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# Characterization of preferential flow in undisturbed, structured soil columns using a vertical TDR probe

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## Abstract

Rapid movement of agricultural chemicals through soil to groundwater via preferential flow pathways is one cause of water contamination. Previous studies have shown that time domain reflectometry (TDR) could be used to characterize solute transport in soil. However, previous studies have only scarcely addressed preferential flow. This study presents an extended application of TDR for determining preferential flow properties. A TDR method was tested in carefully controlled laboratory experiments using 20-cm long and 12-cm diameter undisturbed, structured soil columns. The method used a vertically installed TDR probe and a short pulse of tracer application to obtain residual mass (RM) breakthrough curves (BTC). The RM BTC obtained from TDR were used to estimate mobile/immobile model (MIM) parameters that were compared to the parameter estimates from effluent data. A conventional inverse curve fitting method (CXTFIT) was used to estimate parameters. The TDR-determined parameters were then used to generate calculated effluent BTC for comparison with observed effluent BTC for the same soil columns. Time moments of the calculated and observed BTC were calculated to quantitatively evaluate the calculated BTC. Overall, the RM BTC obtained from TDR were similar to the RM BTC obtained from effluent data. The TDR-determined parameters corresponded well to the parameters obtained from the effluent data, although they were not within the 95% confidence intervals. Correlation coefficients between the parameters obtained from TDR and from effluent data for the immobile water fraction ( $\theta_{im}/\theta$ ), mass exchange coefficient ( $\alpha$ ), and dispersion coefficient ( $D_m$ ) were 0.95, 0.95, and 0.99, respectively. For three of the four soil cores,  $\theta_{im}/\theta$  ranged from 0.42 to 0.82, indicating considerable preferential flow. The TDR-calculated effluent BTC also were

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similar to the observed effluent BTC having an average coefficient of determination of 0.94. Time moments obtained from calculated BTC were representative of those obtained from observed BTC. The vertical TDR probe method was simple and minimally destructive and provided representative preferential flow properties that enabled the characterization of solute transport in soil. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* TDR (time domain reflectometry); Preferential flow; Solute transport; Mobile/immobile model

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## 1. Introduction

Groundwater contamination by agricultural chemicals is a continuing problem. The fate of agricultural chemicals in the environment depends on many factors such as soil type, rainfall, tillage, and chemical management practices. However, the movement of water and solutes in the vadose zone is not fully understood due to the complexities of soil. Time domain reflectometry (TDR) has been used as a tool to monitor solute transport in soil. A number of laboratory studies (Wraith et al., 1993; Vanclooster et al., 1993; Ward et al., 1994; Mallants et al., 1994, 1996; Heimovaara et al., 1995; Risler et al., 1996; Vogeler et al., 1996; Persson, 1997), as well as field studies (Kachanoski et al., 1992; Vanclooster et al., 1995; Ward et al., 1995; Rudolph et al., 1996; Jacques et al., 1998), have been conducted to evaluate the ability of TDR for characterizing solute transport in soil. These studies focused on measuring breakthrough curves (BTC) based on TDR-measured  $\theta$  and bulk electrical conductivity ( $\sigma_a$ ), which was related to soil solution concentration. Wraith et al. (1993) reported a good agreement between  $D_m$  and retardation factor ( $\lambda$ ) estimates from TDR and effluent using unsaturated steady flow soil columns. Vanclooster et al. (1993), Ward et al. (1994), Mallants et al. (1994) and Risler et al. (1996) also utilized TDR measurements to estimate solute transport parameters from BTC.

However, previous studies have only scarcely addressed preferential flow. Rudolph et al. (1996) pointed out that solute transport should be described with models that incorporate macropore flow and exchange of water and solutes between different flow domains. Preferential flow is one of the leading causes of water contamination by agricultural chemicals and may, in part, explain why screening models that ignore preferential flow do not accurately predict observed spatial patterns of groundwater contamination (USEPA, 1992). To date, the experimental evidence as to whether, and to what degree, TDR adequately describes preferential solute transport in soil is not conclusive.

Therefore, the objective of this study was to test whether TDR could be used for determining preferential flow properties. The study was conducted using undisturbed, structured, intact soil cores taken from where preferential flow was previously reported. Vertically installed TDR probes were used to monitor solute transport in the soil cores. The mobile/immobile model (MIM) parameters were estimated using TDR data and compared with estimated parameters obtained by conventional inverse fitting of effluent breakthrough data. The TDR-determined parameters were then used to calculate effluent BTC to be compared with the observed effluent BTC for the same soil cores.

