Estimating soil solute transport under transient water flow conditions using time domain reflectometry
by Patricia Dawn Risler

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Soils
Montana State University
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Abstract:
Prediction and monitoring of solute movement through soils are critical to research and management. Current techniques for monitoring chemical transport are often destructive and time-consuming. Time domain reflectometry (TDR) has become a reliable method of simultaneously and non-invasively measuring in situ soil volume water content (θv) and bulk electrical conductivity (ςa). Recent studies comparing TDR ςa measurements to effluent analyses found TDR to be a practical alternative method for monitoring ionic chemicals under steady flow conditions. Extending these techniques to transient water flow conditions is necessary for monitoring solute transport under natural flow regimes. The objectives of this study were to evaluate the potential of exploiting a previously reported simplified soil-specific relationship between θv and ςa for estimation of soil solution electrical conductivity (ςw), and to apply this relationship to monitoring ionic soil solute transport under transient flow conditions using automated TDR. This relationship was applied to repacked soil column and field transport studies conducted under transient flow conditions. TDR ςw breakthrough curves (BTCs) were compared to BTCs obtained with conventional soil solution collection and analysis procedures. Agreement between TDR ςw and effluent fraction BTCs was generally good. Regions where TDR ςw did not match the effluent curves corresponded to θv extremes during the transient flow cycle. This may be the result of inherent limitations of the simplified relationship in overcompensating for θv In the field, it was difficult to. discern between the influences of fluctuating water and temperature, and discrepancies may also be due to an incomplete temperature compensation. The detailed TDR ςw BTCs had much less scatter and are an advantage over time-consuming effluent analyses. However, quantitative comparison of TDR ςw to effluent BTCs is not straightforward under transient flow because of the lack of an appropriate comparative method. Initial results are quite promising with respect to monitoring ionic solutes, but additional work will be required before this methodology may be applied as an alternative to related steady flow techniques for determination of model transport parameters.

ESTIMATING SOIL SOLUTE TRANSPORT UNDER TRANSIENT WATER FLOW CONDITIONS USING TIME DOMAIN REFLECTOMETRY

by

Patricia Dawn Risler

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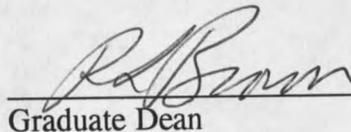12-15-94
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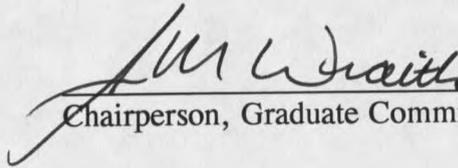
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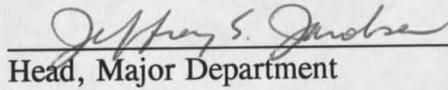
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VITA

Patricia Dawn Risler was born on November 18, 1969 in Mondovi, Wisconsin to Allen "Pat" and Nancy Risler. Patty grew up on her parents' dairy farm and was very active in 4-H and FFA. Patty attended Sacred Heart Catholic School in Mondovi during elementary years, and completed Junior and Senior High at Mondovi Public Schools.

Upon graduation from high school, Patty attended college at University of Wisconsin - River Falls where she completed a Bachelor's Degree in Soil Science in May, 1992. In August, 1992, Patty began her Master's program in Soil Science at Montana State University under the guidance of Dr. Jon M. Wraith. On April 22, 1995, Patty will marry Douglas George in Mondovi, Wisconsin.

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NOMENCLATURE

BTCs	Breakthrough curves
CDE	Convective-dispersive equation
PVC	Polyvinyl chloride
TDR	Time domain reflectometry
C_R	Resident concentration
D	Dispersion coefficient ($cm^2\ h^{-1}$ or $cm^2\ d^{-1}$)
K	Bulk dielectric constant
M_1	First time-moment
M_2	Second time-moment
R_f	Retardation factor
T	Transmission coefficient
v	Mean pore water velocity ($cm\ h^{-1}$ or $cm\ d^{-1}$)
θ_v	Volume soil water content ($m^3\ m^{-3}$)
λ	Dispersivity (cm)
σ	Electrical conductivity ($dS\ m^{-1}$)
σ_a	Bulk soil electrical conductivity ($dS\ m^{-1}$)
σ_s	Bulk soil surface electrical conductivity ($dS\ m^{-1}$)
σ_w	Soil solution electrical conductivity ($dS\ m^{-1}$)

