Estimation of soil water content and resident and effluent solute concentrations using time domain reflectometry

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Estimation of soil water content and resident and effluent solute concentrations using time domain reflectometry

by

Fulin Shen

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Soil Science (Soil Physics)

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Iowa State University

Ames, Iowa

1999

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This is certify that the Doctoral dissertation of

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has met the dissertation requirements of Iowa State University

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For the Major Program

For the Graduate College
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published models. An increase in flow velocity increased variation of TDR-measured $\sigma$, and thus variation of TDR-estimated C, for measurements on undisturbed soil cores over a range of pore water velocity ($v$, 0.5 - 86.1 cm hr$^{-1}$). The effluent breakthrough curve (BTC) predicted with solute transport models using solute transport parameters obtained by fitting the same models to TDR-estimated Cr BTC usually deviated from the measured effluent BTC; whereas, a simple mass balance method demonstrated the capability of accurately predicting effluent BTC.
CHAPTER 1. GENERAL INTRODUCTION

Groundwater contamination is a widespread problem where intensive agricultural operations exist. A study shows that concentrations of nitrate and other inorganic constituents within the surficial aquifers are significantly elevated due to applications of commercial fertilizers and manure in five agricultural regions in the United States (Hamilton and Helsel, 1995). Best resource management practice may protect the groundwater from pollution (Boyer and Pasquarell, 1996). The implementation of such management requires knowledge of how and in what rate agricultural chemicals such as nitrate-N are transported from top soil to groundwater.

Ideally, the solute transport process can be monitored in the field. But, traditional methods for measuring solute concentration, such as solution sampler, either are limited to a relatively narrow range of soil water content or require destructive sampling (Dalton and Van Genuchten, 1986). An alternative methods of understanding solute transport assumes that solute transport is a process that can be mathematically simulated, thus the coordinates of a certain chemical molecules or ions in soil can be determined at any time for known initial and boundary conditions. However, these mathematical models are usually not thoroughly tested due to the difficulty in obtaining measured values (Kachanoski et al., 1994) and their usefulness is questionable (Brusseau and Rao, 1990).

Since time domain reflectometry (TDR) was successfully used in the measurements of soil water content (Topp et al., 1980) and bulk soil electrical conductivity (Dalton et al., 1984), it has been shown to have the potential to monitor soil solute transport (Kachanoski et
Baker and Allmaras (1990) developed a TDR system capable of automated multiple measurements, which makes massive and continuous field determinations of solute transport possible. Although TDR has been used to obtain solute transport parameters (Vanclooster et al., 1993; Risler et al., 1996), its capability of predicting effluent solute concentration has not been fully evaluated.

The objectives of this dissertation are to evaluate TDR’s abilities to accurately estimate soil water content and solute concentration for packed and undisturbed soil cores in the laboratory, and to predict effluent solute concentration from TDR measurements using either solute transport models or a simple mass budget method.

**Dissertation Organization**

This dissertation adopted the manuscript format as defined by the Thesis Office of Iowa State University. Three technical articles, which will be submitted to professional journals, are included. The first article (Chapter 3) discusses the development of a theoretical relationship of TDR-measured soil dielectric constant to water content and the effects of bulk soil electrical conductivity on this relationship. The second article (Chapter 4) describes a study that relates TDR-measured bulk soil electrical conductivity to soil solute concentration and TDR-estimated soil water content for both packed and undisturbed soil cores. The third article (Chapter 5) includes an evaluation of TDR’s capability to predict effluent concentration using both solute transport models and a simple mass budget method. Chapter 2 is a literature review on both basic electromagnetic theory used in TDR method and recent developments in the TDR application to measurements of soil water content, bulk soil
electrical conductivity, and solute transport. General conclusions are given in Chapter 6. The appendix includes comparison of soil solute mass balance obtained using TDR-estimated resident solute concentration with input-effluent mass balance measurements, and compares them with effluent breakthrough curves for five experiments.

References


CHAPTER 2. LITERATURE REVIEW

Development of TDR

TDR measurement of soil water content

Soil water content, $\theta_v$, is an important index of both soil physical and chemical properties. Accurate, intensive, frequent, and nondestructive measurements of $\theta_v$, are desired in order to conduct a number of different types of studies. The gravimetric method, which is direct and also destructive, is the standard technique used to determine $\theta_v$. Many indirect methods have been developed in order to either save time and effort or make large scale nondestructive field measurements feasible. The common ground for these methods is to utilize the most prominent property of soil water, which is remarkably different either in quality or in quantity from other soil constituents (e.g., soil particle or air).

Time domain reflectometry (TDR), originally used for cable testing, was developed to determine permittivity of material (Fellner-Feldegg, 1969). Traditional determination of permittivity requires a number of measurements over a wide frequency. Advances in technology allow the measurement to be conducted in time domain with a pulse, which contains all the frequencies of interest. A few years later, TDR was used to measure soil relative permittivity (dielectric constant), $\varepsilon_r$, with the following relationship (Davis & Chudobiak, 1975; Davis, 1975)

$$\varepsilon_r = \left(\frac{ct}{1}\right)^2 \quad [1]$$

where $c$ = the velocity of electromagnetic wave in free space, $3 \times 10^8 \text{ m s}^{-1}$

and $t = \text{travel time of electromagnetic wave along the transmission line in the soil}$
\( l = \) length of transmission line in the soil

Based on the relationship between soil relative permittivity and \( \theta_v \), Davis and Chudobiak (1975) concluded that TDR was a useful technique to determine \( \theta_v \). Equation [1] was rewritten by Davis and Annan (1977) as

\[
K_a = \left( \frac{c}{l} \right)^2 \tag{2}
\]

where \( K_a \) is called the apparent dielectric constant, whose main component is \( \varepsilon_r \). Laboratory measurements in three different soils (Rideau clay, Uplands Sand, and clay-till) gave a relationship between \( K_a \) and volumetric \( \theta_v \) as (Davis & Annan, 1977)

\[
K_a = (3.34 \pm 1.05) \exp((4.56 \pm 0.21)\theta_v) \tag{3}
\]

The uncertainties of the coefficients in Eq. [3] can be viewed as taking into account the variations due to density and soil type. Topp et al. (1980) proposed the following polynomial relationship between \( \theta_v \) and \( K_a \)

\[
\theta_v = -5.3 \times 10^{-2} + 2.92 \times 10^{-2}K_a - 5.5 \times 10^{-4}K_a^2 + 4.3 \times 10^{-6}K_a^3 \tag{4}
\]

and stated that this relationship is independent of soil type, soil density, soil temperature, and soluble salt content. Since this equation is broadly applicable it is called the universal equation for TDR \( \theta_v \) measurement (Topp et al., 1994).

Researchers have proposed a number of relationships between the dielectric constant of a system \( \varepsilon_m \) and the dielectric constant of individual components in the system \( \varepsilon_i \) (\( i \) represents the \( i \)th component). For example, Landau-Lifshitz found for an \( n \)-phase mixture the expression as cited by Bunget & Popescu (1984):

\[
(\varepsilon_m)^{1/3} = \sum_{i=1}^{n} k_i (\varepsilon_i)^{1/3} \tag{5}
\]
where $k_i$ is volume fraction of the $i$th component. For soil, Roth et al. (1990) verified the following model

$$\varepsilon_{\text{soil}}^\alpha = \theta \varepsilon_w^\alpha + (1 - P) \varepsilon_s^\alpha + (P - \theta) \varepsilon_a^\alpha$$  \hspace{1cm} [6]

where $\varepsilon_w$, $\varepsilon_s$, and $\varepsilon_a$ are dielectric constants of the liquid, solid, and gaseous phases, respectively. $P$ is the soil porosity and $\alpha = 0.5$. Rearranging Eq. [6] gives

$$\varepsilon_{\text{soil}}^\alpha = \theta(\varepsilon_w^\alpha - \varepsilon_a^\alpha) + \varepsilon_s^\alpha + P(\varepsilon_a^\alpha - \varepsilon_s^\alpha)$$  \hspace{1cm} [7]

Like any other new technique, the effort to improve TDR measurement has not ended. Zegelin et al. (1992) suggested that Eq. [4] works best in coarser textured soils, but has problems in fine textured, dense, heavy clay soils. Dalton (1992) stated that Eq. [4] will require adjustment for peat and heavy clay soils or in any case where great accuracy is required. These reports indicated that TDR estimated $K_a$ in one type of soil could differ from that in another type. In other words, TDR-measured $K_a$ could be affected by factor(s) induced by different types of soil. Identifying these effects will improve TDR $\theta_v$ measurement.

**TDR measurement of bulk soil electrical conductivity**

Since Dalton et al. (1984) first proposed simultaneous TDR measurement of $\theta_v$ and bulk soil electrical conductivity ($\sigma_a$), a number of research studies have been conducted to evaluate the effectiveness of TDR in measuring $\sigma_a$. Dasberg and Dalton (1985) suggested that $\sigma_a$ measured by TDR using an algorithm developed by Dalton et al. (1984) had a high correlation with that obtained by the four electrode probe (4P), but not a 1:1 relation. But, Nadler et al. (1991) reported that $\sigma_a$ values obtained for uniform and layered matrices by the 4P technique were in excellent agreement with values obtained by calibrating TDR
measurements with solutions of known electrical conductivity. Topp et al. (1988) reported that the electrical conductivity of KCl solutions measured by TDR using an algorithm developed by Yanuka et al. (1988) had a good 1:1 relationship with that determined using a Wheatstone resistance bridge. A linear relationship (not 1:1) exists between $\sigma_a$ measured by TDR and that obtained with Wheatstone resistance bridge. Zegelin et al. (1989) showed that $\sigma_a$ of a fine sand determined by TDR using the Giese-Tiemann thin layer model was in a good agreement with that measured by an AC conductivity bridge.

**Monitoring solute transport using TDR**

Chemical fate and solute transport in soil have been intensively studied in the past decades in response to increasing public concern about possible groundwater pollution. Monitoring solute transport in soil can either provide data needed for testing solute transport theory or be a precaution against possible pollution. Traditional methods for monitoring solute transport require separate instrumentation or procedures for $\theta_v$ and solution concentration measurement. These procedures are usually destructive, labor-intensive, and time-consuming. Due to its capability of measuring simultaneously $\theta_v$ and $\sigma_a$, TDR provides a powerful tool in solute transport research.

Current application of TDR to solute transport focuses on constructing solute breakthrough curves (BTC) based on TDR-measured $\theta_v$ and $\sigma_a$ (Wraith et al., 1993; Elrick et al., 1992; Ward et al., 1994 & 1995; Mallants et al., 1994 & 1996; Persson, 1997; Vanclooster et al., 1993 & 1995; Vanderborght et al., 1996; Kachanoski et al., 1992 & 1994; Risler et al., 1996; Heimovaara et al., 1995; Hart and Lowery, 1998), and estimating transport parameters utilizing established BTCs (Wraith et al., 1993; Elrick et al., 1992;
There are two questions that need to be answered: 1) Since BTC are commonly presented by plotting relative effluent or resident solute concentration versus time, how can TDR-measured \( \sigma_a \) be transformed into resident solute concentration, \( C_r \)? 2) How do TDR BTC compare to BTC obtained by other methods?

Rhoades et al. (1976) suggested a linear relationship between \( \sigma_a \) and solution conductivity, \( \sigma_w \), when \( \theta_v \) is constant,

\[
\sigma_a = \gamma_0 \sigma_w + \sigma_s \tag{8}
\]

where \( \gamma_0 \) is a constant. Eq. [8] can be rewritten as

\[
Z^{-1} = \beta_0 C + \beta_1 \tag{9}
\]

due to the relationship of \( \sigma_a \) to soil impedance, \( Z \) and \( \sigma_w \) to \( C_r \) (discussed later), where \( \beta_0 \) and \( \beta_1 \) are constants. Thus relative solute concentration \( \bar{C} \) at any given soil depth, when the TDR probe is horizontally positioned, can be represented by

\[
\bar{C} = \frac{C - C_i}{C_0 - C_i} = \frac{Z^{-1} - Z_i^{-1}}{Z_0^{-1} - Z_i^{-1}} \tag{10}
\]

where \( C_i \) and \( Z_i \) are background solute concentration and TDR-measured impedance at that concentration, respectively; \( C_0 \) is the input tracer concentration and \( Z_0 \) the TDR-measured impedance assuming soil matrix is completely filled with tracer solution (Wraith et al., 1993; Mallants et al., 1994 & 1996). \( \bar{C} \) can be replaced by relative mass \( \bar{M} \) when a TDR probe is vertically inserted (Kachanoski et al., 1992 & 1994; Ward et al. 1994 & 1995; Golabi et al., 1995). Although widely used, this approach has limitations. First, it can only be applied to steady flow conditions under which \( \theta_v \) is presumably constant at a given depth. Second, \( Z_0 \) is
difficult to determine when the probe is horizontally installed (Mallants et al., 1994).

One approach to obtain $Z_0$, used by Mallants et al. (1994), is to add enough tracer solution that the solution concentration at given soil depth reaches tracer concentration, $C_0$. Another approach, used by Vanclooster et al. (1993), obtains $(Z_0^{-1} - Z_i^{-1})$ by integrating the observed $(Z^{-1} - Z_i^{-1})$ vs. time curve. The first approach requires long time tracer application while the second assumes 100% mass recovery. These requirements are difficult to achieve for structured soil. The third limitation is that for structured soil the linear $\sigma_a - \sigma_w$ relation exists only when $\sigma_w > 3.5$ dS m$^{-1}$ (Nadler and Frenkel, 1980; Shainberg et al., 1980). These limitations may partly explain why the majority of studies of solute transport using TDR are on sand or sandy loam. An alternative to avoid the difficulty of determining $Z_0$ is to obtain a calibration between $Z^{-1}$ and $C_i$, i.e., to determine $\beta_0$ and $\beta_1$ in Eq. [2] prior to the measurement of BTC. This alternative method has been practiced by Vanclooster et al. (1995), Vanderborght et al. (1996), and Ward et al. (1994). Under transient flow conditions $\sigma_a - \theta_v - \sigma_w$ or $\sigma_a - \theta_v - C_r$ relations rather than the simple $Z^{-1} - C_r$ relation are needed to construct BTCs. The $\sigma_a - \theta_v - C_r$ relation can be purely empirical based on calibration data as obtained by Hart and Lowery (1998) and Vogeler et al. (1996), or, it can be obtained by fitting experimental data to published models (Mallants et al., 1996; Heimovaara et al., 1995; Persson, 1997; Risler et al., 1996). Calibration of $Z^{-1} - C_r$ or $\sigma_a - \theta_v - C_r$ to determine $\sigma_w$ of the small soil volume sampled by the TDR probe measurement remains difficult. Commonly used calibration procedures are: 1) Equating $\sigma_w$ to input solution or effluent electrical conductivity after long time application of such input solution. A series of input solutions are used to obtain a series of $\sigma_w - \sigma_a$ measurements. This approach has been adopted by Risler et
al. (1996). 2) Measuring $\sigma_w$ using a solution sampler as done by Heimovaara et al. (1995), Persson (1997), Vanderborght et al. (1996), and Vanclooster et al. (1995). 3) Equating $\sigma_w$ to known concentration of solution mixed with soil (Ward et al., 1994; Mallants et al., 1996). Procedure 1 is simple and straightforward, but it has the same problem mentioned before for determining $Z_b$. It requires long time application of input solution to ensure the solution concentration in the soil matrix is uniform and the concentration is the same as the inflow concentration. As for procedure 2, the solution sampler may fail to collect a sufficient number of samples, especially at low $\theta_v$ (Ward et al., 1994). And, TDR measures the electrical conductivity of the total soil solution, whereas the solution samplers only sample the solution from the mobile region (Heimovaara et al., 1995). This disparity may bring error to BTC based on TDR measurements. The assumption for procedure 3 is that no salt from the soil matrix will dissolve or precipitate when solution is mixed with soil. This assumption might be valid for sand but may not apply to agricultural soil.

BTC obtained by TDR have been compared to that determined by effluent (Kachanoski et al., 1992; Wraith et al., 1993), solution sampler (Kachanoski et al., 1992; Heimovaara et al., 1995), or transport theory (Persson, 1997; Ward et al., 1994). Though a number of studies suggested TDR determined BTC were in a good or excellent agreement with effluent BTC (Kachanoski et al., 1992; Wraith et al., 1993), discrepancy between the two BTC measurement methods was also reported (Risler et al., 1996). While Kachanoski et al. (1992) reported good agreement between BTC determined by TDR and measured with solution sampler, Heimovaara et al. (1995) showed a difference between BTC obtained from the two methods of measurement. Solute transport parameters are another index for evaluating TDR performance in determining BTC. Solute transport models such as the convection-dispersion
equation (CDE), convective lognormal transfer function (CLT), and mobile/immobile (MIM) were used to obtain the parameters by fitting TDR determined BTC to these models (Elrick et al., 1992; Wraith et al., 1993; Vanclooster et al., 1993; Risler et al., 1996). Elrick et al. (1992) showed that fitting the measured TDR reading to the CDE and CLT models for both field and laboratory data gave good estimates of the transport parameters.

In summary, most studies conclude that TDR is fast, inexpensive, nondestructive, and highly automatic in determining BTC and estimating solute transport parameters (Elrick et al., 1992; Kachanoski et al., 1994; Risler et al., 1996). But, Mallants et al. (1994) suggested that TDR should not be a substitute for existing monitoring techniques. In my opinion, with proven capability in measuring $\sigma_a$, TDR determined BTC do not depend on TDR itself, but on the correct interpretation of $\sigma_a-C_r$ (or $Z^{-1}-C_r$) or $\sigma_a-\theta_r-C_r$ relationships.

**TDR Theory**

**Theory for $\sigma_a$ measurement**

Time domain reflectometry detects reflections made by discontinuities upon sending an electrical pulse down the cable (Tectronix, 1990). A commercial TDR (e.g., Tektronix, 1502b) contains three main components: a pulse generator, a sampler, and an oscilloscope (Fellner-Feldegg, 1969; Davis & Chudobiak, 1975; Spaans & Baker, 1993). The pulse generator produces a square wave signal (Vadoze Zone Equipment Co., 1994). The frequency of the signal varies depending on the rise time of the signal generated by the TDR (Spaans & Baker, 1993; Zegelin et al., 1992; White et al., 1994). Usually, a coaxial cable, which connects the TDR at one end to a probe inserted in soil at the other end, is used to transmit the signal. The probe can be a coaxial (Topp et al., 1980), parallel two-wire (Topp et
al. 1982), or other multi-wire transmission line (Zegelin et al. 1989;).

A property of coaxial and two-wire transmission lines is that the electrical and magnetic fields on the line are transverse to the direction of wave propagation. Such transverse electromagnetic fields are known as TEM modes (An electromagnetic wave which has only components transverse to the direction of propagation is called a TEM wave). For TEM modes the scalar quantities \( V \) and \( I \) are uniquely related to the vector \( E \) and \( H \) fields of the transmission line (Plonus, 1978). To study wave propagation in a transmission line, one needs to use both the general fields and lumped circuits approaches since: first, unlike in free space, a wave propagating in a transmission line is in certain boundaries; second, the usual electrical circuit parameters—resistance, capacitance, inductance—are considered as distributed rather than lumped (Shadowitz, 1975). Theoretically, when a wave in one medium impinges upon a second medium with different permittivity, permeability, or conductivity, the wave will in general be partially transmitted into the second medium and be partially reflected (Plonus, 1978). Figure 1 shows an incident wave \((E', H')\), a reflected wave \((E'', H'')\), and a transmitted wave \((E', H')\) in a two dielectric media.

Let \(E(x, t)\) represents scalar quantity of electric field strength at time \(t\) and distance \(x (x < 0)\) in medium 1, then

\[
E(x, t) = E_0^i e^{j(\omega t - kx)} + E_0^r e^{j(\omega t + kx)}
\]

[11]

where \(j = \sqrt{-1}\). \(E_0^i\) is the amplitude of the forward, or incident, wave and \(E_0^r\) is the amplitude of the reflected wave. \(\omega\) and \(k\) are angular frequency and wave propagation constant of the wave, respectively. An equivalent expression to equation [11] using circuits approach gives
Fig. 1. Incident, reflected, and transmitted waves at the interface of two media where $E$ and $H$ represent scalar quantity of electric field strength and magnetic field strength, respectively. Superscript $i$, $r$, and $t$ represent incident, reflected, and transmitted wave, respectively.

$$V(x, t) = V_0^i e^{i(\alpha x - \beta x)} + V_0^r e^{i(\alpha x + \beta x)}$$  \[12\]

where $V(x, t)$ is voltage at time $t$ and distance $x$ from source.

According to field theory, the TDR signal passes three cascaded media when measuring $\theta_v$. First, the signal travels along a lossless coaxial cable; second, the signal travels along a lossy two-wire transmission line; third, the signal radiates in a conducting medium (soil) without boundary. Reflection occurs at the interface of any two neighboring medium. When a wave is reflected by a loss dielectric, the reflection coefficient $\Gamma(x)$ anywhere along the negative $x$ axis is defined as

$$\Gamma(x) = \frac{E'(x)}{E''(x)} = \frac{E_0'}{E_0''} e^{2\alpha x} e^{i2\beta x} = \Gamma e^{2\alpha x} e^{i2\beta x}$$  \[13\]

where $\alpha$ and $\beta$ are the attenuation and phase factor, respectively. $\alpha$ is given by
\[ \alpha = \left( \frac{\sigma}{2} \right) \sqrt{\frac{\mu}{\varepsilon}} \]  

where \( \sigma \), \( \mu \), and \( \varepsilon \) are electrical conductivity, permittivity, and permeability of the medium. \( \Gamma \) in Eq. [13] is the reflection coefficient evaluated at \( x = 0 \) (Fig. 1).

On the other hand, according to circuits theory (contrast to fields theory), transmission lines with two parallel conductors can be considered as a parameter network in which series inductance (L) and resistance (R) as well as shunt capacitance (C) and conductance (G) distribute uniformly along the line (Plonus, 1978). Thus, the electromagnetic fields on the transmission line can be described in terms of voltage, current, and impedance, and conventional instruments such as voltmeters, ammeters, and oscilloscopes can be used to measure the voltage and current (Magnusson, 1970). By the theory, the characteristic impedance of the transmission line \( (Z_0) \) in lossless media is given by

\[ Z_0 = \sqrt{\frac{L}{C}} \]  

[15]

where \( L \) has units of \( \text{H m}^{-1} \) and \( C \) has units of \( \text{F m}^{-1} \). For a coaxial line

\[ Z_0 = \frac{\eta}{2\pi} \ln \left( \frac{r_b}{r_a} \right) \]  

[16]

where \( r_a \) and \( r_b \) are radii of inner and outer conductors, respectively. Coaxial cable used for TDR measurement commonly have an impedance of 50 \( \Omega \). \( \eta \) is called characteristic wave impedance of the medium which is independent of the geometry of the transmission line, and

\[ \eta = \sqrt{\mu / \varepsilon} \]  

[17]

When in free space \( \eta \) is a constant and denoted by \( \eta_0 \).
where \( \varepsilon_0 \) denotes the permittivity of air, free space, as well as vacuum. Its value is \( 8.854 \times 10^{-12} \text{ F m}^{-1} \). \( \mu_0 \) is the permeability of vacuum (\( \mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1} \)). For material media it is convenient to express the permittivity of the media normalized with respect to vacuum (Plonus, 1978). It is then known as the relative permittivity or dielectric constant \( \varepsilon_r = \varepsilon / \varepsilon_0 \).

For the same reason, \( \mu_r = \mu / \mu_0 \) is defined as relative permeability. For nonmagnetic material, such as soil, \( \mu_r \) has a value which is very nearly unity.

Eq. [17] can be rewritten as

\[
\eta = \sqrt{\frac{\mu}{\varepsilon}} = \sqrt{(\mu_0 \mu_r)/(\varepsilon_0 \varepsilon_r)} = \eta_0 / \sqrt{\varepsilon_r} \approx 120\pi / \sqrt{\varepsilon_r} \tag{19}
\]

Substituting Eq. [19] into Eq. [16], we obtain

\[
Z_0 = \frac{\eta}{2\pi} \ln \left( \frac{r_b}{r_a} \right) \approx \frac{60}{\sqrt{\varepsilon_r}} \ln \left( \frac{r_b}{r_a} \right) \tag{20}
\]

For a set of two circular conductors parallel to each other, such as 2-rod TDR probe, the \( Z_0 \) is given as

\[
Z_0 = \frac{\eta}{\pi} \ln \left( \frac{d}{r} \right) = \frac{120}{\sqrt{\varepsilon_r}} \ln \left( \frac{d}{r} \right) \tag{21}
\]

where \( d \) and \( r \) are distances between the centers and radii of the two conductors, respectively.

For a two-rod probe with 3.175 mm of rod diameter and 30 mm spacing, as used by Spaans and Baker (1993), in free space \( Z_0 = 352.7 \Omega \). It is obvious that the impedance of the TDR probe does not match that of the coaxial cable. The mismatch is undesirable since it causes reflection, which could be a noise to the reflection caused by changing medium. Hence, a balan is commonly used to eliminate the mismatch.
In a medium with small conductive loss, the characteristic wave impedance is given by

\[ \eta \equiv \sqrt{\frac{\mu}{\varepsilon}} [1 + j \sigma / (2 \omega \varepsilon)] \]  

where \( \sigma / (\omega \varepsilon) \ll 1 \). Clearly, \( \sigma \) and \( \varepsilon \) of a medium determines \( \eta \) and thus \( Z_0 \) in Eq. [21]. When impedance of the coaxial line matches that of the TDR probe, the reflection occurring at the conjunction of the cable and probe should be ascribed to the medium around the probe. The magnitude of the reflection is determined by the impedance of both coaxial cable and TDR probe in the lossy medium.

The simplest circuits to describe the TDR measurement process is a finite length of line with characteristic impedance \( Z_0 \) terminated by a load impedance \( Z_L \), as illustrated in Fig. 2. The reflection coefficient (\( \Gamma \)), the ratio of reflected voltage (\( V' \)) to incident voltage (\( V^i \)), is given as

\[ \Gamma = \frac{V'}{V^i} = \frac{Z_L - Z_0}{Z_L + Z_0} \]  

[23]

For an open circuit, \( Z_L \rightarrow \infty \) and \( \Gamma = +1 \); for a short circuit, \( Z_L \rightarrow 0 \) and \( \Gamma = -1 \). For convenience, the reflection coefficient is designated by the Greek letter \( \rho \) (Tektronix, 1990). \( \Gamma = 1 \) is equivalent to \( \Gamma = 1 \rho = 1000 \text{ m}\rho \) (millirho). A detailed derivation for Eq. [23] can be

Fig. 2. Coaxial cable with characteristic impedance \( Z_0 \) terminated with a load impedance of \( Z_L \). \( V^i \) is the incident voltage and \( V' \) is the reflected voltage.
found in “Applied Electromagnetics” (Plonus, 1978).

Γ can be obtained by measuring $V'$ and $V^i$ shown on TDR waveform. $Z_L$ can then be represented by $Γ$ and $Z_0$. By measuring $Z_L$ in a solution of known electrical conductivity $σ_w$, a simple $Z_L-σ_w$ relationship can be established as done by Nadler et al. (1991) and Wraith et al. (1993):

$$σ_w = k / Z_L$$  \[24\]

where $k$ is an empirical coefficient but has been considered as the cell constant of a TDR probe. $σ_a$ was obtained using Eq. [24] with the same $k$ and $Z_L$ measured in soil. The circuit shown in Figure 2 considers the TDR probe and soil as an integrity. It completely ignores the existence of the TDR probe, though $Z_L$ is determined by both the probe and the medium, soil, and cannot be considered as soil impedance. Despite an obvious flaw in theory, this simple circuit approach has been recommended as a good method by Nadler et al. (1991).

