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

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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 ($\theta_{im}$) and mass exchange coefficient ($\alpha$). Previously, a method for determining $\theta_{im}$ and $\alpha$ using sequential tracers (ST) has been used to characterize solute transport. In this work, we present and evaluate a method to estimate $\theta_{im}$ and $\alpha$ 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 $\theta_{im}$ and $\alpha$. The $\theta_{im}$ and $\alpha$ 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 $\theta_{im}/\theta$ from the TDR method, ST method, and effluent data were 0.31, 0.30, and 0.26, respectively. The means of $\alpha$ from the TDR method, ST method, and effluent data were 0.03, 0.03, and 0.04 h$^{-1}$, respectively. The values of $\theta_{im}/\theta$ and $\alpha$ from the TDR method were very similar to the estimates from the ST method. In all three columns, the $\theta_{im}$ 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 $\alpha$ 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

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DIVISION S-1—SOIL PHYSICS

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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 ($\theta_{im}$) and mass exchange coefficient ($\alpha$). Previously, a method for determining $\theta_{im}$ and $\alpha$ using sequential tracers (ST) has been used to characterize solute transport. In this work, we present and evaluate a method to estimate $\theta_{im}$ and $\alpha$ 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 $\theta_{im}$ and $\alpha$. The $\theta_{im}$ and $\alpha$ estimates from the TDR method were very similar to 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 $\theta_{im}/0$ from the TDR method, ST method, and effluent data were 0.31, 0.30, and 0.26, respectively. The means of $\alpha$ from the TDR method, ST method, and effluent data were 0.03, 0.03, and 0.04 h$^{-1}$, respectively. The values of $\theta_{im}/0$ and $\alpha$ from the TDR method were very similar to the estimates from the ST method. In all three columns, the $\theta_{im}$ estimates from the TDR method were within the 95% confidence intervals (CI) of the estimates from the ST method. In two of three columns, the $\alpha$ estimates from the TDR method were within the 95% CI of the estimates from the effluent data. In two of three columns, the $\alpha$ 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 $\theta$ (m$^3$ m$^{-3}$) is divided into two regions: a mobile region ($\theta_m$) 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)

$$\theta_m \frac{dC_m}{dt} + \theta_{im} \frac{dC_{im}}{dt} = \theta_m D_m \frac{d^2C_m}{dx^2} - q_m \frac{dC_m}{dx}$$

[1]

$$\theta_{im} \frac{dC_{im}}{dt} = \alpha(C_m - C_{im})$$

[2]

where $C_m$ and $C_{im}$ are concentrations in $\theta_m$ and $\theta_{im}$, 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 $\alpha$ (h$^{-1}$) is the chemical mass transfer coefficient between $\theta_m$ and $\theta_{im}$.

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

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


can describe some forms of preferential flow. However, determining the required model parameters, $\theta_m$ and $\alpha$, 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 Wagener, 1989; Gamarndier et al., 1990), obtaining effluent breakthrough data in the field is not always practical.

Clothier et al. (1992) presented a method for determining $\theta_m$ in situ using a tension infiltrometer with a conservative, noninteracting tracer. Similarly, Jaynes carefully controlled laboratory experiments using saturation ($s$) calculated from Eq. [3] by fitting the $\ln(1 - C/C_o)$ vs. $t^*$ relationship between measured resident concentration and tracer application time. Immobile water content and $\alpha$ can be calculated from Eq. [3] by fitting the $\ln(1 - C/C_o)$ vs. $t^*$ intercept and slope of the regression line. The intercept and slope give estimates of both $\theta_m$ and $\alpha$. The ST method provides a means for determining estimates of $\theta_m$ and $\alpha$ 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 $\theta_m$ and $\alpha$ 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 $\theta$ and bulk soil electrical conductivity, $\sigma_r$ (S m$^{-1}$), which is directly related to soil solution concentration, a number of studies (VanCloooster et al., 1993; Ward et al., 1995; Mallants et al., 1996; Persson 1997) have been done to evaluate the performance of TDR in measuring $\theta_r$. These studies focused on constructing breakthrough curves (BTCs) based on TDR measured $\theta$ and $\sigma_r$. To date, no one has reported the use of a shallow TDR probe for determining $\theta_m$ and $\alpha$. If a shallow TDR can be used to determine $\theta_m$ and $\alpha$, it would overcome the shortcomings of the ST method.