ABSTRACT

Prediction and monitoring of solute movement through soils are critical to research and management. Current techniques for monitoring chemical transport are often destructive and time-consuming. Time domain reflectometry (TDR) has become a reliable method of simultaneously and non-invasively measuring *in situ* soil volume water content (θ_v) and bulk electrical conductivity (σ_a). Recent studies comparing TDR σ_a measurements to effluent analyses found TDR to be a practical alternative method for monitoring ionic chemicals under steady flow conditions. Extending these techniques to transient water flow conditions is necessary for monitoring solute transport under natural flow regimes. The objectives of this study were to evaluate the potential of exploiting a previously reported simplified soil-specific relationship between θ_v and σ_a for estimation of soil solution electrical conductivity (σ_w), and to apply this relationship to monitoring ionic soil solute transport under transient flow conditions using automated TDR. This relationship was applied to repacked soil column and field transport studies conducted under transient flow conditions. TDR σ_w breakthrough curves (BTCs) were compared to BTCs obtained with conventional soil solution collection and analysis procedures. Agreement between TDR σ_w and effluent fraction BTCs was generally good. Regions where TDR σ_w did not match the effluent curves corresponded to θ_v extremes during the transient flow cycle. This may be the result of inherent limitations of the simplified relationship in over-compensating for θ_v. In the field, it was difficult to discern between the influences of fluctuating water and temperature, and discrepancies may also be due to an incomplete temperature compensation. The detailed TDR σ_w BTCs had much less scatter and are an advantage over time-consuming effluent analyses. However, quantitative comparison of TDR σ_w to effluent BTCs is not straightforward under transient flow because of the lack of an appropriate comparative method. Initial results are quite promising with respect to monitoring ionic solutes, but additional work will be required before this methodology may be applied as an alternative to related steady flow techniques for determination of model transport parameters.

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CHAPTER ONE

INTRODUCTION

Movement of soluble chemicals through soils is an important environmental concern for many industries and farmers. The fate of soil-applied fertilizers, pesticides, and other chemicals needs to be monitored and predicted to facilitate development of preventative and remedial water quality procedures and policies. Transport parameters estimated from solute breakthrough curves (BTCs) provide useful information for predicting fate and transport of chemicals in soils, but it is often difficult to obtain detailed and reliable BTCs.

Hydraulic and chemical transport properties of intact field soils play a critical role in unsaturated transport phenomena. However, *in situ* field measurements of relevant transport properties have often been considered approximate values because of the simplifying assumptions used in many field methods and the difficulty in collecting undisturbed soil samples for laboratory use (Nielsen et al., 1986).

Time domain reflectometry (TDR) has become recognized as a potential means of accurately and non-destructively monitoring ionic solute transport in soil columns or field profiles (Kachanoski et al., 1992; Wraith et al., 1993; Ward et al., 1994). The application of automated TDR has allowed simultaneous and unattended measurement of *in situ* soil water content and soil salinity, providing an alternative method to often destructive and time-consuming procedures which have conventionally been used.

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Many solute transport studies have been conducted under unsaturated steady-state flow conditions, but most contamination and leaching occurs under transient flow regimes. Evaluation of solute transport characteristics under transient water flow conditions is necessary to quantify the movement of fertilizers and other chemicals. There is therefore substantial need for a relatively simple method of estimating solute transport parameters in laboratory and field applications.

Literature Review

Electrical conductivity (σ) is a measure of soil salinity and can be used to detect and quantify the presence of certain solutes. Conventional methods of measuring soil salinity are often destructive and time-consuming, and do not lend themselves to continuous field determinations. Shea and Luthin (1961) developed a method of measuring soil salinity *in situ* with the four-electrode probe, but the relationship they developed between soil salinity and σ was limited to water contents ranging from saturation to 30 cm tension. After further investigations by Rhoades and Ingvalson (1971), it was recommended that σ measurements be taken at field capacity soil water content for increased accuracy of the four-electrode probe measurement because their proposed relationship between soil conductivity and soil salinity was established for specific soils at a known volume water content (θ_v). They suggest that field capacity is a reasonably reproducible θ_v that occurs throughout the year following irrigation or rainfall.

The application of TDR has provided an ability to simultaneously measure θ_v and bulk electrical conductivity (σ_a) in soils with relatively high accuracy and precision. Topp et al. (1980) developed a correlation between the apparent bulk dielectric constant (K) and

θ_v, and found little dependence of the relationship on mineralogy, bulk density, or salinity status. Topp et al. (1984) subsequently confirmed the independence of K with respect to soil texture. TDR has since become a well-accepted and established method for measuring θ_v (Dalton, 1992; Zegelin et al., 1992; Dane and Molz, 1991).