Another circuits approach to simulate TDR measurement was introduced by Topp et al. (1988) following the thin sample method of Giese and Tiemann (1975). The approach is diagrammed in Fig. 3. A section of coaxial line of length $l$ and of characteristic impedance $Z_i = Z_0 / z$ ($z =$ mismatch factor) is filled up with the dielectric under test and terminated with a load impedance $Z_L$ (Giese and Tiemann, 1975). Solutions for this approach were summarized by Clarkson et al. (1977). One of the solutions (Eq. 6c), cited by Topp et al. (1988), states that

$$σ_a = (ε_0 c / l)(Z_l / Z_0)((1-Γ)/(1+Γ))$$  \[25\]

when $Z_L \rightarrow \infty$, where $c = 1 / \sqrt{ε_0 μ_0}$ is the velocity of electromagnetic wave in free space. $Γ$ is the reflection coefficient for the first air-dielectric interface. Eq. [25] can be
Fig. 3. Coaxial cable partially exposed in a dielectric with impedance $= Z_i$ before terminated by a load impedance $Z_L$.

rewritten as

$$\sigma_a = \frac{1}{120\pi l} \frac{(Z_i/\varepsilon_0)\Gamma(1-\Gamma)/(1+\Gamma)}{(1-r)/(1+n)} \quad \text{[26]}$$

if Eq. [18] is used. Topp et al. (1988) found that $\sigma_a$ measured using Eq. [25] was at least 15% higher than that measured by a Wheastone resistance bridge. Note that thin sample analysis is merely an approximation to real TDR procedure: first, TDR probe in soil measures a "thick" rather "thin" sample; second, the mismatch factor $\Gamma$ is presumably greater than 1, i.e., $Z_1 < Z_0$, which is not true for the configuration of the TDR probe; third, when soil is wet, $Z_L \neq \infty$.

Dalton and Van Genuchten (1986) suggested that

$$\sigma_a = \frac{\sqrt{\varepsilon_r}}{120\pi l} \ln\left(\frac{V_T}{V^r}\right) \quad \text{[27]}$$

where $V_T$ and $V^r$ are incident and reflected voltage at the end of TDR probe, respectively. Eq. [27] was probably derived based on the theory stated by Eq. [13]. The assumption made by Dalton and Van Genuchten (1986) is that a perfect reflection occurs at the end of the TDR probe and thus
\[ V' = V_T e^{(-2\alpha t)} \]  

where \( \alpha \) is an attenuation coefficient. Eq. [28] is somewhat questionable because for perfect reflection conditions either

\[ V' = V_T \quad \text{for open circuit} \]  

or

\[ V' = -V_T \quad \text{for short circuit} \]  

In fact, data presented by Dalton and Van Genuchten (1986) seemed not to support Eq. [27] when it was applied to TDR measurements on soil. However, Nadler et al. (1991) concluded that TDR \( \sigma_a \) calculated using Eq. [27] agreed with \( \sigma_a \) measured with the 4P method.

\( \Gamma \) in Eq. [23] and Eq. [26] can be obtained by analyzing the TDR waveform. Figure 4 illustrates a waveform obtained for a 2-rod, 15-cm TDR probe, where \( V_0, V_1 \) and \( V_f \) are amplitudes (or voltages) of TDR pulse, signal at the end of probe before reflection, and signal after multiple reflections. Topp et al. (1988) and Wraith et al. (1993) used the following equation to calculate \( \Gamma \)

\[ \Gamma = (V_f - V_0)/V_f \]  

It is obvious that current approaches in determining \( \sigma_a \) from TDR measurements are not exact in theory. Though some good results have been obtained, various uncertainties remain undiscussed. More detailed and exact circuit analysis may be needed to better understand TDR.
Theory for $\theta_v$ measurement

The behavior of an electromagnetic wave can be described by the following equations (Plonus, 1978)

\[ \nabla^2 E - \mu \varepsilon \frac{\partial^2 E}{\partial t^2} = \mu \frac{\partial A}{\partial t} + \nabla \rho / \varepsilon \]  \[32\]

and

\[ \nabla^2 H - \mu \varepsilon \frac{\partial^2 H}{\partial t^2} = \nabla \times J \]  \[33\]

where $E$ = electric field strength, $H$ = magnetic field strength, $J$ = current density, $\rho$ = charge density.

An equation whose left-hand side has the form of [32] or [33] is called a wave equation,
since solutions to such equations give propagating waves. The right hand side represents merely the sources for the wave fields $E$ and $H$. In free space, $J = \rho = 0$ since no sources can be present. Fields in such a region must satisfy the wave equation

$$\nabla^2 E - \mu \frac{\partial^2 E}{\partial t^2} = 0$$

[34]

In a conducting medium, such as sea water or wet soil, $J = \sigma E$. If $\rho$ and $\varepsilon$ are homogeneous in the media, i.e., $\nabla(\rho/\varepsilon) = 0$. The wave equations are

$$\nabla^2 E - \mu \frac{\partial^2 E}{\partial t^2} - \sigma \mu \frac{\partial E}{\partial t} = 0$$

[35]

and

$$\nabla^2 H - \mu \frac{\partial^2 H}{\partial t^2} - \sigma \mu \frac{\partial H}{\partial t} = 0$$

[36]

Note that Maxwell's equation states

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

[37]

where $B = \mu H$, is magnetic flux density.

Sinusoidal wave solutions are part of the many different solutions to Eq. [35] or [36] (Shadowitz, 1975). Let $\psi$ represent any one of the six components of $E$ or $H$, then a sinusoidal plane wave moving along the $x$ axis toward $+x$ may be represented by

$$\psi = \psi_0 \sin \left[ 2\pi (ft - \frac{x}{\lambda}) + \theta \right] = \psi_0 \sin \left[ (\omega t - kx) + \theta \right]$$

[38]

where $f$ is frequency, $\lambda$ is wave length, $\omega = 2\pi f$ is the angular frequency, $k = 2\pi/\lambda$ is the propagation constant, $\theta$ is a phase angle, $t$ is plane time, and the amplitude $\psi_0$ is a constant. By setting $\theta = 90^\circ$ equation [38] can be simplified to a complex exponential form,
\[ \psi = \psi_0 e^{i(\alpha x - kx)} \]  

[39]

Note that the physical wave of concern is actually given only by the real part of \( \psi \). The velocity of the wave \( (v) \) is given by

\[ v = \frac{\lambda}{T} = \lambda f = \omega/k \]  

[40]

where \( T \) is the period of the wave. The term \( v \) changes when an electromagnetic wave passes an interface between a vacuum and a conducting medium. If the incident wave is normal to the plane of interface, \( f \) does not change after the wave travels into the medium, but the wave length decreases (Fig. 5)

Wave length can be inferred from \( k \) values. So can velocity. Substituting equation [39] in equation [35] or [36] gives

\[ k^2 - \varepsilon \mu \omega^2 + j \sigma \mu \omega = 0 \]  

[41]

---

**Fig. 5.** A sketch of an electromagnetic wave passing a interface between a vacuum (wave length = \( \lambda \)) and a conducting medium (wave length = \( \lambda_m \)).
It is clear that $k$ is related to $\varepsilon$ and $\mu$. Equation [39] indicates that the fields do not attenuate in conducting medium due to constant $\psi_0$. To present an attenuation term, we make $k$ complex. Let

$$k = \beta - j\alpha. \ (\beta > 0, \alpha > 0) \quad [42]$$

and substitute for $k$ in equation [39]. Then,

$$\psi = (\psi_0 e^{-\alpha}) e^{j(\alpha x - \beta t)} \quad [43]$$

where $\alpha$ is the attenuation factor and $\beta$ the phase factor (Hippel, 1954). The fields now experiences a small exponential attenuation. The relative size of attenuation will be discussed later. Substituting $k = \beta - j\alpha$ in Equation [41] gives

$$(\beta^2 - \alpha^2) - j(2\alpha \beta) = \varepsilon \mu \omega^2 - j\sigma \mu \omega \quad [44]$$

To satisfy Eq. [44] requires that

$$(\beta^2 - \alpha^2) = \varepsilon \mu \omega^2 \quad \text{and} \quad 2\alpha \beta = \sigma \mu \omega \quad [45]$$

Solving equation system [45] gives

$$\alpha = \omega \sqrt{\frac{\varepsilon \mu}{2} \left( \sqrt{1 + Q^2} - 1 \right)} \quad [46]$$

and

$$\beta = \omega \sqrt{\frac{\varepsilon \mu}{2} \left( \sqrt{1 + Q^2} + 1 \right)} \quad [47]$$

where $Q = \varepsilon \omega / \sigma$. It can be shown that $Q$ is the ratio of the "displacement current density" to the conduction current density.

Eq. [43] gives the wave velocity $v = \omega / \beta$. So
\[ v = \frac{1}{\sqrt{\varepsilon \mu}} \left[ \frac{2}{\sqrt{1 + Q^{-2}} + 1} \right]^{1/2} \]  \[ [48] \]

If \( Q > 10 \), then \( v \approx 1/\sqrt{\varepsilon \mu} \); on the other hand, when \( Q < 0.1 \) then \( v \approx \sqrt{2Q} (1/\sqrt{\varepsilon \mu}) \).

Putting \( \varepsilon = \varepsilon_0 \varepsilon_0 \) and \( \mu = \mu_0 \mu_0 \) in Equation [48] gives

\[ v = \frac{1}{\sqrt{\varepsilon_0 \mu_0} \sqrt{\varepsilon_0 \mu_0}} \left[ \frac{2}{\sqrt{1 + Q^{-2}} + 1} \right]^{1/2} \]  \[ [49] \]

Recall that in free space the velocity of an electromagnetic wave \( c = 1/\sqrt{\varepsilon_0 \mu_0} \) and for nonmagnetic material \( \mu_r = 1 \). Eq. [49] can be simplified as

\[ v = \frac{c}{\sqrt{\varepsilon_r}} \left[ \frac{2}{\sqrt{1 + Q^{-2}} + 1} \right]^{1/2} \]  \[ [50] \]

Rearranging Eq. [50], we obtain

\[ \varepsilon_r \left( \sqrt{1 + Q^{-2}} + 1 \right) / 2 = \left( \frac{c}{v} \right)^2 \]  \[ [51] \]

Topp et al. (1980) and White et al. (1994) suggested that relative permittivity can be represented as a complex quantity, \( \varepsilon_r^* \), with real (in-phase), \( \varepsilon_r'(\omega) \), and imaginary (out-of-phase), \( \varepsilon_r''(\omega) \), components when an electromagnetic wave travel through wet porous materials. That is

\[ \varepsilon_r^* = \varepsilon_r'(\omega) - j\varepsilon_r''(\omega) + \sigma / \omega \varepsilon_0 \]  \[ [52] \]

They also gave a relationship similar to Equation [51] as follows:
\[ \varepsilon_r \left(1 + \sqrt{1 + \tan^2 \delta} \right)/2 = \left(\frac{c}{v}\right)^2 \]  

where

\[ \tan \delta = \left[ \varepsilon_r''(\omega) + \sigma / \omega \varepsilon_0 \right] / \varepsilon_r'(\omega) \]

is called the loss tangent.

Combining Eq. [2] and Eq. [51] gives

\[ K_a = \left(\frac{c}{v}\right)^2 = \varepsilon_r \left(\sqrt{1 + Q^2} + 1\right)/2 \]

If we can measure the velocity \( v \) of electromagnetic wave propagation in a material medium, then we can determine the value of the right hand side of Eq. [55]. Furthermore, we can determine \( \varepsilon_r \) if \( Q^2 \) or \( \tan^2 \delta \) is negligible.

TDR is the right tool to determine \( v \). When the TDR signal reaches the junction of a coaxial cable and probe, a partial open circuit occurs which results in a reflection of the signal, which increases the signal strength. On the other hand, a signal transmitted into a probe in moist soil is also partially reflected due to the resulting partial short circuit, and signal strength decreases. The increase and decrease of the signal produce a peak in the TDR trace. The signal encounters a partially open circuit at the end of the probe and another reflection occurs which increases the strength of the signal. A signal sampler in the TDR measures signal strength (voltage) over time (Tektronix, 1990). This information is then displayed on an oscilloscope in terms of distance and reflection coefficient (or ohms) on the abscissa and the ordinate, respectively (Tektronix, 1990; Spaans & Baker, 1993).

Figure 6 illustrates a TDR trace plotted using data points obtained from the oscilloscope.
display using an algorithm (Baker & Allmaras, 1990). This trace was obtained with a 15-cm, two-wire probe horizontally positioned in an undisturbed soil core. The peak A and valley B indicate where the wave enters and ends on the probe, respectively. The LCD of the oscilloscope is scaled into ten divisions horizontally and 8 divisions vertically. Initial settings for the measurement were: \( v_p = 0.99(c) \), VERT SCALE = 76 m\( \rho \), and DIST/DIV = 0.25 m. \( v_p \) is the speed of a signal down the cable given as a percentage of the speed of the signal in free space. VERT SCALE sets sensitivity per division. DIST/DIV determines the number of meters per division across the display (Tektronix, 1990). The \( v_p \) setting allows the oscilloscope to display distances on the horizontal axis of the screen rather than time, which is what TDR actually determines (Vadose Zone Equ. Co., 1994). Note that Baker & Allmaras’ algorithm gives only relative byte position rather than actual number of m\( \rho \) of each data point on the ordinate.

Assuming the time required for the TDR signal to travel along a probe of length of 1 is \( \Delta t \), the actual wave propagation velocity \( v \) is given as

\[
v = \frac{1}{\Delta t}
\]  

[56]

Upon obtaining a steady TDR trace, the TDR displays distance \( d \) at any given time \( t \) after an internal conversion based on

\[
d = v_p t
\]

[57]

Recall that A and B on the TDR trace mark the beginning and ending points of the probe. The horizontal distance between A and B, \( \Delta d \) is then given as

\[
\Delta d = v_p \Delta t
\]

[58]

Combining equation [56] and [58] gives
\[ v = \left( \frac{\ell}{\Delta d} \right) v_p \] [59]

A number of different algorithms to measure \( \Delta d \) have been developed (e.g., Baker & Allmaras, 1990; Heimovaara & Bouten, 1990; Zegelin et al., 1989). For instance, the algorithm described by Baker & Allmaras (1990) gives \( \Delta d = 0.796 \text{ m} \) for the waveform shown in Fig. 6 by obtaining the distance between the first reflection point, C, and the second reflection point, D.

Using Eq. [55], Eq. [59], \( \Delta d = 0.796 \text{m} \), and \( 1 = 0.15 \text{m} \) yields \( K_a = 28.73 \). Putting this value in Eq. [4] gives \( \theta_v = 0.4339 \text{ m}^3 \text{ m}^{-3} \). Note that \( K_a \) is an approximation of the soil dielectric constant. This approximation is valid if: a) the sampled soil has a uniform dielectric
constant and charge density, i.e., $\nabla(\rho/\varepsilon) = 0$, so that Eqs. [35] and [36] can be used; b) $Q$ is large, i.e., the ratio of $\varepsilon/\sigma$ is large so that Eq. [51] can be simplified as

$$\varepsilon_r = \left(\frac{\sigma}{\varepsilon}\right)^2$$

[60]

**Effects of $\sigma_a$ on TDR-measured $\theta_v$**

It can be shown that $\sigma_a$ has little influence on TDR $\theta_v$ measurement in theory. $Q$ usually is large enough so that the approximation, $K_a = \varepsilon_r$, can be used when the measurement is made on soil. For instance, for a soil with $\sigma_a = 2$ dS m$^{-1}$, $\varepsilon_r = 25$, and TDR measuring frequency of 2.5 Ghz, $Q = 17.38$ and the term $[(1+Q^2)^{1/2}+1]/2$ in Eq. [55] is 1.0008, i.e., $K_a = 1.0008\varepsilon_r$. This small difference is non-measurable since it is beyond the resolution of TDR measurement of $\theta_v$ (Zegelin et al. 1992).

There are few reports on the influence of electrical conductivity on TDR estimated $K_a$ and $\theta_v$. By measuring $K_a$ in KCl solution with concentration varied from 0 to 0.05 N, Topp et al. (1992) concluded that determination of $K_a$ using the travel time of the TDR signal was accurate for various KCl concentrations provided that there was sufficient reflected signal strength. Dalton et al. (1984) reported that for a soil column with bulk electrical conductivity ($\sigma_a$) varying from 0.3 to about 1.3 dS m$^{-1}$, TDR estimated $K_a$ was 19.48±0.53 and $\theta_v$ was 0.34±0.01 m$^3$ m$^{-3}$. They concluded that variation in $\sigma_a$ had negligible effect upon the determinations of $\theta_v$. But, in a later paper Dalton and Poss (1990) reported that TDR overestimated $\theta_v$ for pore water electrical conductivity $\sigma_w$ equal to or greater than 8 dS m$^{-1}$. White et al. (1994) reported that the square root of $K_a$ increased with an increase of $\sigma_a$.
induced by graphite at given volumetric water content for a sand-graphite-water system. So far, few researchers have demonstrated an effect of σₐ in the moderate range on TDR estimated Kₐ or θᵥ for an undisturbed soil core in spite of the fact that undisturbed soil cores under this range of σₐ are commonly used in TDR research. Vanclooster et al. (1993) suggested, without showing their data, that salts had a significant impact on the travel time of the TDR trace. Wyseure et al. (1997) reported that the overestimation of θᵥ caused by σₐ for five soils (from coarse sand to clay loam) stayed within reasonable limits if σₐ was less than 2 dS m⁻¹.

Estimating σᵥ from σₐ Measurement

Solution conductivity and Ohm’s Law

If the resistance between two points of a conductor is R, Ohm’s law relates the current I between two points to the voltage V between the points as

\[ V = IR \]  \[ 61 \]

where the units of R are ohms, I ampere, and V volt.

The resistance of a material is proportional to its length (l) and inversely proportional to its cross-sectional area (A)

\[ R = \frac{\rho l}{A} \]  \[ 62 \]

The coefficient ρ (Ω-m) is called resistivity or specific resistance. The reciprocal of the resistivity is called the conductivity or specific conductance:

\[ \sigma = \frac{1}{\rho} \]  \[ 63 \]

The units of the conductivity, σ, in the older system are in mhos/meter, with mho = 1/ohm. In
the newer SI system of units, \( \sigma \) is in siemens/meter (S m\(^{-1}\)).

The conductivity of a solution is determined by: 1) its equivalent concentration (N); 2) the degree of dissociation of the solute (\( \alpha \)); 3) the mobility of the dissociated ions (\( u \)) (Noggle, 1996), i.e.

\[
\sigma = \alpha (u_+ + u_-) F N \tag{64}
\]

where \( F \) is Faraday's constant (96485 C mole\(^{-1}\)). The signs + and - refer to cation and anion, respectively. The degree of dissociation of the solute is the fraction of solute that is dissociated. The mobility of an ion is defined as the ion's velocity per unit electric field. It is related to the size of the ion, its charge, and the viscosity of the solvent.

Another frequently used term for solution conductance is the equivalent conductivity, \( \Lambda \), which is the ratio of the solution conductivity to the solution equivalent concentration

\[
\Lambda = \frac{\sigma}{N} = \alpha (u_+ + u_-) F \tag{65}
\]

**Soil electrical conductivity and its measurement**

Soil electrical conductivity is generally called bulk soil electrical conductivity, \( \sigma_a \), by soil scientists. Past measurement of \( \sigma_a \) was mainly for salinity appraisal. Recently, it has been used to monitor solute movement in non-saline soil. Most soils when completely dry are non-conductors of electricity (Tagg, 1964). Tagg (1964) summarized the main factors determining soil conductivity as: \( \theta_e \), the concentration and chemical composition of solute, temperature, soil type, soil particle and particle distribution, and closeness of packing and pressure. While Mualem and Friedman (1991) considered \( \sigma_a \) as analogous to soil hydraulic conductivity, Nadler (1991) reported that \( \sigma_a \) measured on disturbed soil was not different
from that determined on undisturbed soil. As a porous medium, soil is electrically conductive
due to the movement of free ions in electrolyte solution contained in the soil pores and to
ions adsorbed to the matrix surface (Nadler & Frenkel, 1980; Mualem & Friedman, 1991). It
is common to use the terms soil solution electrical conductivity, $\sigma_w$, to represent the
contribution of ions in the solution and soil surface conductivity, $\sigma_s$, the contribution of ions
adsorbed on soil particles.

Direct measurement of $\sigma_w$ can be made on: 1) aqueous extracts of soil samples; 2)
samples of soil water per se, obtained from the soil (Rhoades and Oster, 1986). In the first
case $\sigma_w$ equals the electrical conductivity of the extracts multiplied by the ratio of soil sample
weight to water volume of soil sample (Nadler, 1981). This correction assumes no
dissolution or precipitation of salts during extraction (Nadler et al, 1984). Soil water samples
can be obtained either in laboratory or in situ with the following methods: 1) displacement;
2) compaction; 3) centrifugation; 4) molecular adsorption; 5) suction; and 6) pressure
membrane extraction. The suction method is commonly used in the field and less destructive
than other methods. Problems associated with the suction method include: 1) soil water
samples extracted at lower suction may differ from that extracted at higher suction, because
the composition and concentration of soil water are not homogeneous throughout the soil
matrix; 2) it may take several days to get an adequate sample at $\theta_v$ less than field capacity.

The $\sigma_a$ can be determined in several different ways: 1) The “cup” method: This is a
technique used to measure $\sigma_a$ of soil paste, $\sigma_p$. The cup is a 50-cm$^3$ cylindrical conductivity
cell made of hard rubber, with two large electrodes of nickel-plated brass. This method is
quick and reproducible while the apparatus is inexpensive, simple, and rugged (Rhoades et
al., 1989b); 2) Four-electrode method (4P): This is a technique requiring an electric current source and a resistance meter. Four metal electrodes are placed into soil with adequate interelectrode spacing. An alternating current is passed through the soil between two outside electrodes, and the voltage drop between the two inner electrodes is measured. The ratio of the voltage and the current measured enables the calculation of the resistance of a minimally disturbed bulk soil (Rhoades and Oster, 1986; Nadler, 1988). It enables direct, instantaneous, in situ measurements (Nadler and Frenkel, 1980); 3) EM (electromagnetic induction) method: The instrument includes a transmitter and a receiver coil. The transmitter induces circular eddy current loops in the soil. The magnitude of these induced current loops is proportional to the \( \sigma_a \). The receiver detects part of the secondary electromagnetic field generated by the current loops and is proportional to the value of the current (de Jong et al., 1979; Rhoades and Oster, 1986). This is a non-contact, less detail, but faster technique for \( \sigma_a \) measurement; 4) TDR method was previously discussed.

**Estimating \( \sigma_w \) from \( \sigma_a \) measurement**

Due to the facility in measuring \( \sigma_a \) and difficulty in determining \( \sigma_w \), there is considerable interest in the indirect method of estimating \( \sigma_w \) from the measurement of \( \sigma_a \). A number of models have been used to describe the \( \sigma_w-\sigma_a \) relation. It is commonly accepted that the soil solution and soil solid particles can be considered as two resistors connected in either series or parallel (Rhoades et al., 1976). Nadler and Frenkel (1980) concluded that a series model cannot be applied to natural conditions. Another model considers soil as three resistors in parallel: soil solution, conducting solid particles, and the alternating layers of solution and
conducting solid connected in series (Shainberg et al., 1980; Rhoades et al., 1989).

Rhoades et al. (1976) proposed a linear relation between bulk soil electric conductivity, \( \sigma_a \), and soil solution electric conductivity, \( \sigma_w \), by adapting the parallel model.

\[
\sigma_a = \sigma_w \theta_v T + \sigma_s \tag{66}
\]

where \( \theta_v \) is volumetric \( \theta_v \) and \( T \) the transmission coefficient. The transmission coefficient accounts for the tortuosity of soil pores and less mobile ions near the solid-liquid and liquid-gas interfaces. \( T \) can be empirically expressed as

\[
T = a \theta_v + b \tag{67}
\]

where \( a \) and \( b \) are constants. The linearity of the \( \sigma_a-\sigma_w \) relation exists only when \( \sigma_w > 3.5 \text{ dS m}^{-1} \) (Nadler and Frenkel, 1980; Shainberg et al., 1980). Below 3.5 dS m\(^{-1}\), \( \sigma_s \) increases with \( \sigma_w \).

Using the three resistors (or conductors) in parallel model, Shainberg et al. (1980) suggested that under saturated conditions \( \sigma_a \) can be described as

\[
\sigma_a = \frac{\sigma_s \sigma_w}{(1 - d) / d \sigma_s + \sigma_w} + \frac{\sigma_w}{F} \tag{68}
\]

where \( \sigma_s' \) is apparent soil surface electrical conductivity and \( d \) is the length parameter of the solid particles varying between 0.7 to 0.8. It is the solid fraction plus the thickness of the diffuse double layer for a unit length of soil. \( F \) is the formation factor representing tortuosity. Its value is around 4.0 (\( 1/F = 0.25 \)) for a typical soil. Eq. [68] can be simplified as

\[
\sigma_a = \sigma_s' + \sigma_w / F \tag{69}
\]

when \( \sigma_w >> \sigma_s' \), i.e., at high solution concentration. Eq. [69] is equivalent to Eq. [66] if \( 1/F = \theta_v T \). They concluded that for nonsaline soils, Eq. [68] should be used.
They concluded that for nonsaline soils, Eq. [68] should be used.

Nadler and Frenkel (1980) proposed the following relationship between $\sigma_a$ and $\sigma_w$

$$\sigma_a = [\sigma_w(\theta_{act}/\theta_{sat}) + \delta \cdot \lambda C_a^{2+} \cdot \psi_v] (1/F) \quad [70]$$

where $\sigma_a$ and $\sigma_w$ are defined as before, $\theta_{act}$ and $\theta_{sat}$ are volumetric $\theta_v$ at $\sigma_a$ measurement and its volumetric water content at saturation, respectively. The term $(\theta_{act}/\theta_{sat})$ is designed to make Eq. [70] suitable over a wide range of $\theta_v$. $F$ is the formation factor, which is defined as in Eq. [68] and has similar values. Nadler et al. (1984) reported that $F$ decreases with the increase of volumetric $\theta_v$. The $F$ in Eq. [68] and [70] is the formation factor under saturated water content. $\delta$ is the empirical ratio of equivalent conductance of clay counter ions to the maximum value of this equivalent conductance. It increases with the increase of $\sigma_w$.

$\lambda C_a^{2+} \cdot \psi_v \equiv \sigma_s$. Eq. [68] and Eq. [70] actually state that at low $\sigma_w$, electrical conductivity due to ions on the solid surface changes with $\sigma_w$ while Eq. [66] suggests that it is fixed. Eq. [68] and Eq. [70] are similar to each other except that they use different ways to relate the change of solid surface conductivity with $\sigma_w$. A laboratory $\sigma_a$-$\sigma_w$ relation based on Eq. [70] was tested in the field (Nadler, 1981). The results showed that $\sigma_w$ estimated from $\sigma_a$ using Eq. [70] was close to the electrical conductivity of irrigation water and always equal to or smaller than that estimated from $\sigma_w$ of 1:1 soil extracts.