## 2. Theory

In the MIM (Coats and Smith, 1964; van Genuchten and Wierenga, 1976), water-filled pore space is divided into two regions based on flow velocities within the pores. One is a mobile region, where water is free to move and solute transport is by advection and dispersion, and the other is an immobile region, where water is stagnant and solute moves only by diffusion. Based on the mobile/immobile approach, the transport of non-reactive solutes during steady, one-dimensional flow can be written:

$$\theta = \theta_m + \theta_{im} \quad (1)$$

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

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

where  $\theta$  is total volumetric water content,  $\theta_m$  and  $\theta_{im}$  are mobile and immobile water contents, respectively,  $C_m$  and  $C_{im}$  are concentrations in mobile and immobile domains, respectively,  $t$  is time,  $D_m$  is dispersion coefficient,  $q$  is water flux,  $x$  is depth, and  $\alpha$  is chemical mass transfer coefficient between mobile and immobile domains.

This MIM allows for preferential movement of non-sorbing solute in soil, because the effective transport volume ( $\theta_m$ ) is less than the total water-filled pore space ( $\theta$ ). Therefore, infiltrating solute moves preferentially through part of the pore space ( $\theta_m$ ) and bypasses the remainder of the pore space ( $\theta_{im}$ ). In field and laboratory studies, the ratio of immobile water to total soil water content has been found to vary from as little as 0 (i.e. no preferential flow; Cassel, 1971) to 35–55% (Smeetteem, 1984) or even 75% in unstructured desert soil (Jaynes et al., 1988). These latter immobile water fractions mean that water and chemicals could move through the soil profile more than twice as fast as predicted by models not incorporating immobile water concepts (Jaynes et al., 1995). However, a major difficulty in applying the two-domain transport model is estimating the required model parameters: immobile water content ( $\theta_{im}$ ), mass transfer coefficient ( $\alpha$ ), and dispersion coefficient ( $D_m$ ). Under certain water flux conditions,  $q$  can be measured but  $\theta_{im}$ ,  $\alpha$ , and  $D_m$  must be estimated. Although one can determine the three parameters by applying inverse methods to breakthrough data (Parker and van Genuchten, 1984; van Genuchten and Wagenet, 1989; Gamedainger et al., 1990), obtaining breakthrough data in the field is often not practical.

A simple and rapid field applicable procedure for determining solute transport properties based on TDR measurements was proposed by Kachanoski et al. (1992) and tested by Elrick et al. (1992). This method uses vertically installed TDR probes with a very short pulse of tracer application. The TDR measurements of  $\sigma_a$  are used to determine the mass flux of solute past the ends of the TDR probes. In a simple approach,  $\sigma_a$  is related to the impedance load of the TDR probe (Nadler et al., 1991):

$$\sigma_a(t) = kZ^{-1}(t) \quad (4)$$

where  $Z(t)$  is impedance load of the TDR probe at time  $t$ , and  $k$  is a calibration constant. Measurements of  $Z(t)$  obtained by TDR are functions of soil water content,  $\theta$ , and electrical conductivity of the soil solution,  $\sigma_w$ . A linear relationship is generally

observed between the resident solute concentrations,  $C$  ( $\text{kg m}^{-3}$ ), and  $\sigma_a$  for constant water contents and for salinity levels ranging from 0 to  $\approx 50 \text{ dS m}^{-1}$  (Ward et al., 1994). It is assumed that a vertically installed TDR probe to depth  $L$  can measure the total amount of solute between  $x=0$  (soil surface) and  $x=L$  at time  $t$ , regardless of the distribution of the solute along the probes (Kachanoski et al., 1992). After a solute pulse of tracer has been applied, the relative mass of applied tracer can be measured (Kachanoski et al., 1992) by:

$$M_R(t) = \left[ \frac{Z(t)^{-1} - Z(t_i)^{-1}}{Z(t_o)^{-1} - Z(t_i)^{-1}} \right] \quad (5)$$

