2000

A Time Domain Reflectometry Method to Measure Immobile Water Content and Mass Exchange Coefficient

Jaehoon Lee
Iowa State University

Robert Horton
Iowa State University, rhorton@iastate.edu

Dan B. Jaynes
U.S. Department of Agriculture, dan.jaynes@ars.usda.gov

A Time Domain Reflectometry Method to Measure Immobile Water Content and Mass Exchange Coefficient

Abstract

Physical nonequilibrium of water and solute transport in soil has been reported. One of the most common mechanistic models used to describe physical nonequilibrium transport phenomena is the mobile–immobile model (MIM). Two significant parameters in the MIM are immobile water content (θ_{im}) and mass exchange coefficient (α). Previously, a method for determining θ_{im} and α using sequential tracers (ST) has been used to characterize solute transport. In this work, we present and evaluate a method to estimate θ_{im} and α using time domain reflectometry (TDR). The TDR method was tested in laboratory experiments using three 20 cm long by 12 cm diameter undisturbed saturated soil columns. The method used TDR with an application of $CaCl_2$ to obtain resident concentrations as a function of time. The data obtained from TDR were analyzed using a log-linear equation developed based on the ST method to estimate θ_{im} and α. The θ_{im} and α estimates from the TDR method were compared with the estimates from the ST method and from effluent data. A conventional inverse curve fitting method (CXTFIT) was used to estimate parameters from effluent data. The means of θ_{im}/θ from the TDR method, ST method, and effluent data were 0.31, 0.30, and 0.26, respectively. The means of α from the TDR method, ST method, and effluent data were 0.03, 0.03, and 0.04 h^{-1}, respectively. The values of θ_{im}/θ and α from the TDR method were very similar to the estimates from the ST method. In all three columns, the θ_{im} estimates from the TDR method were within the 95% confidence intervals (CI) of the estimates from the effluent data. In two of three columns, the α estimates from the TDR method were within the 95% CI of the estimates from the effluent data. The TDR method is relatively simple, rapid, and had advantages over the ST method and conventional methods for measuring solute transport properties.

Disciplines

Agriculture | Hydrology | Soil Science | Statistical Models

Comments

This article is published as Lee, Jaehoon, Robert Horton, and Dan B. Jaynes. "A time domain reflectometry method to measure immobile water content and mass exchange coefficient." Soil Science Society of America Journal 64, no. 6 (2000): 1911-1917. doi: 10.2136/sssaj2000.6461911x. Posted with permission.

Published November, 2000

SOIL SCIENCE SOCIETY OF AMERICA
JOURNAL

VOL. 64 NOVEMBER–DECEMBER 2000 NO. 6

DIVISION S-1—SOIL PHYSICS

A Time Domain Reflectometry Method to Measure Immobile Water Content and Mass Exchange Coefficient

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

ABSTRACT

Physical nonequilibrium of water and solute transport in soil has been reported. One of the most common mechanistic models used to describe physical nonequilibrium transport phenomena is the mobile–immobile model (MIM). Two significant parameters in the MIM are immobile water content (θ_{im}) and mass exchange coefficient (α). Previously, a method for determining θ_{im} and α using sequential tracers (ST) has been used to characterize solute transport. In this work, we present and evaluate a method to estimate θ_{im} and α using time domain reflectometry (TDR). The TDR method was tested in laboratory experiments using three 20 cm long by 12 cm diameter undisturbed saturated soil columns. The method used TDR with an application of $CaCl_2$ to obtain resident concentrations as a function of time. The data obtained from TDR were analyzed using a log-linear equation developed based on the ST method to estimate θ_{im} and α. The θ_{im} and α estimates from the TDR method were compared with the estimates from the ST method and from effluent data. A conventional inverse curve fitting method (CXTFIT) was used to estimate parameters from effluent data. The means of θ_{im}/θ from the TDR method, ST method, and effluent data were 0.31, 0.30, and 0.26, respectively. The means of α from the TDR method, ST method, and effluent data were 0.03, 0.03, and 0.04 h^{-1}, respectively. The values of θ_{im}/θ and α from the TDR method were very similar to the estimates from the ST method. In all three columns, the θ_{im} estimates from the TDR method were within the 95% confidence intervals (CI) of the estimates from the effluent data. In two of three columns, the α estimates from the TDR method were within the 95% CI of the estimates from the effluent data. The TDR method is relatively simple, rapid, and had advantages over the ST method and conventional methods for measuring solute transport properties.

MANY STUDIES (Kanwar et al., 1985; Rice et al., 1986) have shown that water and chemicals can move through soil along preferred pathways such as macropores, cracks, root channels, and worm holes. The rapid movement of water and solute can significantly enhance leaching of surface-applied chemicals to below root growth area and groundwater. One of the first considerations in dealing with the physical nonequilibrium transport is partitioning the flow area into active and nonactive regions (Coats and Smith, 1964; van Genuchten and Wierenga, 1976). This approach has been successful to describe preferential solute transport in both laboratory and field studies (van Genuchten and Wierenga, 1977; Rao et al., 1980; Nkedi-Kizza et al., 1983). In this approach, volumetric water content θ (m^3 m^{-3}) is divided into two regions: a mobile region (θ_m) where water and solute move by advection and an immobile region ($\theta_{im} = \theta - \theta_m$) where chemical movement is by diffusion alone. Exchange of solute between domains is assumed to be first order, the rate being expressed by a solute exchange coefficient (Eq. [2]). Based on the two-domain approach, the transport of nonreactive solute during steady, one-dimensional flow can be written as follows (Coats and Smith, 1964)

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

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

where C_m and C_{im} are concentrations in θ_m and θ_{im}, respectively, t is time, D_m is the dispersion coefficient (m^2 h^{-1}), q_m is water flux (m h^{-1}), x is depth, and α (h^{-1}) is the chemical mass transfer coefficient between θ_m and θ_{im}.