During their investigations of the relationship between K and θ_v, Topp et al. (1980) detected an attenuation of the TDR signal in saline soil. This attenuation was found to be independent of the transit time used for measuring θ_v, thus allowing the simultaneous and independent measurement of θ_v and σ_a (Dalton et al., 1984; Topp et al., 1988; Zegelin et al., 1989). This provides moisture and salinity data from the same sampling volume (Dalton and van Genuchten, 1986).

Recent applications concerning soil salinity measurement using TDR have focused on relationships previously developed using the four-electrode probe, although Nadler et al. (1991) have recommended the use of TDR over the four-electrode probe for monitoring σ_a because the attenuation of the TDR electromagnetic pulse is insensitive to the presence of a quality contact between the soil and probe.

Because plant responses as well as fate and transport of soluble chemicals are more directly related to soil solution electrical conductivity (σ_w) than to σ_a, considerable effort has gone towards characterizing the relationships between these variables in soil-water systems (Rhoades et al., 1976; Nadler and Frenkel, 1980; Shainberg et al., 1980; Bohn et al., 1982). Rhoades et al. (1976) developed a soil-specific linear relationship between σ_a and σ_w to account for the effect of varying water content:

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

where T is a soil-specific transmission coefficient which accounts for soil tortuosity and decreases in ion mobility near solid/liquid and liquid/gas interfaces, and σ_s is the bulk surface conductivity which is comprised of the contribution of exchangeable ions at the solid/liquid interface. Similar results were found when Bohn et al. (1982) compared this macroscopic approach to microscale soil electrical conduction. Nonlinearity of this relationship has been identified in the low salinity range ($< \sim 4$ dS m^{-1}, depending on soil texture) (Shainberg et al., 1980; Nadler and Frenkel, 1980). However, Rhoades et al. (1989) did not find significant deviation until σ_w became less than about 1 dS m^{-1} in 12 soils varying in texture from sand to clay.

Some recent investigations have evaluated the potential for monitoring solute breakthrough under steady flow conditions using TDR. Kachanoski et al. (1992) monitored solute transport through soils in the field and laboratory under an imposed steady flow regime using TDR. Similar results were obtained when mass breakthrough curves (BTCs) from column effluent samples and field solution samples were compared to TDR σ_a values resulting from the addition of a Cl$^-$ pulse. Wraith et al. (1993) found TDR to be a reliable means of determining steady-state Br$^-$ transport parameters in intact soil columns when TDR-estimated σ_a, effluent Br$^-$ concentration, and effluent σ_w BTCs were compared. Upon fitting the BTCs to the convective-dispersive equation (CDE) using CXTFIT (Parker and van Genuchten, 1984), no significant differences were found among the estimated retardation factors (R_f) for the σ_a (observed and temperature-corrected), Br$^-$,

and effluent σ_w data. Dispersion coefficients (D) for both TDR σ_a BTCs were not different from those based on Br⁻ and effluent σ_w, but D for effluent σ_w was lower than for Br⁻. Ward et al. (1994) monitored Cl⁻ transport through intact soil columns under steady-state conditions by relating TDR σ_a to resident Cl⁻ concentration (C_R). They reported that fitting the measured BTC to the CDE revealed underestimation of C_R (by the CDE) near the end of the BTC in their measurements.

These studies were all conducted, in part, to avoid the limitations of using solution samplers for estimation of solute transport. The common practice of soil solution extraction using porous samplers poses well-known problems for laboratory and field use (van Der Ploeg and Beese, 1977; Nagpal, 1982; Barbee and Brown, 1986; Lord and Shepherd, 1993). The insufficient number of solution samples that may practically be collected, particularly as the soil desaturates, as well as the prohibitive cost of solution samplers plus sample analysis, create substantial limitations in their application (Ward et al., 1994). Hansen and Harris (1975) found variability in porous cup samples due to long sampling intervals, differences in intake rate, plugging, and variable initial vacuum.

