



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 (θ_v) and bulk electrical conductivity (ζ_a). Recent studies comparing TDR ζ_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 ζ_a for estimation of soil solution electrical conductivity (ζ_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 ζ_w breakthrough curves (BTCs) were compared to BTCs obtained with conventional soil solution collection and analysis procedures. Agreement between TDR ζ_w and effluent fraction BTCs was generally good. Regions where TDR ζ_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 overcompensating 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 ζ_w BTCs had much less scatter and are an advantage over time-consuming effluent analyses. However, quantitative comparison of TDR ζ_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.

**ESTIMATING SOIL SOLUTE TRANSPORT UNDER TRANSIENT WATER
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Bozeman, Montana

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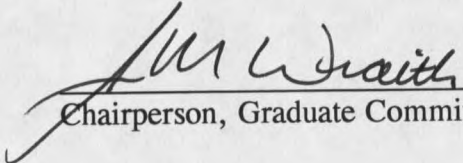
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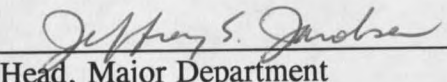
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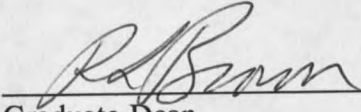
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VITA

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.

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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 ($\text{cm}^2 \text{h}^{-1}$ or $\text{cm}^2 \text{d}^{-1}$)
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 ($\text{m}^3 \text{m}^{-3}$)
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.

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.

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:

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

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 ($< \sim 4 \text{ dS m}^{-1}$, 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_p) 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

Theory

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)

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

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

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

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, NH¹). 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 CaCl₂ 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

¹Mention 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):

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

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

$$M_n = \frac{\int_0^{\infty} t^n \bar{C}(t) dt}{\int_0^{\infty} \bar{C}(t) dt} \quad [4]$$

where M_n is the n th 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

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

and

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

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 $< \sim 4 \text{ dS m}^{-1}$ (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

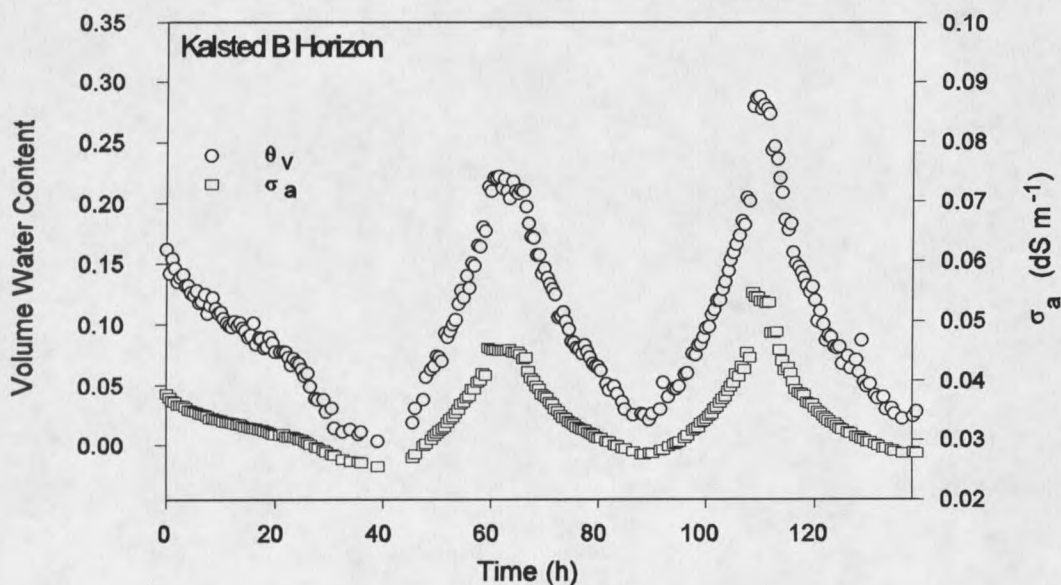


Fig. 1. Measured volume water content (θ_v) and bulk soil electrical conductivity (σ_a) during cyclic wetting and drying of Kalsted sandy loam B horizon soil for estimation of transmission coefficient (T) and surface conductivity (σ_s). Background CaCl_2 solution conductivity (σ_w) was 1.04 dS m^{-1} .