where  $M_R(t)$  is relative specific mass of applied tracer at time  $t$ ,  $Z(t)$  is impedance load of the TDR probe at time  $t$ ,  $Z(t_i)$  is impedance load before tracer application, and  $Z(t_o)$  is impedance load after the specific mass of tracer application, but before any solute has moved past  $L$ . Detailed descriptions of Eq. (5) can be found in Kachanoski et al. (1992). This approach assumes that (i) solute application must be completed before any of the applied solute passes the end of the probe rods, and that (ii) the distribution of solute along the probe has no influence on  $Z^{-1}$  as long as all the applied solute is above the end of the TDR probe. Based on these assumptions and on Eq. (5), the relative mass remaining within depth  $L$  at any time can be obtained. From the observed residual mass BTC using TDR, we can obtain a flux-averaged concentration BTC by taking the first derivative of  $M_R(t)$  in Eq. (5) with respect to volume of outflow. Using the converted flux-averaged concentration BTC, one can estimate MIM parameters by inverse curve fitting of the BTC. The vertical probe approach by Kachanoski et al. (1992) is well suited to in situ measurements in heterogeneous systems and undisturbed soil cores because this method does not need a separate calibration experiment.

### 3. Materials and methods

#### 3.1. Soil column preparation and TDR setup

Undisturbed soil cores were collected during spring 1999 from the Agronomy and Agricultural Engineering Research Center located approximately 11 km west of Ames, IA. The soil is classified as Nicollet silt loam (fine-loamy, mixed, superactive, mesic Aquic Hapludoll) in the Clarion–Nicollet–Webster soil association and has a weak fine subangular blocky structure. Nicollet soils were formed on uplands from glacial till and have a slope of 1–3%. Selected chemical and physical properties of the soil and experimental conditions of the soil cores are listed in Table 1. Everts and Kanwar (1990) and Jayachandran et al. (1994) reported preferential movement of both reactive and non-reactive solutes in this field. To obtain undisturbed soil cores from the field, 50-cm wide and 40-cm deep trenches were dug. For each soil core, a furnace pipe (so-called stove pipe, 12 cm diameter and 30 cm length), whose side was crimped and folded so that it could be opened from the side, was placed on the surface after removing vegetation. Soil around the pipe was gently shaved to form a pedestal approximately 12 cm in diameter. The pipe was then carefully pushed downward to encase the column and

Table 1

Chemical and physical conditions for the soil column experiments

Column	Soil material	Sand/silt/clay fractions (%)	Organic C (%)	Cation exchange capacity (cmol <sub>c</sub> kg <sup>-1</sup> )	Bulk density (Mg m <sup>-3</sup> )	Water content (m <sup>3</sup> m <sup>-3</sup> )	Pore water velocity (cm h <sup>-1</sup> )
A	Ap horizon, sl	30/46/24	2.2	31.8	1.32	0.48	25.6
B					1.49	0.43	22.4
C					1.42	0.45	4.3
D					1.48	0.43	2.7

to avoid smearing. The process continued until 25-cm long soil columns were obtained. The upper surface of each soil column represented the actual field soil surface, with the exception that litter and loose soil had been carefully removed to provide a level surface.

In the laboratory, each furnace pipe was opened from the sides and removed from the undisturbed soil core. The soil cores were trimmed to the desired dimensions (10 cm diameter and 20 cm length). A polyvinyl chloride (PVC) plastic pipe (14 cm diameter) 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 to prevent solute flow along the wall. A wire screen was attached to the bottom of each column and a funnel was positioned beneath each column. A funnel was used to direct effluent to a fraction collector.

A 2.5-mm diameter and 200-mm long, two-wire type, baluned probe (Midwest Special Services, St. Paul, MN) was used for this study. A cable tester (model 1502B, Tektronix, Redmond, OR) and TACQ program (Evet, 1998) were used to obtain  $Z$  and  $M_R$  as a function of time during miscible displacement experiments. The length of the coaxial cable was 150 cm and the experiment was conducted at a constant temperature of  $25 \pm 1^\circ\text{C}$ . In order to obtain  $Z$ , the simplified waveform analysis approach presented by Wraith et al. (1993) was used. The probe was installed vertically at the center of the soil column from soil surface to the bottom end of the soil column. Thus, we assumed that the TDR probe detected the total amount of tracer along the TDR probe regardless of the distribution of the tracer.

