 d^{-1} and from 0.03 to 60 d^{-1}, respectively. The volumetric water content (θ) changed considerably over the course of the experiment for the estimation of α using the single tracer-variance method; thus, the assumptions of this technique were compromised. The measured values of $K(h_0)$ at the five sites ranged from 0.47 to 1.66 $\mu m\ s^{-1}$. There was evidence that the basic single tracer method underestimated θ_{im} and overestimated θ_m, because this method considers $\alpha = 0$ during the tracer application.

Many agricultural problems involve the reactivity and transport of dissolved chemicals in the soil. Chemicals such as fertilizer and pesticide are deliberately added to the soil but may result in significant contamination of the groundwater (Pye et al., 1983). These chemicals can be managed to maximize their effectiveness within the root zone and minimize their transport below the root zone. Chemicals often move preferentially through soil, resulting in a high risk of groundwater contamination. Preferential flow is exemplified by the early breakthrough and long tailing in laboratory column experiments and in field lysimeter experiments (Beven and Germann, 1982; Ressler et al., 1998). The mobile–immobile solute transport model (Coats and Smith, 1964), developed within the field of petroleum engineering, includes preferential flow. This model has been expanded and applied to soil columns (van Genuchten and Wierenga, 1976, 1977; van Genuchten et al., 1977). The mobile–immobile model was also applied to field-scale solute transport by Toride and Leij (1996), who used a stochastic stream tube model.

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The mobile–immobile solute transport model separates θ into θ_m and θ_{im}. The soil solution is stagnant in θ_{im}, and advection and dispersion occur in θ_m. For one-dimensional transport of a noninteracting, conservative solute, the mobile–immobile model can be written as follows:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \qquad [1]$$

where C_m and C_{im} are the solute concentrations in the mobile and immobile domains, t is time, D_m is the dispersion coefficient for θ_m, x is distance, and q is Darcy flux. The two domains are connected by a diffusive transfer of chemical at the boundary of θ_{im} and θ_m:

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}). \qquad [2]$$

The diffusive mass transfer is characterized by α. The mobile–immobile model can account for more rapid solute transport because flow only occurs in a fraction of total θ. It can also account for tailing because of the solute exchange between the domains (Eq. [2]).

Values of θ_{im} and α can be estimated from solute breakthrough curves in laboratory experiments. Matching the observed flux concentrations of tracers in column effluent with concentrations predicted from analytical solutions of the mobile–immobile model results in a set of best-fit solute transport parameters (Parker and van Genuchten, 1984; van Genuchten and Wagenet, 1989; Gamerdinger et al., 1990; Toride et al., 1995). Although the observed and calculated flux concentrations may match closely with this method, the estimated transport parameters may not be a unique set of values. Alternative methods for estimating parameter values are needed so that unique sets of solute transport values can be determined. There also exists a need to estimate these parameters without running extensive column breakthrough experiments. Methods that do not require effluent breakthrough curves to estimate solute transport properties are also useful in estimating these parameters in situ.

Tracer techniques have been proposed for estimating θ_{im} and α in the field. These methods give an alternative approach for the estimation of θ_{im} and α without the need for breakthrough curves or solute distribution profiles. These methods are a single tracer method (Clothier et al., 1992, 1995; Angulo-Jaramillo et al., 1996) and a multiple tracer method (Jaynes et al., 1995; Jaynes and Horton, 1998; Casey et al., 1997, 1998; Lee et al., 1996, 1997). The single and multiple tracer methods have been applied in the field and have received limited validation. The multiple tracer method was field tested by Casey et al. (1997) and further laboratory tested by Lee et al. (1996, 1997), the latter of whom used both the breakthrough curve method and the multiple tracer method to estimate θ_{im} and α in the same aggregated soil columns. In these studies a series of tracers were applied, after which the soil columns were sectioned and analyzed for resident tracer concentrations. The multiple tracer method was used with the resident tracer concentrations to estimate θ_{im} and α. Lee et al. (1996, 1997) were able to use these estimates to accurately predict solute breakthrough curves and resident concentration profiles in soil columns. The single tracer method has been field tested in several studies (Clothier et al., 1992, 1995; Angulo-Jaramillo et al., 1996) but no laboratory validation has been done.

Both the multiple and single tracer methods are simplifications of the full mobile–immobile model. There exist two separate single tracer methods: the basic single tracer method to estimate θ_{im} (Clothier et al., 1992) and the single tracer-variance method to estimate α (Clothier et al., 1995). The basic single tracer method used to estimate θ_{im} assumes that $\alpha = 0$ and that there is no significant solute exchange between θ_m and θ_{im} ($C_{im} = 0$) during the course of the experiment. The single tracer-variance method for estimating α does not assume $\alpha = 0$ but that α can be measured over a long period of time. The multiple tracer method simultaneously estimates α and θ_{im} with the assumption that α is not negligible. Both single and multiple tracer methods assume that there is piston displacement of tracer within θ_m and that C_m behind the tracer front is approximated by the input tracer concentration. There are advantages with both of these methods. The basic single tracer method is simple to use when estimating θ_{im} and the analytical techniques are not complex; however, the single tracer-variance method is more involved when estimating α. Both techniques are capable of simultaneously determining soil hydraulic properties. To date there has not been a critical comparison of the two methods. The objective of this study is to compare the single and multiple tracer methods for estimating α and θ_{im} of a field soil.