Following the same theory, three conductors in parallel, used by Shainberg et al. (1980), Rhoades et al. (1989) suggested the following relationship of $\sigma_a$ to $\sigma_w$

$$\sigma_a = \left[ \frac{(\theta_s + \theta_{ws})^2 \sigma_{ws} \sigma_s}{\theta_s \sigma_{ws} + \theta_{ws} \sigma_s} \right] + \theta_{wc} \sigma_{wc} \quad [71]$$
pathway (large pores), respectively. $\theta_{ws}$ and $\theta_{wc}$ are volumetric water contents in the series-coupled pathway and the separate continuous liquid pathway. $\theta_s$ is volumetric content of solid phase. Eq. [71] is almost the same as Eq. [68] except that Eq. [71] includes the tortuosity effect in the first term while Eq. [68] considers the effect both in the first and the second terms. When $\sigma_{ws} >> \sigma_s$, Eq. [71] can be reduced to

$$\sigma_a = \left[ \frac{(\theta_s + \theta_{ws})^2 \sigma_s}{\theta_s} \right] + \theta_{wc} \sigma_{wc}$$  [72]

Eq. [72] can be considered as the equivalent of Eq. [66] and is applicable only for high solution electrical conductivity (>2–4 dS m$^{-1}$). Working on both saturated soil paste in the laboratory and undisturbed soil in the field with the water content at field capacity, Rhoades et al. (1989) obtained the $\sigma_s$ and $\theta_{ws}$ for Eq. [71] using nonlinear least squares fit. The predicted $\sigma_a$-$\sigma_e$ (electrical conductivity of saturation extract) corresponded to the observed $\sigma_a$-$\sigma_e$ relation very well given the following assumptions and approximations: a) $\sigma_{ws} = \sigma_{wc} = \sigma_w$; b) $\sigma_w$ was estimated from $\sigma_e$. They further suggested that Eq. [71] could be a tool for determining mobile water content. However, Mualem and Friedman (1991) thought this was questionable. The assumptions made by Rhoades et al (1989a) could be questioned by the following facts: a) To estimated $\sigma_w$ by $\sigma_e$, one has to assume no dissolution or precipitation of salts during extraction (Nadler et al., 1984). Thus the estimate is accurate only when $\theta_v$ approaches saturation. b) For structured soil, $\sigma_{wc}$ differs from $\sigma_{ws}$ when soils are undergoing relatively rapid changes in salinity within the large pores (Rhoades et al., 1989c). In practice, Eq. [71] is difficult to use for the purpose of estimating $\sigma_w$ by measuring $\sigma_a$ and $\theta_v$, because it requires pre-measurements of soil bulk density and immobile $\theta_v$. While Rhoades et al.
(1989a) suggested a linear relation of $\theta_{ws}$ (or $\theta_{im}$ as usually used) to $\theta_v$, others (Casey et al., 1997; Smedt et al., 1986) reported that the correlation between $\theta_{ws}$ and $\theta_v$ was not significant. Thus, estimating $\theta_{ws}$ from $\theta_v$, as suggested by Rhoades et al. (1989a) is somewhat questionable.

Criticizing Eq. [71] for having too many parameters that need to be determined, Mualem and Friedman (1991) proposed a conceptual model that assumed the flow lines of electrical current are similar to the flow lines of water molecules

$$\sigma_b(\theta) = \sigma_w(\theta^n/\theta_{sat})$$

[73]

where $\sigma_b(\theta)$ is bulk solution electrical conductivity at effective $\theta_v$, $\theta$, which is the difference between $\theta_v$ and residual water content. $\theta_{sat}$ is $\theta_v$ at saturation. $n = 0.5$ for sand and loam soils with stable structure. $\sigma_b \equiv \sigma_a$ if $\sigma_v \rightarrow 0$. The results showed that Eq. [73] was only suitable for coarse and stable structured soil.

Calibration of $\sigma_w - \sigma_a$ can be carried out on either packed soil core (Shainberg et al. 1980; Nadler and Frenkel, 1980) or undisturbed soil core (Rhoades et al., 1989). Measurement can be made by electrode cup (Rhoades et al., 1989), four probe (Shainberg et al., 1980; Nadler and Frenkel, 1980; Rhoades et al., 1989), or TDR method (Hart and Lowery, 1998; Ward et al., 1995; Risler et al., 1996). $\sigma_w$ is determined on saturation extracts (Nadler, 1981; Rhoades et al., 1989) or free drainage solution produced by leaching soil cores for multiple pore volumes (Shainberg et al., 1980; Nadler and Frenkel 1980; Nadler, 1981; Hart and Lowery, 1998; Risler et al., 1996)
Solute Transport in Soil

Solute transport in soil has long been a subject of research. Understanding the processes of solute transport in soil is important to optimize fertilizer application and control contamination of ground water.

Convection, diffusion, and hydrodynamic dispersion are three mechanisms of solute movement in soil. Convection refers to the movement of solute with soil water flow which is driven by hydraulic pressure gradients or/and gravity forces. Diffusion, caused by Brownian motion, describes solute movement from the region of higher solute concentration to the region of lower solute concentration. Hydrodynamic dispersion, resulting from the nonuniform velocity distribution of water flow in soil, is a process in which faster-moving incoming flow mixes with slower-moving antecedent flow.

When a solution different in composition or concentration from preexisting pore solution is introduced into a soil column, the original solution will be replaced and displaced. The replacement and displacement result in a change in composition or concentration of soil solution with time. How fast and how much the change would be depend on the scale of convection, diffusion, dispersion, and soil properties. A plot of solution concentration versus time at any particular position of the soil column, called breakthrough curve (BTC), is frequently used to characterize the replacement and displacement processes. Since the solute transport in soil is generally not visible and difficult to be visualized and determined, the outflow BTC is commonly used to characterize solute transport from a soil core. A BTC can partly explain what takes place during solute transport in soil. For instance, piston flow has an abrupt change in solution composition while preferential flow has an early breakthrough and a long tail. Numerical models are required to quantitatively describe solute transport.
processes.

For equilibrium transport, the classical convection-dispersion equation (CDE)

\[
R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} + S \tag{74}
\]

describes one-dimensional solute transport, where \( C \) is the solute concentration at time \( t \) and distance \( z \). \( v \) is average pore-water velocity. \( D \) is a lumped diffusion and dispersion coefficient. \( R \) is the retardation factor given by

\[
R = 1 + \rho_b K_d / \theta_v \tag{75}
\]

where \( \rho_b \) and \( K_d \) are soil bulk density and empirical distribution constant, respectively. The source term \( S \) represents degradation and production of solute. If the solute is non-reactive and no degradation and production occur, \( S \) can be dropped. \( K_d = 0 \) and \( R = 1 \) if no adsorption of the solute take place.

For two-region nonequilibrium transport, the liquid phase is assumed to be partitioned into mobile and immobile regions. The two-region solute transport model is given by

\[
R_m \frac{\partial C_m}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - \theta_m v_m \frac{\partial C_m}{\partial z} - \alpha_T (C_m - C_{im}) + S_m \tag{76}
\]

where \( \alpha_T \) is a first-order mass transfer coefficient, subscripts "m" and "im" refer to the mobile and immobile liquid regions. Analytical solutions to Eqs. [74] and [76] can be obtained under various boundary and initial conditions. More details can be found in the U.S. Salinity Laboratory Research Report No. 137 (Toride et al., 1995). The solution can be generalized as

\[
C(t, z) = f(t, z, R, D, v, \alpha_T \ldots) \tag{77}
\]

The exact value of \( C(t, z) \) depends on known values of parameters \( R, D, v, \alpha_T \), and so on, at
given time $t$ and distance $z$. The term $v$ can be obtained by measuring outflow flux while $R$ can be determined by Eq. [75] where $K_d$ is obtained by adsorption isotherm. More frequently, all these parameters are obtained by least-square fitting right hand side of Eq. [77] to a series of known $C(t, z)$, which are usually the outflow concentrations sampled at certain time interval. When fitting many data points, the computation work is tremendous. Computer programs, such as CXTFIT (Toride et al., 1995), have been developed to do this calculation.

References


CHAPTER 3. BULK SOIL ELECTRICAL CONDUCTIVITY EFFECTS ON TIME DOMAIN REFLECTOMETRY WATER CONTENT MEASUREMENTS

A paper to be submitted to Soil Science Society of America Journal

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ABSTRACT

Current TDR-measured apparent soil dielectric constant, \( K_a \), to soil water content, \( \theta \), relationships ignore soil bulk electrical conductivity, \( \sigma_s \). An effect of \( \sigma_s \) on \( \theta \) would decrease the accuracy of solute transport determinations based on TDR-measured \( \theta \) and \( \sigma_s \).

The effect of \( \sigma_s \) on \( K_a \) was evaluated theoretically to have negligible influence on TDR-measured \( K_a \) and \( \theta \), for \( \sigma_s < 2 \) dS m\(^{-1}\). The influence of \( \sigma_s \) on \( K_a \) was measured for packed cores over a range of \( \sigma_s \) of 0.07 to 1.47 dS m\(^{-1}\) and at five depths in an undisturbed soil core over a range of \( \sigma_s \) from 0.65 to 1.38 dS m\(^{-1}\). A \( K_a-\theta \), relationship, theoretically based and ignoring the effect of \( \sigma_s \) on \( \theta \), was more efficient than Topp's universal equation in fitting packed soil core measurements. The theoretically based \( K_a-\theta, \sigma_s \) relationship was unable to properly interpret the same data. However, a semi-empirical \( K_a-\theta, \sigma_s \) relationship, developed by adding a \( \sigma_s \) term as an independent variable to the theoretical \( K_a-\theta \), relationship, significantly better fit the data.

On undisturbed cores, TDR-measured \( K_a \) increased with increasing \( \sigma_s \) while \( \theta \), was

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relatively constant at all five depths. The semi-empirical $K_s-\theta_v-\sigma_s$ relationship based on the full range of $\sigma_s$ for the packed soil measurements overestimated the effect of $\sigma_s$ on $K_s$ measurements for an undisturbed soil core. The same type of relationship calculated over the range of $\sigma_s$ used in the undisturbed core measurements improved estimates of $\theta_v$ for the undisturbed core, but both over- and under-corrected measured $K_s$ values. The error in estimating $\theta_v$ depended on position within the core. A position-specific linear relation of $K_s$ and $\sigma_s$ was required to remove the effect of $\sigma_s$ on $\theta_v$ estimates for individual probe positions.

**INTRODUCTION**

TDR, commonly used for cable testing, was developed to determine permittivity of material by Fellner-Feldegg (1969). Davis and Chudobiak (1975) concluded that TDR was a useful technique to determine $\theta_v$ due to the strong dependence of apparent soil dielectric constant (or relative permittivity), $K_s$, on $\theta_v$. A widely accepted $K_s-\theta_v$ relation was proposed by Topp et al. (1980)

$$\theta_v = -5.3 \times 10^{-2} + 2.92 \times 10^{-2}K_s - 5.5 \times 10^{-4}K_s^2 + 4.3 \times 10^{-6}K_s^3 \quad [1]$$

Eq. [1] was considered to be independent of soil type, soil density, and soluble salt content (Topp et al., 1980). Zegelin et al. (1992), however, suggested that Eq.[1] works best in coarse textured soils, and may not apply to fine textured, dense, and heavy clay soils.

Application of TDR has been extended to determination of soil solute transport since Dalton et al. (1984) proposed simultaneous TDR measurement of $\theta_v$ and $\sigma_s$. Frequently, this application requires estimation of soil solution electrical conductivity ($\sigma_w$) or solute concentration ($C_s$). An accurate estimate of $\theta_v$ is necessary in order to accurately estimate $\sigma_w$. 
and \( C \), since \( \sigma_a \) is a function of both \( \theta_v \) and \( \sigma_w \). Although studies on solute transport under steady flow conditions commonly assume that \( \theta_v \) is constant (Kachanoski et al., 1992; Wraith et al., 1993), Vanclooster et al. (1995) reported that variation in \( \theta_v \) measurements increased with increasing variation in resident solute concentration. Data presented by Hart and Lowery (1998) also showed a possible effect of Br\(^-\) solution on TDR \( \theta_v \) measurements. These reports raise questions about the possible effect of \( \sigma_w \) or \( \sigma_a \) on TDR-measured \( \theta_v \). Dalton et al. (1984) concluded that variation in \( \sigma_a \) had negligible effect upon the TDR determinations of \( \theta_v \). But, in a later paper Dalton (1992) reported that TDR overestimated \( \theta_v \) for pore water electrical conductivity \( \sigma_w \) equal to or greater than 8 dS m\(^{-1}\). White et al. (1994) reported that \( \sqrt{K_s} \) increased with an increase of \( \sigma_a \) induced by graphite at given \( \theta_v \) for a sand-graphite-water system. Wyseure et al. (1997) reported that the overestimation of \( \theta_v \) caused by \( \sigma_a \) for five soils (from coarse sand to clay loam) stayed within reasonable limits if \( \sigma_a \) was less than 2 dS m\(^{-1}\). No other reports have provided supporting evidence although undisturbed soil cores with \( \sigma_a < 2 \) dS m\(^{-1}\) are commonly used in TDR research. Also, few studies have attempted to theoretically explain the effect of \( \sigma_a \) on \( \theta_v \).

The objectives of this study are: 1) to evaluate, both by theory and by laboratory measurements, the effects of \( \sigma_a \) on TDR-measured \( K_s \) for an undisturbed soil core with \( \sigma_a < 2 \) dS m\(^{-1}\), and 2) to develop an adjustment to the determination of \( K_s \) to correct for the effect of \( \sigma_a \) on TDR estimated \( \theta_v \), based on theoretical analysis or experimental measurement, depending on which one is more applicable.
THEORY

\( K_s \) is determined by TDR through the following relationship (Davis and Annan, 1977)

\[
K_s = \left( \frac{ct}{1} \right)^2 \tag{2}
\]

where \( c \) is velocity of an electromagnetic wave in free space, \( 3 \times 10^8 \text{ m s}^{-1} \), \( t \) is travel time of an electromagnetic wave along the transmission line of length \( = 1 \) in the soil and can be measured by TDR.

Shadowitz (1975) derived the following equation without adapting the concept of relative permittivity as a complex quantity, which was embraced by Topp et al. (1980) and White et al. (1994)

\[
\varepsilon_r \left( \frac{v}{\sqrt{1 + Q^2}} + 1 \right) / 2 = \left( \frac{c}{v} \right)^2 \tag{3}
\]

where \( \varepsilon_r \) is relative permittivity (dielectric constant) of the media where the electromagnetic wave travels at a velocity of \( v \). And

\[
Q = \frac{\varepsilon \omega}{\sigma} \tag{4}
\]

where \( \varepsilon \) is the permittivity, \( \sigma \) the electrical conductivity of the media, and \( \omega \) the angular frequency of the electromagnetic wave.

Recall that Eq. [2] actually states

\[
K_s = \left( \frac{c}{v} \right)^2 \tag{5}
\]

Thus, Eq. [3] can be rewritten as

\[
K_s = \varepsilon_r \left( \sqrt{1 + Q^2} + 1 \right) / 2 = k \varepsilon_r \tag{6}
\]

where
While Topp et al. (1980) advocated the purely empirical $K_s$-$\theta_s$ relation, Roth et al. (1990) verified the following semi-empirical model

$$\varepsilon_{\text{mol}}^a = \varepsilon_w^a \theta + (1 - \eta)\varepsilon_s^a + (\eta - \theta)\varepsilon_g^a$$  \[8\]

where $\varepsilon_w$, $\varepsilon_s$, and $\varepsilon_g$ are dielectric constants of the liquid, solid, and gaseous phase, respectively, $\eta$ is the soil porosity and $\alpha = 0.5$. Rearranging Eq. [8] gives

$$\varepsilon_{\text{mol}}^a = \theta (\varepsilon_w^a - \varepsilon_s^a) + \varepsilon_s^a + \eta (\varepsilon_g^a - \varepsilon_s^a)$$  \[9\]

At a given temperature, $\varepsilon_w$, $\varepsilon_s$, and $\varepsilon_g$ can be considered as constant if measured at a given frequency (Hippel, 1954). Let

$$\beta_1 = \varepsilon_w^{05} - \varepsilon_s^{05}$$  \[10\]

and

$$\beta_0 = \varepsilon_s^{05} + \eta (\varepsilon_g^{05} - \varepsilon_s^{01})$$  \[11\]

Eq. [9] can be simplified as

$$\sqrt{\varepsilon_{\text{mol}}} = \beta_0 + \beta_1 \theta$$  \[12\]

where $\beta_1$ is constant if the measurement is conducted at constant temperature and frequency, and $\beta_0$ is constant under the same conditions for $\beta_1$, plus constant soil porosity. Recalling that $K_s = k \varepsilon_r$, we have

$$\sqrt{K_s} = \beta_0 \sqrt{k} + (\beta_1 \sqrt{k}) \theta$$  \[13\]

Let $\gamma_0 = \beta_0 \sqrt{k}$ and $\gamma_1 = \beta_1 \sqrt{k}$, and Eq. [13] can then be simplified as

$$\sqrt{K_s} = \gamma_0 + \gamma_1 \theta$$  \[14\]

where $\gamma_0$ and $\gamma_1$ are constants when soil electrical conductivity, temperature, and
measuring frequency remain unchanged.

Wyseure et al. (1997) proposed an empirical relationship between $K_a$ and $\sigma_a$,

$$K_a = \varepsilon_r + 1.432 \sigma_a$$  \[15\]

where $\varepsilon_r$ is defined as the real part of soil dielectric constant. They concluded the above linear regression performs slightly better than the theoretical model. For multi-depth measurements on an undisturbed soil core, Eq. [15] can be generalized as

$$(K_a)^\wedge_i = (K_{a,\sigma=0})^\wedge_i + c_i(\sigma_a)^\wedge_i$$  \[16\]

where $c_i$ is a site-specific coefficient and $(K_{a,\sigma=0})^\wedge_i$ is the soil dielectric constant at $\sigma_a \to 0$ for the $i$th depth of the undisturbed soil core. In other words, $K_{a,\sigma=0}$ is a TDR measurement with site-specific effects of $\sigma_a$ being eliminated. The estimated $\theta_v$ from $K_{a,\sigma=0}$ can be considered as the $\theta_v$ in a $\sigma_a$-free environment, which does not exist in soil. In fact, $\sigma_a$ is dependent on both $\theta_v$ and solute concentration. With no addition of solute to the undisturbed soil core, $K_a$ for any given $\theta_v$ at any given depth of the soil core should also comply to Eq. [16],

$$(K_{a,\theta_v})^\wedge_i = (K_{a,\sigma=0})^\wedge_i + c_i(\sigma_{a,\theta_v})^\wedge_i$$  \[17\]

where $(K_{a,\theta_v})^\wedge_i$ is soil dielectric constant at $\theta_v$ and $(\sigma_{a,\theta_v})^\wedge_i$ is $\sigma_a$ at $\theta_v$ for the $i$th position in the undisturbed soil core assuming distilled water as inflow. Subtracting Eq. [17] from Eq. [16], we obtain

$$(K_{a,\theta_v}) = (K_a) - c_i[(\sigma_a) - (\sigma_{a,\theta_v})]$$  \[18\]

Eq. [18] suggests that soil dielectric constant at $\theta_v$ ($K_{a,\theta_v}$) equals the TDR-measured apparent soil dielectric constant ($K_a$) minus the effect of $\sigma_a$ due to change in solute concentration.

Substituting $K_a$ in Eq. [14] with $K_{a,\theta_v}$, we have

$$[(K_a) - c_i((\sigma_a) - (\sigma_{a,\theta_v})))]^{\theta_v} = \gamma_0 + \gamma_1 \theta_v$$  \[19\]
Eq. [19] can be considered as a new $K_s - \theta_v$ relation that accounts for solute effects on TDR $K_s$ measurements. By combining Eq. [19] and [25], $\theta_v$ can be solved for numerically.

**MATERIALS AND METHODS**

**Packed soil core measurement and calibration**

Four 15-cm diameter PVC cylinders 20 to 23 cm in length were sealed at the bottom and packed to an approximate bulk density of 1.2 Mg m$^{-3}$ with 2-mm sieved Monona silt loam soil (fine-silty, mixed mesic, Typic Hapludolls). Polyurethane foam and plastic covers were used to minimize evaporation. Four different solution concentrations of distilled water and CaCl$_2$ (0.22, 1.47, and 2.79 g L$^{-1}$ CaCl$_2 \cdot 2$H$_2$O in test 1 and 1.47, 2.79, and 5.58 g L$^{-1}$ CaCl$_2 \cdot 2$H$_2$O in test 2) were used in two calibration sequences (Table 1). Initial $\theta_v$ in test 1 was 0.198 m$^{-3}$ m$^{-3}$ for all four cylinders and in test 2 ranged from 0.109 to 0.111 m$^{-3}$ m$^{-3}$ due to variation of soil bulk density among cores. The electrical conductivity, $\sigma$, of CaCl$_2$ solutions ranged from $<0.001$ to 8.2 dS m$^{-1}$ (Table 1).

The CaCl$_2$ solutions were added sequentially in 140 ml increments to individual cylinders to provide a range of $\sigma$ and $\theta_v$. At each addition of solution, the soil and cylinder were weighed, soil was removed from the cylinder and weighed, 140 ml of solution added by spraying while thoroughly mixing the solution and soil, the soil was repacked in the cylinder and weighed, the TDR probe inserted and the cylinder capped and sealed. Bulk density was determined by measuring soil height in each column and the known constant mass of soil. The $\theta_v$ ranged sequentially from 0.14 to 0.50 m$^{-3}$ m$^{-3}$. The two-rod parallel TDR probes used were 15-cm in length with 8 m cable leads. The probe were made by Midwest Special
Services\(^3\) after a design by Spaans and Baker (1993). Individual probes were tested in five different solutions (distilled water, 0.37, 0.74, 1.10, and 1.47 g L\(^{-1}\) CaCl\(_2\cdot2H_2O\)) for reliability in measuring electrical conductivity prior to the packed core measurements. An F-test indicated no significant difference (P-value=0.333) among probes in determining electrical conductivity of the solutions. Solution electrical conductivity measured by TDR had a 1.05:1 relation (\(r^2 = 0.998\)) with that determined by conductivity meter (Model 30, Fisher Scientific). The TDR signal was recorded using a 286 portable computer, Techtronics 1502B Cable Tester, and 16 channel DYNAMAX multiplexer. The Baker and Allmaras (1990) algorithm was used to analyze TDR waveforms and provide soil dielectric constant (\(K_s\)) measurements. The \(\sigma_s\) was obtained using the method proposed by Topp et al. (1988, Eq.[9]), and corrected to 25°C based on the procedure described in USDA Agriculture Handbook 60 (1954).

**Undisturbed Soil Core Measurement**

An undisturbed core of Montana silt loam soil, 15 cm in diameter and 41 cm in length, and approximate bulk density of 1.35 Mg m\(^{-3}\), was sealed with paraffin inside a 20-cm diameter PVC pipe (Fig. 1). The bottom of the pipe was sealed by a PVC cap enclosing a sintered porous filter plate (Newmet Krebsoge, R. B. Summers & Associates, Olanthe, KS). Glass beads were placed between the soil core and the ceramic plate to ensure good hydraulic contact. A vacuum hose connected the cap with a suction chamber in which a fraction

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\(^3\) Mention of specific products names is for the benefit of the reader, and does not imply endorsement.
collector with 50 tubes (Universal fraction collector, Eldex Laboratories Inc.) was used to collect approximately 50 ml effluent per tube. Five 15-cm probes were horizontally inserted into the soil core at 7 cm intervals. The uppermost probe was 9.5 cm below the soil surface. Soil temperature was monitored by a thermocouple sensor 2 cm below the soil surface. Soil temperature varied during the measurements from 21.6 to 22.6 °C. Soil water matric potential was monitored by pressure transducers installed at the upper (9.5 cm) and lower (37.5 cm) probe placements. Solute was applied to the soil surface using a syringe pump with 6 applicators attached to a polyurethane foam cover (Precision Multichannel Syringe Pump, Soil Measurement Systems). Two separate measurements were conducted. In the first measurement (Exp. 1), the soil core was pre-washed with 0.22 g L⁻¹ CaCl₂•2H₂O background solution until a constant effluent concentration was achieved. Then a pulse of 1.47 g L⁻¹ CaCl₂•2H₂O was applied at a rate of approximate 40 ml hr⁻¹. After 1.5 pore volumes (5000 ml) was applied, inflow was switched back to the background solution. The θ, and σ, were monitored by TDR every 30 minutes. About 5 kPa suction was measured at the bottom of the soil core. The second measurement (Exp. 2) is basically the same as the first one except the suction was 15 kPa. All TDR instrumentation and analysis of waveform are the same as used with the packed core measurement.

RESULTS AND DISCUSSION

Estimating Theoretical Effects of σ, on Ks

Eq. [6] suggests that TDR-measured soil Ks is a function of not only ε but also σ, and ω. Thus, in theory, any change in σ, will result in a change in TDR-measured soil Ks and will
cause error in TDR-estimated \( \theta_v \). Using Eq. [6] and [1], the error can be calculated. For instance, assume soil \( \sigma_s \) changes from 0 to 2 dS m\(^{-1}\), \( \varepsilon_r = 25 \), and \( \omega = 2.5 \) GHz, then

1) \( Q \rightarrow 0, K_s = \varepsilon_r = 25, \theta_v = 0.4004 \text{ m}^3 \text{ m}^{-3} \) when \( \sigma_s = 0 \) dS m\(^{-1}\)

2) \( Q = 17.4, K_s = 1.0008\varepsilon_r = 25.02, \theta_v = 0.4006 \text{ m}^3 \text{ m}^{-3} \) when \( \sigma_s = 2 \) dS m\(^{-1}\)

These results suggest, in theory, that change in \( \sigma_s \) for a range of 0 to 2 dS m\(^{-1}\) has little influence upon TDR-measured \( K_s \) and TDR-estimated \( \theta_v \). In fact, the small theoretical increase in \( K_s \) is non-measurable since it is less than the resolution of TDR measurement of \( \theta_v \) (Zegelin et al., 1992). However, Wyseure et al. (1997) reported that the 2 dS m\(^{-1}\) of \( \sigma_s \) can have a measurable effect on \( \theta_v \) measurement.

**Modeling Packed Soil Core Measurements**

**Ignoring effects of \( \sigma_s \) on \( \theta_v \) (Eq. [14])**

If the effect of \( \sigma_s \) on \( \theta_v \) is ignored, Eq. [14] can be used to theoretically describe the relationship of \( K_s \) to \( \theta_v \) for measurements made under variable \( \sigma_s \) conditions. Fitting Eq. [14] to \( K_s \) and \( \theta_v \) measurements obtained from the packed cores in both tests yielded \( \gamma_0 = 1.14 \) (SE = 0.10) and \( \gamma_1 = 10.03 \) (SE = 0.30) with \( r^2 = 0.951 \). Topp's empirical equation (Eq.[1]) fitted the same data with \( r^2 = 0.949 \) or 0.950, depending on whether the coefficients were fixed or not. Compared with Topp's empirical equation, theoretically based Eq. [14] required fewer variables and had similar \( r^2 \), thus, Eq. [14] was an efficient model in describing \( K_s \) and \( \theta_v \) relationship for our data. The results also suggested that fitting coefficients to Topp's equation did not provide marked improvement.