### 3.2. TDR probe sensitivity test

Detecting the total amount of solute regardless of the distribution in the soil column was critical for this study. To test whether variable distributions of tracer along the TDR probe could affect TDR measurements, we conducted a preliminary experiment using three repacked soil columns. The repacked soil columns had the same dimensions as the undisturbed soil columns used for miscible displacement experiments. Three distributions of tracer were tested. For the first packed column, the bottom half was filled with soil mixed with 0.01 M of  $\text{CaCl}_2$ , and the top half was filled with soil mixed with 0.1 M of  $\text{CaCl}_2$ , representing the condition of having most of the tracer in the top portion of the soil column. For the second packed column, the bottom half was filled with soil

mixed with 0.1 M of  $\text{CaCl}_2$ , and the top half was filled with soil mixed with 0.01 M of  $\text{CaCl}_2$ , simulating the condition of having most of the tracer in the bottom of the soil column. For the third packed column, a bottom and a top quarter of the soil column were filled with soil mixed with 0.01 M of  $\text{CaCl}_2$ , and the middle half of the soil column was filled with soil mixed with 0.1 M of  $\text{CaCl}_2$ , representing the condition of having most of the tracer in the middle of the soil column. The volumetric water content of the soil columns was 0.32. After each soil column was packed, a TDR probe was vertically installed into each soil column. Note that the three packed soil columns had identical amounts of tracer. Two replications were done for this test.

### 3.3. Miscible displacement experiments

Four undisturbed soil columns were used for the miscible displacement study. The soil columns were designated “Column A”, “Column B”, “Column C”, and “Column D”. Each soil column was mounted vertically and slowly saturated from the bottom with a background solution of 0.01 M  $\text{CaCl}_2$ . After saturation, TDR probes were vertically installed by carefully pushing them down through the soil surface. The bottom of each soil column was then opened for free drainage and steady flow with 1-cm surface head was established by applying about 10 pore volumes of 0.01 M  $\text{CaCl}_2$  solution. Physical conditions of the soil columns are shown in Table 1. A steady-flow miscible displacement experiment was conducted to obtain a residual mass BTC using a specific mass of  $\text{CaCl}_2$  and TDR. In order to calculate  $M_R(t)$ , the initial impedance load,  $Z(t_i)$ , of the soil solution was measured by TDR. A total of 0.06 mol of  $\text{CaCl}_2$  (15 ml of 4 M  $\text{CaCl}_2$ ) was quickly applied at the top of each soil column. The input impedance load,  $Z(t_o)$ , was measured right after the tracer application but before any solute had moved out of the bottom of the soil columns. Each soil column was then leached with background solution (0.01 M of  $\text{CaCl}_2$ ).  $Z(t)$  was measured at a time interval equivalent to 0.05 pore volume.  $M_R(t)$  was obtained from measured  $Z(t_i)$ ,  $Z(t_o)$ , and  $Z(t)$  values using Eq. (5). Flux-averaged concentration BTC was then computed based on the  $M_R(t)$ . To obtain the flux-averaged concentration BTC, the first derivative,  $M'_R(t)$ , was computed. This derivative was then converted to mass( $t$ ) by multiplying by the mass applied. Finally, the concentration was computed by dividing the computed mass by leachate volume. Solute transport properties ( $\theta_{im}$ ,  $\alpha$ , and  $D_m$ ) were determined from the TDR-determined flux-averaged concentration BTC using an inverse curve fitting method (CXTFIT, Toride et al., 1995). The values of measured flux,  $q$ , from the miscible displacement experiments were used for the curve fitting of BTC, so that the CXTFIT solves for only the three parameters,  $\theta_{im}$ ,  $\alpha$ , and  $D_m$ . Each 0.05 pore volume of outflow containing the tracer was also collected with a fraction collector from the bottom of the column and stored at 4°C before analysis. The Cl concentrations were determined with a digital chloridometer (Haake Buchler Instruments, Saddle Brook, NJ). From the observed effluent data, a computed  $M_R(t)$  can be obtained by taking total mass (mol) of tracer applied minus integration of effluent BTC as a function of time. The TDR-determined  $M_R(t)$  and the effluent-determined  $M_R(t)$  were compared with each other. MIM parameters estimated using the TDR-determined effluent BTC were compared with the parameters obtained from observed effluent BTC.

### 3.4. Mass recovery test

Mass recovery of applied tracer was calculated using both observed effluent data and TDR measurements. The mass recovery was calculated using data collected after 4 pore volumes of leaching solution was applied. To calculate the mass recovery of the measured effluent data, integration of the observed effluent BTC was used. To calculate the mass recovery of the TDR measurements, the TDR-calculated effluent BTC obtained from the  $M_R(t)$  was used. The values of mass recovery obtained from TDR measurements were compared with those obtained from observed effluent data.