Solute movement through soils may be successfully predicted using computer simulation models, but transient flow models are often avoided because they are relatively complicated. However, transient solute flow can often be approximated with good success using simpler steady-state models (Wierenga, 1977; Beese and Wierenga, 1980). Transient solutions require extensive computer time and additional input information which makes such models more difficult and time-consuming to use. The additional input data often require knowledge of hydraulic conductivity and water retention relationships which

are not always available (Wierenga, 1977). Wierenga (1977) and Beese and Wierenga (1980) concluded that the behavior of noninteracting solutes under transient flow may be approximated using a steady-state flow model, and smooth BTCs were obtained when predicted solute concentration was plotted versus cumulative drainage, rather than time. Also, Beese and Wierenga (1980) and Destouni (1991) found increased agreement between the two flow modeling approaches when root water uptake was included for prediction of solute arrival throughout the soil profile, and differences between the models decreased with an increase in distance from the soil surface. However, even though we may often predict (model) solute transport under transient flow conditions using a simpler steady flow approach, it is critical that we have the ability to monitor such movement under actual conditions of variable soil water content and temperature regimes. If estimation of transport parameters is required, resultant BTCs can be fitted to the one-dimensional CDE (Parker and van Genuchten, 1984), or evaluated by moment analysis (Jury and Sposito, 1985; Valocchi, 1985).

As in many of the studies previously described, laboratory investigations often involve substantial modification of soil pore size distribution, which creates valid concern when evaluating repacked column experiments. Although original field bulk density may be regained, soil structure and the flow paths it provides are destroyed upon repacking. Nadler (1991) investigated this problem by determining σ_a and θ_v at two salinity levels using TDR and four-electrode probe techniques, as compared to conventional σ_a and θ_v methods, on three well-structured soils and one weakly structured soil in the field. The salinity levels were chosen to include the range of expected nonlinearity between σ_a and

σ_w. Measurements were subsequently repeated on the same soils in the laboratory. A portion of these soils were slightly disturbed through repacking to original bulk density while other samples were severely disturbed by drying, grinding, sieving (< 2 mm), and spraying with distilled water to obtain field θ_v. Minimal differences were found in σ_a between the undisturbed and disturbed soils. This result was perhaps not surprising, as the electromagnetic pulse interacts with ions in soil solution, rather than through direct soil contact. Therefore, laboratory column studies may provide valuable data with respect to salinity status when field work is inappropriate or inaccessible.

Structural changes do have strong influence on water movement through the soil profile. The magnitude of hydraulic conductivity is influenced by soil structure and the related macroporosity of the soil. Increased tillage breaks down soil structure and reduces the volume of macropores, resulting in decreased surface soil hydraulic conductivity (Cresswell et al., 1992). Preferential flow results in rapid, downward solute movement which may lead to unexpected groundwater contamination (Bouma, 1991). Repacked laboratory column experiments disregard the possibility of preferential flow due to the disruption of macropores, soil cracks, or biological activity. Estimation of transport parameters from repacked column experiments may therefore not yield accurate assessments of solute transport under natural soil conditions and flow regimes.

Thesis Objectives

The objectives of this research were 1) to evaluate the feasibility of exploiting a previously reported, simplified, soil-specific relationship between θ_v and σ_a for determination of σ_w, and 2) to apply this relationship to monitoring the transport of ionic

soil solutes under transient flow conditions using TDR. Field and repacked laboratory soil column experiments were conducted, with conventional methods of solute collection and analysis compared to results of experimental TDR techniques using several soils and salinity levels.

CHAPTER TWO

TIME DOMAIN REFLECTOMETRY ESTIMATION OF SOLUTE TRANSPORT DURING TRANSIENT FLOW THROUGH SOIL COLUMNS

Introduction

The development of effective water quality procedures and policies requires the ability to monitor and predict solute movement through soils. Transport parameters determined from solute breakthrough curves (BTCs) provide useful predictive information, but it is often difficult to obtain detailed and reliable BTCs. Hydraulic and chemical transport properties of intact field soils play a critical role in unsaturated transport phenomena. However, *in situ* field measurements of relevant transport properties have often been considered approximate values because of the simplifying assumptions used in many field methods and the difficulty in collecting undisturbed soil samples for laboratory use (Nielsen et al., 1986).

Time domain reflectometry (TDR) has become recognized as a potential means of accurately and non-destructively monitoring solute transport in soil columns or field profiles. Recent investigations have evaluated the potential for monitoring solute BTCs under steady flow conditions using TDR. Kachanoski et al. (1992) were able to characterize the Cl⁻ mass BTC when measured TDR bulk soil electrical conductivity (σ_a) values were compared to effluent samples from a Cl⁻ pulse. Wraith et al. (1993) compared TDR σ_a measurements to effluent sample Br⁻ concentrations (ion chromatograph) and soil

solution electrical conductivity (σ_w) (conductivity bridge). Dispersion coefficient (D) and retardation factor (R_f) parameters based on fitting TDR σ_a data to the convective-dispersive equation (CDE) were not different from those estimated using effluent samples. Ward et al. (1994) monitored solute transport through intact soil columns during steady flow using TDR by relating σ_a to resident Cl⁻ concentration (C_R). Their measured BTC closely matched a BTC based on the CDE, with only slight underestimation of C_R near the end of the BTC.