The objective of this study was to develop and evaluate a method to estimate $\theta_m$ and $\alpha$ 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 $\theta_m$ and $\alpha$ observed from the TDR method were compared to parameters estimated by the ST method and by the effluent BTCs.

**THEORY**

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

$$\sigma_r = kZ^{-1}$$

where $k$ is a calibration constant. Measurements of $Z$ obtained by TDR are mostly a function of $\theta$ and soil solution electrical conductivity ($\sigma_r$). Kachanoski et al. (1992) showed that solute concentrations, $C$ (kg m$^{-3}$), can be deduced from TDR-estimated $\sigma_r$. A linear relationship is generally observed between $\ln(C/C_o)$ and $\sigma_r$. In this case, the left side of Eq. [3] can be used for Eq. [1] because

$$\ln\left(1 - \frac{C}{C_o}\right) = \ln\left(\frac{\theta_m}{\theta}\right) - \frac{\alpha}{\theta_m}t^*$$

where $C$ is resident concentration, $t$ is time since the tracer was applied, $t^* = t - h/v$ and is defined as the time required for the tracer front to reach the depth of sampling ($h$), 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 $\alpha$ can be calculated from Eq. [3] by fitting the $\ln(1 - C/C_o)$ vs. $t^*$ intercept and slope of the regression line. The intercept and slope of the regression line give estimates of both $\theta_m$ and $\alpha$. The ST method provides a means for determining estimates of $\theta_m$ and $\alpha$ 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 $\theta_m$ and $\alpha$ 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.

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especially for undisturbed or structured soils exhibiting non-equilibrium 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 $Z$. 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 $t_f$, $C(t_f)$. $Z$ can be determined using Eq. [7] with the TDR measurement at the time $t_i$, $Z(t_i)$ with the $C(t_i)$ and $Z$. Substituting $C(t_i)$ in the left side of Eq. [7], and $Z(t_i)$ and $Z$ into the right side of Eq. [7], $Z$ can be easily calculated. This calibration method based on soil sample extract for determining $Z$ removes possible errors from the continuous application method associated with the nonequilibrium of input solution. Once $Z$ is determined, $C(t)$ values can be calculated using Eq. [7] with the $Z$, $Z$, and $Z$ values. Using Eq. [3], one can estimate both $t_{\theta_a}$ and $\alpha$ 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 stave 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 soil sample. After the space was sealed with paraffin wax, a funnel was positioned beneath the reach equilibrium. Because of the problems with the continuous solute application method, we used another approach to accurately determine $Z$. 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 $t_f$, $C(t_f)$. $Z$ can be determined using Eq. [7] with the TDR measurement at the time $t_i$, $Z(t_i)$ with the $C(t_i)$ and $Z$. Substituting $C(t_i)$ in the left side of Eq. [7], and $Z(t_i)$ and $Z$ into the right side of Eq. [7], $Z$ can be easily calculated. This calibration method based on soil sample extract for determining $Z$ removes possible errors from the continuous application method associated with the nonequilibrium of input solution. Once $Z$ is determined, $C(t)$ values can be calculated using Eq. [7] with the $Z$, $Z$, and $Z$ values. Using Eq. [3], one can estimate both $t_{\theta_a}$ and $\alpha$ 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.