### 3.5. Calculating effluent BTC

Calculated effluent BTC were generated using TDR-determined MIM parameters and the CXTFIT program. The TDR-calculated effluent BTC were compared with the observed effluent BTC. In order to compare the observed and the calculated BTC independently from a particular transport model, time moments were calculated. Time moments are often used to analyze BTC for determining the mean breakthrough time, and the degree of spreading and tailing (Razavi et al., 1978; Jury and Sposito, 1985).

Temporal moments,  $m_p$ , of a concentration distribution,  $C/C_o(t)$ , as a result of a pulse input are defined as:

$$m_p = \int_0^{\infty} T^p (C/C_o) dT \quad p = 0, 1, 2, \dots \quad (6)$$

where  $T$  is the dimensionless time ( $T = vt/L$ , where  $v$  is the pore water velocity,  $L$  is the column length), and  $C_o$  is the influent concentration of the solute pulse. Normalized moments

$$\mu'_p = m_p / m_o \quad (7)$$

and central moments (Leij and Dane, 1992)

$$\mu_p = \frac{1}{m_o} \int_0^{\infty} (T - \mu'_1)^p (C/C_o) dT \quad (8)$$

were calculated based on Eq. (6).

The first, second, third, and fourth moments of the concentration distribution of the BTC can be used to characterize the mean, variance, skewness, and kurtosis, respectively. The skewness characterizes the degree of asymmetry of the distribution around its mean. The kurtosis quantifies the extent of peakedness or flatness of the distribution compared to that of a normal probability distribution. The moments of calculated and observed BTC were compared.

## 4. Results and discussion

### 4.1. TDR probe sensitivity test

The results from the probe sensitivity study showed that there was negligible effect of non-uniform distribution of tracer for measurements of  $Z(t)$ . If the vertical TDR probe

detects the total amount of solute regardless of the horizontal distributions, the measurements of impedance load from the three packed soil columns should be identical. For the three soil columns, the average of the  $R^{-1}$  values was 0.245 having  $\pm 0.4\%$  variance. The results implied that the vertical distribution of tracer in the soil columns did not affect TDR measurements of impedance load. Thus, the assumption that TDR could detect the total mass of tracer regardless of vertical distribution along the probe (Kachanoski et al., 1992) was valid for our soil columns. Although this test does not fully represent the complexity of an undisturbed soil column, the test does provide an idea of sensitivity of the vertical TDR probe where the solute is non-uniformly distributed along the probe.

#### 4.2. Miscible displacement experiments

Fig. 1 shows the relative residual mass BTC from the four undisturbed soil columns. The BTC marked “TDR” were obtained from TDR measurements and Eq. (5), and the BTC marked “Effluent” were obtained from observed effluent data. As explained in Section 3, the “TDR” BTC were measured and the “Effluent” BTC were computed using observed effluent BTC. For Columns A and B in which the average pore water velocity was larger than for Columns C and D, the TDR-determined BTC showed a slight deviation from the BTC obtained from effluent data. For Columns C and D, the