When Eq. [14] was fitted to the data set from each individual soil core for both tests, the
coefficients (both $\gamma_0$ and $\gamma_1$) varied from one soil core to another (Table 1), but were generally similar to the coefficients ($\gamma_0 = 1.14$ and $\gamma_1 = 10.03$) obtained from fitting Eq. [14] to all data points. The slope ($\gamma_1$) of the linear relationship increased as the strength of the added CaCl$_2$ solution increased in both tests. When the same CaCl$_2$ solution was added, lower initial $\theta_v$ (test 2) gave higher slopes due to a more concentrated liquid phase. For example, $\gamma_1 = 10.07$ for initial $\theta_v = 0.198$ m$^3$ m$^{-3}$ and $\gamma_1 = 10.62$ for initial $\theta_v = 0.111$ m$^3$ m$^{-3}$ when 1.47 g L$^{-1}$ CaCl$_2$$\cdot$2H$_2$O solution was added. A t-test suggests that any two slopes shown in Table 1 do not differ at the 95% confidence level, except for the slope (13.56) for the addition of 5.58 g L$^{-1}$ CaCl$_2$$\cdot$2H$_2$O solution, which is significantly different from the other seven slopes. When only data points with $\theta_v < 0.40$ are used, any two of the eight slopes are the same at 95% confidence level, except that the two slopes (9.18 and 9.58) for the addition of water differ significantly from the slope (13.56) for the addition of 5.58 g L$^{-1}$ CaCl$_2$$\cdot$2H$_2$O solution. The data points with $\theta_v > 0.40$ are suspect because soil and added solution was not well-mixed. The results are expected because, in theory, $\sigma_a$ rather than $\sigma_w$ affects $K_a$, and thus the $K_a$ and $\theta_v$ relationship as shown by Eqs. [4] and [6].

Including effects of $\sigma_a$ on $\theta_v$ (Eq. [13])

Eq. [13] (with $k$ as a function of $\sigma_a$) did not fit the measured data as well ($r^2 < 0.950$) as Eq. [14]. However, $\sigma_a$ can be empirically added to Eq. [14] as another explanatory variable in the form of $\sqrt{\sigma_a}$

$$\sqrt{K_a} = 0.94 + 6.86\theta_v + 1.70\sqrt{\sigma_a}$$  \[20\]

with $r^2 = 0.984$, where $\sigma_a$ units are dS m$^{-1}$. An F-test suggests that Eq. [20] is significantly
different from Eq. [14] (Prob>F = 0.0001) and that the addition of $\sqrt{\sigma}$ improves the accuracy of the model. In summary, the effect of $\sigma$ on $\theta$, is not theoretically important for the $\sigma$ range conducted in this study and the theoretical model (Eq. [13]) did not include such an effect. However, the existence of the effect of $\sigma$ on $\theta$, was empirically determined with Eq. [20], which was shown to be the best among several other models with one or more $\sigma$ terms. For instance, adding a term of interaction between $\theta$, and $\sqrt{\sigma}$ to Eq. [20] did not increase $r^2$.

**Undisturbed Soil Core Measurements**

**TDR-measured $K_s$ and $\sigma$ in Exp. 1**

TDR-measured $K_s$ values at five depths increase 4.7 to 9.7% in response to changing $\sigma$, due to an increase in tracer input from 0.22 to 1.47 g L$^{-1}$ CaCl$_2$$\cdot$2H$_2$O under steady state flow (Fig. 2). TDR-measured $\sigma$, ranged from 0.65 to 1.38 dS m$^{-1}$ and differed in value at the five soil depths. At the same time, effluent flowrate and matric pressures at both the top and the bottom of soil core remained relatively constant during the measurement (Fig. 3). Less than one fifth of all data points are outliers caused by stopping the lower boundary vacuum conditions to replace tubes for outflow sample collection. Thus, $\theta$, and $K_s$ should be relatively constant at a given depth. Variation in $\sigma$, caused consistently observable changes in TDR-measured $K_s$. The TDR-measured $K_s$ was correlated to $\sigma$, in opposition to theory (Eq. [13]). The increase in $K_s$ associated with an increase in $\sigma$, varied by position. For instance, at the 9.5 cm depth TDR measured $K_s$ increased only 4.2% as $\sigma$, increased 71.6%, but $K_s$ increased 6.1% as $\sigma$, increased 62.2% at the 23.5 cm depth (Fig. 2). These results suggested that the effect of $\sigma$, on TDR-measured $K_s$ was unique at each soil depth possibly due to
difference in soil structure, porosity, or clay content.

**Estimated \( \theta_v \) using Eq. [14], [20], and Topp's equation for Exp. 1**

Estimated \( \theta_v \) based on TDR-measured \( K_s \) at different soil depths increased 2.5 to 5.4% when Topp's equation (Eq. [1]) was used and 2.9 to 6.1% when Eq. [14] \( (\gamma_0 = 1.14 \text{ and } \gamma_1 = 10.03) \) used (Fig. 4). This increase in TDR-estimated \( \theta_v \) can be considered as error associated with the change in \( \sigma_s \). However, Eq. [20], obtained from packed soil cores, over-corrected the error due to the effect of \( \sigma_s \) on TDR-estimated \( \theta_v \) (Fig. 5). These results indicated that the \( \sigma_s \) effect on TDR-estimated \( \theta_v \) differed between probe positions and depended on soil structure.

**Estimated \( \theta_v \) using modified Eq. [14] for Exp. 1**

We used packed soil data to adjust for \( \sigma_s \) effects on estimates of \( \theta_v \) for the undisturbed soil core. The empirical approach included several steps. A \( K_s-\theta_v \) relation similar to Eq. [14] was obtained by restricting the range of \( \sigma_s \) in the packed core data to that encountered in the undisturbed core. The relation developed was

\[
\sqrt{K_s} = 0.83 + 11.08\gamma_s \quad [21]
\]

with \( r^2 = 0.943 \). Second, a residual \( \sqrt{K_s} \) term, \( r_\sqrt{K_s} \), was calculated from measured \( K_s \) and \( K_s \) estimated using Eq. [21] for packed soil treated with 1.47 g L\(^{-1}\) CaCl\(_2\cdot2\)H\(_2\)O in both tests. A linear correction term \( r_\sqrt{K_s-\sigma_s} \) was obtained.

\[
r_\sqrt{K_s,1.47} = -0.44 + 0.60\sqrt{\sigma_s,1.47} \quad [22]
\]

with \( r^2 = 0.59 \), where \( \sigma_s,1.47 \) represents \( \sigma_s \) obtained for packed core data with different
amounts of 1.47 g L\(^{-1}\) CaCl\(_2\)·2H\(_2\)O added. Eq. [22] was used to adjust the measured \(\sqrt{K_s}\):

\[
adj_{-}\sqrt{K_s} = \sqrt{K_s} - (-0.44 + 0.607\sqrt{\sigma_s})
\]  

[23]

The final step was to obtain a linear relation of \(\theta_v\) and \(adj_{-}\sqrt{K_s}\) from all packed core measurements. The result is as follows:

\[
\theta_v = 0.10(\sqrt{K_s} - 0.60\sqrt{\sigma_s} - 0.79)
\]  

[24]

with \(r^2 = 0.957\). Applying Eq. [24] to the data obtained from the undisturbed soil core under 5 kPa suction reduced error in the estimate of \(\theta_v\) compared with the use of equation [20] (Fig. 6). Eq. [24] both over and under-corrected \(\sigma_s\) effect on \(K_s\) measurements for individual probes indicating an effect of position and/or probe on the \(K_s-\sigma_s\) relationship derived from packed soil.

**Estimated \(\theta_v\) using Eq. [19] for Exp. 2**

The results in previous sections have shown that the effect of \(\sigma_s\) on TDR-measured \(\theta_v\) is site-specific and cannot be eliminated using the \(K_s-\theta_v-\sigma_s\) relationships, Eq. [20] and [24], developed from packed soil core data. Site-specific \(K_s-\theta_v-\sigma_s\) relationships for individual depths are required. Table 2 shows the results of fitting Eq. [16] to TDR measurements in Exp. 1. As expected, the linear \(K_s-\theta_v-\sigma_s\) relationships differed among different soil depths. The coefficient \(c_1\) increased with soil depths and was independent of \(K_s\) values. The low \(K_{s,\sigma=0}\) value at 37.5 cm is caused by a lower water content. Note that \(\sigma_s\) includes the effect of both soil water and solute.

In order to use Eq. [19], the following solute-free \(\sigma_s-\theta_v\) relationship \((r^2 = 0.974)\) was
developed from the measurements on packed soil cores with distilled water

\[ \sigma_{s, ev} = -29.04 \theta_v^3 + 24.75 \theta_v^2 - 4.75 \theta_v + 0.37 \]  \[25\]

As for Exp. 1, \( \sigma_s \) affected TDR-measured \( K_s \) and \( \sigma_s \) for Exp. 2 (Fig. 7). Using Eq. [19] and [25], estimated \( \theta_v \) for Exp. 2 was relatively stable at every soil depth (Fig. 8). This result is in agreement with the relatively constant effluent flowrate and matric potential measurements for Exp. 2 (Fig. 9).

**CONCLUSIONS**

Based on electromagnetic wave theory, \( \sigma_s \) was shown to have negligible effect on TDR-measured \( K_s \) at \( \sigma_s < 2 \text{ dS m}^{-1} \). However, our study found that addition of a \( \sqrt{\sigma_s} \) term significantly improved the \( K_s-\theta_v \) relationship (Eq.[14]) for packed soil when \( \sigma_s \) ranged from 0.07 to 1.47 \text{ dS m}^{-1}. \( K_s \) also depends strongly on \( \sigma_s \) measurements, which ranged from 0.65 to 1.38 \text{ dS m}^{-1}, for an undisturbed soil core under steady unsaturated flow conditions. The semi-empirical \( K_s-\theta_v-\sigma_s \) model (Eq.[24]) generated from packed soil data which adjusts for changes in solute concentration reduced error but both over- and under-corrected individual probes indicating that probe measurements were site-specific. When packed core data containing a greater \( \sigma_s \) range than in BTC measurements was used to develop the \( K_s-\theta_v-\sigma_s \) relationship (Eq.[20]), the \( K_s \) measurements for undisturbed soil core were over-corrected. Combining the depth-specific linear \( K_s-\sigma_s \) relationship (Table 2) and the semi-empirical \( K_s-\theta_v \) relationship (Eq.[14]) minimized the effect of \( \sigma_s \) on \( \theta_v \) for the undisturbed soil core measurement. However, individual calibrations were required for each probe depth apparently due to differences in soil structure or other site specific soil characteristic.
ACKNOWLEDGEMENTS

Drs. John M. Baker and Egbert J.A. Spaans of USDA-ARS and University of Minnesota and Drs. G.L. Hart and B. Lowery of the University of Wisconsin-Madison contributed valuable technical advice and furnished software for water content analysis, TDR control, and data acquisition. The authors thank each of these individuals for their contributions to the project. Research support from USDA-CSREES-Water quality program (Agreement no. 93-34214-8849) is gratefully acknowledged.

REFERENCES


Table 1. Initial water content ($\theta_i$) of packed soil cores, added solution concentration (C) and electrical conductivity ($\sigma$) for two calibration tests, and the goodness of fit and coefficients for Eq. [14] fitted to the measurements on each packed soil core.

<table>
<thead>
<tr>
<th>Test</th>
<th>$\theta_i$</th>
<th>C</th>
<th>$\sigma$</th>
<th>$\gamma_0$</th>
<th>$\gamma_1$</th>
<th>$r^2$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m$^3$ m$^{-3}$</td>
<td>g L$^{-1}$ CaCl$_2$·2H$_2$O</td>
<td>dS m$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.198</td>
<td>0.00</td>
<td>&lt;0.001</td>
<td>1.23</td>
<td>9.18</td>
<td>0.976</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
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<td>0.22</td>
<td>0.38</td>
<td>1.13</td>
<td>9.63</td>
<td>0.973</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
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<td>1.47</td>
<td>2.23</td>
<td>1.00</td>
<td>10.07</td>
<td>0.984</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>0.198</td>
<td>2.79</td>
<td>4.32</td>
<td>0.99</td>
<td>10.23</td>
<td>0.970</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
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<td>0.00</td>
<td>&lt;0.001</td>
<td>1.23</td>
<td>9.58</td>
<td>0.976</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>0.111</td>
<td>1.47</td>
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<td>1.06</td>
<td>10.62</td>
<td>0.974</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>0.110</td>
<td>2.79</td>
<td>4.32</td>
<td>0.95</td>
<td>11.17</td>
<td>0.982</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>0.111</td>
<td>5.58</td>
<td>8.20</td>
<td>0.56</td>
<td>13.56</td>
<td>0.953</td>
<td>7</td>
</tr>
</tbody>
</table>

$n =$ number of observations
Table 2. Linear relationship (Eq. [24]) between $K_s$ and $\sigma_s$ at different depths of the undisturbed soil core under steady flow conditions with a suction of 5 kPa

<table>
<thead>
<tr>
<th>$i$</th>
<th>Soil depth</th>
<th>$K_s$ at $\sigma_s = 0$</th>
<th>$c$</th>
<th>$r^2$</th>
<th>$F_{(1,156)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.5 cm</td>
<td>27.218</td>
<td>1.925</td>
<td>0.915**</td>
<td>5969</td>
</tr>
<tr>
<td>2</td>
<td>16.5 cm</td>
<td>27.209</td>
<td>2.001</td>
<td>0.951**</td>
<td>10960</td>
</tr>
<tr>
<td>3</td>
<td>23.5 cm</td>
<td>27.5</td>
<td>3.315</td>
<td>0.958**</td>
<td>12588</td>
</tr>
<tr>
<td>4</td>
<td>30.5 cm</td>
<td>26.076</td>
<td>3.602</td>
<td>0.955**</td>
<td>11882</td>
</tr>
<tr>
<td>5</td>
<td>37.5 cm</td>
<td>22.765</td>
<td>4.698</td>
<td>0.938**</td>
<td>8411</td>
</tr>
</tbody>
</table>

Note: $F = (n-2)r^2/(1-r^2)$, ** The linear relation is significant at 99% confidence level
Syringe Pump

Suction chamber with fraction collector

Line to vacuum

Data logger for tensiometers

Multiplexer

Laptop computer

Cable tester

Fig. 1. Experimental Setup Diagram
Fig. 2. TDR-measured apparent soil dielectric constant, $K_a$, and bulk soil electrical conductivity, $\sigma_a$, at depths indicated for undisturbed soil core under steady state flow conditions in Exp. 1. For clarity, every fifth data point is shown.
Fig. 3. Soil matric pressure at depths indicated and effluent flowrate for undisturbed soil core under steady state flow conditions in Exp. 1.
Fig. 4. $\theta_v$ estimated from TDR-measured $K_s$ using a) Topp's equation (Eq. [1]) and b) Eq. [14] for undisturbed soil core under steady state flow conditions in Exp. 1. For clarity, only every fifth data point is shown.
Fig. 5. \( \theta_v \) estimated from TDR-measured \( K_s \) using Eq. [20] for undisturbed soil core under steady state flow conditions in Exp. 1. For clarity, only every fifth data point is shown.
Fig. 6. $\theta_v$ estimated from TDR-measured $K_n$ using Eq. [24] for undisturbed soil core under steady state flow conditions in Exp. 1. For clarity, only every fifth data point is shown.
Fig. 7. TDR-measured apparent soil dielectric constant, $K_a$, and bulk soil electrical conductivity, $\sigma_a$, at depths indicated for undisturbed soil core under steady state flow conditions in Exp. 2. For clarity, only every fifth data point is shown.
Fig. 8. \( \theta_v \) estimated from TDR-measured \( K_s \) using Eq. [19] and [25] for undisturbed soil core under steady state flow conditions in Exp. 2. For clarity, only every fifth data point is shown.
Fig. 9. Soil matric pressure at depths indicated and effluent flowrate for undisturbed soil core under steady state flow conditions in Exp. 2.
CHAPTER 4. TIME DOMAIN REFLECTOMETRY RELATIONSHIP OF SOIL BULK ELECTRICAL CONDUCTIVITY, WATER CONTENT, AND SOLUTE CONCENTRATION

A paper to be submitted to Soil Science Society of America Journal

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ABSTRACT

The relationship of soil bulk electrical conductivity, $\sigma_b$, volumetric soil water content, $\theta_v$, and resident solute concentration, $C_r$, is necessary to estimate $C_r$ in solute transport studies. A semi-empirical $\sigma_b-\theta_v-C_r$ relationship was developed on packed cores of a silt loam soil using time domain reflectometry (TDR). The established $\sigma_b-\theta_v-C_r$ relationship (or model) was used on a packed soil column to estimate a time series of $C_r$, or a $C_r$ breakthrough curve (BTC), based on TDR-measured $\sigma_b$ and $\theta_v$ at several different soil depths. The TDR-estimated $C_r$ BTC was compared with the $C_r$ BTC predicted from the measured effluent BTC using the convection-dispersion equation (CDE) and mobile/immobile model (MIM). Also, effluent solute concentration ($C_e$) BTC was predicted from the TDR-estimated $C_r$ BTC with CDE and MIM and was compared with the measured $C_e$ BTC. Our $\sigma_b-\theta_v-C_r$ relationship was compared with published $\sigma_b-\theta_v-C_r$ relationships for the accuracy in estimating $C_r$ and predicting $C_e$.

Our model and Rhoades' 76 and 89 models closely fitted the measured data. The simplified Mualem and Friedman's 91 model failed to interpret the data. For five of six cases

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(three depths by two solute transport models), $C_r$ estimated by our model more closely agreed with $C_r$ predicted from effluent using CDE or MIM models than $C_r$ estimated using three published models. It is inconclusive whether our model or Rhoades’ models gave the more accurate prediction of effluent BTC. Unlike Rhoades’ 1989 and Mualem and Friedman’s 1991 models, our model does not require information other than TDR measurements to estimate $C_r$, which is an advantage when TDR field measurements are used.

INTRODUCTION

Soil solution is a hub predictor of soil processes (Wolt, 1994) reflecting soil chemical processes such as ion adsorption and desorption. Temporal and spatial change in total soil solution or individual ion concentrations have implications on solute transport. Long term non-destructive measurement of soil solution concentration offers obvious advantages in monitoring solute transport. Direct sampling methods, such as centrifugation, vacuum, pressure membrane, and solution sampler, either are time-consuming, laborious, and destructive or can only operate at high soil water content (Wolt, 1994; Dasberg and Dalton, 1985). Due to the existence of cause-effect relationship between resident soil solution concentration, $C_r$, and $\sigma_a$ and the relative ease in determining $\sigma_a$, it is tempting to estimate $C_r$ from $\sigma_a$. Traditional methods of measuring $\sigma_a$ including four electrode (Rhoades and Ingvalson, 1971) and other methods require independent measurement of $\theta_v$ to estimate $C_r$. TDR has been shown to reliably measure both $\sigma_a$ and $\theta_v$ in similar sample volume (Dasberg and Dalton, 1985). Thus, accurate estimation of soil solution concentration or electrical conductivity, $\sigma_w$, relies on quantitatively and accurately interpreting the $\sigma_a-\theta_v-\sigma_w$ relationship.
Published $\sigma_a - \theta_v - \sigma_w$ relationships (or models) such as the linear $\sigma_a - \sigma_w$ relationship by Rhoades et al. (1976, Eq.[5]) have been used to estimate solution concentration from TDR measured $\sigma_a$ and $\theta_v$ (Kachanoski et al., 1992; Risler et al., 1996; Persson, 1997). Value of $C_r$ estimated from TDR measured $\sigma_a$ and $\theta_v$ using such a model may differ from that obtained by soil sampler or estimated by effluent (Heimovaara et al., 1995; Risler et al., 1996). One possible reason for this difference is that published $\sigma_a - \theta_v - \sigma_w$ relationships were improper for TDR use since they were formed and tested using instrumentation other than TDR resulting in systemic error. Several $\sigma_a - \theta_v - \sigma_w$ relationships were established using TDR measurements (Vogeler et al., 1996; Hart and Lowery, 1998; Ferre et al., 1998). However, these relationships were either developed using a sand or with no explanation about parameters, i.e., they were purely empirical.

Verification of established $\sigma_a - \theta_v - \sigma_w$ models are difficult to conduct on the same soil volume since measured $\sigma_w$ is often obtained from aqueous extracts of soil samples for low $\theta_v$ (Rhoades and Oster, 1986). Also, measured $\sigma_w$ could be inaccurate because the assumption of no dissolution and precipitation of salts during extraction may not be met (Nadler et al., 1984). The objectives of this study are to establish a $\sigma_a - \theta_v - \sigma_w$ relationship for a silt loam soil based on TDR measured $\sigma_a$ and $\theta_v$ and to compare this relationship with other published $\sigma_a - \theta_v - \sigma_w$ relationships.

**THEORY**

The factors determining soil resistivity, summarized by Tagg (1964), are: 1) type of soil; 2) chemical composition of soil solution; 3) solution concentration; 4) soil water
content; 5) temperature; 6) soil particle size distribution; and 7) soil bulk density. Nadler and Frenkel (1980) indicated that clay content and the interaction between the bulk and exchangeable ions are also factors affecting $\sigma_a$. Study of the quantitative relationship between $\sigma_a$ and its affecting factors has mainly focused on the dependence of $\sigma_a$ on $\theta_v$ and $\sigma_w$ or $C$. The role of soil properties such as clay content, CEC, and bulk density in determining $\sigma_a$ has not been quantitatively defined.

A linear $\sigma_a$-$\sigma_w$ (or $C$) relationship was assumed for constant $\theta_v$ in a number of studies (Rhoades et al., 1976; Nadler and Frenkel, 1980; Mualem and Friedman, 1991). A curvilinear $\sigma_a$-$\sigma_w$ (or $C$) relationship for $\sigma_w < 2-3$ dS m$^{-1}$ was observed by Shainberg et al. (1980). A widely used $\sigma_a$-$\theta_v$-$\sigma_w$ relationship, proposed by Rhoades et al. (1976), can be given as

$$\sigma_a = \sigma_w \theta_v T + \sigma_s \quad [1]$$

where $\sigma_s$ is surface conductivity of soil particles and $T$ is the transmission coefficient accounting for the tortuosity of soil pores and mobility of ions near the solid-liquid and liquid-gas interfaces. $T$ can be empirically expressed as

$$T = a \theta_v + b \quad [2]$$

where $a$ and $b$ are constants. Thus, Eq.[1] can be rewritten as

$$\sigma_a = \sigma_w (a \theta_v^2 + b \theta_v) + \sigma_s \quad [3]$$

When $\sigma_w$ or $C$ remained unchanged, the reported $\sigma_a$-$\theta_v$ relationship varied. Tagg (1964) illustrated that for a red clay and a sandy loam, soil resistivity of dry soil first decreased rapidly as soil water content increased, but after a value of 14 to 18 per cent gravimetric water content, the rate of decrease in resistivity became much less. Water contents larger than
24 per cent had constant resistivity. Rhoades et al. (1976) and Ferré et al. (1998) used a simple power function to describe the $\sigma_a-\theta_v$ relationship. Mualem and Friedman (1991) considered bulk soil electrical conductivity an analogy of soil hydraulic conductivity and proposed a complex $\sigma_a-\theta_v$ relationship, which can be reduced to a power function relationship:

$$\sigma_a(\theta) = \frac{\sigma_w(\theta_v)^{n^2}}{\theta_{sat}} \quad [4]$$

where $\sigma_a(\theta)$ is bulk solution electrical conductivity at effective soil water content, $\theta_e$, which is the difference between $\theta_v$ and residual water content. $\theta_{sat}$ is the soil water content at saturation and $n = 0.5$ for sand and loam soils with stable structure.

A linear $\sigma_a-\theta_v$ relationship was used by Nadler and Frenkel (1980) and Rhoades et al. (1989). However, Rhoades et al. (1989) differentiated the role of mobile soil water from that of immobile soil water in determining $\sigma_a$ and proposed that

$$\sigma_a = \left[\frac{(X_s + \theta_{ws})^2 \sigma_s}{X_s}\right] + (\theta_v - \theta_{ws})\sigma_{wc} \quad [5]$$

where $\sigma_{wc}$ is solution electrical conductivity in the separate continuous liquid pathway (large pores). $\theta_{ws}$ and $\theta_{wc}$ are volumetric water contents in the series-coupled pathway and the separate continuous liquid pathway. $X_s$ is volumetric content of solid phase.

Bulk surface conductivity, $\sigma_s$, is associated with exchangeable ions at the solid/liquid interface (Rhoades et al., 1976). Although $\sigma_s$ has been considered a constant in Eq.[1] and [5], Nadler and Frenkel (1980) demonstrated that it increased with the increase of $\sigma_w$.

Mualem and Friedman (1991) suggested that $\sigma_s$ was negligible.

Solution conductivity, $\sigma_w$, was linearly dependent on solution concentration, $C$ (Noggle,
\[ \sigma_w = \alpha (u_+ + u_-)FN \]  

where \( F \) is Faraday's constant (96485 C mole\(^{-1}\)), \( N \) is solution equivalent concentration, \( u \) is the ion mobility defined as the ion's velocity per unit electric field. It is related to the size of the ion, the charge the ion carries, and the viscosity of the solvent. The signs + and - refer to cation and anion, respectively. The term \( \alpha \) is the degree of dissociation of the solute, which is the fraction of solute that is dissociated.

**METHODS AND MATERIALS**

**Establishment of \( \sigma_w - \theta_i - \sigma_w \) relationship**

The soil used for this study is Monona silt loam soil (fine-silty, mixed mesic, Typic Hapludolls) from Treynor, Iowa. Mechanical composition for the soil is: 2% sand, 71% silt, and 27% clay for the Ap horizon, and 1% sand, 72% silt, and 27% clay for the 45-90 cm depth. Four 15-cm diameter PVC cylinders 20 to 23 cm in length were sealed at the bottom and packed to a range in bulk density of 1.20 to 1.39 Mg m\(^{-3}\) with 2-mm sieved soil. Polyurethane foam and plastic covers were used to minimize evaporation. Four different solutions (0.00, 0.22, 1.47, and 2.79 g L\(^{-1}\) \( \text{CaCl}_2\cdot2\text{H}_2\text{O} \) in test 1 and 0.00, 1.47, and 2.79 g L\(^{-1}\) \( \text{CaCl}_2\cdot2\text{H}_2\text{O} \) in test 2) were used in two calibration sequences (Table 1). Electrical conductivity of each solution (\( \sigma_w \)) determined by a conductivity meter (Model 30, Fisher Scientific)\(^3\) and initial soil water content, \( \theta_i \), are listed in Table 1. A relationship between the concentration (\( C \)) and meter measured \( \sigma_w \) of six \( \text{CaCl}_2 \) solutions (from 0.22 to 5.58 g L\(^{-1}\))

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\(^3\) Company names are provided for the benefit of the reader and do not imply an endorsement by the authors or Iowa State University
CaCl₂·2H₂O) was

\[ C (g \, L^{-1}) = 0.686\sigma_w (dS \, m^{-1}) - 0.074 \]  \hspace{1cm} [7]

with \( r^2 = 0.9996 \).

The CaCl₂ solutions were added sequentially in 140 ml increments to individual cylinders to provide a range of \( \sigma_a \) and \( \theta_v \). At each addition of solution, the soil and cylinder were weighed, soil was removed from the cylinder and weighed, 140 ml of solution added by spraying while thoroughly mixing the solution and soil, the soil was repacked in the cylinder and weighed, the TDR probe was inserted and the cylinder capped and sealed. Bulk density was determined by measuring soil height in each column and the known mass of soil.