The MIM is used because it is simple to apply and it

Jaehoon Lee and R. Horton, Dep. of Agronomy, Iowa State Univ., Ames, IA 50011; and D.B. Jaynes, USDA-ARS, National Soil Tilth Lab., 2150 Pammel Dr., Ames, IA 50011. Journal paper no. 18616 of the Iowa Agric. and Home Econ. Exp. Stn., Ames; Projects no. 3262 and 3287 and supported by Hatch Act and State of Iowa. Received 16 Sept. 1999. *Corresponding author (rhorton@iastate.edu).

Published in Soil Sci. Soc. Am. J. 64:1911–1917 (2000).

Abbreviations: BTC, breakthrough curve; CI, confidence interval; MIM, mobile–immobile model; PVC, polyvinyl chloride; ST, sequential tracers; TDR, time domain reflectometry; α, mass exchange coefficient; θ_{im}, immobile water content.

can describe some forms of preferential flow. However, determining the required model parameters, θ_{im} and α, in the field is not as easy as in the laboratory. Although one can determine the parameters by applying inverse methods to effluent breakthrough data (Parker and van Genuchten, 1984; van Genuchten and Wagenet, 1989; Gamerdinger et al., 1990), obtaining effluent breakthrough data in the field is not always practical.

Clothier et al. (1992) presented a method for determining θ_{im} in situ using a tension infiltrometer with a conservative, noninteracting tracer. Similarly, Jaynes et al. (1995) extended the method to estimate both θ_{im} and α using a sequence of tracers. This ST method uses a sequence of two or more different fluorobenzoate tracers applied through a ponded or a tension infiltrometer for a step input. The ST method assumes that the initial tracer concentration in the soil is zero, the tracers move identically through the soil, tracer concentration in the mobile domain is constant and equal to the input concentration (C_o), and samples of soil solution are well behind the tracer solute front so that dispersion in θ_m is negligible at the time of sampling. To estimate θ_{im} and α, the following expression was developed by separation of variables in Eq. [2] (Jaynes and Horton, 1998)

$$\ln\left(1 - \frac{C}{C_o}\right) = \ln\left(\frac{\theta_{im}}{\theta}\right) - \frac{\alpha}{\theta_{im}} t^* \qquad [3]$$

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

Equation [3] describes a log-linear relationship between measured resident concentration and tracer application time. Immobile water content and α can be calculated from Eq. [3] by fitting the $\ln(1 - C/C_o)$ vs. t^*. The intercept and slope of the regression line give estimates of both θ_{im} and α. The ST method provides a means for determining estimates of θ_{im} and α in situ by using resident tracer concentrations. The ST method has been tested both in the laboratory (Lee et al., 2000) and the field (Casey et al., 1997), and the results show that the ST method provides reasonable estimates of θ_{im} and α from easy to obtain soil samples. The ST technique, however, has shortcomings. Since each tracer results in only one data point, applying a series of tracers can be expensive and time consuming. The flow characteristics of the tracers may not be exactly identical, which can result in inaccurate parameter estimates. Lifting of the infiltrometers also disrupts solute flow when changing tracer solutions. Therefore, there is a need to develop an additional method for determining the solute transport parameters of field soil.

The ability to take measurements continuously and automatically, in a low-disturbance way, makes TDR a potentially valuable tool for observing solute transport. Since Dalton et al. (1984) first proposed simultaneous TDR measurement of θ and bulk soil electrical conductivity, σ_a (S m^{-1}), which is directly related to soil solution concentration, a number of studies (Vanclooster et al., 1993; Ward et al., 1995; Mallants et al., 1996; Persson 1997) have been done to evaluate the performance of TDR in measuring σ_a. These studies focused on constructing breakthrough curves (BTCs) based on TDR measured θ and σ_a. To date, no one has reported the use of a shallow TDR probe for determining θ_{im} and α. If a shallow TDR can be used to determine θ_{im} and α, it would overcome the shortcomings of the ST method.

The objective of this study was to develop and evaluate a method to estimate θ_{im} and α using TDR. The method was based on the ST method and was tested in carefully controlled laboratory experiments using saturated, undisturbed, soil columns. The parameter estimates of θ_{im} and α obtained from the TDR method were compared to parameters estimated by the ST method and by the effluent BTCs.

THEORY

The σ_a is inversely related to impedance load, Z (Ω), of the TDR probe and the relationship can be expressed (Nadler et al., 1991)

$$\sigma_a = kZ^{-1} \qquad [4]$$

where k is a calibration constant. Measurements of Z obtained by TDR are mostly a function of θ and soil solution electrical conductivity (σ_w). Kachanoski et al. (1992) showed that solute concentrations, C (kg m^{-3}), can be deduced from TDR-estimated σ_a. A linear relationship is generally observed between the C and σ_a for constant water contents and for salinity levels ranging from 0 to ≈50 dS m^{-1} (Ward et al., 1994; Mallants et al., 1996)

$$C = \delta + \beta\sigma_a \qquad [5]$$

where δ and β are calibration constants. Combining Eq. [4] and [5], solute concentration under steady-state conditions can be expressed as (Kachanoski et al., 1992; Ward et al., 1994)

$$C = a_1 Z^{-1} + a_2 \qquad [6]$$

where a_1 and a_2 are constants.