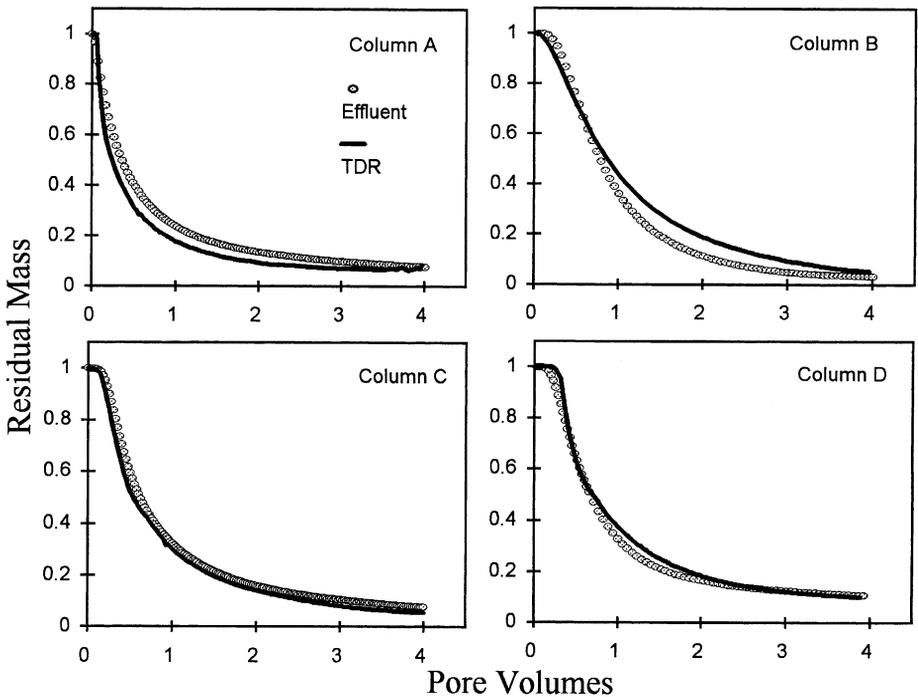


Fig. 1. Residual mass breakthrough curves (BTC) obtained from TDR and from effluent data.

BTC obtained from TDR and effluent data were similar to each other. Column A showed faster leaching of tracer than the other columns. But, no visual large pores were observed on the surface or bottom of Column A. Overall, the BTC obtained from TDR were similar to the BTC obtained from observed effluent data, and the BTC were indicative of MIM behavior.

In order to determine MIM parameters, flux-averaged concentration BTC were computed using the TDR-determined  $M_R(t)$  BTC and used with an inverse curve fitting method to estimate  $\theta_{im}$ ,  $\alpha$ , and  $D_m$ . Table 2 shows the parameter estimates from the observed effluent BTC and from TDR measurements. In Column A, the estimates of  $\theta_{im}$ ,  $\alpha$ , and  $D_m$  from both TDR and effluent BTC were large, indicating the early breakthrough of tracer. Overall, the TDR-determined parameters corresponded well to the parameters obtained from the effluent data, although they were not within the 95% confidence interval (CI). Note that the 95% CI of the parameter estimates for both effluent data and TDR were very narrow, especially for  $\alpha$  and  $D_m$ . In Column C, the estimates of  $\theta_{im}$  and  $\alpha$  obtained from TDR were similar to those obtained from effluent data, but the  $D_m$  from effluent data was larger than the  $D_m$  from TDR. Correlation coefficients,  $r$ , between the parameters obtained from TDR and those obtained from effluent data were calculated based on Goldman and Weinberg (1985). The values of  $r$  for the immobile water fraction ( $\theta_{im}/\theta$ ),  $\alpha$ , and  $D_m$  were 0.95, 0.95, and 0.99, respectively. For three of the four soil cores,  $\theta_{im}/\theta$  ranged from 0.42 to 0.82, indicating considerable preferential flow.

#### 4.3. Mass recovery test

Mass recovery of the BTC was calculated to evaluate TDR measurements. For the observed effluent BTC, mass recovery for Columns A, B, C, and D was 92%, 97%,

Table 2  
Comparison of the estimated parameters from effluent data and TDR

		Effluent	TDR
Column A	$\theta_{im}/\theta$	0.64 ( $\pm 0.02$ ) <sup>†</sup>	0.82 ( $\pm 0.07$ )
	$\alpha$ ( $h^{-1}$ )	5.23 ( $\pm 0.43$ )	5.45 ( $\pm 0.32$ )
	$D_m$ ( $cm^2 h^{-1}$ )	653 ( $\pm 65$ )	476 ( $\pm 27$ )
Column B	$\theta_{im}/\theta$	0.14 ( $\pm 0.01$ )	0.21 ( $\pm 0.02$ )
	$\alpha$ ( $h^{-1}$ )	0.79 ( $\pm 0.04$ )	0.41 ( $\pm 0.05$ )
	$D_m$ ( $cm^2 h^{-1}$ )	136 ( $\pm 11$ )	157 ( $\pm 23$ )
Column C	$\theta_{im}/\theta$	0.45 ( $\pm 0.01$ )	0.42 ( $\pm 0.02$ )
	$\alpha$ ( $h^{-1}$ )	0.34 ( $\pm 0.03$ )	0.33 ( $\pm 0.03$ )
	$D_m$ ( $cm^2 h^{-1}$ )	79 ( $\pm 8$ )	125 ( $\pm 8$ )
Column D	$\theta_{im}/\theta$	0.48 ( $\pm 0.02$ )	0.59 ( $\pm 0.05$ )
	$\alpha$ ( $h^{-1}$ )	2.34 ( $\pm 0.11$ )	0.78 ( $\pm 0.08$ )
	$D_m$ ( $cm^2 h^{-1}$ )	34 ( $\pm 4$ )	76 ( $\pm 7$ )

<sup>†</sup>( ) 95% confidence interval.