MATERIALS AND METHODS

Research took place in a ridge-tilled corn field between 30 August and 14 September 1996 at the Agronomy and Agricultural and Biosystems Engineering Research Center west of Ames, IA. The soil was mapped as a Nicollet series derived from glacial till. Five infiltration sites were located in the interrow areas of adjacent corn rows. The infiltration sites were cleared of corn debris and weeds to ensure suitable hydraulic contact between the infiltrometer disk and the soil surface. Experiments to estimate soil hydraulic properties preceded experiments to estimate the solute transport coefficients θ_{im} and α.

Near each site a soil core was taken using a beveled brass ring with height 37 mm and diameter 73 mm. These soil cores were used to determine the antecedent θ and bulk density. A large-base diameter (230 mm, Perroux and White, 1988) tension infiltrometer was filled with a 4-mmol L^{-1} solution of KCl and placed on the flat soil surface. Infiltration began at a pressure head of -30 mm and the early cumulative infiltration (I) volumes were automatically recorded every second for the first 100 s. These early I values were later used to calculate sorptivity (S). The infiltrometers were automated with transducers as described by Ankeny et al. (1988). After the first 100 s of cumulative infiltration, the automated recording interval was changed to read every 576 s for 16 h. These later I values were used to determine the steady state infiltration rates (i) according to White and Sully (1987).

To estimate S, early stages of I values were used with the following expression (Philip, 1957; White and Sully, 1987, 1988):

$$I = St^{1/2} \quad [3]$$

where t is the infiltration time. Sorptivity was estimated from the slope of the measured I vs. $t^{1/2}$, and coefficients of determination were determined for the regression.

To estimate $K(h_0)$, the White and Sully (1987) method was used. White and Sully (1987) derived the following expression for the matrix flux potential (ϕ):

$$\phi = bS^2/(\Delta\theta) \quad [4]$$

where b is a shape factor between $\frac{1}{2}$ and $\pi/4$, and $\Delta\theta$ is the change in θ during the entire infiltration period. Taking a reasonable approximation for b of 0.55 (Smettem and Clothier, 1989) and substituting Eq. [4] into Wooding's (1968) solution for unconfined steady state infiltration from a disk results in the following expression:

$$K(h_0) = i - (2.2S^2)/(\Delta\theta\pi R) \quad [5]$$

where R is the base radius of the infiltrometer (115 mm) and h_0 is the pressure head (-30 mm).

After the 4-mmol L^{-1} KCl solution had reached steady state infiltration rate, a series of four benzoic acid tracer solutions was applied to each site. The tracer solutions were mixed in the same manner as described by Jaynes et al. (1995) and Casey et al. (1997, 1998). The tracers used were *o*-trifluoromethylbenzoate; 2,6-difluorobenzoate; pentafluorobenzoate; and 2,3,6-trifluorobenzoate. Tracer application order was randomized to minimize any error caused by nonidentical transport, recovery, and analysis. Each tracer solution was applied using a separate infiltrometer; detailed laboratory experiments have shown that infiltration rates quickly return to steady state after brief removal of a tension infiltrometer (Clothier et al., 1992). The final tracer solution was applied for approximately 1 to 2.5 h so that the tracer front was well beyond the soil sampling depth of 15 mm. Clothier et al. (1995) determined that infiltrating 25 to 30 mm of tracer was sufficient to sample soil 10 to 15 mm deep while well avoiding the tracer front. We used the same criteria as the Clothier et al. (1995) study for tracer application and sampling depth.

Within seconds after the final tracer application the infiltrometer was removed, and the soil was sampled from the area that had been beneath the tension infiltrometer. The infiltration area was sectioned into four equal parts, and eight cylindrical samples (15 mm deep and 10.6 mm diameter) were taken from one of the quarters (Fig. 1) at the same time. The infiltration area was sectioned into four quarters so that sampling disturbance was localized to a single quarter and minimized at the other quarters. The infiltration sites were then covered with plastic and loose soil was spread over the plastic. This was done to prevent water loss by evaporation and infiltration from precipitation. During the course of the experiment there was no precipitation. Approximately 2 d