Then, relative solute concentration $\underline{C}(t)$ can be calculated by

$$\underline{C}(t) = \frac{C(t) - C_i}{C_o - C_i} = \frac{Z^{-1}(t) - Z_i^{-1}}{Z_o^{-1} - Z_i^{-1}} \qquad [7]$$

where C_i is background solute concentration, Z_i^{-1} is TDR-measured impedance load for C_i, and Z_o^{-1} is impedance load for C_o. Because of the linear relationship between Z^{-1} and C, the empirical constants a_1 and a_2 in Eq. [6] need not be determined to calculate $\underline{C}(t)$. In other words, the constants a_1 and a_2 in the linear relationship between Z^{-1} and C cancel out and, therefore, we can directly use Z^{-1}, Z_i^{-1}, and Z_o^{-1} values to determine $\underline{C}(t)$. Under steady-state conditions, TDR-determined $\underline{C}(t)$ can be directly used for Eq. [3] to estimate θ_{im} and α. In this case, the left side of Eq. [3] can be reduced to $\ln[1 - \underline{C}(t)]$ because $\underline{C}_o = 1$. However, for better understanding, the expression "$\ln(1 - C/C_o)$" was used for this paper.

In order to compute $\underline{C}(t)$, Z_i and Z_o should be determined. Z_i can be directly measured, but determining Z_o is somewhat difficult. Ward et al. (1994) and Mallants et al. (1996) determined Z_o by applying a long (continuous) solute pulse until the solutes were distributed uniformly throughout the soil profile. However, Mallants et al. (1996) reported that the continuous solute application method may be problematic, especially for undisturbed or structured soils exhibiting nonequilibrium solute transport. Some of their undisturbed soil columns required solute applications for more than 660 h to reach equilibrium. Because of the problems with the continuous solute application method, we used another approach to accurately determine Z_o. The new approach uses a soil sample taken from the 0- to 2-cm surface area where the TDR probe is installed. The soil sample taken after applying tracer provides relative resident concentration at final time t_f, $\underline{C}(t_f)$. Z_o can be determined using Eq. [7] with the TDR measurement at the time t_f, $Z(t_f)$ with the $\underline{C}(t_f)$ and Z_i. Substituting $\underline{C}(t_f)$ in the left side of Eq. [7], and $Z(t_f)$ and Z_i into the right side of Eq. [7], Z_o can be easily calculated. This calibration method based on soil sample extract for determining Z_o removes possible errors from the continuous application method associated with the nonequilibrium of input solution. Once Z_o is determined, $\underline{C}$(t) values can be calculated using Eq. [7] with the Z_o, Z_i, and $Z(t)$ values. Using Eq. [3], one can estimate both θ_{im} and α from simple TDR measurements. Detailed explanation is given in the Materials and Methods section. This TDR method is well suited to in situ measurements in heterogeneous systems as well as to undisturbed soil columns.

MATERIALS AND METHODS

Undisturbed Soil Sampling

Undisturbed soil cores were collected during fall 1998 from the Agronomy and Agricultural Engineering Research Center located ≈11 km west of Ames, IA. The sampling depth was 0 to 30 cm. The plot had been chisel-plowed and planted in corn (*Zea mays* L.). The soil at the experimental site is classified as Nicollet silt loam (fine-loamy, mixed, superactive, mesic Aquic Hapludolls) in the Clarion–Nicollet–Webster soil association. Selected physical properties of the soil are listed in Table 1. The particle density was measured using the pycnometer method described by Blake and Hartge (1986).

To obtain undisturbed soil columns from the field, 50-cm-wide trenches were dug. The depth of each trench was ≈40 cm. For each soil core, a furnace pipe (so-called stove pipe, 12-cm diam. and 30-cm length) whose side is crimped and folded so that it can be opened from the side was placed on the surface after removing vegetation. Soil around the pipe was gently shaved to form a pedestal of ≈12 cm in diameter. The pipe was then carefully pushed downward to encase the column and to avoid smearing. The process continued until 30-cm-long soil columns were obtained. The upper surface of each soil column was preserved and represented the actual field soil surface, with the exception that litter and loose soil had been carefully removed to provide a level surface. Each soil column was then wrapped in a plastic bag and stored at 4°C to minimize biological activity.

In the laboratory, the furnace pipe was opened from the sides and removed from the undisturbed soil column. The soil cores were trimmed to the desired dimensions (12-cm diam. and 20-cm length). A polyvinyl chloride (PVC) plastic pipe (14-cm diam.) was put around each soil column so that the soil core was at the center of the PVC pipe. The space between the soil core and the PVC pipe was filled with molten paraffin wax. The paraffin wax was used to eliminate wall flow of the soil column. After the space was sealed with paraffin wax, a wire screen was attached to the bottom of the column to prevent soil loss and a funnel was positioned beneath the column. The funnel was used to direct effluent to a fraction collector.

Table 1. Physical conditions of the three soil columns used.