92%, and 89%, respectively. In other words, 3–11% of applied tracer remained in the soil column after four pore volumes of leaching. For the TDR-calculated BTC, mass recovery for Columns A, B, C, and D was 92%, 95%, 96%, 90%, respectively. The mass recovery obtained from TDR measurements was very similar to those obtained from measured effluent data.

*4.4. Calculating effluent BTC*

The values of moments obtained from observed and calculated BTC are listed in Table 3. The mean residence time,  $\mu'_1$ , ranged from 0.54 to 0.96 with an average of 0.76, and the variance,  $\mu_2$ , ranged from 0.31 to 0.43. Hornberger et al. (1990) and Ma and Selim (1994) reported that  $\mu'_1$  decreased exponentially with increasing pore water velocity,  $v$ , but no significant correlation was found in this study. For all soil columns, the values of skewness,  $\mu_3$ , and kurtosis,  $\mu_4$ , were positive with an average of 0.34 and 0.67, respectively. The positive values of  $\mu_3$  result from the tailing of the BTC, and the positive values of  $\mu_4$  are indicative of peakedness of the BTC. In general, the moments from TDR-calculated BTC were in good agreement with those from observed BTC.

We evaluated the TDR method by comparing the TDR-calculated BTC with observed effluent BTC. Fig. 2 shows the TDR-calculated BTC and observed BTC. For Column A, the calculated BTC was very similar to the observed effluent BTC except at very early times. Calculated BTC concentrations from TDR were a little bit higher than measured values at the beginning of the BTC. For Columns B, C, and D, the calculated BTC from TDR deviated slightly from the observed effluent data. A quantitative measure, coefficient of determination,  $r^2$ , was computed for the non-linear relationship based on Snedecor and Cochran (1967) to evaluate the accuracy of the calculations. For Columns A, B, C, and D, the  $r^2$  values for the calculated BTC and the observed BTC were 0.997, 0.87, 0.96, and 0.95, respectively. Note that this comparison using  $r^2$  values presented in this study did not incorporate uncertainties of model parameters and measurements. Statistical tests based on various factors such as the MIM assumptions, degree of non-equilibrium, boundary conditions may be required to precisely describe the differences between calculated and observed BTC (Vanderborght et al., 1997). However, the  $r^2$  values presented in this study provide an approximation for the differences between calculated and observed BTC. The results from both curve fitting and time moments analysis show the feasibility of the vertical TDR probe to characterize preferential solute transport in soil.

Table 3

The values of central moments<sup>a</sup> of the observed effluent breakthrough curves (BTC) and the TDR-determined BTC

	Column A				Column B				Column C				Column D			
	$\mu'_1$	$\mu_2$	$\mu_3$	$\mu_4$												
Effluent	0.54	0.34	0.37	0.74	0.96	0.39	0.33	0.66	0.78	0.36	0.34	0.66	0.78	0.31	0.27	0.52
TDR	0.57	0.39	0.43	0.87	0.87	0.36	0.26	0.53	0.86	0.43	0.35	0.73	0.74	0.36	0.34	0.67

<sup>a</sup> $\mu'_1$  is the mean residence time;  $\mu_2$ ,  $\mu_3$ , and  $\mu_4$  are second, third, and fourth central moments, respectively.