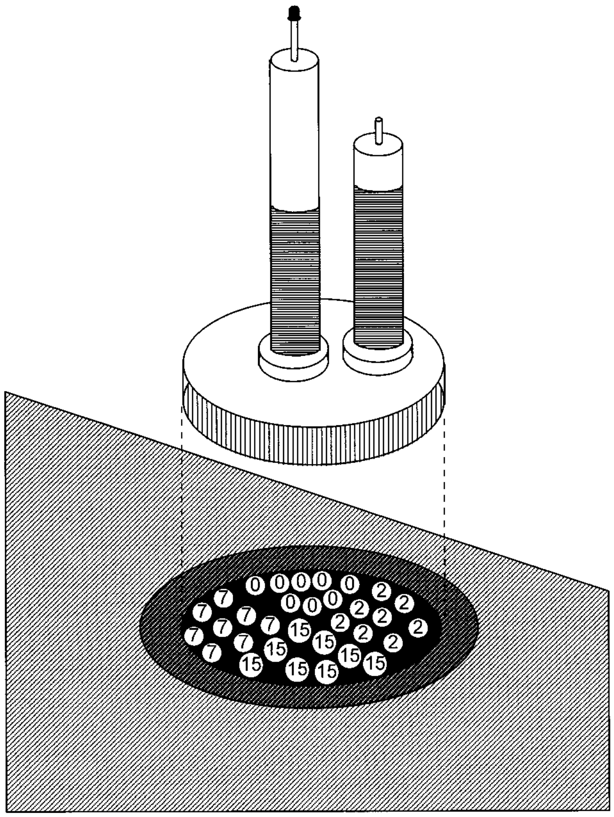

Fig. 1. A diagram of the soil sampling scheme beneath the tension infiltrometer. The soil sampled immediately after the tracer application was used to estimate θ_{im} and α with the Jaynes et al. (1995) method, and to estimate θ_{im} with the Clothier et al. (1992) method. All sampling dates were used to estimate α with the Clothier et al. (1995) method. The sampling dates immediately after the final tracer application, 0, 2, 7, and 15 d, correspond to the numerals, 0, 2, 7, and 15 within the white circles, respectively.

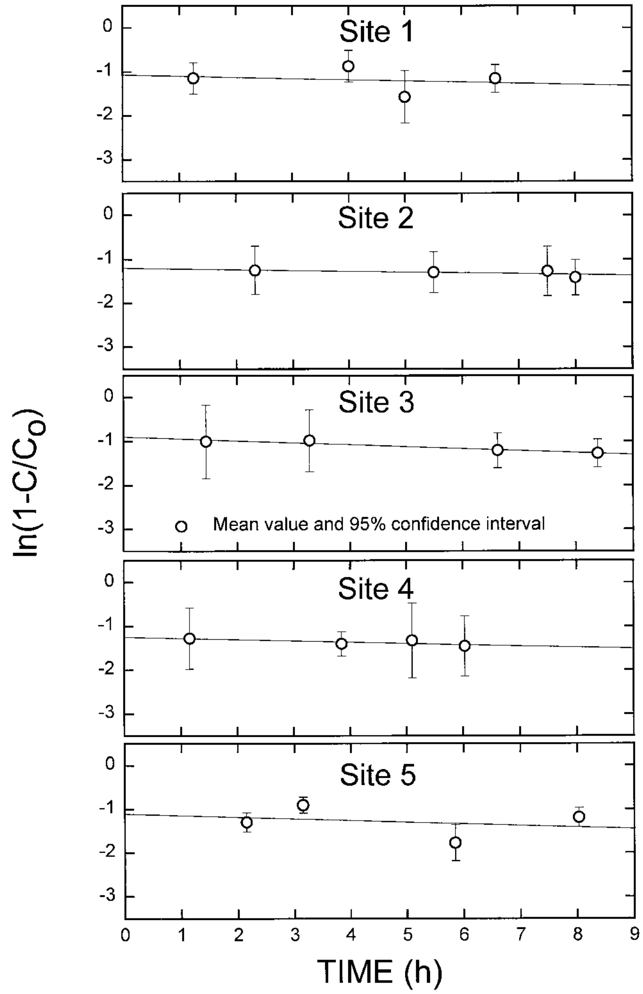

Fig. 2. Regressions of the ln(1 − C/C_0) vs. time used by the Jaynes et al. (1995) method to estimate θ_{im} and α at each site. The slope gives $-\alpha/\theta_{im}$ and the intercept gives $\ln(\theta_{im}/\theta) + \ell\theta_m/(\theta_{im}q)$.

after the start of the tracer application, the soil and plastic sheets were taken off the infiltration sites and eight more soil samples were taken from another quarter of the infiltration site. The soil was then covered again with the plastic and loose soil. This procedure was repeated at approximately 7 d and 15 d after the start of the tracer application. Figure 1 shows the sampling scheme. All soil samples were weighed and placed in plastic zip-lock bags and refrigerated to prevent any loss of tracer or change in θ.

The soil samples were taken to the laboratory for tracer extraction and θ measurements. Tracer extractions of the soil samples were done in 150-mL Erlenmeyer flasks using ≈1:1 soil/0.0005 M $CaSO_4$ solution. The extraction mixture was shaken for 5 min on a wrist shaker and allowed to settle for 5 min. The solution was then decanted through no. 40 filter paper and stored at 2°C until analysis. Approximately 10 mL of filtered solution was needed for tracer solution determination. The remaining decant and soil retained on the filter paper were oven dried at 105°C to compute θ.

Analysis for the fluorobenzoate tracers was done on a Dionex Series 4500i ion chromatograph (Dionex, Sunnyvale, CA) as described by Bowman and Gibbens (1992). For the fluorobenzoates, a SAX column (Regis Chemical Co., Morton Grove, IL)[1] was used with 230 mM KH_2PO_4, adjusted to a pH of 2.65 with H_3PO_4 and 20 mL L^{-1} acetonitrile as the eluting solution. The flow rate was 1 mL min^{-1} and the detection wavelength was set to 205 nm.

Extracted tracer concentrations from the soil sampled immediately after the tracer application were used to estimate θ_{im} and α with the modified Jaynes et al. (1995) method (Casey et al., 1997; Jaynes and Horton, 1998):

$$\ln(1 - C/C_0) = -\alpha t/\theta_{im} + \ln(\theta_{im}/\theta) + \ell\alpha\theta_m/(\theta_{im}q) \quad [6]$$

where C is the measured tracer concentration from the extract, C_0 is the tracer concentration from the input tracer solution, t is tracer application time, and ℓ is the soil sampling depth. It is assumed that $C_0 = C_m$ when the soil is sampled. Plotting $\ln(1 - C/C_0)$ as a function of t should result in a straight line with the intercept of $[\ln(\theta_{im}/\theta) + \ell\alpha\theta_m/(\theta_{im}q)]$ and the slope $-\alpha/\theta_{im}$ (Fig. 2). Since θ_{im} is in both the intercept and slope, a least squares optimization has to be done to estimate α and θ_{im}.