Column	Particle density	Bulk density	Saturated water content	Velocity	K_{sat}
	g cm^{-3}		cm^3 cm^{-3}	cm h^{-1}	
A	2.56	1.42	0.45	17.9	7.8
B	2.59	1.32	0.49	20.9	9.7
C	2.58	1.40	0.46	26.2	11.5

TDR Setup

A two-rod, 2-mm-diam. and 80-mm-long TDR probe was used along with a cable tester (model 1502B, Tektronix Corp., Redmond, OR) and TACQ program (Evett, 1998) to obtain Z values as a function of time during miscible displacement experiments. The probe was installed diagonally from the surface to a depth of 2 cm (Fig. 1) to simulate a field condition. In the field, one can minimize soil disturbance by installing the TDR probe diagonally instead of horizontally. Thus, we assume that the TDR probe measures the average σ_a of the top 2-cm layer of soil. The experiment was conducted at a constant temperature of 25 ± 1°C, and the length of coaxial cable was 100 cm.

Miscible Displacement Experiments

Three soil columns were used for miscible displacement experiments. The soil columns were designated Column A, Column B, and Column C. Two continuous steady-flow miscible displacement experiments, (i) a step application of $CaCl_2$ (TDR method) and (ii) a step input of ST application, were successively conducted on each soil column. Each undisturbed soil column equipped with TDR probe was positioned vertically and slowly saturated from the bottom with a background solution of 0.01 M $CaCl_2$. After saturation, a steady downward flow was established with a 1-cm surface head. The volume rate of outflow was measured as a function of time during each experiment to confirm the steady flow conditions.

Before starting the first step input experiment, Z_i of the soil solution was measured using TDR. This value represented a concentration of background solution and was used to calculate $\underline{C}(t)$ values in Eq. [7]. Input solution of 0.5 M $CaCl_2$ was applied using a mariotte bottle with 1-cm constant head. Approximately four pore volumes (based on whole soil column) of input solution were applied. We assumed that the background (0.01 M) and input (0.5 M) concentrations of $CaCl_2$ satisfied the linear relationships between the Z and σ_a reported in the previous studies (Nadler et al., 1991; Vogeler et al., 1996). The duration of four pore volumes, ≈4 h, of

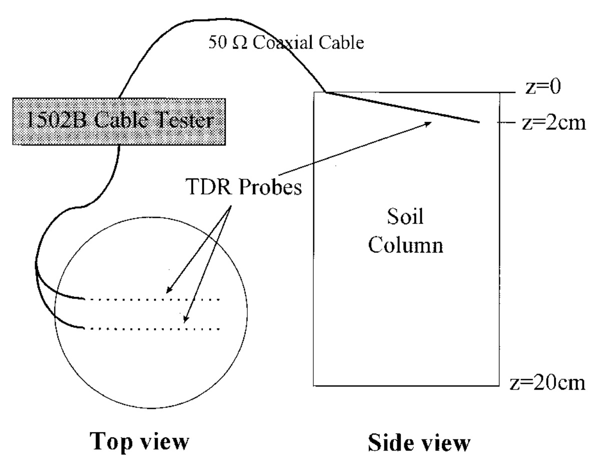

Fig. 1. Schematic diagram of time domain reflectometry (TDR) setup. A two-wire type 8-cm-long probe was diagonally installed in the surface 2-cm layer of the each soil column.

input application were equivalent to 40 pore volumes of input application for the top 2-cm sampling layer where the TDR probe was diagonally installed. The $Z(t)$ values were measured at a time interval equivalent to 0.025 pore volume for the whole experiment. During the experiment, θ was estimated with the TDR using the Topp et al. (1980) equation. The estimated θ was used in Eq. [3] to estimate θ_{im} and α.

After we measured $Z(t)$ values, each soil column was leached with 0.003 M $CaCl_2$ until each soil column was saturated with 0.003 M $CaCl_2$ solution to establish a constant molar concentration for ST experiments. After saturation with 0.003 M $CaCl_2$ solution, ST miscible displacement experiments were conducted using sequences of three fluorobenzoate tracer solutions.

The sequences of the tracer solutions were applied at the top of each column with a 1-cm surface head. The first solution was composed of 0.002 M $CaCl_2$ and 0.001 M of either 2,6-difluorobenzoate, pentafluorobenzoate, or *o*-trifluoromethylbenzoate tracer. After leaching the column with about one pore volume (of whole soil core) of the first solution, a second solution was applied containing 0.001 M $CaCl_2$, 0.001 M of the first benzoate tracer, and 0.001 M of a second benzoate tracer. The second solution was applied for about two pore volumes. Finally, the third solution was applied for about one pore volume. The third solution contained no $CaCl_2$, and the three benzoate tracers were each at a concentration of 0.001 M. Two tracer application orders were made, and the orders were randomized for the columns so that any bias caused by nonidentical tracer transport, recovery, and analysis would be lessened. Each 0.025 pore volume of outflow containing the tracers was collected from each column with a fraction collector, and the samples were stored at 4°C before analysis.