<table>
<thead>
<tr>
<th>Column</th>
<th>Particle density</th>
<th>Bulk density</th>
<th>Saturated water content</th>
<th>Velocity</th>
<th>$K_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.56</td>
<td>1.42</td>
<td>0.45</td>
<td>17.9</td>
<td>7.8</td>
</tr>
<tr>
<td>B</td>
<td>2.59</td>
<td>1.32</td>
<td>0.49</td>
<td>20.9</td>
<td>9.7</td>
</tr>
<tr>
<td>C</td>
<td>2.58</td>
<td>1.40</td>
<td>0.46</td>
<td>26.2</td>
<td>11.5</td>
</tr>
</tbody>
</table>

**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 $\sigma_s$ 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 CaCl₂ (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 CaCl₂. 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, $Z$ of the soil solution was measured using TDR. This value represented a concentration of background solution and was used to calculate $C(t)$ values in Eq. [7]. Input solution of 0.5 M CaCl₂ was applied using a maritote 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 CaCl₂ satisfied the linear relationships between the $Z$ and $\sigma_s$ reported in the previous studies (Nadler et al., 1991; Vogeler et al., 1996). The duration of four pore volumes, ~4 h, of 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.

![Fig. 1. Schematic diagram of time domain reflectometry (TDR) setup.](image-url)
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, \( \theta \) was estimated
with the TDR using the Topp et al. (1980) equation. The
estimated \( \theta \) was used in Eq. [3] to estimate \( \theta_m \) and \( \alpha \).

After we measured \( Z(t) \) values, each soil column was
leached with 0.003 \( M \) CaCl\(_2\) until each soil column was satu-
rated 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 \( \alpha \)-trifluoromethyl-
benzoate 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
two 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 non-
identical 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 collec-
tor, 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 \( \theta \). Analysis for the fluorobenzoate tracers was done
on a Dionex Series 4500i ion chromatograph (Dionex, Sun-
nyville, 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\(_2\)PO\(_4\) ad-
justed to a pH of 2.65 with H\(_2\)PO\(_4\) 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 \( Z_r \).

**Parameter Estimation: TDR Method**

In order to obtain \( Z \), a simplified waveform analysis
approach was used. The impedance load, \( Z, (\Omega) \) 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 \( \Omega \)), and
\( \rho \) 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 \( \xi(t) \) values based on Eq. [7]. As briefly explained in the Theory
section, \( Z \) and \( \xi \) should be determined to calculate \( \xi(t) \). \( \xi \),
was measured before applying input (0.5 \( M \) CaCl\(_2\)) solution.
\( Z \) was computed using Eq. [7] based on the relative resident
concentration, \( C(t) \), from the top 2-cm soil sample. We assume
that the TDR probe measures the average \( \sigma_t \) of the top 2-cm
layer of soil. The soil sample is also taken from the top 2-cm
layer of soil. Thus, \( C(t) \) and the last measured \( Z(t) \) after
applying four pore volumes of input tracer have identical
sampling depth. \( Z \), was determined using Eq. [7] with \( Z(t) \),
\( Z_t \), and \( C(t) \). For example, the relative \( C(t) \) from the soil
sample for Column C was 0.86. Substituting 0.86 with \( C(t) \)
to into Eq. [7] with \( Z(t) \) and \( Z_0 \), \( Z_t \), or \( Z_m \) can be easily
determined. Using the \( Z_t \) and measured \( Z(t) \) values, \( C(t) \)
values were obtained. The normalized \( C(t) \) values represent
relative resident concentrations of the top 2-cm soil layer,
where the TDR probe was installed. The \( C(t) \) values and \( \theta \)
were analyzed by Eq. [3] to estimate \( \theta_m \) and \( \alpha \).