Extracted tracer concentrations from the soil sampled immediately after the tracer application were also used to estimate θ_{im} with the basic single tracer method (Clothier et al., 1992):

$$\theta_{im} = \theta(1 - C/C_0) \quad [7]$$

Equation [7] is identical to Eq. [6] if α is zero. Extracted tracer concentrations that were used to estimate θ_{im} from Eq. [7]

[1] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may be suitable.

were of the longest applied tracer in the series. The basic single tracer method assumed $\alpha = 0$ for the entire tracer experiment, so it should not have mattered which tracer we chose. However, to diminish concern that the assumption that $C_m = C_0$ was not being violated, we chose to use to final tracer in the series. The longer the tracer was applied the higher the probability that $C_m = C_0$ was true.

Clothier et al. (1995) proposed a single tracer-variance method to estimate α by measuring the variance of tracer concentration over time. First, Clothier et al. (1995) analytically expressed the decrease of C_m through time:

$$C_m(t) = C^*[1 + [(\theta - \theta_m)/\theta_m]\exp[-\alpha(\theta_{im}/\theta_m)\theta t]] \quad [8]$$

and the simultaneous increase of C_{im} through time:

$$C_{im}(t) = C^*[1 - \exp[-\alpha(\theta_{im}/\theta_m)\theta t]] \quad [9]$$

where C^* is the equilibrium tracer concentration when $C^* = C_m = C_{im} = C_0\ (1 - \theta_{im}/\theta)$ as t approaches infinity. Finally, Clothier et al. (1995) developed the following expression to predict the normalized variance in tracer concentration under the infiltrometer through time:

$$s^2(t)/s_0^2 = \frac{(\theta_m/\theta)[C_m(t) - C^*]^2 + (\theta_{im}/\theta)[C_{im}(t) - C^*]^2}{C^*(C_0 - C^*)} \quad [10]$$

where $s^2(t)/s_0^2$ is the predicted normalized variance in the soil samples over time. The temporal decline in $[C_m(t) - C^*]$ and $[C_{im}(t)]$ incline in $[C_{im}(t) - C^*]$ can be found using the analytical expressions of Eq. [8] and Eq. [9]. At the time the soil is first sampled it is assumed that the values of $C_{im} = 0$ and the value of $C_m = C_0$. Also, the values for θ_m and θ_{im} that were used in Eq. [8], [9], and [10] came from Eq. [7].

The variance of each of the tracer concentrations from each application site was determined at approximately 0, 2, 7, and 15 d after the tracer infiltration. The time at 0 d was the time the first tracer was applied, and the first sampling occurred at the completion of the last tracer infiltration. The following expression was used to determine the sample variance (s^2) of the tracer concentrations (Steel and Torrie, 1980):

$$s^2 = \sum_{i=1}^{n} \frac{(C - \overline{C})^2}{n - 1} \quad [11]$$

where n is the number of the soil samples ($n = 8$), and $\overline{C}$ is the mean value of the n samples. The sample variance values from Eq. [11] were normalized by dividing through by the initial sample variance, s_0^2, calculated from all of the tracers. This approach for estimating α assumed that the soil samples that were taken from the infiltration site were either sampled from θ_m or θ_{im} (Clothier et al., 1995).

All four tracers were used in estimating the measured $s^2(t)/s_0^2$ values. The tracers were assumed to move through the soil identically, and the tracers were applied at different times. Each tracer was used to estimate an $s^2(t)/s_0^2$ value. Figure 3 shows the observed $s^2(t)/s_0^2$ values (Eq. [11]) from all four tracers and corresponding model curves that were calculated from Eq. [10]. To calculate Eq. [10] it was necessary to calculate $C_m(t)$ and $C_{im}(t)$ values which were calculated using Eq. [8] and Eq. [9], respectively. The varying calculated $s^2(t)/s_0^2$ values from Eq. [10] were obtained by using various α values, which are reported in Fig. 3.

To evaluate the basic single tracer method's assumption that $\alpha \approx 0$, calculations were made with the α values from Eq. [6] to estimate the amount of solute accumulation in θ_{im} during the time of the experiment. The program CXTFIT 2.0 (Toride et al., 1995) was used to calculate the accumulation of tracer in θ_{im} with time.