The TDR probes were two rod parallel probes, 0.3 cm in diameter, and 15-cm in length with 8 m cable leads purchased from Midwest Special Services after a design by Spaans and Baker (1993). The TDR signal was recorded using a 286 portable computer, Techtronics 1502B Cable Tester, and 16 channel DYNAMAX multiplexer. The Baker and Allmaras (1990) algorithm was used to obtain soil dielectric constant (\( K_a \)) measurements. Soil water content was estimated from TDR-measured \( K_a \) using the \( K_a-\theta_v \) relationship of Shen et al. (1999, Eq. [14]). The \( \sigma_a \) was obtained using the method of Topp et al. (1988, Eq.[9]), and corrected to 25°C based on the procedure described in USDA Agriculture Handbook 60 (1954). There was no significant difference among probes (P-value=0.333) in determining electrical conductivity of the five different solutions (distilled water, 0.37, 0.74, 1.10, and 1.47 g L⁻¹ CaCl₂·2H₂O). TDR \( \sigma_w \) had a 1.05:1 relation (\( r^2 = 0.998 \)) with that determined by conductivity meter. The CaCl₂ concentration of soil solution, \( C_r \), was defined as a ratio of the total mass of added CaCl₂·2H₂O to the total volume of added solution plus initial soil water content.
The proposed model, Eq.[3], [4], and [5] were fitted to measured TDR $\sigma_s$, $\theta_v$, and $C_r$ or $\sigma_w$ values using non-linear regression programs. When Eq.[3], [4], and [5] were used, $\sigma_w$ was considered as the sum of solution conductivity of added CaCl2 and other inherent salts in the soil. The part of $\sigma_w$ contributed from added CaCl2 solution was calculated using Eq.[7]. The part of $\sigma_w$ contributed from inherent salts, hereafter referred to as $\sigma_{in}$, was regarded as unchanged and obtained by curve-fitting. Residual water content required by Eq.[4] was assumed to be the water content at pressure equal -15 bar and had a value of 0.146 Mg Mg$^{-1}$ (Bargar et al., 1999).

Model Comparison

The same soil used for calibration was packed into a PVC pipe (diameter = 15.2 cm, height = 38.7 cm) to a height of 35 cm. The bottom of the PVC pipe was sealed with a PVC cap enclosing a sintered porous filter plate (Newmet Krebsoge, R. B. Summers & Associates, Olanthe, KS), which provided direct contact with the packed soil in the core. The average bulk density ($\rho_b$) of the soil core was 1.23 g cm$^{-3}$ (0~10 cm, 1.30 g cm$^{-3}$; 10~19 cm, 1.14 g cm$^{-3}$; 19~35 cm, 1.24 g cm$^{-3}$). Five TDR probes were horizontally inserted into the soil core at depths of 3, 10, 17, 24, and 31 cm, respectively.

The soil core was leached with 0.88 g L$^{-1}$ CaCl2$\cdot$2H2O solution for 3.2 pore volumes until outflow electrical conductivity was steady. A 0.27 g L$^{-1}$ CaCl2$\cdot$2H2O solution was introduced from a Marriot bottle to the soil surface and 1.5 cm water head maintained at the surface for 4.1 pore volumes. TDR measurements of $\sigma_s$ and $\theta_v$ at 30 minute intervals, started a half hour before the change of inflows. Then a 1.56 g L$^{-1}$ CaCl2$\cdot$2H2O solution was applied
for 3.84 pore volume. Effluent was sampled by a fraction collector (Universal fraction collector, Eldex Laboratories Inc.) containing tubes each with a maximum volume of 65 ml. Effluent electrical conductivity ($\sigma_e$) was measured with a conductivity meter and a digital chloridometer (Haake-Buchler Instruments Inc.).

Resident CaCl$_2$ solution concentration ($C_r$) at each soil depth was estimated from TDR measured $\sigma_a$ and $\theta_v$ using Eq.[3], [4], [5], and the proposed model. $C_r$ was also predicted using solute transport parameters obtained from fitting CDE and MIM models to the effluent BTC. The cumulative absolute deviation ($\Delta C_r$) of one $C_r$ BTC from the other was determined from the area between the two BTC. This area has the unit of the mass and can be expressed as:

$$\Delta C_r = \int_0^t |C_r^1 - C_r^2| \, dt \quad [8]$$

where $t$ refers a relative time, expressed as pore volume of effluent. $C_r^1$ is resident solute concentration for $C_r$ BTC 1 and $C_r^2$ is resident solute concentration for $C_r$ BTC 2 at any time $t$ over a time period $t_1$.

The estimated $C_r$ BTC at 31 cm obtained from TDR measurements was fitted with CDE and MIM. Solute transport parameters obtained from this curve-fitting together with known boundary and initial conditions were used to predicted effluent CaCl$_2$ concentration, $C_e$. The cumulative absolute deviation of the predicted from the measured $C_e$ BTC, $\Delta C_e$, was calculated the same way as in Eq.[8].
RESULTS AND DISCUSSION

Establishment of \( \sigma_a - \theta_v - \sigma_w \) (or \( C_r \)) relationship

Increasing TDR \( \theta_v \) increased TDR \( \sigma_a \) over most of the range of TDR \( \theta_v \) measurement (Fig. 1). However, when the added solution was distilled water or a low concentration of CaCl\(_2\) solution (0.22 g L\(^{-1}\)), TDR \( \sigma_a \) was relatively unchanged for TDR \( \theta_v > 0.40 \text{ m}^3\text{ m}^{-3} \). This relationship is similar to the resistivity-soil moisture relationship described by Tagg (1964) and differs from Eq. [3], [4], and [5], which have either a power function or a linear relationship between \( \sigma_a \) and \( \theta_v \). When added solution concentration was 1.47 or 2.79 g L\(^{-1}\), the relationship of TDR \( \sigma_a \) and TDR \( \theta_v \) was generally linear. However, the slope of this linear relationship was less for TDR \( \theta_v < 0.2 \text{ m}^3\text{ m}^{-3} \) than for TDR \( \theta_v > 0.2 \text{ m}^3\text{ m}^{-3} \) (Table 2).

Our data suggested that: 1) the discontinuity of soil solution in soil pores for \( \theta_v < 0.2 \text{ m}^3\text{ m}^{-3} \) resulted in a smaller slope \( (\Delta \sigma_a / \Delta \theta_v) \) than for \( \theta_v > 0.2 \text{ m}^3\text{ m}^{-3} \); 2) when solution in the soil core was effectively continuous, a further increase in TDR \( \theta_v \) did not increase TDR \( \sigma_a \). Rather, soil solution was diluted and TDR \( \sigma_a \) was decreased if no solute was added to the soil solution or the solute concentration was 0.22 g CaCl\(_2\)\(\cdot2\text{H}_2\text{O}\) L\(^{-1}\). Based on the above discussion, the following semi-empirical relationship of TDR \( \sigma_a \) and TDR \( \theta_v \) was developed:

\[
\sigma_a = \beta_0 (1 + e^{-2x})^{-1}(C_r + C_{soil})
\]

where \( x = \beta_1 + \beta_2 \theta_v \) with \( \beta_0, \beta_1, \) and \( \beta_2 \) being constants, and \( \sigma_a \) and \( \theta_v \) are TDR measured \( \sigma_a \) and \( \theta_v \). The term \( \beta_0 (1 + e^{-2x})^{-1} \) defines ion mobility in soil pores and reflects the relationship of \( \sigma_a \) and \( \theta_v \). \( C_r \) is the mass of CaCl\(_2\)\(\cdot2\text{H}_2\text{O}\) per volume of soil solution resulting from added solution. \( C_{soil} \) represents total mass (equivalent to CaCl\(_2\)\(\cdot2\text{H}_2\text{O}\)) of all soil ions, caused by dissolution and precipitation, per volume of soil solution. \( C_{soil} \) might change with
θν depending on soil buffering power and with Cν depending on ion competition. In order to make the calibration simple we ignored the effect of ion competition and assumed a simple Csoil-θν relationship:

\[ C_{\text{soil}} = \frac{\beta_3}{\theta_\nu} \]  

[10]

where \( \beta_3 \) is constant and can be considered as total mass of soluble ions per volume of soil. Thus, \( \sigma_\nu \) can be expressed as:

\[ \sigma_\nu = \beta_0 (1 + e^{-2x})^{-1} (C_{\text{CaCl}_2} + \frac{\beta_3}{\theta_\nu}) \]  

[11]

Parameters or coefficients in Eq.[11] were determined by fitting Eq. [11] to the measured data using the method of least squares. The estimated parameters and the goodness of the curve fitting is illustrated in both Fig. 1 and Table 3. Also shown in Table 3 are the estimated parameters for and the goodness of the fit of the \( \sigma_\nu - \theta_\nu - \sigma_w \) relationships proposed by Rhoades et al. (1976 & 1989) and by Mualem & Friedman (1991).

The relationships proposed by this study (Eq.[11]) and Rhoades et al. (1976 and 1989) closely fitted the measured data \( (r^2 > 0.996) \). The simplified Mualem and Friedman's model (1991) had the lowest \( r^2 \), but fewest parameters. Note that nine measurements with \( \theta_\nu \) less than the water content at the wilting point were not used to fit Eq.[4]. Fitted \( \sigma_{\text{in}} \) has the value of 2.43, 1.55, and 7.28 dS m\(^{-1}\) for the \( \sigma_\nu - \theta_\nu - \sigma_w \) relationships proposed by Rhoades et al. (1976), Rhoades et al. (1989), and Mualem and Friedman (1991), respectively. These values appear high compared to the electrical conductivity of added CaCl\(_2\) concentrations. Also, estimated \( \sigma_\nu \) for Eq.[3] has a negative value, which violates the definition given by Rhoades et al. (1976). Estimated \( \sigma_\nu \) for Eq.[5] is 0.173 dS m\(^{-1}\) while calculated \( \sigma_\nu \) based on clay content using the relationship presented by Rhoades et al. (1989, Fig. 5) is 0.60 dS m\(^{-1}\). These
unusual values of $\sigma_{in}$ and $\sigma_s$ may result from: 1) In the studies for the three published models, $\sigma_w$ was assumed to equal the effluent electrical conductivity after the soil core was leached with a solution of constant concentration, whereas, in this study $\sigma_w$ was partially fitted. 2) The three published conceptual models describing $\sigma_a$- $\theta_v$- $\sigma_w$ relationships were not applicable to the soil used in this study.

Regardless of the physical meaning of each fitting parameter, the goodness of a regression model can be examined through a residual plot. Fig. 2 shows residual $\sigma_a$ values, the difference between corresponding measured and fitted $\sigma_a$ values, plotted against the measured $\sigma_a$ value. For all four models, the residual $\sigma_a$ values were randomly distributed over the range of $\sigma_a$ measurements and no dependence of residual $\sigma_a$ values on measured $\sigma_a$ was found. Eq.[11] has the largest portion of residual $\sigma_a$ with absolute value less than 0.05 dS m$^{-1}$, indicating that Eq.[11] best fitted the measured data in most cases. The average absolute residual $\sigma_a$ values, or the average distance of data points to $y = 0$ line in Fig. 2, for Eq. [3], [4], [5], and [11] are 0.033, 0.026, 0.194, and 0.024 dS m$^{-1}$, respectively. In other words, the residual $\sigma_a$ for Mualem and Friedman’s model (Eq.[5]) are more widely spread or have greater absolute values, suggesting that Eq.[5] less accurately described the data than did the other three models. More residual $\sigma_a$ values were closer to zero for Eq.[5] (Rhoades et al., 1989) than for Eq.[3] (Rhoades et al., 1976).

Fig. 3 shows the relation between residual $\sigma_a$ values and TDR measured $\theta_v$ for the four models. For Mualem and Friedman’s model, the residual $\sigma_a$ values over the range of TDR measured $\theta_v$ had a definite pattern, i.e., they were not randomly distributed. Thus, the $\sigma_a$-$\theta_v$ relationship suggested by Mualem and Friedman (1991) was biased. The results also showed
that for TDR measured $\theta_v > 0.40 \text{ m}^3 \text{ m}^{-3}$ the variation in residual $\sigma_a$ values increased for Eq.[3], [5], and [11], possibly due to non-uniform mixture of soil and added CaCl$_2$ solution. For TDR $\theta_v < 0.40 \text{ m}^3 \text{ m}^{-3}$, average absolute residual $\sigma_a$ values for Eq. [3], [5], and [11] were 0.026, 0.017, 0.015 dS m$^{-1}$, respectively. In other words, Eq. [11] had the smallest variation in the residual $\sigma_a$ values, and these values were more concentrated near zero compared with Eq.[3] and [5] (Fig. 3).

The plots of residual $\sigma_a$ values vs. soil CaCl$_2$ concentration, $C_r$, shows that the residual $\sigma_a$ values for Eq.[11] were randomly distributed over the range of CaCl$_2$ concentration (Fig. 4). Eq. [3], [5], and [11] underestimated $\sigma_a$ for $C_r > 1.2$ g CaCl$_2$$\cdot$2H$_2$O L$^{-1}$. For $0.4 < C_r < 1.2$ g CaCl$_2$$\cdot$2H$_2$O L$^{-1}$, Eq.[5] tended to overestimate $\sigma_a$. Eq.[11] showed a similar tendency as Eq.[5], but for Eq. [11] the overestimation of $\sigma_a$ was generally < 0.05 dS m$^{-1}$.

The above results suggest that overall Eq.[11] fitted the experimental data better than the three published models. However, the advantage of Eq.[11] over Eq.[5] in accurately describing the experimental data is relatively small, based on the analysis of the residual plots and the values of $r^2$ for both equations. Since it used one fewer parameter than Eq. [11], Eq. [5] could be a more efficient model of $\sigma_a-\theta_v-\sigma_w$ (or $C_r$) relationships. However, Eq. [5] requires information of soil bulk density for the sample volume when used to estimate $C_r$. This can result in an additional source of error for the use of Eq.[5] in field measurements.

**Estimating $C_r$ using four different $\sigma_a-\theta_v-\sigma_w$ (or $C_r$) relationships**

The $C_r$ at 10, 17, and 31 cm depths, estimated from TDR measured $\sigma_a$ and $\theta_v$ using the four $\sigma_a-\theta_v-\sigma_w$ (or $C_r$) relationships, are shown over the range of effluent pore volumes in
Fig. 5a, 5b, and 5c, respectively. Data for the 3 and 24 cm depths was of poor quality due to either probe failure or noise and was omitted. Also shown are $C_r$ predicted using solute transport parameters obtained from fitting CDE and MIM models to effluent BTC. The simplified $\sigma_a - \theta_n - \sigma_w$ (or $C_r$) relationship proposed by Mualem and Friedman (1991) did not give reasonable estimates of $C_r$ for the three depths, probably due to its inaccurate interpretation of the $\sigma_a - \theta_n$ relationship. $C_r$ estimated using Eq.[11] agreed closely with $C_r$ estimated using Rhoades 76 and 89 models for all three depths. The cumulative absolute deviation between any two $C_r$ BTC estimated using Eq.[11] and Rhoades’ $\sigma_a - \theta_n - \sigma_w$ (or $C_r$) relationships or predicted using CDE and MIM is given in Table 4. For all three depths, the cumulative absolute deviation of $C_r$ BTC estimated using Eq.[11] from MIM-predicted $C_r$ BTC is less than the cumulative absolute deviation of $C_r$ BTC estimated using either of the two Rhoades’ models (Table 4 and Figures 5a, 5b, and 5c). For 17 and 31 cm depths, the $C_r$ BTC estimated using Eq.[11] was also the closest to the CDE- predicted $C_r$ BTC compared with $C_r$ BTC estimated using the two Rhoades’ models.

However, this appears insufficient to conclude that Eq.[11] was more accurate in estimating $C_r$ than the two Rhoades’ models (Eq.[3] and [5]) due to the lack of knowledge of real $C_r$ values. The cumulative absolute deviation between the CDE-predicted and MIM-predicted $C_r$ BTC, which ranged from 2.90 to 3.50 g CaCl$_2$•2H$_2$O for the three depths, was large compared with the cumulative absolute deviation between any two estimated $C_r$ BTC, which ranged from 0.75 to 1.97 g CaCl$_2$•2H$_2$O. Thus, the credibility of the predicted $C_r$ BTC as a reference is questionable.

Another practical use of TDR measurements is the estimation of solute transport parameters. Table 5 listed the solute transport parameters obtained by fitting CDE and MIM
to the BTC of Cr estimated from TDR measured $\sigma_a$ and $\theta_v$ using Eq.[3], [5], and [11] for 31 cm depths. Solute transport parameters obtained from effluent measurements are also shown.

Dispersion coefficients (D) obtained from estimated resident Cr using Eq. [3], [5], and [11] differed from D estimated from effluent by CDE (Table 5). These results are consistent with those of Wraith et al. (1993) and Risler et al. (1996). Similar results were obtained when MIM was used and are not unexpected because the solute transport parameters obtained from effluent characterize the flow in the entire core whereas those obtained from a specific depth describe only flow on a local scale. Vanclooster et al. (1993) showed that solute transport parameters obtained from TDR measurements varied among soil horizons for undisturbed coarse sandy soil. Thus, the difference between solute transport parameters obtained from effluent and those obtained from estimated Cr may be consider as an extension of variation of those parameters among soil horizons. Although the soil core used in this study is disturbed, it was not completely homogeneous. In fact, its bulk density varied along its profile. For MIM, D obtained from estimated Cr using Eq.[11] was less close to that obtained from effluent than was D obtained from estimated Cr using Eq.[3] or Eq.[5]. But for CDE, D obtained from estimated Cr using Eq.[11] was closest to that obtained from effluent. Thus, it is not clear which $\sigma_a$ - $\theta_v$ - $\sigma_w$ (or Cr) relationship resulted in a more accurate estimation of solute transport parameters.

Solute transport parameters obtained from least square fit are just fitting parameters. An increase in the value of one parameter may be compensated by a decrease in the value of another parameter. This could be what happened to the $\omega$ and $\beta$ terms obtained from fitting non-equilibrium CDE to Cr BTC estimated using Eq.[11] (Table 5). Thus, the similarity between a parameter obtained from estimated resident Cr and that obtained from effluent may
not provide meaningful information. Prediction of effluent concentration based on solute transport parameters obtained from TDR measurements is more important in practice than the above comparison of parameters.

The similarity of measured and predicted effluent BTC is shown in Fig. 6. The cumulative absolute deviation of each predicted from the measured Ce BTC is given for each model in Table 6. Compared with Rhoades's models (Eq.[3] and [5]), Eq.[11] gave more accurate prediction of effluent BTC with the use of CDE and less accurate prediction of effluent BTC with the use of MIM (Table 6). However, the less accurate prediction resulted mainly from the mismatch of the tail (pore volume of effluent > 5.0) of the measured effluent BTC (Fig. 6). Quantitatively, the accuracy in the prediction of effluent BTC varied in a relatively small range: 0.29 g CaCl₂·2H₂O for CDE and 0.62 g CaCl₂·2H₂O for MIM, or 1.18% of total mass for CDE and 2.53% for MIM. It is inconclusive whether or not Eq.[11] gave a better prediction of effluent BTC than do Eq.[3] and [5]. One observation worth noting is that the Rhoades' models (Eq.[3] and [5]) have been modified by adding another parameter to account for initial salt of the soil core. This modification was actually a major innovation of Eq.[11]. Thus, adding another parameter to Rhoades' models might have improved their accuracy in the estimation of Cᵢ. Supporting evidence for this argument is that the predicted effluent BTC based on Cᵢ estimated from Rhoades' model (Eq.[3] and [5]) is visually more accurate than that reported by Risler et al. (1996). Also, Eq. [11] fitted the measured data better than did Eq. [3] and [5] when θᵥ < 0.4 m³ m⁻³ (Fig. 3). But application of these equations was at θᵥ > 0.4 m³ m⁻³ (average θᵥ at 10, 17, and 31 cm during the BTC measurement was 0.474, 0.460, and 0.457, respectively). Thus, the advantage of Eq. [11] was not fully presented.
For all three $\sigma_a - \theta_v - \sigma_w$ (or $C_r$) relationships (Eq. [3], [5], and [11]), the use of MIM can improve the accuracy of effluent prediction compared with the use of CDE, used by Risler et al. (1996). This indicated that two-region flow may exist in the packed soil core.

While the resident $C_r$ BTC estimated using Eq. [11] had the smallest discrepancy with the $C_r$ BTC predicted from the measured $C_e$ BTC using MIM (Table 4), the predicted effluent BTC using MIM from $C_r$ BTC estimated using Eq. [11] had the least agreement with the measured $C_e$ BTC. These results indicate that the possibility exists that the TDR-estimated $C_r$ BTC did not contain sufficient information for the MIM model to accurately simulate the measured effluent BTC.

**CONCLUSION**

Eq. [11] fitted packed soil core data with $r^2$ no less than did $\sigma_a - \theta_v - \sigma_w$ (or $C_r$) relationships suggested by Rhoades et al. (1976) and Mualem and Friedman (1991). Resident $C_r$ estimated by Eq. [11] was more accurate, with reference to the $C_r$ predicted from effluent using CDE or MIM models, than that estimated by any of the three published $\sigma_a - \theta_v - \sigma_w$ (or $C_r$) relationships (Eq. [3], [4], and [5]) for most cases. The simplified $\sigma_a - \theta_v - \sigma_w$ (or $C_r$) relationship presented by Mualem and Friedman (1991) did not give a reasonable estimation of $C_r$ for the data in this study.

Dispersion coefficients obtained from fitting CDE and MIM models to resident $C_r$ BTC at 31 cm, estimated from TDR measured $\theta_v$ and $\sigma_a$ using the $\sigma_a - \theta_v - C_r$ relationships proposed by this study, were different from those obtained from effluent BTC. Similar results were observed for the $\sigma_a - \theta_v - \sigma_w$ (or $C_r$) relationships reported by Rhoades et al. (1976 and 1989).
Both CDE and MIM predicted effluent BTC, based on resident $C_e$ BTC estimated from Eq.[3], [5], or [11], agreed well with the measured effluent BTC. The prediction by the MIM model was slightly more accurate than that by the CDE model. It is inconclusive whether Eq.[11] gave a more accurate prediction of effluent BTC than did Eq.[3] and [5].

Unlike that suggested by Rhoades et al. (1989), Eq.[11] does not require any information other than TDR measured $\sigma_a$ and $\theta_v$ to estimate soil solution concentration $C_r$. Thus, Eq.[11] provides easily used alternative for interpreting the $\sigma_a$-$\theta_v$-$\sigma_w$ (or $C_r$) relationships obtained in field measurements, maximizing the potential of TDR application.

ACKNOWLEDGEMENTS

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REFERENCES


Table 1. Initial soil water content, $\theta_i$, and concentration and electrical conductivity, $\sigma$, of added solutions for each core.

<table>
<thead>
<tr>
<th>Core#</th>
<th>Run</th>
<th>$\theta_i$ m$^{-3}$ m$^{-3}$</th>
<th>Added solutions g L$^{-1}$ CaCl$_2$•H$_2$O</th>
<th>$\sigma$ dS m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.198</td>
<td>0.00</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.198</td>
<td>0.22</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.198</td>
<td>1.47</td>
<td>2.23</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.198</td>
<td>2.79</td>
<td>4.32</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>0.110</td>
<td>0.00</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0.111</td>
<td>1.47</td>
<td>2.23</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>0.110</td>
<td>2.79</td>
<td>4.32</td>
</tr>
</tbody>
</table>
Table 2. Slopes of the linear TDR $\sigma_s$-$\theta_v$ relationship for repacked soil cores

<table>
<thead>
<tr>
<th>Added solutions (CaCl$_2$•H$_2$O)</th>
<th>$\theta_v &lt; 0.20$ m$^3$ m$^{-3}$</th>
<th>$\theta_v &gt; 0.20$ m$^3$ m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope ($b$) $^\dagger$</td>
<td>$r^2$ (observations)</td>
</tr>
<tr>
<td>1.47 g L$^{-1}$</td>
<td>1.94</td>
<td>0.910 (5)</td>
</tr>
<tr>
<td>2.79 g L$^{-1}$</td>
<td>2.30</td>
<td>0.904 (5)</td>
</tr>
</tbody>
</table>

$^\dagger$$\sigma_s = a + b\theta_v$
Table 3. The goodness of the fit of four $\sigma_s - \theta_s - \sigma_w$ relationships to packed soil core data and estimated parameters for each relationship.