After infiltrating the third solution, the application and outflow were stopped and the top 2-cm surface soil was collected. This sampling depth was identical to the sampling depth of the diagonally installed TDR probe. The soil sample was then extracted by adding 30 mL of a 0.002 M $CaSO_4$ solution. Each sample was shaken for 10 min and allowed to settle for 8 h. The extractions were then centrifuged at 9200 g for 20 min and decanted for analysis. The remaining soil was oven-dried at 105°C, and the dry weight of the sample was used to calculate θ. Analysis for the fluorobenzoate tracers was done on a Dionex Series 4500i ion chromatograph (Dionex, Sunnyville, CA) and UV detector by the method described by Bowman and Gibbens (1992) using a SAX column (Regis Chemical Co., Morton Grove, IL) with 0.03 M 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 of the UV detector was set to 205 nm. The resident concentration from the soil extracts along with TDR data was used to determine Z_o.

Parameter Estimation: TDR Method

In order to obtain Z, a simplified waveform analysis approach was used. The impedance load, Z, (Ω) is (Wraith et al., 1993)

$$Z = Z_{Ref}\frac{(1 + \rho)}{(1 - \rho)} \quad [8]$$

where Z_{Ref} is output impedance of the cable tester (50 Ω), and ρ is the reflection coefficient of the TDR waveform. Detailed descriptions to determine Z can be found in Wraith et al. (1993).

The TDR-measured values of $Z(t)$ were normalized to $\underline{C}(t)$ values based on Eq. [7]. As briefly explained in the Theory section, Z_i and Z_o should be determined to calculate $\underline{C}(t)$. Z_i was measured before applying input (0.5 M $CaCl_2$) solution. Z_o was computed using Eq. [7] based on the relative resident concentration, $\underline{C}(t_f)$, from the top 2-cm soil sample. We assume that the TDR probe measures the average σ_a of the top 2-cm layer of soil. The soil sample is also taken from the top 2-cm layer of soil. Thus, $\underline{C}(t_f)$ and the last measured $Z(t_f)$ after applying four pore volumes of input tracer have identical sampling depth. Z_o was determined using Eq. [7] with $Z(t_f)$, Z_i, and $\underline{C}(t_f)$. For example, the relative $\underline{C}(t_f)$ from the soil sample for Column C was 0.86. Substituting 0.86 with $\underline{C}(t)$ into Eq. [7] with $Z^{-1}(t_f)$ and Z_i^{-1}, Z_o (or Z_o^{-1}) can be easily determined. Using the Z_o and measured $Z(t)$ values, $\underline{C}(t)$ values were obtained. The normalized $\underline{C}(t)$ values represent relative resident concentrations of the top 2-cm soil layer, where the TDR probe was installed. The $\underline{C}(t)$ values and θ were analyzed by Eq. [3] to estimate θ_{im} and α.

Jaynes et al. (1995) assumed that soil solution that was well behind the front of the tracers was free of dispersive effects of the tracer in the mobile domain. To satisfy this assumption, we used data obtained after one pore volume (identical to 10 pore volumes for the 2-cm sampling layer) of tracer application, because the tracer front was well beyond the 2-cm depth probes. The resident concentrations over time were fitted to Eq. [3] plotting vs. t^*. Fitting Eq. [3] to the resident concentrations obtained from TDR measurements provides α and θ_{im} values from the slopes and intercepts. The intercept of the least-square regression gave $\ln(\theta_{im}/\theta)$, and α was obtained from the slope (shown in Fig. 2).

Parameter Estimation: Sequential Tracers Method

Equation [3] was applied to the resident concentration data from the 2-cm top soil extracts obtained with ST application to estimate θ_{im} and α. The procedure for determining θ_{im} and α was very similar to the procedure used in the TDR method. Detailed descriptions to calculate θ_{im} and α using the ST resident concentrations can be found in Jaynes et al. (1995), Casey et al. (1997), and Lee et al. (2000).

Parameter Estimation: Effluent Data

The effluent BTCs obtained from all three tracers were used to estimate θ_{im}, α, and D_m by the conventional inverse curve fitting method. 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 three BTCs were then combined to produce a single group BTC for analysis, and the three MIM parameters, θ_{im}, α, and D_m, were estimated by the program CXTFIT, version 2 (Toride et al., 1995). Eventually, three sets of θ_{im} and α were generated from each column: from the (i) TDR method, (ii) ST method, and (iii) effluent method. We should note that the parameter estimates from the effluent BTCs were obtained from the 20-cm-long soil column, whereas the parameter estimates from the ST and TDR methods were obtained from the surface 2-cm soil layer.

RESULTS AND DISCUSSION

Figure 2a shows the normalized $\underline{C}(t^*)$ values from the TDR method plotted as $\ln(1 - C/C_o)$ vs. t* and regression lines fitted to the data using Eq. [3]. The TDR measurements were obtained from the top 2-cm soil layer. The average coefficient of determination (r^2) value for the regression from the Eq. [3] was 0.92, indicating relevance of the expression, Eq. [3], for physical nonequilibrium solute transport processes in this soil.