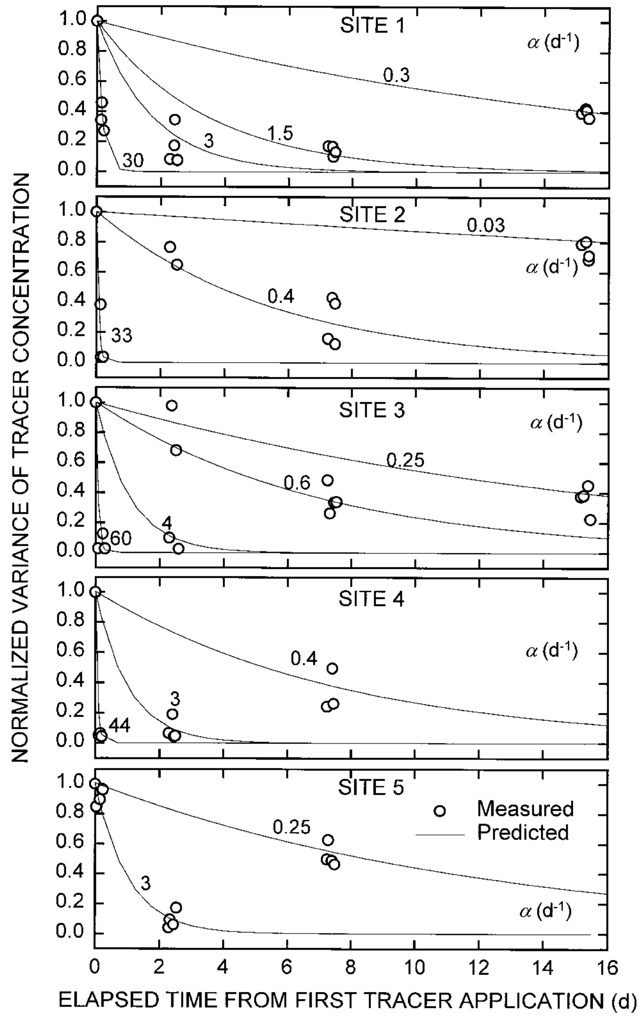

Fig. 3. The predicted and measured normalized sample variance ($s^2(t)/s_0^2$) as a function of time elapsed from the start of the tracer application for each site. Here the predicted α values next to the curves are derived from Eq. [10]. Note that measured $s^2(t)/s_0^2$ values that were >1 were excluded from Site 2 on the second sampling date and from Site 4 and 5 on the last sampling date.

Values of θ_{im}/θ and α from this study were compared with the Casey et al. (1997) study using a one-way ANOVA at a 0.05 significance level (Steel and Torrie, 1980, p. 64, 137–167).

RESULTS

Soil Hydraulic Properties

The first objective of this study was to estimate the hydraulic properties of the soil at −30 mm pressure head; these values are presented in Table 1 for the five

Table 1. Physical and hydraulic properties of the five measurement sites. Hydraulic conductivity ($K(h_0)$) was calculated by the White and Sully (1987) method.

Site	i	$K(h_o)$	S	Antecedent θ	Final θ	Bulk density
	$\mu m\ s^{-1}$		$m^3\ s^{-1/2}$	$m^3\ m^{-3}$		$Mg\ m^{-3}$
1	2.27	1.66	73.98	0.25	0.31	1.11
2	0.49	0.47	20.32	0.28	0.43	1.09
3	2.16	1.02	23.95	0.23	0.34	1.13
4	1.05	1.55	107.80	0.33	0.41	1.20
5	1.45	1.46	0.39	0.21	0.32	1.02

measurement sites. The coefficients of determination for the estimation of S that used the early time infiltration data ranged from 0.77 to 0.99 with a mean of 0.87. Estimations of $K(h_0)$ from the longtime steady state infiltration data using the White and Sully (1987) method were reasonable and fell within the ranges that others have found in soils near this research area (Logsdon and Jaynes, 1996; Logsdon, 1993). Under similar tillage systems and time of the season, Logsdon and Jaynes (1996) found the mean $K(h_0)$ values at $h_0 = -30$ mm to be 4.52 μm s^{-1} with a plus or minus one standard deviation range of 1.81 to 10.70 μm s^{-1}. These values are slightly higher than the values reported in the present study. Also, Logsdon (1993) found $K(h_0)$ values in similar soils to range from 0.67 to 2.2 μm s^{-1}, which were similar to our values (Table 1).

Soil Transport Properties

Multiple Tracer Method

Figure 2 shows the graphs of $\ln(1 - C/C_0)$ vs. t from the first sampling, where only the mean $\ln(1 - C/C_0)$ values and 95% confidence intervals of the eight samples were plotted to avoid clutter. As plotted, the slopes and intercepts of the regression from the eight soil samples at the five sites were quite similar. The estimated median values of θ_{im} from the multiple tracer method for Sites 1, 2, 3, 4, and 5 were 0.17, 0.29, 0.16, 0.19, and 0.10 m^3 m^{-3}, respectively. The variances in θ_{im} values were relatively low for all sites, ranging from 5.0×10^{-4} m^6 m^{-6} at Site 1 to 3×10^{-3} m^6 m^{-6} at Site 5. The corresponding θ_{im}/θ values were 0.52, 0.48, 0.44, 0.44, and 0.30 for the respective Sites 1, 2, 3, 4, and 5. An ANOVA comparison with the Casey et al. (1997) study showed that θ_{im}/θ values in this study were not statistically different at a 0.05 significance level. The Casey et al. (1997) study was conducted two years earlier on the same research field, using the same pressure head.

The median α values for Sites 1, 2, 3, 4, and 5 were 0.6, 0.9, 0.3, 0.7, and 0.1 d^{-1}, respectively. The variances of α values were low, ranging from 2.5×10^{-5} d^{-2} at Site 5 to 0.4 d^{-2} at Site 2. The α values from this study were not significantly different from the Casey et al. (1997) study at a 5% level.