The use of TDR to detect changes in σ_a during steady-state flow of ionic chemicals through soils therefore appears practical, but extending current TDR techniques to transient flow conditions is desirable for monitoring ionic solutes under natural flow regimes. The common practice of soil solution extraction using porous samplers poses well-documented problems for field and laboratory use (van Der Ploeg and Beese, 1977; Nagpal, 1982; Barbee and Brown, 1986; Lord and Shepherd, 1993). The limited number of solution samples which may be acquired, particularly as the soil desaturates, as well as the prohibitive cost of solution samplers themselves plus analysis of acquired samples, create substantial limitations in their application (Ward et al., 1994). Sample variability also makes the use of porous ceramic solution samplers unfavorable (Hansen and Harris, 1975); however, few practical alternative methods exist.

The objectives of this study were to evaluate the potential to exploit a previously reported simplified soil-specific relationship between volume water content (θ_v) and σ_a for determination of σ_w, and to apply this relationship to monitoring the transport of ionic solutes through soils under transient flow conditions. Repacked soil column experiments

were conducted, with conventional methods of solute collection and analysis compared to results of a proposed technique based on TDR estimates of σ_w.

Materials and Methods

<u>Theory</u>

Many soil reactions of importance to the fate and transport of soluble chemicals in soils are more directly related to σ_w than to σ_a, and considerable effort has gone towards characterizing the relationships between these variables in soil-water systems (Rhoades et al., 1976; Shainberg et al., 1980; Nadler and Frenkel, 1980; Bohn et al., 1982). A simplified relationship between σ_a and σ_w to account for the effects of variable θ_v in specific soils is given by Rhoades et al. (1976)

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

where T is a soil-specific transmission coefficient which accounts for soil tortuosity and decreases in ion mobility near solid/liquid and liquid/gas interfaces, and σ_s is the surface conductivity which is comprised of the contribution of exchangeable ions at the solid/liquid interface. This simplified relationship does not require specific knowledge of soil physical/chemical properties (particle size distribution, clay mineralogy, etc.). Nonlinearity in this relationship has been identified in the low salinity range ($< \sim 4$ dS m^{-1}, depending on soil texture) (Shainberg et al., 1980; Nadler and Frenkel, 1980). However, Rhoades et al. (1989) did not find significant deviation from linearity until σ_w became less than about 1 dS m^{-1} in 12 soils of varying texture.

If θ_v and σ_a are simultaneously monitored during successive soil wetting and drying

at constant known σ_w, T and σ_s may be determined using eq. [1] by linear regression of σ_a against $(\sigma_w \cdot \theta_v)$. With T and σ_s known, eq. [1] may be rearranged as

$$\sigma_w = \frac{\sigma_a - \sigma_s}{T\,\theta_v} \qquad [2]$$

for estimation of unknown σ_w during transient water and chemical flow in the same soil.

Experimentation

Column transport studies were conducted under transient flow conditions using fine-to-very fine silica sand (grade 70 silica sand sieved through 149 μm screen), a Bridger loam soil (fine, mixed Argic Cryoborolls), and surface and subsurface horizons of Kalsted sandy loam soil (coarse-loamy, mixed Borollic Calciorthids). Polyvinyl chloride (PVC) columns were packed with soil (Table 1) and sealed at both ends using Plexiglas caps.

Table 1. Relevant characteristics and dimensions of repacked soil columns.

Soil Type	Soil Height (m)	Soil Diameter (m)	Bulk Density (Mg m^{-3})	Waveguide Length (m)
V-Fine Sand	0.33	0.15	1.44	0.15
Kalsted A	0.32	0.15	1.45	0.15
Kalsted B	0.21	0.05	1.47	0.043
Bridger	0.21	0.05	1.34	0.043

Column setup and waveguide construction are detailed in Wraith et al. (1993), and their schematic diagram (Wraith et al., 1993; Fig. 2) illustrates the automated TDR acquisition and analysis apparatus used in these investigations. Constant temperature was

maintained by wrapping each column in polyethylene tubing for circulation of water at 25°C (RTE-220D, Neslab Instruments, Inc., Newington, NH[1]). The tubing and column were then covered with aluminum foil and spun fiberglass insulation. One TDR waveguide was installed horizontally 4 cm from the bottom of each column (see Wraith et al., 1993; Fig. 2). The repacked columns were then connected to a vacuum chamber apparatus (Soil Measurement Systems, Tucson, AZ), and preconditioned by flushing with $CaCl_2$ solution (Table 2) until constant effluent σ_w was attained. Eluants for the Kalsted B and Bridger loam soil columns also contained 0.1% liquid bleach to inhibit growth of microorganisms.