Figure 2b shows the resident concentrations plotted

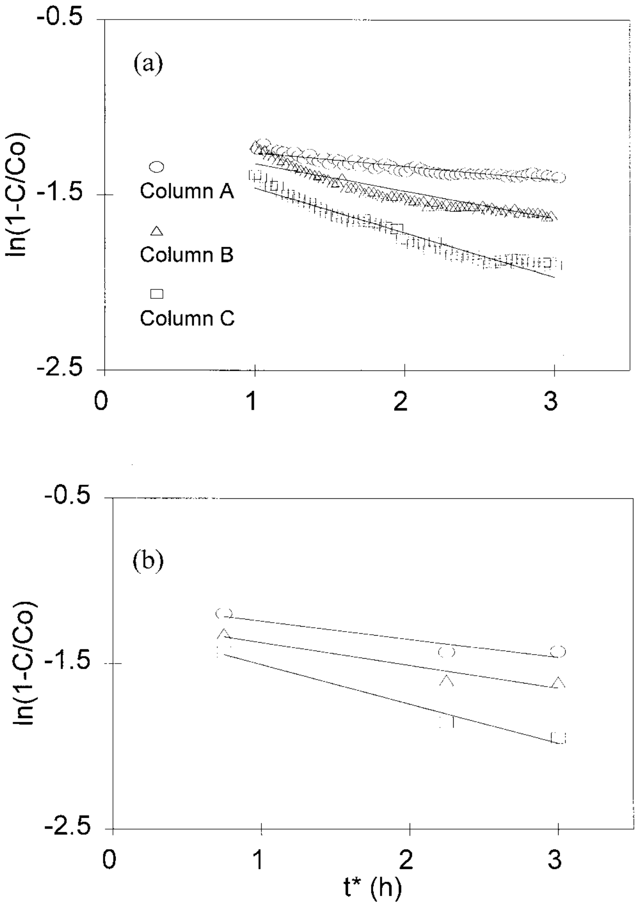

Fig. 2. (a) The relative resident concentrations obtained from TDR are plotted as ln(1 − C/C_o) vs. t^*, and the regression lines are fitted to the data using Eq. [3]. (b) The resident concentrations are plotted as ln(1 − C/C_o) vs. t^*, and the regression lines are fitted to the data using Eq. [3]. The data are obtained from surface 2-cm soil extracts sampled after applying a series of three different fluorobenzoate tracers.

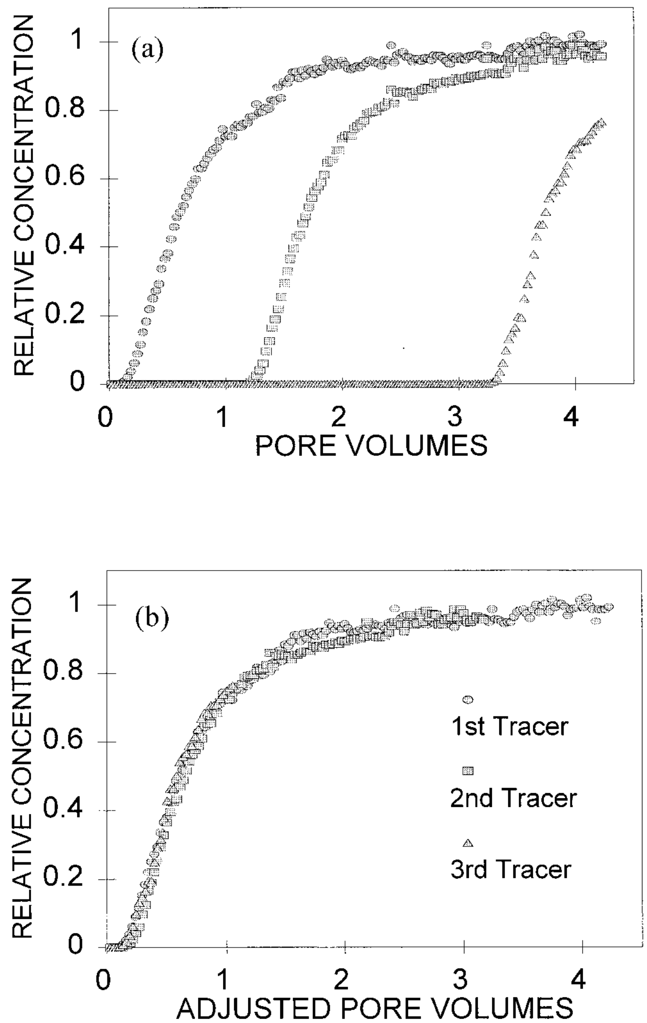

Fig. 3. (a) Flux-averaged concentration BTCs of the three different tracers for Column C. (b) The BTCs are adjusted so that $t = 0$ when each tracer is first applied to Column C.

as ln(1 − C/C_o) vs. t^* with regression lines from Eq. [3] fitted to the data from the ST method. The ST resident concentrations were obtained from the top 2-cm of surface soil. This sampling depth was identical to the sampling depth of the diagonally installed TDR probe. For all three columns, the overall average of r^2 for the regression lines was 0.95. The relative resident concentrations from each soil extract for Column A, B, and C were 0.76, 0.80, and 0.86, respectively. The θ values from TDR and soil extracts were almost identical having only 0.01 cm^3 cm^{-3} difference. The θ from TDR were used for Eq. [3] for the TDR method, and the θ from soil extracts were used for the ST method.

Data were obtained more easily using the TDR method than the ST method. While the ST method provided only three data points after applying three different tracers, the TDR method produced an extensive series of data points because of our chosen data acquisition time interval. The extensive data points can reduce any potential error caused by tracer analysis.