Single Tracer Methods

The estimates of θ_{im} that used the basic single tracer method for Sites 1, 2, 3, 4, and 5 were 0.10, 0.15, 0.10, 0.14, and 0.10 m^3 m^{-3}, respectively. The variances of θ_{im} values ranged from 1.0×10^{-4} m^6 m^{-6} at Site 1 to 2.1×10^{-5} m^6 m^{-6} at Site 2, which was lower than the variance values estimated by the multiple tracer method. The θ_{im}/θ values estimated by the basic single tracer technique were 0.24, 0.35, 0.26, 0.33, and 0.24 for the respective Sites 1, 2, 3, 4, and 5.

Although the exact same soil samples were used, the estimates of θ_{im} and θ_{im}/θ from the single tracer method were lower than the estimates from the multiple tracer method. The single tracer method assumes that the tracer enters the soil surface and moves through θ_m exclusively. The single tracer technique assumes that $\alpha = 0$; therefore, there is no mass exchange between θ_{im} and θ_m and no accumulation of tracer in θ_{im}. If $\alpha = 0$, then the concentration of the tracer should not change through time, which is contrary to the negative slopes shown for the $\ln(1 - C/C_0)$ vs. t function (Fig. 2). Clothier et al. (1995) expressed concern that some of their samples did not reach final concentration due to dispersion. As a result Clothier et al. (1995) recommended that a tracer should infiltrate to depths of 25 to 30 mm for soil samples taken to the 10 to 15 mm depth. This sampling criterion was exceeded in this study. Since the Clothier et al. (1995) sampling recommendation was exceeded, it is less likely the tracer concentrations changed with time because of dispersion rather than as a consequence of α. The Clothier et al. (1995) recommendation is supported by several studies showing that dispersion approaches zero close to the solute application source at the soil surface (Yates, 1992; Gimmi, 1994). Our soil samples were taken at a shallow depth so that the effect of dispersion approached zero. A likely explanation of the increase in tracer concentration through time in Fig. 2 [i.e., decrease of $\ln(1 - C/C_0)$ vs. t] was diffusion of tracer into θ_{im}.

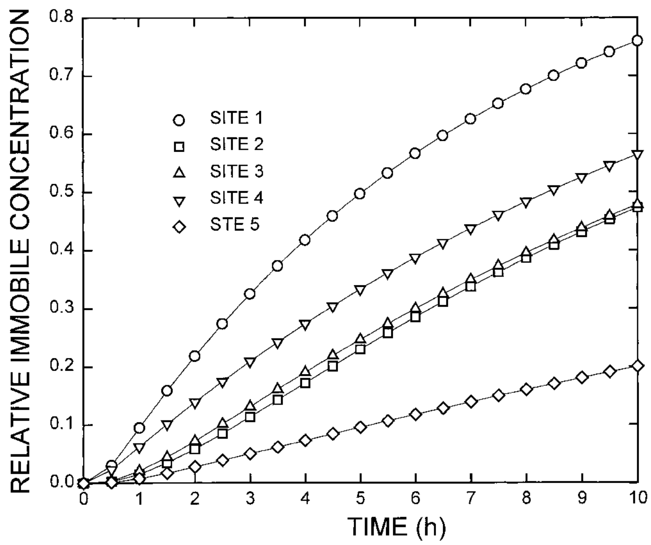

Fig. 4. The calculated relative tracer concentration in the immobile domain as a function of time. Relative immobile tracer concentrations were calculated using CXTFIT 2.0 (Toride et al., 1995), and α values were obtained from the multiple tracer method.

Assuming $\alpha = 0$ does not appear realistic. For instance, using α of 0.5 d^{-1}, as estimated by Clothier et al. (1995), a measurable diffusion of solute into θ_{im} occurs within a few hours (Jaynes and Horton, 1998). Ignoring this diffusion with the basic single tracer method leads to an underestimation of θ_{im}/θ. As a demostration, C_{im} was calculated using CXTFIT 2.0 (Toride et al., 1995) with α values from the multiple tracer method (Eq. [6]). Figure 4 shows the relative C_{im} as a function of time and indicates appreciable accumulation of tracer in θ_{im} at the time of the first soil sampling. This gives further evidence for the underestimation of θ_{im} with the basic single tracer method.

The normalized variance calculated from the mea-

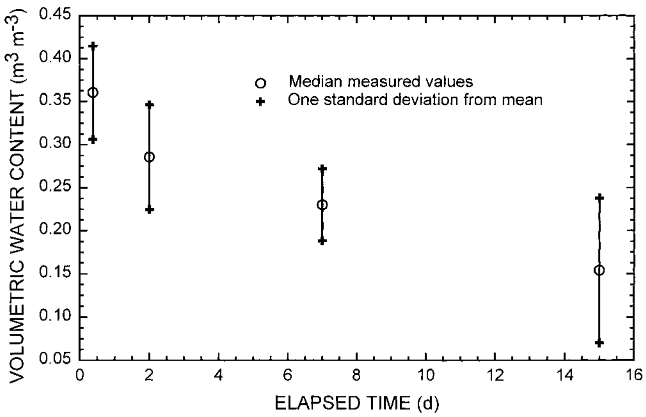

Fig. 5. Soil volumetric water content as a function of time.

sured tracer concentrations with time did not fit the single tracer model (Eq. [10]) very well (Fig. 3). For each of the sampling dates a separate α value can be estimated using this method, so there was not a single α value that characterized the decrease in $s^2(t)/s_0^2$ with time for any of the sites. Also, at any one site the estimated α values ranged from two to three orders of magnitude. The range of α values for all the sites was 0.03 to 60 d^{-1}.