Table 2. Salinity attributes during column conditioning and transport.

Soil Type	$CaCl_2$ Matrix (dS m^{-1})	Effluent σ_w[†] (dS m^{-1})	Br Pulse (dS m^{-1})
V-Fine Sand	1.00	1.00	5.96[‡]
Kalsted A	0.53	0.74	3.91[§]
Kalsted B	0.87	1.04	3.89[§]
Bridger	0.87	1.32	3.89[§]

[†]Used in calculation of T and σ_s.
[‡]As LiBr
[§]As KBr

After conditioning the soil columns, an electronic datalogger (21X, Campbell Scientific, Inc., Logan, UT) was utilized to deliver a quasi-sinusoidal eluant application rate by controlling a power relay to a precision low flow syringe pump (Soil Measurement

[1]Mention of company names or commercial products is for the convenience of the reader and does not imply endorsement.

Systems, Tucson, AZ). Soil θ_v and σ_a were continuously monitored over several wetting and drying cycles using automated TDR (Wraith et al., 1993). T and σ_s were then estimated using eq. [1] based on measured changes in θ_v and σ_a at constant σ_w. This procedure was repeated for several σ_w levels to evaluate consistency in calculated values for T and σ_s.

TDR estimation of σ_a was based on the Giese and Tiemann (1975) approach as modified by Topp et al. (1988):

$$\sigma_{GT} = \frac{Z_o}{120 \, \pi \, L \, Z_L} \qquad [3]$$

with the probe impedance (Z_o) determined by immersing each probe in deionized water (25°C) having negligible conductivity and known dielectric (Heimovaara, 1992; Baker and Spaans, 1993), the resistive impedance load (Z_L) across the embedded probe calculated using the simplified waveform analysis procedure developed by Wraith et al. (1993), and L being the length (m) of the TDR probe.

Following addition of a Br⁻ pulse (Table 2), BTCs were monitored in the soil columns by continuously measuring σ_a and θ_v. These were measured at intervals of 2 to 10 minutes, depending on soil and flow rate. Effluent was collected over pre-determined time intervals by a fraction collector (Retriever II, ISCO, Lincoln, NE) housed within the vacuum chamber. One to three pore volumes of background $CaCl_2$ solution were flushed through the column before and after addition of the Br⁻ pulse. TDR estimates of σ_w using eq. [2] were compared with Br⁻ concentration in effluent samples as analyzed using a

Dionex 4000i ion chromatograph (Dionex Corp., Sunnyvale, CA) with a Dionex AS4A

column, or a Br⁻-specific electrode with Orion pH meter (Model 720A, Orion Research

Inc., Boston, MA). Measurements of σ_w determined at 25°C using a conductivity bridge

(Model 4010, Jenway Ltd., Essex, England) were also made on all effluent fractions for

comparative purposes. All solute concentration indices were expressed in relative form

$[(C-C_{min})/(C_{max}-C_{min})]$ for presentation and comparison of BTCs.

Transport parameters were estimated from each BTC by fitting the measured data

to the CDE using the computer program CXTFIT (Parker and van Genuchten, 1984), and

by time-moment analysis (Jury and Sposito, 1985; Valocchi, 1985). Resident

concentration mode was employed in CXTFIT for TDR σ_w while the effluent BTCs were

considered as measures of flux-averaged concentration. D, R_f, and mean pore water

velocity (v) for each BTC were fitted for comparative purposes. Two scenarios were

examined in the CXTFIT analyses. In the first run, R_f was fixed to 1.0 while v and D

were fitted to measured BTCs. R_f and D were subsequently fitted, with v fixed to a

predetermined value. This value of v ($v=J_w/\theta_v$, where J_w is water flux density) was

averaged over a single 48 hour sinusoidal water application cycle by measuring the volume

of eluant pumped into the column and by averaging measured θ_v over the duration of each

measured BTC.