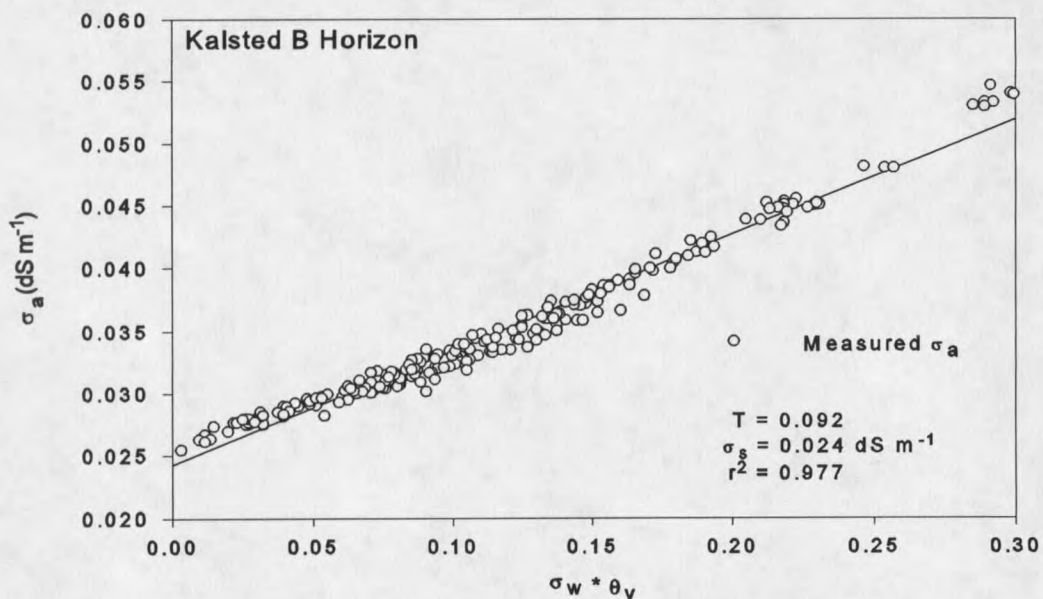


Fig. 2. Linear regression results for estimation of transmission coefficient (T) and surface conductivity (σ_s) during cyclic wetting and drying for Kalsted sandy loam B horizon soil corresponding to Fig. 1.