The calculated $s^2(t)/s_0^2$ values did not decrease with time as the assumptions of this method predict. Furthermore, the spread of $s^2(t)/s_0^2$ values between the tracers at each sampling date did not diminish with time (Fig. 3). Values of $s^2(t)/s_0^2$ even went above one for Site 2 on the second day of sampling and again at Sites 4 and 5 on the last day of sampling. The $s^2(t)/s_0^2$ values that were >1 were excluded when we created Fig. 3.

The single tracer-variance method requires constant θ throughout the course of the experiment to estimate α (Clothier et al., 1995). Although the infiltration areas were covered by plastic and loose soil between each of the sampling periods, θ values decreased either from lateral distribution, drainage, condensation on the plastic, or transpiration during the experiment (Fig. 5). An increase in tracer concentration over time at some of the sites was measured and was consistent with the occurrence of transpiration. Corn plants may have drawn soil water from the experimental volume and concentrated the tracer. The large decrease in θ during the 15-d period compromised the single tracer-variance method and probably added variability in the tracer concentration with time. During the first two sampling dates the mean θ values changed the least: 20%; but there still was no consistent decrease in $s^2(t)/s_0^2$ values within the first 2 d. We speculate that the variation in θ for the first two sampling dates was caused by the wetting properties of the soil as affected by the interface with the infiltrometer base, not by the exchange of tracer between θ_m and θ_{im}. Clothier et al. (1995) showed the same disagreement between the single tracer-variance model and their measured $s^2(t)/s_0^2$ values but attributed the disagreement to advective transport. As a rule, the multiple tracer method fit the C data better than the single tracer-variance method.

An additional coinsideration is that the single tracer-variance method assumes that soil samples taken from the infiltration site are either sampled from θ_m or θ_{im} (Clothier et al., 1995). This macroscopic interpretation of θ_m and θ_{im} is a fundamental difference between the single and multiple tracer methods. The multiple tracer method assumes that the domains of solute transport are on a small scale and not found in large pockets of the soil. The single tracer method assumes that the solute transport domains are on a large scale and can be sampled individually.

CONCLUSION

Two single tracer (basic and variance) methods and a multiple tracer method have been proposed for the estimation of the mobile–immobile model transport parameters α and θ_{im}, but they have not been used on the same site. By using these methods at one site, we estimated the hydraulic parameters along with the solute transport parameters. The multiple tracer method consistently gave θ_{im} values that were larger than those given by the basic single tracer method, and we attributed this result to an invalid assumption of $\alpha = 0$ used in the basic single tracer method. The single tracer-variance method for estimating α was less practical than the multiple tracer method because it took a long time and was less consistent with the measured data. The single tracer-variance method gave biased estimates of α because of decreasing soil water during the test period.

ACKNOWLEDGMENTS

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REFERENCES

Angulo-Jaramillo, R., J.P. Gaudet, J.L. Thony, and M. Vauclin. 1996. Measurement of hydraulic properties and mobile water content of a field soil. Soil Sci. Soc. Am. J. 60:710–715.

Ankeny, M.D., T.C. Kaspar, and R. Horton. 1988. Design for an automated tension infiltrometer. Soil Sci. Soc. Am. J. 52:893–896.

Beven, K., and P. Germann. 1982. Macropores and water flow in soils. Water Resour. Res. 18:1311–1325.

Bowman, R.S., and J.F. Gibbens. 1992. Difluorobenzoates as nonreactive tracers in soil and ground water. Ground Water. 30:8–14.

Casey, F.X.M., S.D. Logsdon, R. Horton, and D.B. Jaynes. 1997. Immobile water content and mass exchange coefficient of a field soil. Soil Sci. Soc. Am. J. 61:1030–1036.

Casey, F.X.M., S.D. Logsdon, R. Horton, and D.B. Jaynes. 1998. Measurement of field soil hydraulic and solute transport parameters. Soil Sci. Soc. Am. J. 62:1172–1178.

Clothier, B.E., M.B. Kirkham, and J.E. McLean. 1992. In situ measurements of the effective transport volume for solute moving through soil. Soil Sci. Soc. Am. J. 56:733–736.

Clothier, B.E., L. Heng, G.N. Magesan, and I. Vogeler. 1995. The measured mobile-water content of an unsaturated soil as a function of hydraulic regime. Aust. J. Soil Res. 33:397–414.

Coats, K.H., and B.D. Smith. 1964. Dead end pore volume and dispersion in porous media. SPE J. 4:73–84.

Gamerdinger, A.P., R.J. Wagenet, and M.Th. van Genuchten. 1990. Application of two-site/two-region models for studying simultaneous nonequlibrium transport and degradation of pesticides. Soil Sci. Soc. Am. J. 54:957–963.

Gimmi, T.F. 1994. Transport of reactive gases in unsaturated, structured media-modeling and experimental aspects. Ph.D. diss. Swiss Federal Institute of Technology, Zurich.

Jaynes, D.B., S.D. Logsdon, and R. Horton. 1995. Field method for measuring mobile/immobile water content and solute transfer rate. Soil Sci. Soc. Am. J. 59:352–356.