<table>
<thead>
<tr>
<th>relationships</th>
<th>Authors</th>
<th>Estimated Parameters</th>
<th>$r^2$ (observations)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq.[11]</td>
<td>Shen et al. (1999)</td>
<td>$\beta_0 = 0.614, \beta_1 = -2.36, \beta_2 = 6.49, \beta_3 = 0.597$</td>
<td>0.997 (51)</td>
</tr>
<tr>
<td>Eq.[3]</td>
<td>Rhoades et al. (1976)</td>
<td>$a = 0.662, b = 0.305, \sigma_s = -0.030, \sigma_in = 2.43$</td>
<td>0.996 (51)</td>
</tr>
<tr>
<td>Eq.[5]</td>
<td>Rhoades et al. (1989)</td>
<td>$\theta_w = 0.159, \sigma_s = 0.173, \sigma_in = 1.55$</td>
<td>0.997 (51)</td>
</tr>
<tr>
<td>Eq.[4]</td>
<td>Mualem &amp; Friedman (1991)</td>
<td>$\sigma_in = 7.28$</td>
<td>0.864 (42)</td>
</tr>
</tbody>
</table>
Table 4. The cumulative absolute deviation ($\Delta M_c$) between paired $C$, BTC either estimated from TDR measured $\sigma_x$ and $\theta_x$ using one of three $\sigma_x$, $\theta_x$, $C$ relationships or predicted from effluent using CDE and MIM models.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Shen</th>
<th>Rhoades 76</th>
<th>Rhoades 89</th>
<th>Predicted, CDE</th>
<th>Predicted, MIM</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 cm depth</td>
<td>1.97</td>
<td>0.87</td>
<td>2.53</td>
<td>3.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.26</td>
<td>0.75</td>
<td>5.18</td>
<td>5.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.60</td>
<td>0.87</td>
<td>2.81</td>
<td>4.26</td>
<td></td>
</tr>
<tr>
<td>17 cm depth</td>
<td>1.26</td>
<td>0.75</td>
<td>5.18</td>
<td>5.18</td>
<td></td>
</tr>
<tr>
<td>31 cm depth</td>
<td>1.60</td>
<td>0.96</td>
<td>4.38</td>
<td>5.86</td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Values of estimated solute transport parameters with 95% confidence intervals and goodness of fit for CDE and MIM models fitted to effluent Ce and Cr, estimated from TDR measured \( \sigma_s \) and \( \theta_s \) at 31 cm depth using Eq.[3], [5], and [11]

<table>
<thead>
<tr>
<th></th>
<th>CDE</th>
<th>MIM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D, \text{ cm}^2 \text{ hr}^{-1} )</td>
<td>( r^2 )</td>
</tr>
<tr>
<td>Effluent</td>
<td>10.90±0.20</td>
<td>0.960</td>
</tr>
<tr>
<td>Estimated</td>
<td>Eq.[3]</td>
<td>2.11±0.27</td>
</tr>
<tr>
<td></td>
<td>Eq.[5]</td>
<td>2.60±0.25</td>
</tr>
<tr>
<td></td>
<td>Eq.[11]</td>
<td>3.51±0.21</td>
</tr>
</tbody>
</table>

Note: \( D \) = dispersion coefficient, \( \beta \) = fraction of mobile water content, \( \omega \) = dimensionless mass transfer coefficient. Retardation factor, \( R \), was fixed to 1 and pore water velocity was measured by effluent data.
Table 6. The cumulative absolute deviation, $\Delta M_e$, between the measured and predicted $C_x$ BTC. The $C_x$ BTC was predicted with CDE and MIM models based on estimated solute transport parameters from inverse use of the same models to resident $C_x$ BTC estimated from TDR measurements at 31 cm depth using Eq.[3], [5], and [11]

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>CDE</td>
<td></td>
<td></td>
<td></td>
<td>MIM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g CaCl_2\cdot 2H_2O$</td>
<td>3.15</td>
<td>3.18</td>
<td>2.89</td>
<td>1.46</td>
<td>1.51</td>
<td>2.13</td>
</tr>
</tbody>
</table>

Note: The total mass represented by the measured effluent BTC was 24.53 g $CaCl_2\cdot 2H_2O$
Fig. 1. Soil bulk electrical conductivity, $\sigma_d$, measured with TDR and fitted with Eq. [11] at different soil water content ($\theta_v$) for packed soil cores treated with sequential additions of CaCl$_2$.2H$_2$O solutions of the indicated concentration.
Fig. 2. Residual $\sigma_a$ values (measured - expected) vs. TDR-measured $\sigma_a$ for four $\sigma_a - \sigma_w(C_v)-\theta_v$ relationships.
Fig. 3. Residual $\sigma_a$ values (measured - expected) vs. TDR-estimated $\theta_v$ for four $\sigma_a - \sigma_w(C_{\theta}) - \theta_v$ relationships.
Fig. 4. Residual $\sigma_a$ values (measured - expected) vs. soil CaCl$_2$ concentration ($C_r$) for four different $\sigma_a - \sigma_w(C_r) - \theta_v$ relationships.
Fig. 5a. Resident CaCl₂ concentration at 10 cm depth estimated from TDR-measured $\sigma_a$ and $\theta_v$ using four $\sigma_a$-$\sigma_w$ (or $C_r$)-$\theta_v$ relationships and predicted from effluent using CDE and MIM models.
Fig. 5b. Resident CaCl$_2$ concentration at 17 cm depth estimated from TDR-measured $\sigma_a$ and $\theta_v$ using four $\sigma_a$-$\sigma_w$ (or $C_r$)-$\theta_v$ relationships and predicted from effluent using CDE and MIM models.
Fig. 5c. Resident CaCl₂ concentration at 31 cm depth estimated from TDR-measured $\sigma_a$ and $\theta_v$ using four $\sigma_a - \sigma_w$ (or $C_r$)-$\theta_v$ relationships and predicted from effluent using CDE and MIM models.
Fig. 6. Effluent concentration, $C_e$, measured and predicted from resident solution concentration, $C_r$, using CDE and MIM models, $C_r$ estimated using Eq. [11] and two Rhoades' models.
CHAPTER 5. PREDICTING EFFLUENT CONCENTRATION FOR UNDISTURBED SOIL CORES UNDER STEADY STATE FLOW CONDITIONS USING TIME DOMAIN REFLECTOMETRY

A paper to be submitted to Soil Science Society of America Journal

F. Shen¹, J. Swan¹, D. Jaynes², and R. Horton¹

ABSTRACT

Four solute flux experiments were conducted on two undisturbed soil cores under steady state conditions to evaluate the effectiveness of time domain reflectometry (TDR) in determining effluent solute concentration. Five 15-cm, two-rod TDR probes vertically spaced 7 cm apart were horizontally inserted into each soil core. The convection-dispersion equation (CDE) and mobile/immobile (MIM) models were fitted to resident solute concentration, \( C_r \), estimated based on TDR measurements at each soil depth for each soil core. Solute transport parameters obtained by curve fitting, combined with known initial and boundary conditions, were used to predict effluent breakthrough curves (BTC). The effluent BTC was also predicted by balancing the input and soil core storage solute mass balance. Predicted and measured BTC were compared by measuring the closeness between the two BTC and total solute mass for each BTC. In general the MIM model fitted the TDR-estimated \( C_r \) BTC better than did the CDE model. The goodness of fit, choice of models, or flux alone was not correlated with the accuracy of prediction of effluent BTC by individual solute transport models. However, probe placement and pore water velocity were factors determining the

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accuracy of predicted effluent BTC when the mass balance method was used. The simple mass balance method was potentially capable of accurately predicting the effluent BTC.

INTRODUCTION

Time domain reflectometry (TDR) has proven to be a useful tool in measuring soil volumetric water content, $\theta_v$ (Topp et al., 1980), and soil bulk electrical conductivity, $\sigma_a$ (Dalton et al., 1984; Dasberg and Dalton, 1985). Since soil resident solute concentration, $C_r$, is correlated to $\sigma_a$ and $\theta_v$ (Tagg, 1964; Rhoades et al., 1976), $C_r$ can be determined with TDR, which is more flexible than solution samplers (Ward et al., 1994). With an automatic measurement system similar to that described by Baker and Allmaras (1990), TDR facilitates determination of time and space dependencies of chemical transport through soil (Wraith et al., 1993). Since TDR measured $\sigma_a$ is related to the resident concentration of the probe’s measurement zone while the effluent concentration is a flux averaged over the flow area, understanding the relationship of TDR measured resident concentration to the effluent BTC is of critical importance. Kachanoski et al. (1992) worked on a repacked soil column under steady state flows and concluded that TDR was a quick, non-destructive method to obtain the solute travel-time density function. TDR was also used to measure solute velocity and cumulative travel time on a packed sand column (Kachanoski et al., 1994).

Solute transport models such as the CDE and MIM which account for the relationship between resident and flux averaged concentration are used with TDR measurements (Risler et al., 1996; Vanclooster et al., 1993; Vogeler et al., 1997; Wraith et al., 1993) to estimate solute transport parameters. Mixed results have been reported on the goodness of the model fitting data and the accuracy of the estimated parameters. Risler et al. (1996) reported that
transport parameters estimated using the CDE model with TDR measurements agreed well with those from effluent. Vanclooster et al. (1993) indicated that for coarse sandy soil, the CDE model fitted packed core TDR data well, but failed to fit TDR data from an undisturbed soil core. While Wraith et al. (1993) suggested that solute transport parameters obtained from TDR and effluent BTC were similar for an undisturbed soil core. However, Vogeler et al. (1997), working also on an undisturbed soil core, concluded that TDR was useful in estimating solute transport parameters, but only when the relative bulk soil electrical conductivity was used with a continuous solute application. With known initial and boundary conditions, and the estimated parameters, TDR can be used to predict the effluent BTC. This application has more practical meaning than just estimating parameters. However, few reports have demonstrated the application of TDR to predict effluent solute concentration. Moreover, no report has shown the effects of TDR probe placement and water flux on the accuracy of effluent concentration prediction. The objectives of this study are to evaluate the usefulness of TDR in predicting effluent concentration from TDR estimated resident concentration and to determine the effects of TDR probe placement and solution flux on the accuracy of the prediction.

**MATERIALS AND METHODS**

$\sigma_0$ and $\theta_0$, Measurements and $C_r$ Estimation

A 15 cm diameter and 37 cm long undisturbed soil core (Core #1) of Monona silt loam soil (fine-silty, mixed messic, Typic hapludolls) was inserted into a PVC pipe, 15-cm in diameter and 47-cm in length, after covering the side of the soil core with a slurry of soil. The soil core was seated on 1 cm of glass beads on the surface of a sintered porous filter
plate (Newmet Krebsoge, R. B. Summers & Associates, Olanthe, KS)\(^3\), and enclosed in a
PVC cap that sealed the bottom of the core. Five 15-cm TDR probes were horizontally
inserted into the soil core at depths of 4, 11, 18, 25, and 32 cm. Soil temperature was
monitored by a thermocouple sensor 2-cm below the soil surface. A vacuum hose connected
the PVC cap with a suction chamber containing a fraction collector as described by Shen et
al. (1999b). For all experiments on core #1, background solution (0.22 g CaCl\(_2\cdot2\)H\(_2\)O L\(^{-1}\))
was applied to the column until effluent concentration was constant to obtain a uniform soil
solution concentration in the soil profile before measurement commenced. Two experiments
were conducted under steady flow conditions:

**Exp. 1**, Unsaturated flow with a flowrate of approximately 40 ml h\(^{-1}\). Solute was applied
to the soil surface using a syringe pump (Precision Multichannel Syringe Pump, Soil
Measurement Systems) with 6 applicators attached to a polyurethane foam cover. After
leaching with background solution, 1.4 pore volumes of tracer solution (1.47 g CaCl\(_2\cdot2\)H\(_2\)O
L\(^{-1}\)) followed by 1.5 pore volumes of background solution was applied to the core surface
and 5 kPa suction was maintained in the suction chamber.

**Exp. 2**, Unsaturated flow with flowrate of approximately 500 ml h\(^{-1}\) (pumping rate: 10
ml every 1.2 minutes). Solute application was done in the same manner as in Exp. 1. Tracer
was applied for 1.37 pore volumes followed by 1.68 pore volumes of background solution
with 2 kPa suction maintained in the suction chamber.

A second undisturbed soil core (Core #2), 15 cm in diameter and 41 cm in length, was
prepared. The sides of the core were sealed with paraffin inside a 20-cm diameter PVC pipe
and the core bottom connected to a sintered porous filter plate by glass beads and enclosed by

\(^3\) Mention of specific product names is for the benefit of the reader, and does not imply endorsement.
a PVC cap as in Exp. 1. Five 15-cm probes were horizontally inserted into the soil core at 7-cm intervals. The uppermost probe was 9.5 cm below the soil surface. Soil matrix potential was monitored by pressure transducers at the upper (9.5 cm) and lower (37.5 cm) probe settings. Soil temperature was monitored as in Core #1. Two experiments were conducted under steady flow conditions:

**Exp. 3,** Unsaturated flow: This experiment was done in the exact same way as Exp. 1 on core #1 except that 1.8 pore volume of background solution was applied after application of 1.4 pore volume of tracer solution.

**Exp. 4,** Saturated flow: The sintered porous filter plate was replaced with three cascaded screens, which were $1 \times 1 \text{mm}^2$ nylon, $6.5 \times 6.5 \text{mm}^2$, and $12.5 \times 12.5 \text{mm}^2$ galvanized steel screens. The glass beads were removed. Mariotte bottles were used to maintain a constant solution head of 1 cm on the soil surface. Approximately 4.58 pore volume of tracer and 9.44 pore volume of background solution were applied.

The soil and TDR instrumentation used were described by Shen et al. (1999a). Average soil bulk density, determined at five different soil depths after finishing all experiments, was 1.23 Mg m$^{-3}$ for core #1 and 1.25 Mg m$^{-3}$ for core #2. Soil water content was estimated from TDR-measured apparent soil dielectric constant ($K_a$) using Eq. [14] of Shen et al. (1999a). $C_r$ was determined from TDR-measured $\sigma_z$ and $\theta_v$ using the $\sigma_z$-$\theta_v$-$\sigma_w$ ($C_r$) relationship described by Shen et al. (1999b, Eq.[11]). Although relative concentration, as used by Wraith et al. (1993) and Vanclooster et al. (1993), can be obtained from TDR-measured $\sigma_z$ and does not require an explicit $\sigma_z$-$\theta_v$-$\sigma_w$ ($C_r$) relationship, it seemed inappropriate for use in this study due to the difference in application times of the tracer solution among the studies. For Exp. 1, 2, and 3, effluent was collected using a fraction collector and solute concentration determined
using a conductivity meter as described by Shen et al. (1999b). The high flow rate in Exp. 4 required that effluent was manually collected with beakers. Effluent CaCl₂ concentration (Cₑ) was calculated based on measured σₑ using the relationship presented by Shen et al. (1999b. Eq. [7]).

**TDR-measured σₑ Correction for Local Soil Induced Differences**

To minimize the effect of soil related difference in σₑ among probe locations in estimated Cr, TDR-measured σₑ was corrected (normalized) by assuming that Cr at t = 0, Cₑ(0), was uniform in a soil core and equal to Cₑ at t = 0, Cₑ(0), for all four experiments. This procedure includes four steps: 1) For each experiment, σₑ was calculated from Cₑ(0) and initial TDR-measured θₑ for individual depths using the σₑ-θₑ-σ_w (Cₑ) relationship proposed by Shen et al. (1999b), 2) The difference between TDR-measured initial σₑ and calculated σₑ was obtained for each depth, 3) The depth-specific difference was added to all σₑ values measured at that depth, producing corrected σₑ values, and 4) The corrected C_r was estimated from the corrected σₑ values and TDR-measured θₑ using the σₑ-θₑ-σ_w (C_r) relationship.

**Transport Parameter Estimation and Cₑ Prediction**

Solute transport models, the equilibrium CDE and non-equilibrium CDE (MIM), were fitted to BTC of estimated resident and measured effluent concentrations for all four experiments using CXTFIT. The CDE model for one-dimensional solute transport can be written as (Toride et al., 1995)
where $R$ is the retardation factor, $D$ is the dispersion coefficient, $v$ is the average pore-water velocity, $x$ is distance, and $t$ is time. The governing equations of the MIM model, excluding chemical adsorption and production, can be described as

$$ R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} $$  \hspace{1cm} \text{[1]}

where $\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - J_w \frac{\partial C_m}{\partial x} $  \hspace{1cm} \text{[2]}

$$ \theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) $$  \hspace{1cm} \text{[3]}

$$ \theta_v = \theta_m + \theta_{im} $$  \hspace{1cm} \text{[4]}

where the subscripts $m$ and $im$ refer to the mobile and immobile liquid regions, respectively, $J_w (= v\theta)$ is the volumetric water flux density, and $\alpha$ is the first-order mass transfer coefficient. Dimensionless forms for Eq. [2] and [3] are

$$ \beta R \frac{\partial C_m}{\partial T} + (1 - \beta) R \frac{\partial C_{im}}{\partial T} = \frac{1}{P} \frac{\partial^2 C_m}{\partial Z^2} - \frac{\partial C_m}{\partial Z} $$  \hspace{1cm} \text{[5]}

and

$$ (1 - \beta) R \frac{\partial C_m}{\partial T} = \omega (C_m - C_{im}) $$  \hspace{1cm} \text{[6]}

where $T = vt/L$ (L is the length of the soil column) is dimensionless time, and $Z = x/L$ is dimensionless distance, $P = vL/D$ is the Peclet number, $\beta = \theta_m/\theta_v$ is the fraction of mobile water, and $\omega = (\alpha L)/(v\theta_v)$ is the dimensionless mass transfer coefficient. Detailed solutions to Eq.[1] and system of equations [5] and [6] can be found in the report by Toride et al. (1995). Least square fits of these solutions to time series of measured $C_e$ and TDR-estimated $C_r$ allow an estimation of solute transport parameters such as $D$, $\beta$, and $\omega$. 
When the equilibrium CDE model was used, \( R = 1 \) and no chemical adsorption was considered; \( v \) was based on measurements of effluent flowrate. Only \( D \) was estimated. With the MIM model, two more parameters, \( \beta \) and \( \omega \), were estimated while \( v \) and \( R \) were fixed as discussed above. Effluent BTC was predicted from model parameters fitted to resident BTC based on TDR measured \( \sigma_s \) for individual soil depths and compared with the measured \( C_e \) BTC.

**Solute Mass Balance and \( C_e \) Prediction**

The core mass balance was calculated as the change in resident solute mass, \( \Delta M_r \)

\[
(\Delta M_r)_i = \sum_{j=1}^{k} [(M_r)_{j,i} - (M_r)_{j, i-1}] \tag{7}
\]

where \( i \) refers to the \( i \)th TDR measurement which was synchronized to \( i \)th effluent determination, \( j \) refers to the TDR probe at the \( j \)th soil depth of total \( k \) depths. At \( j \)th soil depth, \( M_r \) is defined as

\[
M_r = V_{soil} \cdot \theta_v \tag{8}
\]

where \( C_r \) and \( \theta_v \) are TDR-estimated resident solute concentration using corrected TDR-measured \( \sigma_s \) and volumetric water content, respectively, for \( j \)th soil depth, \( V_{soil} \) is the \( j \)th sample core volume, formed by dividing the entire soil column at the center cross-section between any two neighboring probes. Using the core mass balance, \( C_e \) was calculated based on the difference between the input solute mass and the change in resident solute mass, \( \Delta M_r \).

The \( i \)th predicted \( C_e \) is given as

\[
(C_e)_i = [(C_{in})_i - (C_{in})_{i-1}] - (\Delta M_r)_i / [(V_e)_i - (V_e)_{i-1}] \tag{9}
\]

where \( C_{in} \) is input solute concentration and \( V_e \) is cumulative effluent volume.
Comparison of the Predicted and Measured $C_e$ BTC

Predicted and measured $C_e$ BTC were compared using two categories: total mass of effluent solute ($M_e$) and cumulative absolute deviation ($\Delta M_e$) of predicted from measured $C_e$ BTC. The $M_e$ is the area under the predicted or measured $C_e$ BTC, obtained with numerical integration. In this study, the composite trapezoid rule (Kincaid and Cheney, 1991) was applied, i.e.,

$$M_e \approx \frac{1}{2} \sum_{i=1}^{n} [(V_e)_i - (V_e)_{i+1}] [(C_e)_i + (C_e)_{i+1}]$$

where $n$ is the number of total effluent measurements. The cumulative absolute deviation is measured by the absolute difference, i.e., the area between the predicted and the measured BTC

$$\Delta M_e \approx \frac{1}{2} \sum_{i=1}^{n} [(V_e)_i - (V_e)_{i+1}] \left| (C_e^p)_i - (C_e^m)_{i+1} \right| + \left| (C_e^p)_i - (C_e^m)_i \right|$$

where superscripts $p$ and $m$ refer to the predicted and the measured, respectively.

RESULTS AND DISCUSSION

TDR-measured $\sigma_a$ and $\theta_v$,

For each experiment, TDR-measured $\sigma_a$ BTC for individual depths have different initial and maximum values and amplitudes (Fig. 1). For instance, the amplitude of TDR-measured $\sigma_a$ BTC ranged from 0.39 dS m$^{-1}$ at 18 cm to 0.51 dS m$^{-1}$ at 32 cm for Exp. 1, and from 0.23 dS m$^{-1}$ at 18 cm to 0.47 dS m$^{-1}$ at 32 cm for Exp. 2. This difference or variation could be caused by three factors singly or in combination: 1) difference of solute concentrations and/or $\theta_v$, among different soil depths, 2) difference of soil properties, such as bulk density,
soil structure, and clay content, among soil depths, which affected ion mobility in soil pores, and 3) differences among probes which may produce a different TDR signal for the same electrical conductivity. Since the probes used all have the same geometry and were linked to the cable tester with cables of the same length, they should have identical response. In addition, the probes used with core #2 showed no difference in measuring electrical conductivities of five different solutions (Shen et al., 1999b). Thus, it is unlikely that differences among probes caused the observed variation of $\sigma_s$ among soil depths. Note that no data was available for undisturbed soil core #1 at 11 cm due to probe failure.

The variation of TDR-measured $\sigma_s$ among soil depths for Exp. 1 and 3 should be attributed to the differences in soil properties along the soil column, since: 1) $\theta_v$ was nearly constant with depth in Exp. 1 and Exp. 3 (Table 1), and 2) $C_r$ appeared well equilibrated at least in the mobile region of soil solution along the soil profile, as indicated by flat peaks and tails of TDR-measured $\sigma_s$ BTC. Given possible nonuniformity in the undisturbed soil used and the documented influence of soil matrix nonuniformity on $\sigma_s$ measurement (Nadler, 1988), these results are not unexpected. For Exp. 2 and 4 ($\nu \geq 5.6 \text{ cm h}^{-1}$), the BTC showed tailing and abrupt transitions between the upward and downward limbs at all depths, suggesting bypass flow and that miscible displacement of soil solution had not reached an equilibrium. Thus, the variation of TDR-measured $\sigma_s$ could result from heterogeneity of both soil properties and soil solution. These results support the conclusion made by Vanderborght et al. (1997) that heterogeneity of solute transport increases with the increasing water flux. Although the variation of $\theta_v$ among soil depths was larger in Exp. 4 than any of the other three experiments (Table 1), it appears that it is not the main reason for larger variation of
TDR-measured $\sigma_a$. The lack of response to tracer at depth of 18 cm for Exp. 2 and at 9.5 cm for Exp. 4 suggests that macro-pore flow occurred with flow bypassing much of the sampling volumes of TDR probes at those depths.

**TDR-estimated $C_r$**

BTC of resident CaCl$_2$ concentration, estimated from TDR-measured $\sigma_a$ and $\theta_v$ using the $\sigma_a$-$\theta_v$-$\sigma_w$ ($C_r$) relationship proposed by Shen et al. (1999b), are shown in Fig. 2 for the four experiments. Ideally the TDR-estimated $C_r$ BTC for each experiment should have an orderly sequence with soil depth. However, they were as disordered as the TDR-measured $\sigma_a$ BTC. This disorder may have reflected the fact that the portions of background solution displaced by tracer solution within individual TDR sample volumes was different, and measurements in the TDR sample area may not accurately represent what occurred in the entire cross-section area of the column. It is likely that TDR-estimated $C_r$ differed because the $\sigma_a$-$\theta_v$-$\sigma_w$ ($C_r$) relationship developed on packed cores was used for multiple soil depths with different soil structures or pore systems. Evidence for bias is that TDR-estimated $C_r$ exceeded tracer concentration, $C_0$, at certain depths for Exp. 1, 3, and 4. For instance, in Exp. 1 TDR-estimated $C_r$ at 25 cm ranged from 1.48 to 1.65 g L$^{-1}$ CaCl$_2$$\cdot$2H$_2$O, which was greater than $C_0$ (=1.47 g L$^{-1}$ CaCl$_2$$\cdot$2H$_2$O) for 0.61 to 1.71 pore volume of effluent (Fig. 2).

The overestimated $C_r$ was associated with a high TDR-measured $\sigma_a$ value. In Exp. 1, for instance, for the 25 cm depth at > 0.61 pore volume of effluent, TDR-measured $\sigma_a$ > 1.15 dS m$^{-1}$, whereas calculated $\sigma_a$, based on the $\sigma_a$-$\theta_v$-$\sigma_w$ ($C_r$) relationship by Shen et al. (1999b) and the assumption that $C_r = C_0$, was 1.14 dS m$^{-1}$. The high TDR $\sigma_a$ values may have resulted
from a soil structure favoring ion movement or greater $C_r$ value in the sample volume than that in the soil outside the sample volume due to soil heterogeneity. They also may have resulted from an increase in $\sigma_w$ due to cation exchange (Vogeler et al., 1996). It appears that a specific $\sigma_r-\theta_r-\sigma_w (C_r)$ relationship is needed for each depth, as indicated by Ward et al. (1994), to improve the accuracy of TDR-estimated $C_r$. However, Risler et al. (1996) reported that discrepancy existed between the TDR-estimated $C_r$ BTC and those obtained from effluent even though in situ calibration was adopted. In addition, the calibration procedure for an in situ $\sigma_r-C_r-\theta_r$ relationship is time-consuming and virtually impossible to carry out in the field.

**Fit of MIM and CDE models to $C_e$ and TDR-estimated $C_r$ BTC**

In general, the MIM model, with two additional parameters, fitted the measured data better than did the CDE model as shown by greater $R^2$ values for the MIM model (Table 2). These results are similar to that reported by Vancloster et al. (1993). For effluent BTC, a near perfect fit ($r^2 \geq 0.999$) was achieved when the MIM model was used (Table 2). The CDE model fitted $C_e$ BTC with $r^2 \geq 0.992$ for Exp. 2 and 4 ($v \geq 5.6 \text{ cm h}^{-1}$) while the lack of fit, with measured BTC lagging fitted BTC, was obvious for Exp. 1 and 3 with $v \leq 0.6 \text{ cm h}^{-1}$ (Fig. 3).

The goodness of fit generally decreased with depth with the CDE model fitted TDR-estimated $C_r$ BTC for experiments with $v \leq 0.6 \text{ cm h}^{-1}$ (Table 2 and Fig. 4). It appears that the CDE model could not fit accelerated movement of the tracer solution, suggesting preferential flow. The MIM model fitted the data well ($r^2 \geq 0.958$) in most cases for experiments under
unsaturated flow conditions (Exp. 1, 2, and 3). Lack of fit occurred either when TDR-estimated $C_r$ was well above tracer’s concentration as for the lower three depths in Exp. 4 (Fig. 5) or when possible bypass flow existed as for 18 cm depth in Exp. 2.

**Estimation of Solute Transport Parameters**

Estimated transport parameters from TDR-estimated $C_r$ were similar among soil depths and to those determined from effluent BTC for experiments with $v \leq 0.6 \text{ cm h}^{-1}$ (Table 2, Exp. 1 and 3). For instance, $D$ estimated from $C_r$ with the MIM model ranged from 0.52 to 0.81 cm$^2$ h$^{-1}$ while that from $C_e$ was 0.57 cm$^2$ h$^{-1}$ for Exp. 1. These results are in agreement with those for a repacked soil core reported by Risler et al. (1996). However, variation in estimated transport parameters among soil depths and between those from $C_r$ and $C_e$ increased with the increase in $v$. For example, $D$ estimated with MIM for Exp. 4 varied from $6.01 \times 10^2$ to $1.07 \times 10^5$. Again, this result can be due to the heterogeneity of solute transport, which increases with the applied water flux (Vanderborght et al., 1997). Since the variation in local advection velocity was identified by Vanderborght et al. (1997) as the cause for the heterogeneity of solute transport, fixing $v$ during the least square fit could have resulted in greater variation in values of other solute transport parameters. For an undisturbed soil core, Vanclooster et al. (1993) showed that fairly large variation in $D$, $\beta$, and $\omega$ among different soil layers existed even if $v$ was a fitting parameter.

It is not unexpected that transport parameters estimated from $C_e$ BTC differ from those estimated from TDR-estimated $C_r$ BTC for an undisturbed soil core, because $C_e$ BTC characterizes the transport process in the entire column while TDR-estimated $C_r$ BTC features the process in the sample region. It is likely that local solute transport deviates from
that of column-averaged solute transport. In most cases, the value of a transport parameter estimated from effluent was within the range of the same parameters obtained from Cr at different soil depths. In Exp. 2 for instance, D has a value of 285 cm² h⁻¹ when Ce was used whereas it ranges from 85.8 to 635 cm² h⁻¹ with Cr (Table 2).

Estimated β for experiments with v ≤ 0.6 cm h⁻¹ (Exp. 1 and 3) was less than or equal to 0.77, indicating a substantial fraction of immobile water (≥0.23) existed. This could explain why the CDE model poorly fitted both the Cr and Ce BTC for these two experiments. A high degree of uncertainty existed in estimation of β and ω for experiments with v ≥ 5.6 cm h⁻¹ (Exp. 2 and 4). Also, large variation in the values of estimated β and ω was observed along the soil profile for the same experiments (Table 2). For instance, β values ranged unreasonably from 0.0 at 16.5 cm depth to 1.0 at 30.5 cm depth for Exp. 4. It is likely that BTC measured in Exp. 2 and 4 did not provide sufficient information on the tailing, which is vital to clearly defining each parameter.