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

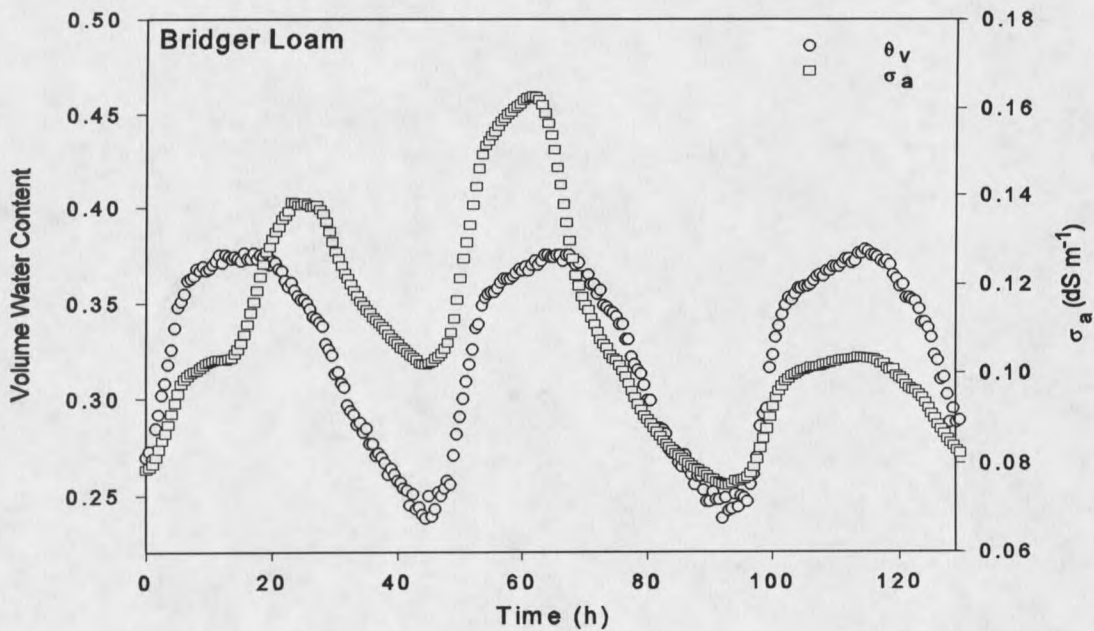


Fig. 3. Measured volume soil water content (θ_v) and bulk electrical conductivity (σ_a) during quasi-sinusoidal application of a Br^- pulse in Bridger loam soil.

measurement and effluent collection of corresponding soil solution volumes for significant variation in concentration to occur under transient water flow. These latter concerns may be minimized in future trials by placing TDR waveguides nearer the terminus of soil columns. Differences in the BTCs may also result from the length of time needed to collect effluent samples during low θ_v . The median collection time was plotted for each effluent sample, but substantial time intervals required to collect samples may alter the true position of time-weighted concentrations. In addition, several Kalsted B horizon and Bridger loam effluent samples had to be combined to obtain adequate sample volume for analysis during portions of the BTCs. Under steady flow conditions (Kachanoski et al., 1992; Wraith et al., 1993; Ward et al., 1994), many of these difficulties are avoided. For example, the temporal separation of TDR and effluent measurements can be accounted for

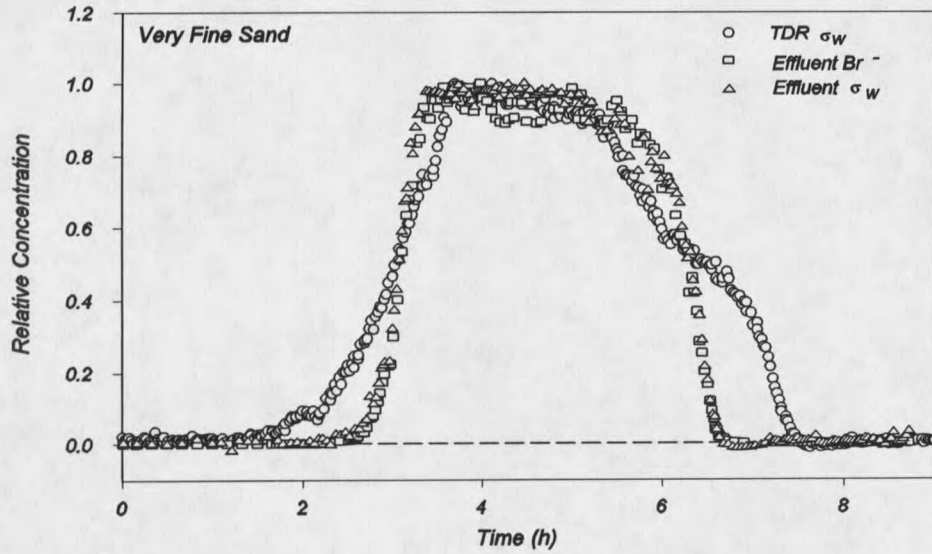


Fig. 4. Measured Br⁻ breakthrough curves for very fine silica sand.