Figure 3a shows the BTCs of three tracers in outflow from Column C. Since we applied three tracers sequentially at an interval of about one pore volume, the results produced three separate BTCs. The BTCs for all three soil columns were similar. In Fig. 3b, 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. Overall, the BTCs for all three soil columns showed early arrival of tracers and tailing, which is representative of preferential flow or physical nonequilibrium (van Genuchten and Wierenga, 1977; Rao et al., 1980; Nkedi-Kizza et al., 1983). The effluent BTC data were used to estimate MIM parameters (θ_{im}, α, and D_m) by the curve fitting method using the program CXTFIT.

Table 2 is a summary of the estimated MIM parameters by the TDR method, ST method, and effluent method for the three soil columns. The 95% CIs were also reported. The CIs for the effluent method were provided by the CXTFIT program (Toride et al., 1995). The CIs for the TDR method and the ST method were calculated based on a technique described by Goldman and Weinberg (1985). The CIs were calculated based on analysis of variance for the regression. The technique used the log-linear relationship between the measured

Table 2. Comparison of parameter estimates from the time domain reflectometry (TDR) method, sequential tracers (ST) method, and effluent method.

Column		TDR method	ST method	Effluent
A	θ_{im}/θ	0.31 (0.30–0.31)†	0.32 (0.20–0.53)	0.26 ± 0.05‡
	α (h^{-1})	0.01 (0.01–0.01)	0.02 (−0.04–0.73)	0.07 ± 0.03
	D_m (cm^2 h^{-1})	–	–	108 ± 0.01
B	θ_{im}/θ	0.32 (0.32–0.33)	0.29 (0.17–0.50)	0.22 ± 0.11
	α (h^{-1})	0.03 (0.03–0.03)	0.02 (−0.13–0.76)	0.03 ± 0.04
	D_m (cm^2 h^{-1})	–	–	160 ± 0.01
C	θ_{im}/θ	0.30 (0.30–0.31)	0.28 (0.17–0.46)	0.30 ± 0.03
	α (h^{-1})	0.04 (0.03–0.04)	0.05 (0.03–0.83)	0.03 ± 0.02
	D_m (cm^2 h^{-1})	–	–	124 ± 0.01

† 95% confidence intervals (CI) obtained based on analysis of variance.
‡ 95% CI provided by the CXTFIT program.

resident concentrations and time. The lower and upper limits of 95% CI for the TDR method and the ST method were not identical due to the log-linear relationship. The 95% CI for the ST method were notably larger than the 95% CI for the TDR method. The number of observations influenced the size of CI. While the estimated immobile water fraction (θ_{im}/θ) for the effluent method ranged from 0.22 to 0.30, the θ_{im}/θ for the TDR method ranged from 0.30 to 0.32, and from 0.28 to 0.32 for the ST method, indicating the consistency of the Eq. [3] and [8]. The means of θ_{im}/θ from the TDR method, ST method, and effluent method were 0.31, 0.30, and 0.26, respectively. The estimated α values ranged from 0.01 to 0.04 for the TDR method, from 0.02 to 0.05 for the ST method, and from 0.03 to 0.07 for the effluent method. The means of α from the TDR method, ST method, and effluent method were 0.03, 0.03, and 0.04, respectively. In most cases, the θ_{im} and α estimates from the ST method were within the 95% CI of the estimates from the effluent data. Similar results were reported by Lee et al. (2000). The values of θ_{im}/θ and α from the TDR method were very similar to the estimates from the ST method. In all three columns, the θ_{im} estimates from the TDR method were within the 95% CI of the estimates from the effluent data. In two of three columns, the α estimates from the TDR method were within the 95% CI of the estimates from the effluent data. Overall, the estimates of θ_{im}/θ and α from the TDR method were very similar to estimates from the ST method and effluent data. Jaynes and Shao (1999) tested the assumption of negligible D_m, which is used for the ST method, by using analytical solutions to MIM. They reported 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 (peclet number) is larger than 100. In this study, ω was smaller than 0.02 with an average of 0.006, and P was larger than 100 for all soil cores. Snow (1999) also examined the effect of the assumptions used for the ST method using a semianalytical solution to MIM. She concluded that when dispersivity (λ) is $<$20 mm and water flux (q) is $>$10 mm h^{-1}, then accurate values of θ_{im} and α can be measured for a wide range of flow conditions. She also reported that if $\lambda > 20$ mm, sampling conditions became very restrictive due to curvilinear behavior in $\ln(1 - C/C_o)$, which is owing to a violation of the assumption that $C_m = C_o$ for all $t^* \geq 0$. In this study, the values of q for all soil columns were higher than 10 mm h^{-1} with an average of 101 mm h^{-1} while, λ calculated from the estimated D ranged from 47 to 77 mm, with an average of 61 mm. Note that while the ST method has restrictive sampling conditions at low q and high λ, the TDR method can reduce the possible errors caused by the curvilinear behavior. Since, the TDR method produces an extensive series of data points, one can eliminate the curvilinear data before applying Eq. [3]. However, in this study, adjustment for curvilinear data was not considered because the main purpose of this study was to directly compare the ST method and the TDR method.

Note the simplicity of the TDR method compared with the ST method. The ST method was time consuming because a series of fluorobenzoate tracers was required to obtain a few data points, and there was a chance to disturb the soil surface when shifting to different infiltrometers. The TDR method needed only a step application of $CaCl_2$ and provided extensive data points. From a simple salt solution BTC experiment, one can determine θ_{im} and α.