**Prediction of Effluent BTC**

The predicted total mass of effluent solute (Mₑ,p) and its percentage to the measured total mass of effluent solute (Mₑ,m) are given in Table 3. Except at 23.5, 30.5, and 37.5 cm depths for Exp. 3, the difference between Mₑ,p and Mₑ,m was within ±8.0%. The over-predicted total mass at 23.5, 30.5, and 37.5 cm for Exp. 3 resulted from high initial TDR-estimated Cr (Fig. 2). The error in Mₑ,p was not correlated with the goodness of fit, soil depth, or the model used. Moreover, v did not appear to influence the accuracy of the total mass prediction.

The relative (cumulative absolute) deviation (ΔMₑ/Mₑ,m) for all depths in Exp. 1 and 3 (v
is higher with the CDE model than with the MIM model (Table 3). For Exp. 2 and 4 \((v \geq 5.6 \text{ cm h}^{-1})\), the relative deviation is higher with the MIM model than with the CDE model for all except 9.5 and 37.5 cm depths of Exp. 4. For any given experiment, variation in the relative deviation among soil depths existed, but showed no pattern. For instance, \(\Delta M_e/M_{e,m}\) is 3.6% at 16.5 cm depth while it is 11.2% at 37.5 cm depth for Exp. 4 with the CDE model. \(\Delta M_e\) was not correlated with the goodness of fit. Furthermore, the closeness in values of solute transport parameters estimated from \(C_e\) to those from \(C_e\) did not relate to the closeness between the predicted and the measured \(C_e\) BTC. For instance, \(\Delta M_e\) is not the smallest at 37.5 cm though \(D\) estimated from TDR measured \(\sigma_a\) at this depth is the closest to \(D\) estimated from effluent for Exp. 1. An example of TDR predicted BTC is illustrated in Fig. 5, which shows that at certain soil depths the deviation occurred at the beginning. This suggests that non-uniform TDR-estimated \(C_e\) among soil depths was partly responsible for the deviation. Adjustment is required to ensure that TDR-estimated \(C_e\) BTC and \(C_e\) BTC start from the same origin. The error in \(M_{e,p}\) is usually less than \(\Delta M_e\) for a given soil depth in a given experiment. In other words, the difference between the total area under a given predicted \(C_e\) BTC and that under the measured \(C_e\) BTC is smaller than the area between the two BTC. These results suggest that TDR will give a more accurate result if it is used to predict \(M_e\) over a period of time than to produce a time series of \(C_e\).

**Using Corrected TDR-measured \(\sigma_a\)**

TDR-measured \(\sigma_a\) was corrected to remove bias created by soil structure or pore system difference among depths. Figure 6 shows the \(C_e\) estimated from corrected TDR-measured \(\sigma_a\)
for Exp. 3 and 4. Using corrected TDR-measured $\sigma_a$ reduced the vertical variation of estimated Cr in amplitude, initial, and maximum values. Overestimation of Cr was basically eliminated. Vertical variation of Cr along soil profile depth should now be due to heterogeneity of miscible displacement. Thus, soil solute was more uniformly displaced at all depths for Exp. 3 than for Exp. 4 (Fig. 6).

The goodness of fit for CDE and MIM models fitted to corrected TDR-estimated Cr was improved in most cases (Table 2 and 4). However, worse fits occurred with no obvious causes in some incidents such as the CDE fit in Exp. 3. In most cases, no significant changes were observed in the values of estimated solute transport parameters due to use of corrected TDR-estimated Cr. Also, it is not evident that using corrected TDR-estimated Cr reduced the difference, if any, between the values of solute transport parameters estimated from Cr and Ce (Table 2 and 4).

Using corrected TDR-estimated Cr reduced the error in predicting total mass of effluent solute, i.e., $M_{e,p}/M_{e,m}$ was closer to 100%, for most cases in Exp. 3 and Exp. 4 (Table 5). However, similar improvement was not observed for Exp. 1 and 2. When the CDE model was used, the relative deviation ($\Delta M_e/M_{e,m}$) of the predicted BTC from the measured BTC with corrected TDR-estimated Cr was only slightly different from the uncorrected. When the MIM model was used, the value of the relative absolute error term $\Delta M_e/M_{e,m}$ decreased at most soil depths for experiments with $v \leq 0.6$ cm h$^{-1}$ (Exp. 1 and 3); it increased at some depths and decreased at the other depths for experiments with $v \geq 5.6$ cm h$^{-1}$ (Exp. 2 and 4).

It appears that a better fit of CDE or MIM to either corrected or uncorrected TDR-estimated Cr does not guarantee a more accurate prediction of either $M_e$ or $\Delta M_e$ (Table 3 and 5). For instance, the prediction of total mass became more accurate as the goodness of fit
decreased for CDE fitted to corrected TDR-estimated Cr rather than the uncorrected at 23.5, 30.5, and 37.5 cm depths of Exp. 3. In this case, an initial Cr similar to Ce obviously played an important role in reducing the prediction error (Fig. 7a). These results demonstrate the inability of the CDE model to accurately predict effluent BTC under conditions of this study. The inability of the CDE model to accurately fit either the TDR Cr measurements (Fig. 4) or effluent BTC measurements (Fig. 3) severely limits the accuracy of prediction of total effluent mass. For \( v < 0.6 \) cm h\(^{-1}\), the effluent BTC was more closely approximated by BTC predicted with parameters obtained from fitting the MIM model (Fig. 7b) than those obtained using the CDE model (Fig. 7a). The predicted BTC for depths closest to the outflow agreed more closely with the effluent BTC than did BTC for depths nearer the upper boundary. Correction of the initial TDR \( \sigma_a \) measurements to calibration data improved the fit with effluent BTC of predicted BTC obtained by fitting the MIM model to TDR-estimated Cr BTC. The MIM model underpredicted the maximum effluent Ce, possibly due to underestimation of the immobile fraction shown in the input-effluent mass balance estimate of Ce (Appendix 1, Fig. 2).

**Prediction of Ce BTC through Mass Balance**

For Exp. 4 with \( v = 86.1 \) cm h\(^{-1}\) the mass balance prediction of effluent BTC gave a value of \( M_{e,p}/M_{e,m} = 102.7\% \), close to those obtained using the CDE or MIM models. The relative absolute error term, \( \Delta M_e/M_{e,m} \), had a value of 4.8\%, which was smaller than most obtained from the CDE or MIM models (Fig. 8 and Table 5). Good prediction was also observed for Exp. 2 with \( v = 5.6 \) cm h\(^{-1}\). However, the relative deviation of the predicted BTC from the measured BTC was considerably larger for experiments with \( v \leq 0.6 \) cm h\(^{-1}\).
(Exp. 1 and 3). For instance, $\Delta M_e/M_{e,m}$ (37.2%) obtained through mass balance for Exp. 3 was greater than any of those obtained from CDE and MIM (Table 5). This large deviation mainly occurred at the time when inflow was switched. Although the storage of solute in the soil core changed immediately after switching tracer concentrations, the upper TDR probe at 4.5 cm did not detect the change until new input reached the sample volume of the probe. Thus, when inflow was switched from high to low concentration (or from tracer to background solution) at pore volume $\equiv 1.4$ for Exp. 1 and 3, the predicted $C_e$ was low due to the combination of a low input concentration with little or no decrease in storage (Fig. 8). The $C_e$ was under-predicted by a larger amount in Exp. 3 than in Exp. 1 due to a greater distance from soil surface to the upper TDR probe in Core #2 (9.5 cm). When the lower concentration solution reached the sample volume of the uppermost probe, the solute storage term suddenly decreased, creating a large negative storage change that resulted in an over prediction of $C_e$. When inflow was switched from low to high concentration (or from background to tracer solution) at pore volume $\equiv 0$, the $C_e$ was first over-predicted and then under-predicted. With the high $v$ in Exp. 2 and 4, the delay for the uppermost probe detecting the change in input was short and only one or two values of predicted $C_e$ were affected. The high random error in storage estimates is to be expected since the change in storage is small at any time step and is calculated as the difference between two large numbers derived from TDR measured $\sigma a$ and $\theta$ both of which have error components.

The results also show that the predicted $C_e$ through mass balance is randomly distributed around the measured $C_e$ (Fig. 8). Whereas, the predicted $C_e$ using CDE or MIM is usually systemically biased (Fig. 5 and 7). The random error for the predicted $C_e$ through mass balance could mathematically be reduced by smoothing the predicted BTC. Given the
simplicity and potential accuracy of mass balance method, this method can be a promising one for predicting effluent BTC with TDR. The accuracy can be improved by placing the uppermost probe as close to the soil surface as possible or using vertical probe placement, and by reducing the soil volume that each probe needs to represent through use of multiple probes.

CONCLUSIONS

TDR-measured $\sigma_a$ BTC varied in initial and maximum values and amplitude among depths for all four experiments. This variation increased as $v$ increased. Estimated $C_r$ from TDR-measured $\sigma_a$ and $\theta_v$ also varied among soil depths due to the structural difference and flow heterogeneity.

In general, the MIM model fitted the TDR-estimated $C_r$ and measured $C_e$ BTC better than the CDE model for all four experiments. Solute transport parameters estimated from TDR-estimated $C_r$ at one depth were similar to those from other depths or to that from effluent for experiments with $v \leq 0.6$ cm h$^{-1}$ (Exp. 1 and 3). For experiments with $v \geq 5.6$ cm h$^{-1}$ (Exp. 2 and 4), solute transport parameters estimated from different soil depths differed from each other and from solute transport parameters estimated from effluent. The use of TDR-measured $\sigma_a$ corrected to remove soil related differences in $\sigma_a$ improved the fits of CDE and MIM models to the $C_r$ BTC in most cases. However, significant changes were not observed for the estimated solute transport parameters obtained from these fits.

The predicted $C_e$ BTC using parameters obtained by fitting CDE and MIM models to TDR-estimated $C_r$ deviated from the measured $C_e$ BTC in different degrees for different experiments and soil depths. When data for the four experiments are considered together,
neither goodness of fit, soil depths, the choice of models, or $v$ alone was well correlated with the accuracy of the prediction. However, for Exp. 1 and 3 the parameters for the lowest two depths most closely agreed with parameters derived from effluent measurements. Initial or boundary conditions were vital for an accurate prediction of $C_e$.

A simple mass balance method demonstrated a potential capability to accurately predict $C_e$ BTC. The accuracy of this method is affected by placement of TDR probes and $v$, but could be improved by placing TDR probes near to the boundaries of soil column, by narrowing the space between neighboring probes, and by smoothing to remove random error.

ACKNOWLEDGEMENTS

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REFERENCES


Table 1. Background solution electrical conductivity, \( \sigma_s(0) \), initial effluent electrical conductivity, \( \sigma_s(i) \), average pore water velocity, \( v \), and average TDR-estimated \( \theta_v \) for experiments and soil depths indicated

<table>
<thead>
<tr>
<th>Experiments</th>
<th>( \sigma_s(0) )</th>
<th>( \sigma_s(i) )</th>
<th>( v )</th>
<th>4 cm</th>
<th>18 cm</th>
<th>25 cm</th>
<th>32 cm</th>
<th>Entire core</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 1</td>
<td>0.38</td>
<td>0.47</td>
<td>0.5</td>
<td>0.400</td>
<td>0.399</td>
<td>0.401</td>
<td>0.403</td>
<td>0.401</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>0.38</td>
<td>0.44</td>
<td>5.6</td>
<td>0.427</td>
<td>0.417</td>
<td>0.431</td>
<td>0.432</td>
<td>0.427</td>
</tr>
<tr>
<td>Exp. 3</td>
<td>0.38</td>
<td>0.45</td>
<td>0.6</td>
<td>0.423</td>
<td>0.424</td>
<td>0.441</td>
<td>0.430</td>
<td>0.407</td>
</tr>
<tr>
<td>Exp. 4</td>
<td>0.38</td>
<td>0.39</td>
<td>86.1</td>
<td>0.421</td>
<td>0.429</td>
<td>0.446</td>
<td>0.476</td>
<td>0.462</td>
</tr>
</tbody>
</table>
Table 2. Values of estimated solute transport parameters with 95% confidence intervals and goodness of fit for CDE and MIM fitted to effluent C_v and TDR-estimated C, for experiments and depths indicated.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Soil Depth</th>
<th>D</th>
<th>r^2</th>
<th>D</th>
<th>β</th>
<th>ω</th>
<th>r^2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td>CDE</td>
<td>cm^2 hr.^{-1}</td>
<td>r^2</td>
<td>MIM</td>
<td>cm^2 hr.^{-1}</td>
<td></td>
</tr>
<tr>
<td>Exp. 1</td>
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<td>0.35±0.14</td>
<td>0.995</td>
<td>0.52±0.17</td>
<td>0.80±0.10</td>
<td>0.11±0.15</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>1.00±0.39</td>
<td>0.963</td>
<td>0.53±0.10</td>
<td>0.61±0.10</td>
<td>0.47±0.12</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.90±0.60</td>
<td>0.936</td>
<td>0.75±0.37</td>
<td>0.68±0.23</td>
<td>0.00±0.35</td>
<td>0.983</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>3.14±0.78</td>
<td>0.869</td>
<td>0.81±0.15</td>
<td>0.61±0.10</td>
<td>0.00±0.14</td>
<td>0.996</td>
</tr>
<tr>
<td>Effluent</td>
<td></td>
<td>5.98±0.52</td>
<td>0.934</td>
<td>0.57±0.04</td>
<td>0.66±0.03</td>
<td>0.00±0.33</td>
<td>1.000</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>4</td>
<td>298±0.20</td>
<td>0.985</td>
<td>550±4.00</td>
<td>0.50±2.68</td>
<td>0.11±1.21</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>635±0.20</td>
<td>0.958</td>
<td>647±2.00</td>
<td>1.00±0.89</td>
<td>0.00±0.48</td>
<td>0.958</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>85.8±0.20</td>
<td>0.977</td>
<td>44.4±0.30</td>
<td>0.19±0.39</td>
<td>4.40±0.61</td>
<td>0.984</td>
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<tr>
<td></td>
<td>32</td>
<td>114±0.40</td>
<td>0.947</td>
<td>7.36±0.16</td>
<td>0.28±0.22</td>
<td>1.32±0.18</td>
<td>0.996</td>
</tr>
<tr>
<td>Effluent</td>
<td></td>
<td>285±0.20</td>
<td>0.992</td>
<td>129±0.100</td>
<td>0.63±0.07</td>
<td>0.00±0.05</td>
<td>1.000</td>
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<tr>
<td>Exp. 3</td>
<td>9.5</td>
<td>1.08±0.26</td>
<td>0.976</td>
<td>1.67±0.39</td>
<td>0.74±0.15</td>
<td>0.23±0.40</td>
<td>0.986</td>
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<tr>
<td></td>
<td>16.5</td>
<td>1.30±0.25</td>
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<td>0.88±0.04</td>
<td>0.74±0.04</td>
<td>0.29±0.05</td>
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</tr>
<tr>
<td></td>
<td>23.5</td>
<td>2.07±0.41</td>
<td>0.964</td>
<td>3.18±0.44</td>
<td>0.77±0.40</td>
<td>0.00±0.38</td>
<td>0.975</td>
</tr>
<tr>
<td></td>
<td>30.5</td>
<td>2.43±0.43</td>
<td>0.958</td>
<td>2.96±0.39</td>
<td>0.75±0.35</td>
<td>0.00±0.36</td>
<td>0.979</td>
</tr>
<tr>
<td></td>
<td>37.5</td>
<td>3.01±0.46</td>
<td>0.951</td>
<td>2.84±0.33</td>
<td>0.74±0.26</td>
<td>0.00±0.32</td>
<td>0.982</td>
</tr>
<tr>
<td>Effluent</td>
<td></td>
<td>5.36±0.43</td>
<td>0.945</td>
<td>0.72±0.06</td>
<td>0.72±0.05</td>
<td>0.05±0.06</td>
<td>0.999</td>
</tr>
<tr>
<td>Exp. 4</td>
<td>9.5</td>
<td>1.11±10^5±0.01</td>
<td>0.932</td>
<td>8.67±10^4±0.01</td>
<td>0.09±1.04</td>
<td>100±1.1</td>
<td>0.945</td>
</tr>
<tr>
<td></td>
<td>16.5</td>
<td>1.60±10^5±0.01</td>
<td>0.968</td>
<td>4.87±10^4±0.01</td>
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<td>35.1±0.05</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>23.5</td>
<td>1.11±10^5±0.01</td>
<td>0.929</td>
<td>1.07±10^5±0.01</td>
<td>0.00±0.12</td>
<td>3.59±0.15</td>
<td>0.975</td>
</tr>
<tr>
<td></td>
<td>30.5</td>
<td>2.55±10^3±1.00</td>
<td>0.922</td>
<td>601±0.80</td>
<td>1.00±3.24</td>
<td>8.33±3.23</td>
<td>0.930</td>
</tr>
<tr>
<td></td>
<td>37.5</td>
<td>2.52±10^3±1.00</td>
<td>0.902</td>
<td>2.52±10^3±1.00</td>
<td>1.00±1.32</td>
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<td>0.902</td>
</tr>
<tr>
<td>Effluent</td>
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<td>1.80±10^5±0.00</td>
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<td>1.06×10^5±0.01</td>
<td>0.69±0.12</td>
<td>0.01±0.06</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Note: r^2 represents the ratio of sum square of regression to sum square of uncorrected total.
Table 3. The measured and predicted total mass of effluent solute ($M_{c,m}$ and $M_{c,p}$), in grams of CaCl$_2$$\cdot$2H$_2$O, and the cumulative relative deviation ($\Delta M_e$, defined by Eq. [11]) of predicted $C_e$ BTC from the measured $C_e$ BTC

<table>
<thead>
<tr>
<th>Experiments (M$_{c,m}$)</th>
<th>Soil Depth</th>
<th>CDE</th>
<th>MIM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td>$M_{c,p}$</td>
<td>$\frac{M_{c,p}}{M_{c,m}}$</td>
</tr>
<tr>
<td>Exp. 1 (8.35)</td>
<td>4</td>
<td>8.32</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>8.86</td>
<td>106.1</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>8.95</td>
<td>107.2</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>7.91</td>
<td>94.8</td>
</tr>
<tr>
<td>Exp. 2 (8.27)</td>
<td>4</td>
<td>7.75</td>
<td>93.7</td>
</tr>
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<td></td>
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<td>7.90</td>
<td>95.5</td>
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<td>Exp. 3 (8.77)</td>
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<td>8.99</td>
<td>102.5</td>
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<tr>
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<tr>
<td></td>
<td>37.5</td>
<td>9.95</td>
<td>113.5</td>
</tr>
<tr>
<td>Exp. 4 (28.31)</td>
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<td>29.05</td>
<td>102.6</td>
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<tr>
<td></td>
<td>16.5</td>
<td>28.69</td>
<td>101.3</td>
</tr>
<tr>
<td></td>
<td>23.5</td>
<td>29.84</td>
<td>105.4</td>
</tr>
<tr>
<td></td>
<td>30.5</td>
<td>30.43</td>
<td>107.5</td>
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<tr>
<td></td>
<td>37.5</td>
<td>30.51</td>
<td>107.8</td>
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</table>
Table 4. Values of estimated solute transport parameters with 95% confidence intervals and goodness of fit for CDE and MIM fitted to effluent $C_e$ and TDR-estimated $C_i$ from corrected $C_a$ for experiments and depths indicated.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Soil Depth</th>
<th>CDE</th>
<th>MIM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td>D</td>
<td>r&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Exp. 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.33±0.17</td>
<td>0.996</td>
<td>0.55±0.19</td>
</tr>
<tr>
<td>18</td>
<td>1.00±0.58</td>
<td>0.944</td>
<td>1.70±0.52</td>
</tr>
<tr>
<td>25</td>
<td>1.30±0.63</td>
<td>0.952</td>
<td>0.55±0.06</td>
</tr>
<tr>
<td>32</td>
<td>3.59±0.79</td>
<td>0.931</td>
<td>0.71±0.09</td>
</tr>
<tr>
<td>Effluent</td>
<td>5.98±0.52</td>
<td>0.934</td>
<td>0.57±0.04</td>
</tr>
<tr>
<td>Exp. 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>187±0.10</td>
<td>0.999</td>
<td>181±0.50</td>
</tr>
<tr>
<td>18</td>
<td>717±0.20</td>
<td>0.980</td>
<td>2515±1.00</td>
</tr>
<tr>
<td>25</td>
<td>111±0.20</td>
<td>0.993</td>
<td>55.8±0.20</td>
</tr>
<tr>
<td>32</td>
<td>112±0.40</td>
<td>0.974</td>
<td>6.62±0.17</td>
</tr>
<tr>
<td>Effluent</td>
<td>285±0.20</td>
<td>0.992</td>
<td>129±0.100</td>
</tr>
<tr>
<td>Exp. 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>1.08±0.22</td>
<td>0.983</td>
<td>1.46±0.33</td>
</tr>
<tr>
<td>16.5</td>
<td>1.31±0.28</td>
<td>0.977</td>
<td>1.05±0.11</td>
</tr>
<tr>
<td>23.5</td>
<td>2.38±0.40</td>
<td>0.945</td>
<td>1.08±0.14</td>
</tr>
<tr>
<td>30.5</td>
<td>1.94±0.49</td>
<td>0.917</td>
<td>1.06±0.15</td>
</tr>
<tr>
<td>37.5</td>
<td>7.46±0.52</td>
<td>0.904</td>
<td>0.99±0.17</td>
</tr>
<tr>
<td>Effluent</td>
<td>5.36±0.43</td>
<td>0.945</td>
<td>0.72±0.06</td>
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<tr>
<td>Exp. 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>1.40×10&lt;sup&gt;4&lt;/sup&gt;±0.01</td>
<td>0.918</td>
<td>1.43×10&lt;sup&gt;4&lt;/sup&gt;±0.01</td>
</tr>
<tr>
<td>16.5</td>
<td>2.11×10&lt;sup&gt;4&lt;/sup&gt;±0.01</td>
<td>0.988</td>
<td>7.65×10&lt;sup&gt;4&lt;/sup&gt;±0.01</td>
</tr>
<tr>
<td>23.5</td>
<td>1.43×10&lt;sup&gt;4&lt;/sup&gt;±0.01</td>
<td>0.988</td>
<td>5.53×10&lt;sup&gt;4&lt;/sup&gt;±0.01</td>
</tr>
<tr>
<td>30.5</td>
<td>2.04×10&lt;sup&gt;3&lt;/sup&gt;±0.01</td>
<td>0.972</td>
<td>1.20×10&lt;sup&gt;3&lt;/sup&gt;±0.01</td>
</tr>
<tr>
<td>37.5</td>
<td>2.01×10&lt;sup&gt;3&lt;/sup&gt;±0.01</td>
<td>0.976</td>
<td>9.60×10&lt;sup&gt;3&lt;/sup&gt;±0.30</td>
</tr>
<tr>
<td>Effluent</td>
<td>1.80×10&lt;sup&gt;4&lt;/sup&gt;±0.01</td>
<td>0.999</td>
<td>1.06×10&lt;sup&gt;3&lt;/sup&gt;±0.69</td>
</tr>
</tbody>
</table>

Note: $r^2$ represents the ratio of sum square of regression to sum square of uncorrected total
Table 5. The measured and predicted total mass of effluent solute ($M_{c,m}$ and $M_{c,p}$), in grams of CaCl$_2$$\cdot$2H$_2$O, using corrected TDR-measured $\alpha_n$, and the cumulative absolute deviation ($\Delta M_e$, defined by Eq. [11]) of predicted $C_e$ BTC from the measured $C_e$ BTC

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Soil Depth cm</th>
<th>CDE</th>
<th>MIM</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(M$_{c,m}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp. 1</td>
<td>4</td>
<td>8.65</td>
<td>103.6</td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td>(8.35)</td>
<td>9.51</td>
<td>113.8</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>8.19</td>
<td>98.0</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>7.46</td>
<td>89.4</td>
<td>2.28</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>4</td>
<td>7.68</td>
<td>92.9</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>(8.27)</td>
<td>8.68</td>
<td>105.0</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>7.67</td>
<td>92.8</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>7.59</td>
<td>91.8</td>
<td>1.64</td>
</tr>
<tr>
<td>Exp. 3</td>
<td>9.5</td>
<td>9.09</td>
<td>103.7</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>(8.77)</td>
<td>9.07</td>
<td>103.5</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>23.5</td>
<td>8.98</td>
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<td>2.25</td>
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<td>98.7</td>
<td>2.32</td>
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<tr>
<td>Exp. 4</td>
<td>9.5</td>
<td>28.33</td>
<td>100.1</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>(28.31)</td>
<td>28.47</td>
<td>100.5</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>23.5</td>
<td>28.51</td>
<td>100.7</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>30.5</td>
<td>29.01</td>
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<td>4.31</td>
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<tr>
<td></td>
<td>37.5</td>
<td>29.01</td>
<td>102.5</td>
<td>4.33</td>
</tr>
</tbody>
</table>
Fig. 1. TDR-measured bulk soil electrical conductivity, $\sigma_a$, at depths indicated. Average pore water velocity ($v$) is shown in ().
Fig. 2. Resident solute concentration, $C_r$, estimated from TDR-measured $\sigma_s$ and $\theta_v$ at depths indicated. Average pore water velocity ($v$) is shown in ( ).
Fig. 3. Effluent solute concentration, $C_e$, measured and fitted using CDE and MIM for experiments indicated. Average pore water velocity ($v$) is shown in (Q).
Fig. 4. Resident solute concentration, $C_r$, estimated from TDR measurements and fitted using CDE and MIM for Exp. 1 at depths indicated.
Fig. 5. Effluent BTC measured and predicted with solute transport parameters obtained from independently fitting CDE and MIM to TDR-estimated C$_r$BTC at depths indicated for Exp. 1.
Fig. 6. Resident solute concentration, $C_r$, estimated from TDR-measured $\sigma_s$ (corrected) and $\theta_v$ for Exp. 3 and 4 at depths indicated. For clarity, only one out of two data points is shown.
Fig. 7a. Effluent BTC measured and predicted with solute transport parameters obtained from independently fitting CDE to a) TDR-estimated \(C_7\) BTC and b) corrected TDR-estimated \(C_7\) BTC at depths indicated for Exp. 3.
Fig. 7b. Effluent BTC measured and predicted with solute transport parameters obtained from independently fitting MIM to a) TDR-estimated C, BTC and b) corrected TDR-estimated C, BTC at depths indicated for Exp. 3.
Fig. 8. Effluent BTC—measured and predicted by budgeting input and TDR-estimated resident solute mass for Exp. 1-4. Both $M_{e,p}$ and $\Delta M_e$ are in g CaCl$_2$·2H$_2$O L$^{-1}$. 
CHAPTER 6. GENERAL CONCLUSIONS

Bulk soil electrical conductivity, $\sigma_a$, affected TDR-measured soil apparent dielectric constant, $K_s$, and thus soil water content, $\theta_v$, on both packed and undisturbed soil cores. These effects were site-specific and not explained by the electromagnetic theory on which TDR is based. A semi-empirical relationship of $K_s$ to $\sigma_a$ and $\theta_v$ developed from packed soil core data did not adequately describe the effects of $\sigma_a$ on $K_s$ measured on an undisturbed soil core. Individual calibrations for each soil depth were required to remove effects of $\sigma_a$ on $K_s$ or $\theta_v$.