All BTCs were also evaluated using time-moment analysis

$$M_n = \frac{\int\limits_0^\infty t^n \bar{C}(t)\,dt}{\int\limits_0^\infty \bar{C}(t)\,dt} \qquad\qquad [4]$$

where M_n is the nth normalized time-moment, t is the travel time to measurement depth Z, and $\bar{C}(t)$ is mean concentration at time t. M_1 is then the mean travel time to the measurement depth, and M_2 is the variance of the distribution. From these time-moments, CDE transport parameters v and D were calculated as

$$v = \frac{Z}{M_1} \qquad\qquad [5]$$

and

$$D = \frac{Z^2}{2}\frac{(M_2 - M_1^2)}{M_1^3} \qquad\qquad [6]$$

The method of moments does not assume a particular transport model formulation. Utilization of both CXTFIT and time-moment analysis therefore provides independent estimates of D and v.

Results and Discussion

Calculated T and σ_s

Changes in measured σ_a corresponded closely to θ_v during cyclic wetting and drying (Fig. 1) because water is an excellent electrical conductor that modifies σ_a even

under constant σ_w. Figure 2 illustrates estimation of T and σ_s from these transient wetness data by linear regression using eq. [1]. The consistency of T and σ_s estimation was evaluated under several σ_w levels (Table 3) within and outside the reported nonlinearity range of $< \sim 4$ dS m^{-1} (Shainberg et al., 1980; Nadler and Frenkel, 1980). The calculated values of T were generally somewhat different from one another (Table 3), but were within 22% of the mean value for each soil. No consistent relationships between T and σ_w or σ_s and σ_w were evident. Sensitivity of the estimated TDR σ_w BTCs was then evaluated by applying eq. [2] to measured θ_v and σ_a data using each pair of T and σ_s values from Table 3. The resulting σ_w BTCs were not substantially altered by this range in paired T and σ_s values. It is therefore concluded that the relationship of Rhoades et al. (1976) appears practical for estimating T and σ_s even at relatively low salinity levels for subsequent determination of TDR σ_w BTCs.

TDR and Effluent BTCs

Raw transient flow BTCs as measured using TDR (i.e., σ_a vs. time) (Fig. 3) corresponded closely to θ_v as expected and as discussed above. Estimated TDR σ_w BTCs generally agreed well with those based on effluent fractions (Figs. 4-7). The earlier Br$^-$ breakthrough for TDR σ_w compared to the effluent BTCs in some cases was expected due to the vertical difference in measurement location. Regions where TDR σ_w did not match the effluent curves correspond to θ_v extremes during the transient flow cycle. Greatest discrepancies exist where low θ_v occurred during peak Br$^-$ concentrations (Figs. 6,7). This may be due to inherent limitations of eq. [2] in over-compensating for θ_v and/or to differences in resident and flux-averaged Br$^-$ concentrations as intensified by
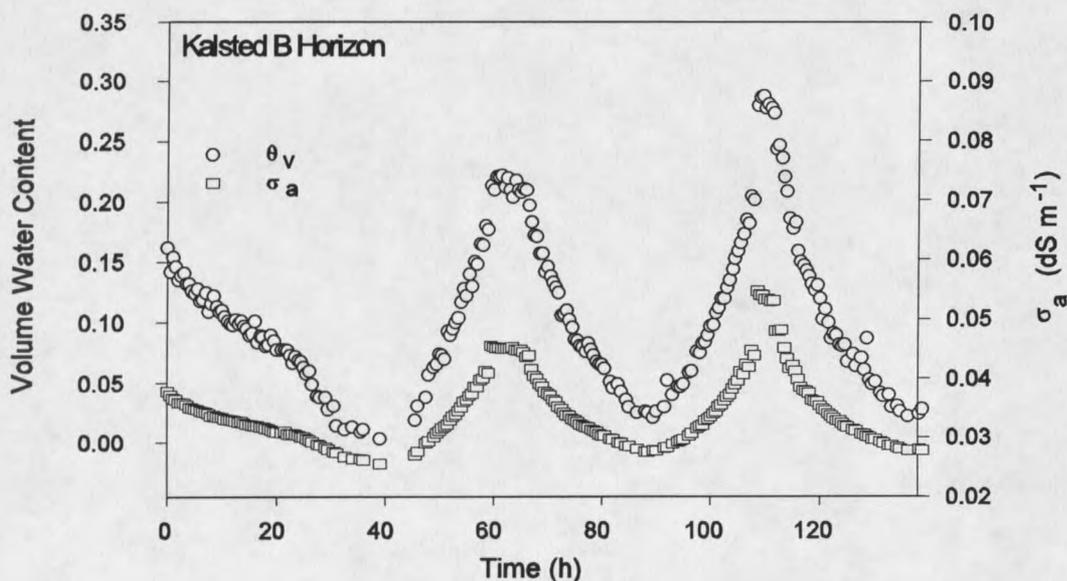
Fig. 1. Measured volume water content (θ_v) and bulk soil electrical conductivity (σ_a) during cyclic wetting and drying of Kalsted sandy loam B horizon soil for estimation of transmission coefficient (T) and surface conductivity (σ_s). Background $CaCl_2$ solution conductivity (σ_w) was 1.04 dS m^{-1}.
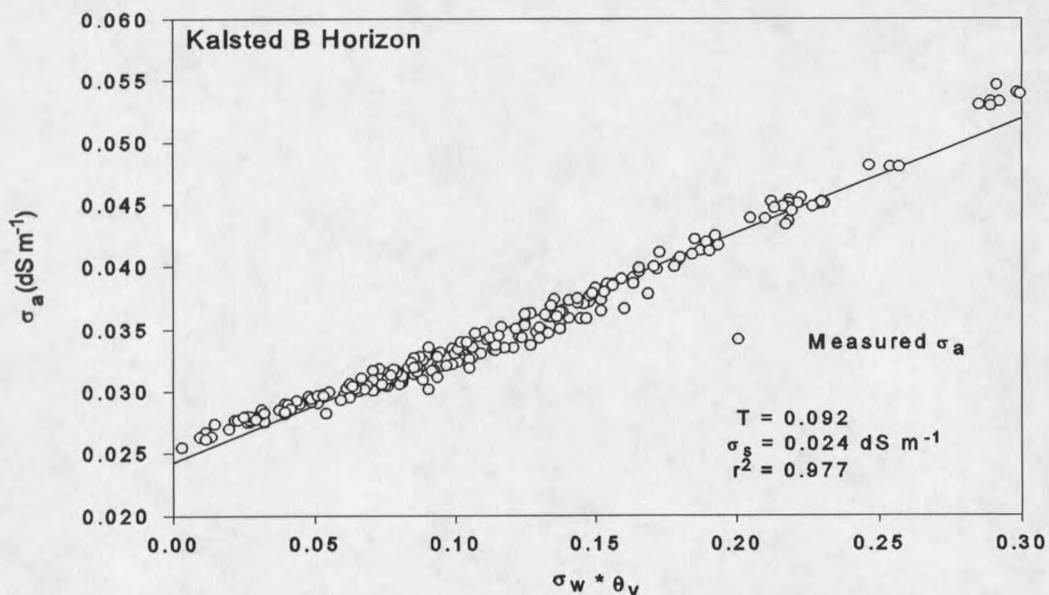