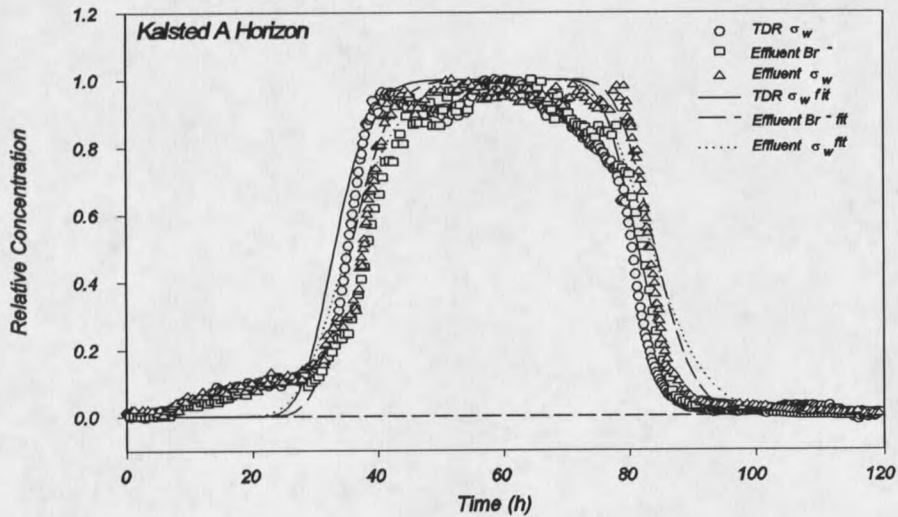


Fig. 5. Measured and fitted (CXTFIT) Br⁻ breakthrough curves for Kalsted sandy loam A horizon soil.

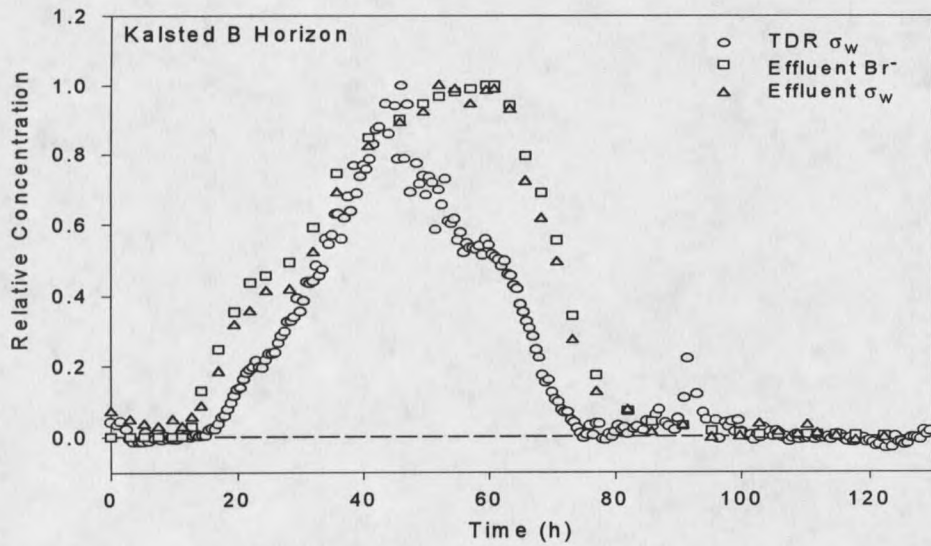


Fig. 6. Measured Br^- breakthrough curves for Kalsted sandy loam B horizon soil.

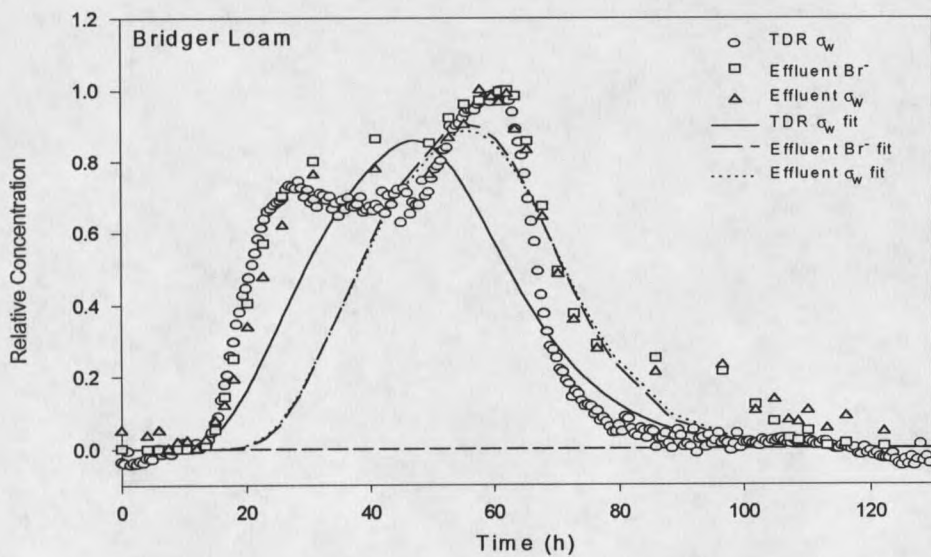


Fig. 7. Measured and fitted (CXTFIT) Br^- breakthrough curves for Bridger loam soil.