Accurate estimation of soil resident solute concentration, $C_r$, from TDR-measured $\sigma_a$ and $\theta_v$ requires an accurate description of the $\sigma_a$-$\theta_v$-$C_r$ relationship. The $\sigma_a$-$\theta_v$-$C_r$ relationship developed in this study fitted packed soil core data with higher $r^2$ than three published models and gave more accurate $C_r$ estimation compared with $C_r$ predicted from effluent with solute transport models. Moreover, our model does not require information other than TDR-measured $\sigma_a$ and $\theta_v$ to estimate $C_r$, and thus provides an easily used alternative for interpreting the $\sigma_a$-$\theta_v$-$C_r$ relationships obtained in field measurements. Mass balance of $C_r$ calculated using TDR measured $\theta_v$ and $\sigma_a$ and the $\sigma_a$-$\theta_v$-$C_r$ relationship from packed cores closely agreed with input-effluent $C_r$ measurements on undisturbed cores for pore water velocity $< 0.6$ cm hr$^{-1}$. This result implies that the $\sigma_a$-$\theta_v$-$C_r$ relationship developed for packed cores accurately described the $\sigma_a$-$\theta_v$-$C_r$ relationship for undisturbed soil cores.

An increase in water flux increased variation of TDR-measured $\sigma_a$, and thus variation of TDR-estimated $C_r$. The effluent breakthrough curve (BTC) predicted with solute transport
models using solute transport parameters obtained by fitting the same models to TDR-estimated C, BTC usually deviated from the measured effluent BTC. The degree of this deviation was not directly correlated with the goodness of fit, choice of models, soil depth, or pore water velocity.

A simple mass balance method, based on the mass of input and TDR measured change in resident solute mass, demonstrated the capability of accurately predicting effluent BTC under steady flow conditions over a range of flow velocity and with possible macropore flow. This method potentially could be used to estimate effluent BTC under transient flow conditions if TDR can accurately estimate the flow region Cr and input conditions are known. Probe placement and number were critically important factors for the accuracy of the mass budget method.

Suggestions for Additional Research

To maximize the potential of TDR application, further study should be conducted on the effects of soil properties, such as soil bulk density, porosity, and clay content, on the TDR-measured $\sigma_z$. The applicability of solute transport models on structured soil should be examined. The capabilities of the mass balance method to estimate effluent BTC under transient flow conditions should be determined.
APPENDIX 1. SOIL CORE MASS BUDGET APPROACH

INTRODUCTION

Use of budgets to determine mass balance in solving problems involving mass transport is a commonly used technique (Bird et al., 1960). While mass recovery is often reported, other than Hart and Lowery (1997) and Kachanoski et al. (1992), relatively few research publications relating to solute movement in the field or in soil cores have used a mass balance approach to relate estimates of resident concentration, $C_r$, obtained from TDR measured bulk soil electrical conductivity, $\sigma_b$, to effluent concentration, $C_e$, or effluent electrical conductivity, $\sigma_e$. This lack is in part due to probe location within a soil core that does not represent the average solute concentration of the entire soil core volume and to the difficulty of determining the relationship of $C_r$ to $\sigma_e$ and to TDR measured $\sigma_b$ and $\theta_v$ for a particular soil or soil conditions of the experiment. Using vertical TDR probe placement, Kachanoski et al. (1992) experimentally related the time-dependent mass of solute in the probe depth to $\sigma_b$. They developed a calibration obtained by equating the specific mass of tracer applied to the difference in $\sigma_b$ before and after the application of the tracer pulse. This procedure was described by Ward et al. (1994) in Eq. [5] and [6].

MATERIALS AND METHODS

Our study used step change of solute as described by Shen et al. (1999). Two methods of estimating the mass balances for soil cores were compared. The first method was based on measured differences between input and effluent concentrations while the second method
used TDR measured $\sigma_a$ and the $\sigma_a-\theta_v-C_r$ relationship to estimate the change in $C_r$. The input-effluent equation:

\[
\text{Mass tracer} = \sum_{i=1}^{n} [(\text{input-effluent concentration}) \times \text{incremental effluent volume}] \quad [1]
\]

The TDR method required the determination of:

\[
\text{Mass tracer} = \sum_{j=1}^{m} \sum_{i=1}^{n} [\text{TDR estimated } C_r \times \theta_i \times \text{core volume}i_j] \quad [2]
\]

where $i$ refers to $m$ numbers of probe depths and $j$ to $n$ increments of effluent. The estimated mass of tracer was divided by the volume of solution in the core to determine $C_r$ using the following equation:

\[
\text{Volume of solution} = \sum_{i=1}^{n} [\text{TDR } \theta_i \times \text{volume represented by probe}_i] \quad [3]
\]

Initial concentration for the input-effluent mass balance was assumed to be the same as that measured by the TDR mass balance. The TDR probe concentration was calculated using Eq. [11] of Shen et al. (1999). Individual probe volumes were calculated from surface to midpoint between probes for the upper and lower probes and between midpoints above and below probes 2 to 4. Dissolution and precipitation of tracer or other solute were assumed negligible. Initial TDR $\sigma_a$ were adjusted (normalized) to packed core $\sigma_a$ values corresponding to measured $\sigma_a$ which tended to equalized initial $C_r$ estimates. This approach was supported by the work of Malants, et al. (1996) who found reference impedance underpredicted 50% using direct calibration approach with calibrations obtained on repacked soil columns.
RESULTS AND DISCUSSION

Core 2 Unsaturated Flow ($v = 0.6 \text{ cm hr}^{-1}$)

Both methods for determining mass balance have the same general shape as the effluent BTC (Fig. 1). The TDR mass balance and input-effluent mass balance agree within 0.2 gm at the point where tracer solution was switched and at the end of the run. The delayed initial response of the TDR mass balance compared to input-effluent mass balance was due to the time required for infiltrating tracer solution to reach the sphere of influence of the upper probe at 9.5-cm depth. A similar delay occurred when tracer solutions were switched. Vertical placement or additional probes located closer to the surface would reduce the difference in the response time for the two methods. Both mass balances lead the effluent BTC and lag the input concentration as expected. The general shape of both mass balances is similar to the shape of the effluent BTC since core volume ($\theta =$ constant) did not change and steady state flow conditions were maintained.

The two mass balances expressed as resident concentration had maximum values that were less than the maximum effluent concentration indicating that part of the soil solution was immobile (Fig. 2). The fractions of the soil solution volume in the mobile and immobile phases can be estimated by extending the slope of the peak of the mass BTC backward to pore volume=0. The BTC from both mass balance conform closely with the effluent BTC when lagged by the number of pore volumes indicated (Table 1).

Core 2 Saturated Flow ($v = 86 \text{ cm hr}^{-1}$)

The TDR measured $\sigma a$ differed among individual probe depths and from the effluent BTC (Fig. 3) but the two mass balance methods appear in general agreement (Fig. 4). Such
agreement between the two mass balance methods may at first appear surprising given the
divergence among individual TDR σa BTC and with σe BTC. The methods of determining
mass balance agree within 0.05 g L⁻¹ at the point when solutions were changed and at the end
of the experiment. Both methods had much lower r² values than the unsaturated flow case
indicating neither method accurately described the effluent BTC probably due to bypass flow
associated with the high flow rate (Table 1). The lagged input-effluent balance more closely
conformed to the effluent BTC than did the lagged TDR mass balance. Apparently the 5
TDR probes did not accurately reflect the average Cₑ for the core. Maximum Cₑ values
estimated by both mass balance methods were about half the maximum value of the Cₑ
indicating a high percentage of immobile soil solution possible associated with bypass flow.

Core 1 Unsaturated Flow (ν = 0.5 cm hr⁻¹)

The shape of both mass balance BTC related closely to the effluent BTC, but, as in Core
2 the maximum concentration of the mass balance BTC was less than the maximum
concentration for the effluent BTC (Fig. 5 and Table 1). By 1.5 pore volumes, effluent
concentration exceeded input concentration probably due to calibration error for the unit used
to measure effluent EC. Overestimation of effluent concentration would explain part of the
lower estimated input-effluent mass balance concentration compared with the TDR mass
balance, and also account for part of the underestimation of the final input-effluent mass
balance concentration. The input-effluent BTC leads the TDR BTC but the difference was
less than that observed for Core 2 unsaturated flow case because the upper probe was 5.5 cm
nearer the surface in Core 1 than in Core 2.
Core 1 Unsaturated Flow \((v = 5.6 \text{ cm hr}^{-1})\)

The pore volumes of tracer solution applied were insufficient for either effluent or mass balance BTC to approach a plateau either when input solutions were switched or at the end of the experiment (Fig. 6). The TDR mass balance over predicted solute concentration following the change in tracer concentrations at 1.3 pore volumes. The greater flow velocity and possibility of bypass flow may explain part of the discrepancy between TDR and input-effluent mass balance BTC (Table 1). The mass balance BTC leads the effluent BTC and the TDR mass balance concentration again lagged the input-effluent mass balance concentration.

Core 1 Saturated Flow \((v = 16.8 \text{ cm hr}^{-1})\)

The pore volumes of tracer solution applied were insufficient for either effluent or mass balance BTC to approach a plateau either when input solutions were switched or at the end of the experiment (Fig. 7). The maximum concentration of the TDR mass balance was less than half that of the input-effluent BTC which in turn was about half that of the effluent BTC. The probable explanation is that significant bypass flow occurred and that the TDR estimate of \(C_r\) did not accurately reflect the average \(C_r\) of the core. This implies that TDR estimated BTC may not accurately represent the mass balance or the effluent BTC under conditions of significant bypass flow as indicated by much lower \(r^2\) for TDR mass balance than for input-effluent mass balance. Thus bypass flow is probably when the TDR mass balance under predicts \(C_r\) estimated by the input-effluent mass balance. Therefore, comparison of the BTC estimated by the two methods may offer a way to assess the impact on solute movement of bypass flow.
CONCLUSIONS

TDR estimated mass balance calculated using normalized $\sigma_a$ agreed well with input-effluent mass balance indicating that TDR measured $\sigma_a$ and the $\sigma_a$-$\theta$-$C_r$ relationship together accurately estimated $C_r$ for flow velocities of 0.6 cm hr$^{-1}$ or less where bypass flow did not noticeable distort the TDR mass balance BTC. Accuracy of estimated generally decreased as flow velocity increased and as probability of bypass flow increased. TDR estimated mass balance agreed in general with effluent BTC if bypass flow was not apparent. Comparison of BTC generated by TDR and input-effluent mass balance provides a possible method of assessing the probability of occurrence and significance on solute transport of bypass flow. Neither mass balance method was closely correlated with effluent BTC at flow velocity of 86 cm hr$^{-1}$ indicating that changes in $C_r$ and $C_e$ were poorly related at high flow velocity apparently due to bypass flow. This implies that the TDR method of directly estimating effluent BTC is limited to conditions where bypass flow is minimal and where the TDR measurements of $\sigma_a$ are sufficiently numerous and probes are placed so as to accurately reflect changes in $C_r$.

REFERENCES


Table 1. Coefficients of linear relationship of lagged TDR mass budget and Input-Effluent Cr BTC to effluent BTC for solute transport measurements.

**Mass balance method**

<table>
<thead>
<tr>
<th>Core</th>
<th>Flow type</th>
<th>velocity $\text{cm hr}^{-1}$</th>
<th>$r^2$</th>
<th>TDR PV $\text{lagged}$</th>
<th>Input-Effluent $r^2$</th>
<th>PV $\text{lagged}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>unsaturated</td>
<td>0.5</td>
<td>0.979</td>
<td>0.29</td>
<td>0.981</td>
<td>0.29</td>
</tr>
<tr>
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<td>unsaturated</td>
<td>5.6</td>
<td>0.796</td>
<td>0.08</td>
<td>0.982</td>
<td>0.08</td>
</tr>
<tr>
<td>1</td>
<td>saturated</td>
<td>16.8</td>
<td>0.506</td>
<td>0.0</td>
<td>0.963</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>unsaturated</td>
<td>0.6</td>
<td>0.985</td>
<td>0.30</td>
<td>0.978</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>saturated</td>
<td>86.</td>
<td>0.464</td>
<td>0.0</td>
<td>0.723</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^1$ PV = Pore volume
Fig. 1. TDR estimated and input-effluent measured mass balance, and input and effluent concentrations plotted against effluent pore volume for Core #2 under unsaturated flow conditions with $v = 0.6$ cm hr$^{-1}$. 
Fig. 2. Effluent, input, and mass balance concentrations plotted against effluent pore volume for Core #2 under unsaturated flow conditions with $v = 0.6$ cm hr$^{-1}$. 
Fig. 3. Corrected TDR-measured bulk soil electrical conductivity ($\sigma_a$) for five depths and effluent electrical conductivity ($\sigma_e$) plotted against effluent pore volume for core #2 under saturated flow conditions.
Fig. 4. Effluent, input, and mass balance concentrations plotted against effluent pore volume for Core #2 under saturated flow conditions.
Fig. 5. Effluent, input, and mass balance concentrations plotted against effluent pore volume for Core #1 under unsaturated flow conditions ($v = 0.5 \text{ cm hr}^{-1}$)
Fig. 6. Effluent, input, and mass balance concentrations plotted against effluent pore volume for Core #1 under unsaturated flow conditions ($v = 5.6 \text{ cm hr}^{-1}$)
Fig. 7. Effluent, input, mass balance concentrations plotted against effluent pore volume for Core #1 under saturated flow conditions.
APPENDIX 2. COMPARISON OF TDR MEASURED SOIL BULK ELECTRICAL CONDUCTIVITY WITH EFFLUENT ELECTRICAL CONDUCTIVITY BREAK THROUGH CURVES.

INTRODUCTION

Recent literature contains several reports in which TDR measured soil bulk electrical conductivity, $\sigma_a$, break through curves, BTC, have been compared with effluent BTC. By analyzing BTC, Wraith et al. (1993) found that the TDR $\sigma_a$ waveform agreed well with Br$^-$ effluent BTC. Using nonlinear least squares fit of BTC to the Convective Dispersion Equation, CDE, they found the retardation factors, $R_f$, and dispersion coefficients, $D$, for $\sigma_a$ BTC were not significantly different from corresponding $R_f$ and $D$ values for effluent electrical conductivity, $\sigma_e$, and Br$^-$ BTC. Ward et al. (1994) used TDR to measure $\sigma_a$ at different depths in a layered soil column to obtain a measure of tracer resident concentration, $C_r$. They directly calibrated $C_r$ vs. $\theta_v$ and TDR measured $\sigma_a$ on packed soil columns and found that $C_r$ was linearly related to $\Delta\sigma_a$ depending on solute concentration and $\theta_v$. Since $\sigma_e$ is a nearly linear function of concentration over the range of our measurements, these results imply that $\sigma_e$ will be linearly related to $\sigma_a$ over a limited range of $\theta_v$ and solute concentrations. Ward et al. (1994) conducted one dimensional transport experiments on undisturbed columns of loamy sand (Typic Hapludalf) using step inputs of KCl with TDR measurements of $\sigma_a$ at five depths from 10 to 40 cm. They found a near linear increase in mean travel time, $\tau$, with depth and decreased amplitude of concentration and a broadening of the concentration BTC. Similar effects of depth on TDR measured resident concentration was observed by Hart and Lowery (1998) for Br- flux over the 15 to 75-cm depth in soil.
columns of Sparta sand under steady state flow conditions. Differences in TDR measurements on disturbed and undisturbed cores were reported by Malants, et al. (1996), who found reference impedance underpredicted 50% using a direct calibration approach compared with calibrations obtained on repacked soil columns.

Our objective was to assess the agreement between $\sigma_s$ and $\sigma_c$ BTC directly through correlation. The even spacing of TDR probes along the core allowed the displacement of TDR curves from effluent BTC curves to be determined with respect to depth.

**RESULTS AND DISCUSSION**

TDR measured $\sigma_s$ values were correlated with associated $\sigma_c$ BTC generated by step changes in tracer concentration. To account for differences in timing of penetration of the infiltrating solute due to location in the core, individual TDR measured $\sigma_s$ BTC were shifted (lagged) the specific numbers of pore volumes (PV) relative to the effluent BTC which maximized $R^2$. As a result, the two BTC share a common center of mass to a close approximation (Fig. 1-9). Slope and intercept coefficients were compared to determine whether effects due to depth in core, core treatment, and flow velocity were detectable (Table 1). For the nine measurements on three cores, $\sigma_c$ BTC and lagged TDR measured $\sigma_s$ were closely correlated for flow velocities <5.6 cm hr$^{-1}$, but were poorly correlated under saturated flow for most depths of undisturbed cores 1 and 2 (Table 1).

For unsaturated flow on undisturbed cores and saturated flow on the packed core the $\sigma_s$ BTC for individual depths were closely related to $\sigma_c$ BTC for the same core and flow
condition with the exception of the 18-cm depth of Core 1 with 5.6 cm hr\(^{-1}\) flow velocity.

This method gave a unique relationship of \(\sigma_s\) for individual depth, core, and flow condition with the associated \(\sigma_c\).

The packed core had the lowest standard error (se) for coefficients. The slopes (b defined as \(\Delta\sigma_s/\Delta\sigma_c\)) for the packed core were within one se for three of four core depths indicating that in these three cases core depth did not affect the accuracy of fitting the slope relationship between \(\sigma_s\) and \(\sigma_c\) BTC. However intercept (a) values differed among depths, implying that \(\sigma_s\) BTC were offset from each other in spite of the normalization of initial \(\sigma_s\) values to calibration \(\sigma_s\) values. The b values for undisturbed cores were more variable among depths. The lower and upper depths of core 1 and upper three depths of core 2 were within one se for flow velocity<0.6-cm hr\(^{-1}\). However increasing flow velocity for core 1 to 5.6 cm hr\(^{-1}\) increased the b values but upper and lower depths remained within one se. The b values and most a values for undisturbed cores were consistently greater by more than one se than those for the packed core indicating possible difficulty of using packed core calibration to represent undisturbed soils. For core 1 the b values generally increased with higher flow rate indicating greater movement of the infiltrating solution and less displacement of resident solution per unit of PV as flow rate increased. The opposite was observed for 30.5- and 37.5-cm depths in core 2 which may be partly explained by the incomplete BTC and lower R\(^2\) values with saturated flow. For both undisturbed cores the measured values for an individual core depth was affected by flow rate.
The number of relative PV the TDR BTC were lagged decreased with depth as expected and was linearly related to depth for flow velocities \(<6 \text{ cm hr}^{-1}\) (Table 2). The change in PV with core depth was the same for the two undisturbed cores for flow velocities \(<0.6\text{ cm hr}^{-1}\). This may represent similar replacement of resident solution with depth by the infiltrating solute. As flow velocity increased, the slope (PV cm\(^{-1}\)) and intercepts generally increased for Core No.1, possibly indicating less complete replacement of resident solution by the infiltrating solution with higher flow rate.

For flow velocity \(<0.6\text{ cm hr}^{-1}\) the TDR BTC had more rapid change in slope per unit PV than \(\sigma_e\) BTC and differences decreased with depth. This effect may be explained by the expected increase in dispersion with depth in the core as observed by Ward et al. (1994) and Hart and Lowery (1998).

**CONCLUSIONS**

1) For packed cores, effluent and TDR BTC were closely correlated in 3 out of 4 measurements over a range of core depths but TDR BTC were offset from each other. Most depths for undisturbed cores required individual calibrations of TDR and effluent BTC and the slope and intercept term for a given depth depended on flow velocity. This implies that development of calibrations of \(\sigma_e\) from measurements of \(\sigma_r\) on packed cores will not necessarily apply to undisturbed cores and that individual calibrations for depth and flow velocity may be required for undisturbed soil conditions. Under field conditions between site variation would apparently require a large number of replicated sites for
each depth to obtain an average calibration and to determine whether differences in calibration exist between soil depths.

2) Qualitative conclusions on the effect of depth on dispersion and on uniformity of dispersion with depth for individual cores was made by comparing changes with depth in the shape of lagged TDR BTC.

3) Uniformity of solute displacement with depth can be qualitatively assessed through the relationship of depth to number of PV $\sigma_x$ BTC must be lagged to conform to $\sigma_e$ BTC.

REFERENCES


Table 1. Regression of bulk soil electrical conductivity ($\sigma_a$) by depth on effluent electrical conductivity by core and flow type.

<table>
<thead>
<tr>
<th>CORE</th>
<th>FLOW Type</th>
<th>DEPTH cm</th>
<th>R2</th>
<th>LAG/LEAD</th>
<th>COEFFICIENTS$^8$</th>
<th>Pore Volume</th>
<th>a (se)</th>
<th>b (se)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed</td>
<td>Sat.</td>
<td>0.8</td>
<td>10</td>
<td>0.237 Lag</td>
<td>-1.742 (0.026)</td>
<td>3.100 (0.025)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>17</td>
<td>0.140 Lag</td>
<td>-1.856 (0.023)</td>
<td>3.325 (0.023)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24</td>
<td>0.072 Lag</td>
<td>-1.702 (0.012)</td>
<td>3.106 (0.011)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>31</td>
<td>0.0</td>
<td>-1.618 (0.011)</td>
<td>3.095 (0.011)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No. 1</td>
<td>Sat.</td>
<td>16.7</td>
<td>4</td>
<td>0.112 Lag</td>
<td>-8.42 (0.869)</td>
<td>11.26 (1.03)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18</td>
<td>0.0</td>
<td>6.08 (5.84)</td>
<td>-6.66 (7.66)</td>
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<td>-11.23 (5.70)</td>
<td>15.65 (7.29)</td>
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<td></td>
<td>32</td>
<td>0.0</td>
<td>-3.79 (1.99)</td>
<td>5.62 (2.34)</td>
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<td>No. 1</td>
<td>Unsat.</td>
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<td>4</td>
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<td>-1.88 (0.056)</td>
<td>3.27 (0.054)</td>
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<td>18</td>
<td>0.289 Lag</td>
<td>-2.19 (0.052)</td>
<td>4.27 (0.059)</td>
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<td>25</td>
<td>0.212 Lag</td>
<td>-2.10 (0.021)</td>
<td>3.43 (0.020)</td>
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<td></td>
<td></td>
<td>32</td>
<td>0.098 Lag</td>
<td>-2.07 (0.023)</td>
<td>3.33 (0.023)</td>
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</tr>
<tr>
<td>No. 1</td>
<td>Unsat.</td>
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<td>4</td>
<td>0.508 Lag</td>
<td>-1.75 (0.054)</td>
<td>3.29 (0.055)</td>
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<td>0.328 Lag</td>
<td>-2.43 (0.031)</td>
<td>4.15 (0.033)</td>
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<td>25</td>
<td>0.212 Lag</td>
<td>-1.96 (0.020)</td>
<td>3.43 (0.020)</td>
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<tr>
<td></td>
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<td>32</td>
<td>0.098 Lag</td>
<td>-1.95 (0.022)</td>
<td>3.33 (0.022)</td>
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<td>No. 1</td>
<td>Unsat.</td>
<td>2.4</td>
<td>4</td>
<td>0.082 Lag</td>
<td>-2.96 (0.072)</td>
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<td>11</td>
<td>0.113 Lead</td>
<td>-4.11 (0.197)</td>
<td>5.69 (0.201)</td>
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<td>18</td>
<td>0.456 Lead</td>
<td>-5.96 (0.353)</td>
<td>8.33 (0.410)</td>
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<td>25</td>
<td>0.082 Lead</td>
<td>-3.63 (0.133)</td>
<td>5.02 (0.137)</td>
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<tr>
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<td>32</td>
<td>0.082 Lead</td>
<td>-2.75 (0.063)</td>
<td>4.11 (0.065)</td>
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<td>Unsat.</td>
<td>4.7</td>
<td>4</td>
<td>0.10 Lead</td>
<td>-4.99 (0.260)</td>
<td>6.61 (0.272)</td>
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<tr>
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<td>11</td>
<td>0.93 Lead</td>
<td>-7.97 (0.447)</td>
<td>10.04 (0.483)</td>
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<td>18</td>
<td>0.76 Lead</td>
<td>-16.47 (1.18)</td>
<td>20.90 (1.37)</td>
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<tr>
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<td>25</td>
<td>0.10 Lead</td>
<td>-3.33 (0.104)</td>
<td>4.85 (0.109)</td>
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<td>32</td>
<td>0.16 Lead</td>
<td>-2.98 (0.072)</td>
<td>4.33 (0.072)</td>
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<td>No. 1</td>
<td>Unsat.</td>
<td>5.6</td>
<td>4</td>
<td>0.113 Lag</td>
<td>-2.68 (0.081)</td>
<td>4.30 (0.088)</td>
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<td>-1.96 (0.666)</td>
<td>3.86 (0.808)</td>
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<td>25</td>
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<td>-3.30 (0.171)</td>
<td>4.84 (0.182)</td>
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<td>32</td>
<td>0.052 Lead</td>
<td>-2.70 (0.061)</td>
<td>4.17 (0.064)</td>
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Table 1. Continued

<table>
<thead>
<tr>
<th>CORE</th>
<th>FLOW DEPTH R2 LAG/LEAD COEFFICIENTS$</th>
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</thead>
<tbody>
<tr>
<td>Type</td>
<td>Velocity cm hr$^{-1}$ cm Pore Volume a (se) b (se)</td>
</tr>
<tr>
<td>No. 2</td>
<td>Sat. 86.1</td>
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<tr>
<td>9.5</td>
<td>0.295</td>
</tr>
<tr>
<td>16.5</td>
<td>0.170</td>
</tr>
<tr>
<td>23.5</td>
<td>0.189</td>
</tr>
<tr>
<td>30.5</td>
<td>0.905</td>
</tr>
<tr>
<td>37.5</td>
<td>0.730</td>
</tr>
</tbody>
</table>

| No. 2 | Unsat. 0.6 |
| 9.5 | 0.978 | 0.501 Lag | -1.80 (0.055) | 3.39 (0.058) |
| 16.5 | 0.989 | 0.395 Lag | -1.89 (0.040) | 3.42 (0.041) |
| 23.5 | 0.995 | 0.296 Lag | -1.94 (0.027) | 3.37 (0.027) |
| 30.5 | 0.995 | 0.203 Lag | -2.03 (0.026) | 3.55 (0.028) |
| 37.5 | 0.994 | 0.105 Lag | -2.07 (0.027) | 3.84 (0.031) |

$^*$ Coefficients a and b from equation Effluent EC=a+b*(TDR Soil Bulk EC)

Table 2. Correlation of depth in core with number of pore volumes (PV) TDR measured soil bulk electrical conductivity lagged .

<table>
<thead>
<tr>
<th>CORE</th>
<th>FLOW COEFFICIENTS$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Velocity cm hr$^{-1}$ PV PV cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>a b R$^2$</td>
</tr>
<tr>
<td>Packed</td>
<td>sat. 0.8</td>
</tr>
<tr>
<td>0.34</td>
<td>-0.011</td>
</tr>
<tr>
<td>No. 1</td>
<td>unsat. 0.5</td>
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<tr>
<td>0.54</td>
<td>-0.014</td>
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<tr>
<td>No. 1</td>
<td>unsat. 5.6</td>
</tr>
<tr>
<td>0.13</td>
<td>-0.006</td>
</tr>
<tr>
<td>No. 2</td>
<td>unsat. 0.6</td>
</tr>
<tr>
<td>0.63</td>
<td>-0.014</td>
</tr>
</tbody>
</table>

$^*$ Coefficients a and b from equation PV = a + b*depth (cm)