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 applica-
tion, 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 concentra-
tions obtained from TDR measurements provides \( \alpha \) and \( \theta_m \)
values from the slopes and intercepts. The intercept of the
least-square regression gave \( \ln(\theta_m/0) \), and \( \alpha \) 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 \( \theta_m \) and \( \alpha \). The procedure for determining \( \theta_m \)
and \( \alpha \) was very similar to the procedure used in the TDR method.
Detailed descriptions to calculate \( \theta_m \) and \( \alpha \) using the ST resi-
dent 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 \( \theta_m \), \( \alpha \), 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, \( \theta_m \), \( \alpha \), and \( D_m \), were estimated
by the program CXTFIT, version 2 (Toride et al., 1995). Even-
tually, three sets of \( \theta_m \) and \( \alpha \) 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 \( \xi(t^*) \) values from the
TDR method plotted as \( \ln(1 - C/C_0) \) 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, indicat-
ing relevance of the expression, Eq. [3], for physical nonequilibrium solute transport processes in this soil.

Figure 2b shows the resident concentrations plotted
as \( \ln(1 - C/C_0) \) 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 \( r^* \) 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 \( \theta \) values from TDR and soil extracts were almost identical having only 0.01 cm\(^3\) cm\(^{-3}\) difference. The \( \theta \) from TDR were used for Eq. [3] for the TDR method, and the \( \theta \) 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 y axis (poro 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 (\( \theta_m, \alpha, \) 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.

<table>
<thead>
<tr>
<th>Column</th>
<th>TDR method</th>
<th>ST method</th>
<th>Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>θim/0</td>
<td>α (h⁻¹)</td>
<td>θim/0</td>
</tr>
<tr>
<td></td>
<td>0.31 (0.30–0.31)</td>
<td>0.01 (0.01–0.01)</td>
<td>0.26 ± 0.05‡</td>
</tr>
<tr>
<td></td>
<td>α (h⁻¹)</td>
<td>0.03 ± 0.03</td>
<td>0.03 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.30 ± 0.02</td>
<td>0.10 ± 0.01</td>
<td>0.02 (0.01–0.03) ± 0.01</td>
</tr>
<tr>
<td>B</td>
<td>0.32 (0.32–0.33)</td>
<td>0.03 (0.03–0.03)</td>
<td>0.22 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>α (h⁻¹)</td>
<td>0.05 ± 0.04</td>
<td>0.03 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.30 ± 0.03</td>
<td>0.10 ± 0.01</td>
<td>0.03 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.04 (0.03–0.05)</td>
<td>0.28 (0.17–0.46)</td>
<td>0.30 ± 0.03</td>
</tr>
<tr>
<td>C</td>
<td>0.00 (0.00–0.01)</td>
<td>0.00 (0.00–0.01)</td>
<td>0.00 (0.00–0.01)</td>
</tr>
<tr>
<td></td>
<td>0.03 ± 0.03</td>
<td>0.10 ± 0.01</td>
<td>0.03 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>α (h⁻¹)</td>
<td>0.05 ± 0.04</td>
<td>0.03 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.30 ± 0.40</td>
<td>0.10 ± 0.01</td>
<td>0.02 (0.01–0.03) ± 0.01</td>
</tr>
</tbody>
</table>

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

CONCLUSIONS

The estimates of θim and α from the TDR method agreed well with the estimates from the effluent data and the ST method. The TDR method provided reasonable θim 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 θim 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 θim and α using a shallow TDR probe in situ.

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REFERENCES


residual 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 (θim/θ) for the effluent method ranged from 0.22 to 0.30, the θim/0 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 θim/0 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 θim 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 θim/θ and α from the TDR method were very similar to the estimates from the ST method. In all three columns, the θim 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 θim/0 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 Dm, which is used for the ST method, by using analytical solutions to IMM. They reported that the estimates for ω = αL/q (where L is depth of measurement and q is Darcy flux density) and θim 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 IMM. She concluded that when dispersivity (λ) is <20 mm and water flux (q) is >10 mm h⁻¹, then accurate values of θim and α can be measured for a wide range of flow conditions. She also reported that if λ > 20 mm, sampling conditions became very restrictive due to curvilinear behavior in ln(1 – C/C0), which is owing to a violation of the assumption that Cim = Cim for all t ≥ 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 CaCl₂ and provided extensive data points. From a simple salt solution BTC experiment, one can determine θim and α.