using known (and constant) v . However, extensive knowledge of column flow conditions is required for this purpose under non-steady conditions. Use of computer simulation may prove useful in this regard. For the current study, evaluation of possible limitations of eq. [2] in compensating for θ_v are complicated by uncertainty resulting from transient flow conditions.

CDE Transport Parameters

Fitting R_f and D using estimated time- and space-averaged v resulted in values of R_f much greater than 1.0 (i.e., $R_f=2.3$ to 3.5) for 2 soils. The values of v for TDR σ_w can be expected to be different from those corresponding to the effluent fractions because of continual changes in the water flow path during transient soil wetness. Error in the assumed v is then associated with the fitted values of D and R_f . More reasonable results were gained when R_f was fixed to 1.0 for the non-reactive tracer (van Genuchten and Wierenga, 1986; Gaber et al., 1992), and D and v were fitted to the data (Table 4). However, symmetrical curves were fit to all measured BTCs (Figs. 5,7) because the CDE assumes steady flow conditions and local equilibrium. These did not adequately represent some transient flow BTCs (e.g., Fig. 7) where the CDE failed to describe the bimodal BTC. The earlier BTCs obtained from fitting TDR σ_w data compared to effluent data (Figs. 5,7) are partially a result of vertical difference in measurement location. Fitted D and v for TDR σ_w were generally significantly different than the values for effluent Br and σ_w (Table 4), although appropriateness of CXTFIT fitted values is highly questionable under the imposed transport conditions.

Estimations of D , v , and dispersivity (λ) from time-moment analysis (M_n) for TDR

Table 4. Dispersion coefficients (D) and pore water velocities (v) determined by fitting measured transient flow breakthrough curves to the convective-dispersive equation (CDE) using CXTFIT. Retardation factor (R_p) was fixed at 1.0. Fitted parameter values followed by the same letter within a soil type are not significantly different ($P < 0.05$).

Soil Type		D			v			fit r^2
		Value	Confidence Interval [†]		Value	Confidence Interval		
		cm ² h ⁻¹			cm h ⁻¹			
V-Fine Sand	TDR σ_w	9.17 a	8.46	9.88	9.46 a	9.40	9.53	0.973
	Effluent Br ⁻	1.10 b	0.84	1.36	11.00 b	10.93	11.07	0.962
	Effluent σ_w	1.31 b	1.05	1.57	11.01 b	10.95	11.07	0.971
Kalsted A	TDR σ_w	0.25 a	0.22	0.29	0.80 a	0.80	0.81	0.960
	Effluent Br ⁻	0.48 b	0.39	0.57	0.88 b	0.87	0.89	0.949
	Effluent σ_w	0.25 a	0.21	0.29	0.87 b	0.87	0.88	0.960
Kalsted B	TDR σ_w	0.93 a	0.81	1.05	0.57 a	0.56	0.59	0.912
	Effluent Br ⁻	0.27 b	0.11	0.43	0.51 b	0.48	0.54	0.860
	Effluent σ_w	0.25 b	0.12	0.37	0.51 b	0.49	0.53	0.901
Bridger	TDR σ_w	0.79 a	0.60	0.97	0.56 a	0.54	0.58	0.807
	Effluent Br ⁻	0.39 a	0.11	0.67	0.52 a	0.47	0.58	0.755
	Effluent σ_w	0.43 a	0.17	0.68	0.52 a	0.47	0.57	0.778

[†]Lower and upper 95% confidence limits.