CONCLUSIONS

The estimates of θ_{im} and α from the TDR method agreed well with the estimates from the effluent data and the ST method. The TDR method provided reasonable θ_{im} and α values so that one could use this method as a first approximation before applying other methods to characterize solute transport in soil. The TDR method was relatively simple, rapid, and reliable. The TDR method had advantages over the ST method and the conventional BTC method. We conclude that the TDR method is a promising method to estimate θ_{im} and α from a simple experiment. The TDR method only needs a step application of salt and a surface soil sample under steady flow condition. One can then easily estimate θ_{im} and α using a shallow TDR probe in situ.

ACKNOWLEDGMENTS

We thank Dr. James B. Swan from the Agronomy Department at the Iowa State University; Dr. Kosuke Noborio from the Department of Agricultural Engineering at the Iwate University, Japan; Dr. Steven R. Evett at the USDA-ARS, Bushland, TX; and Dr. Sally Logsdon at the USDA-ARS, Ames, IA; for helpful comments and suggestions.

REFERENCES

Blake, G.R., and K.H. Hartge. 1986. Particle density. p. 377–382. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Agron. Monogr. 9. ASA, Madison, WI.

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.

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.

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

Dalton, F.N., W.N. Herkelrath, D.S. Rawlins, and J.D. Rhoades. 1984.

Time domain reflectometry: Simultaneous measurement of soil water content and electrical conductivity with a single probe. Science 224:898–990.

Evett, S.R. 1998. The TACQ computer program for automatic measurement of water content and bulk electrical conductivity using time domain reflectometry. ASAE meeting presentation. Paper no. 983182. USDA-ARS, Bushland, TX.

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

Goldman, R.N., and J.S. Weinberg. 1985. Statistics. An introduction. Prentice-Hall, Englewood Cliffs, NJ.

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, Ann Arbor, MI.

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

Jaynes, D.B., and M. Shao. 1999. Evaluation of a simple technique for estimating two-domain transport parameters. Soil Sci. 164:82–91.

Kanwar, R.S., J.L. Baker, and J.M. Laflen. 1985. Nitrate movement through the soil profile in relation to tillage system and fertilizer application method. Trans. ASAE 28:1802–1807.

Lee, J.H., D.B. Jaynes, and R. Horton. 2000. Evaluation of a simple method for estimating solute transport parameters: Laboratory studies. Soil Sci. Soc. Am. J. 64:492–498.

Mallants, D., M. Vanclooster, N. Toride, J. Vanderborght, M.Th. van Genuchten, and J. Feyen. 1996. Comparison of three methods of calibrate TDR for monitoring solute movement in unsaturated soil. Soil Sci. Soc. Am. J. 60:747–754.

Nadler, A., S. Dasberg, and I. Lapid. 1991. Time domain reflectometry measurements of water content and electrical conductivity of layered soil columns. Soil Sci. Soc. Am. J. 55:938–943.

Nkedi-Kizza, P., J.W. Biggar, M.Th. van Genuchten, P.J. Wierenga, H.M. Selim, J.M. Davidson, and D.R. Nielsen. 1983. Modeling tritium and chloride 36 transport through an aggregated Oxisol. Water Resour. Res. 19:691–700.

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.

Persson, M. 1997. Soil solution electrical conductivity measurements under transient conditions using time domain reflectometry. Soil Sci. Soc. Am. J. 61:997–1003.

Rao, P.S.C., D.E. Rolston, R.E. Jessup, and J.M. Davidson. 1980. Solute transport in aggregated porous media: Theoretical and experimental evaluation. Soil Sci. Soc. Am. J. 44:1139–1146.

Rice, R.C., R.S. Bowman, and D.B. Jaynes. 1986. Percolation of water below an irrigated field. Soil Sci. Soc. Am. J. 50:855–859.

Snow, V.O. 1999. In situ measurement of solute transport coefficients: Assumptions and errors. Soil Sci. Soc. Am. J. 63:255–263.

Topp, G.C., J.L. Davis, and A.P. Annan. 1980. Electromagnetic determination of soil water content: Measurement in coaxial transmission lines. Water Resour. Res. 16:574–582.

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

Vanclooster, M., D. Mallants, J. Diels, and J. Feyen. 1993. Determining local-scale solute transport parameters using time domain reflectometry (TDR). J. Hydrol. 148:93–107.

van Genuchten, M.Th., and R.J. Wagenet. 1989. Two-site/two-region models for pesticide transport and degradation. 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., and P.J. Wierenga. 1977. Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium (^3H_2O). Soil Sci. Soc. Am. J. 41:272–278.

Vogeler, I., B.E. Clothier, S.R. Green, D.R. Scotter, and R.W. Tillman. 1996. Characterizing water and solute movement by time domain reflectometry and disk permeametry. Soil Sci. Soc. Am. J. 60:5–12.

Ward, A.L., R.G. Kachanoski, and D.E. Elrick. 1994. Laboratory measurements of solute transport using time domain reflectometry. Soil Sci. Soc. Am. J. 58:1031–1039.

Ward, A.L., R.G. Kachanoski, and D.E. Elrick. 1995. Analysis of water and solute transport away from a surface point source. Soil Sci. Soc. Am. J. 59:699–706.

Wraith, J.M., S.D. Comfort, B.L. Woodbury, and W.P. Inskeep. 1993. A simplified waveform analysis approach for monitoring solute transport using time domain reflectometry. Soil Sci. Soc. Am. J. 57:637–642.