Jaynes, D.B., and R. Horton. 1998. Field parameterization of the mobile/immobile domain model. p. 297–310. *In* H.M. Selim and L. Ma (ed.) Physical nonequilibrium in soils: Modeling and application. Ann Arbor Press, Chelsea, MI.

Lee, J., D.B. Jaynes, and R. Horton. 1996. Using resident concentrations to estimate two-domain solute transport parameters: Laboratory studies. p. 194. *In* Agronomy abstracts. ASA, Madison, WI.

Lee, J., D.B. Jaynes, and R. Horton. 1997. Laboratory experiments to identify solute transport parameters for saturated soil columns. p. 173. *In* Agronomy abstracts. ASA, Madison, WI.

Logsdon, S.D. 1993. Negative head hydraulic properties of the soil surface at different times. Soil Sci. 156:373–379.

Logsdon, S.D., and D.B. Jaynes. 1996. Spacial variability of hydraulic conductivity in a cultivated field at different times. Soil Sci. Soc. Am. J. 60:703–709.

Parker, J.C., and M.Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments. Bull. 84-3. Virginia Agric. Exp. Stn., Blacksburg.

Perroux, K.M., and I. White. 1988. Design for disk permeameters. Soil Sci. Soc. Am. J. 52:1205–1215.

Philip, J.R. 1957. The theory of infiltration: 4. Sorptivity and algebraic infiltration equation. Soil Sci. 84:257–264.

Pye, V., R. Patrick, and J. Quarles. 1983. Ground water quality in the United States. Univ. of Pennsylvania Press, Philadelphia.

Ressler, D., R. Horton, J.L. Baker, and T. Kaspar. 1998. Evaluation of localized compaction and doming to reduce anion leaching losses using lysimeters. J. Environ. Qual. 27:910–916.

Smettem, K.R.J., and B.E. Clothier. 1989. Measuring unsaturated sorptivity and hydraulic conductivity using multiple disk permeameters. J. Soil Sci. 40:563–568.

Steel, R.G.D., and J.H. Torrie. 1980. Principles and procedures of statistics: A biometric approach. 2nd ed. McGraw-Hill, St. Louis.

Toride, N., F.J. Leij, and M.Th. van Genuchten. 1995. The CXTFIT code for estimating transport parameter from laboratory or field tracer experiments. Version 2.0. Res. rep. 137. U.S. Salinity Lab., ARS-USDA, Riverside, CA.

Toride, N., and F.J. Leij. 1996. Convective–dispersive stream tube model for field scale solute transport: I. Moment analysis. Soil Sci. Soc. Am. J. 60:324–352.

van Genuchten, M.Th., and R.J. Wagenet. 1989. Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solution. Soil Sci. Soc. Am. J. 53:1303–1310.

van Genuchten, M.Th., and P.J. Wierenga. 1976. Mass transfer studies in sorbing porous media: I. Analytical solutions. Soil Sci. Soc. Am. J. 40:473–480.

van Genuchten, M.Th., P.J. Wierenga, and G.A. O'Connor. 1977. Mass transfer studies in sorbing porous media: III. Experimental evaluation with 2,4,5-T. Soil Sci. Soc. Am. J. 41:278–285.

White, I., and M.J. Sully. 1987. Macroscopic and microscopic capillary length and time scales from field infiltration. Water Resour. Res. 23:1514–1522.

White, I., and M.J. Sully. 1988. Field characteristics of macroscopic capillary length or alpha parameter. p. 517–524. *In* P.J. Wierenga and D. Bachelet (ed.) Validation of flow and transport models for the unsaturated zone. Int. Conf. Worksh. Proc. Riudose, NM. 22–26 May, 1988.

Wooding, R.A. 1968. Steady infiltration from a shallow circular pond. Water Resour. Res. 4:1259–1273.

Yates, S.R. 1992. An analytical solution for one-dimensional transport in porous media with an exponential dispersion function. Water Resour. Res. 28:2149–2154.

ERRATUM

Scaling Water Retention Curves for Soils with Lognormal Pore-Size Distribution

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Soil Sci. Soc. Am. J. 62:1496–1505 (November–December 1998).

The following is a list of errors found in the paper above.

1. On the right-hand side of Eq. [10], [11], [15], [16], [17], and [27], the square root notation must exclude the standard deviation parameter, σ.
2. The last sentence of the Physically Based Scaling Approach section on p. 1499 should read:

   Using the scaling theory approach as outlined above, the PDF of ln r for the reference soil, $\hat{f}(\ln r)$, is defined by

$$\hat{f}(\ln r) = \frac{1}{\sqrt{2\pi}\hat{\sigma}} \exp\left[-\frac{(\ln r - \ln \hat{r}_m)^2}{2\hat{\sigma}^2}\right] \quad [27]$$

3. In the sentence immediately following Eq. [34] on p. 1500, $S_e(\alpha_i h^{i,j})$ must be replaced by $\hat{S}_e(\alpha_i h^{i,j})$. Moreover, in the fourth sentence of the Results and Discussion section on p. 1500, ln h_m must be replaced by ln $\hat{h}_m$.
4. In the second paragraph of the Scaling Results section on p. 1501, all occurrences of ln σ_i must be replaced by ln α_i.
5. In the first integrand of Eq. [A2] in Appendix A, $r_{m,i}$ must be replaced by ln $r_{m,i}$.