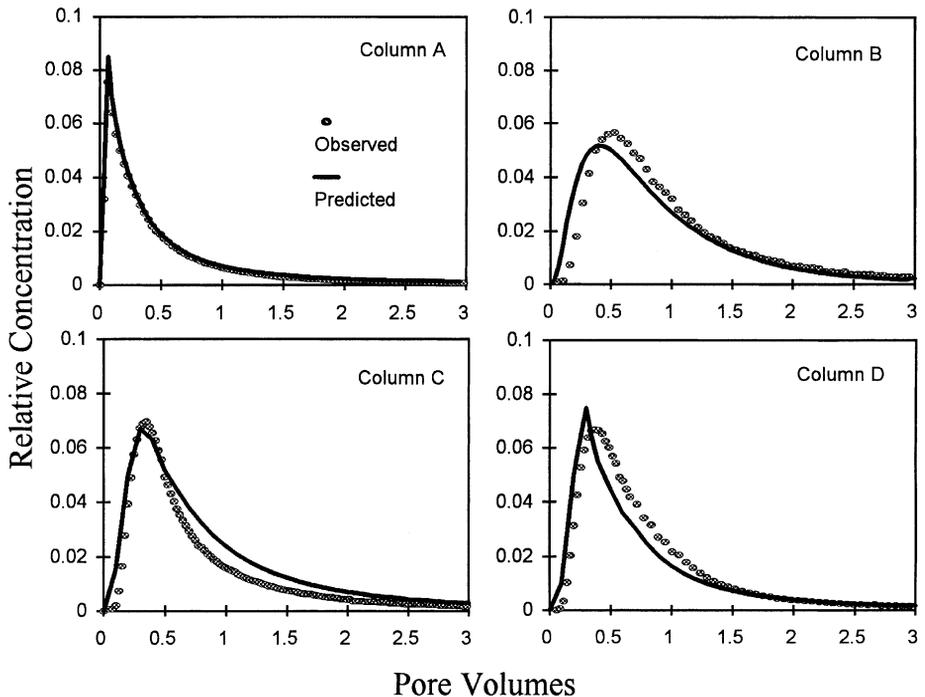


Fig. 2. Observed and calculated effluent BTC. Calculated BTC were obtained using TDR-determined mobile/immobile model parameters and the CXTFIT program.

However, there were slight discrepancies between residual mass BTC obtained from TDR and those obtained from effluent data as well as between measured effluent BTC and calculated effluent BTC. The discrepancies might be due to the following reasons. Although the length of soil cores was relatively short, 20 cm, the water content values from the upper (0–5 cm) soil layer were a little larger than those from deeper soil layers (10–20 cm), having an average of  $\pm 0.03$  variance. Nadler et al. (1984) reported that bulk electrical conductivity of soil,  $\sigma_a$ , was a function of water content,  $\theta$ , and Noborio et al. (1994) and Risler et al. (1996) also presented a relationship between  $\sigma_a$  and  $\theta$ . The relationship between  $\sigma_a$  and  $\theta$  was more complicated in clayey soil than in sandy soil (Nadler, 1997). Based on these studies, if the  $\theta$  was not vertically uniform along the TDR probe, the  $Z(t)$  values might not accurately represent  $\sigma_a$ , which was related to soil solution concentration. Another possible reason for the discrepancies may be a slight non-linear relationship between  $\sigma_a$  and  $C$  for small salinity values. Nadler (1997) reported discrepancies and non-linearity between  $C$  estimates obtained by TDR and aqueous extracts for  $\leq 2$  dS  $m^{-1}$ . The main causes of the non-linearity are physical (tortuosity effects) and physico-chemical phenomena (contribution of clay and other cations and anions to the  $\sigma_a$ ).

Lateral variation of TDR probe sensitivity should also be addressed. Knight et al. (1994) presented a study dealing with the lateral sensitivity and sampling volume of a

TDR probe based on a spatial weighting function. They reported that if the probe wires were too thin in comparison with their spacing, then most of the measurement sensitivity was very close to the wires, which could lead to inaccuracies. But, it was difficult to test the theory of lateral sensitivity in this study because of the complexity of TDR and undisturbed soil, and it will be a challenge to apply this method in situ for soils with large vertical cracks or channels. In spite of its potential shortcomings, the TDR method provided representative BTC and solute transport model parameters from a simple salt solution experiment. The TDR method was shown to have good potential for measuring solute transport in soil, even in a soil with documented preferential flow characteristics.

## **5. Conclusions**

A simple TDR method was evaluated by determining preferential flow properties using undisturbed, structured soil cores. The TDR method responded well for the early breakthrough of solutes and the MIM parameters obtained from the TDR method corresponded well to the parameters obtained from the effluent data. The simulation study calculating effluent BTC from the TDR-determined parameters showed a feasibility of the vertical TDR method to delineate preferential water and solute transport in soil. Mass recovery obtained from TDR were very similar to the mass recovery obtained from effluent data. The vertical TDR probe method is simple and rapid with minimum disturbance of soil, and it is a promising technique for characterizing preferential solute transport.

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