Fig. 2. Linear regression results for estimation of transmission coefficient (T) and surface conductivity (σ_s) during cyclic wetting and drying for Kalsted sandy loam B horizon soil corresponding to Fig. 1.

Table 3. Comparison of calculated (eq. [1]) transmission coefficient (T) and bulk surface conductivity (σ_s) during cyclic wetting and drying in 4 soils using several soil solution electrical conductivity (σ_w) levels. Values followed by the same letter within a soil type are not significantly different (P < 0.05).

Soil Type	CaCl$_2$ (mM)	σ_w (dS m^{-1})	T	T Std Error	σ_s (dS m^{-1})	fit r^2
V-Fine Sand	0.50	0.172	0.6586 a	0.0057	0.0716	0.982
	1.00	0.348	0.5982 b	0.0023	0.0704	0.996
	2.00	0.692	0.5960 b	0.0046	0.0750	0.983
	3.00[†]	1.00	0.5742 c	0.0064	0.0750	0.941
	4.00	1.27	0.5676 c	0.0026	0.1220	0.998
	8.50	2.69	0.6319 d	0.0026	0.0350	0.990
	20.08	5.92	0.5040 e	0.0025	0.0509	0.994
Kalsted A	1.50[†]	0.74	1.1100	0.0173	0.1240	0.932
Kalsted B	2.24[†]	1.04	0.0922 a	0.0096	0.0242	0.977
	4.22	1.60	0.0958 a	0.0005	0.0247	0.993
	9.01	3.10	0.0662 b	0.0003	0.0323	0.996
Bridger	2.24[†]	1.32	0.1578 a	0.0019	0.0219	0.961
	4.22	1.65	0.1652 b	0.0049	0.0170	0.777
	9.01	3.13	0.1182 c	0.0006	0.0130	0.991

[†]Background solution used during measured breakthrough curve.

spatial and temporal separation of measurements. TDR measurements are instantaneous and confined to within ~2 cm vertical distance over the length of the waveguide but highly concentrated towards the region immediately adjacent to the center rod, whereas effluent samples represent a time-averaged concentration measured 4 cm distal to the waveguide position. During low θ_v, there may have been sufficient time lag between TDR