σ_w and effluent BTCs cannot be statistically compared, but there was generally good agreement between TDR and effluent samples (Table 5). The values of v and D for TDR σ_w were generally somewhat lower than effluent values in all soils, except the very fine sand column (Table 5). Values of v were within 9% of the mean value for each soil, with variation in D ranging up to 52% of the mean (Table 5). The greatest deviations of v and D from the mean value came from Bridger loam (Fig. 7), with smaller variations from Kalsted B (Fig. 6) and very fine sand (Fig. 4). This can be expected as time-moment analysis weights concentrations at later times (eq. [4]). In each of these soils most of the disagreement between TDR σ_w and effluent fraction BTCs occurred near the end of the breakthrough. Differences between transport parameters generated by CXTFIT and time-moment analysis are evident (Tables 4,5). The values of v from moment analysis are lower, but D is generally greater with this analysis method. However, these values likely represent less biased estimations of v and D because moment analysis evaluates the data directly rather than fitting the data to the CDE. The values of λ (Table 5) are in the expected range specified by Jury et al. (1991), with values of 0.5 to 2 cm being typical in repacked laboratory column studies.

Under steady flow conditions (Wraith et al., 1993), the CDE can be utilized to quantify agreement between measurement/analysis methods, but as discussed above, quantitative comparison of TDR σ_w to effluent BTCs is not straightforward under transient water flow because of the lack of an appropriate comparative method. Moment analysis (Jury and Sposito, 1985; Valocchi, 1985) is only partially suited for comparative purposes because 1) the time shift in the center of mass for TDR σ_w BTCs due to measurement

Table 5. Pore water velocity (v), dispersion coefficient (D), and dispersivity (λ) parameters determined from analysis of the first (M_1) and second (M_2) time-moments.

Soil Type		M_1 (h)	M_2 (h ²)	v (cm h ⁻¹)	D (cm ² h ⁻¹)	λ (cm)
V-Fine Sand	TDR σ_w	4.696	23.71	6.175	6.745	1.09
	Effluent Br ⁻	4.654	22.57	7.090	4.898	0.69
	Effluent σ_w	4.635	22.51	7.120	5.648	0.79
Kalsted A	TDR σ_w	56.24	3426	0.498	0.580	1.16
	Effluent Br ⁻	58.56	3680	0.546	0.638	1.18
	Effluent σ_w	58.59	3710	0.546	0.706	1.29
Kalsted B	TDR σ_w	46.883	2401	0.373	0.301	0.81
	Effluent Br ⁻	49.11	2678	0.428	0.496	1.16
	Effluent σ_w	48.75	2637	0.431	0.497	1.16
Bridger	TDR σ_w	47.94	2510	0.365	0.295	0.81
	Effluent Br ⁻	52.48	3172	0.400	0.639	1.60
	Effluent σ_w	53.49	3383	0.393	0.751	1.91

position cannot be adequately corrected under transient flow, and 2) lack of a confidence interval for calculated parameters (M_n , v , D , λ) restricts statistical comparison among BTCs. The steady flow studies of Kachanoski et al. (1992) and Ward et al. (1994) utilized moment analysis, and therefore did not provide any quantitative comparisons between CDE transport parameters derived from TDR and independent methods.

Summary and Conclusions

The relationship of Rhoades et al. (1976) was utilized to estimate changes in σ_w based on simultaneous measurement of θ_v and σ_a using TDR during transient Br⁻ transport through soil columns. A primary advantage of this approach is its relative simplicity,

whereby specific knowledge of soil physical or chemical properties is not required. Additional advantages of automated TDR over time-consuming effluent analyses are its ability to provide highly detailed BTCs and the capability for continuous unattended operation. However, TDR provides a measure of total ionic solute concentration and cannot characterize the soil solution constituents.

Satisfactory results were achieved when this linear relationship was applied to estimation of σ_w , even within the range of reported nonlinearity ($< \sim 4 \text{ dS m}^{-1}$). Variations in T and σ_s during replicate calibration over a range of soil solution concentrations were generally within 22% of the mean values, and did not notably alter the shape of the resulting TDR σ_w BTCs. There were no evaporative losses from the soil columns to cause changes in σ_w during calibration of T and σ_s , but this technique should not be used within several cm of the soil surface under normal field conditions.

In contrast to steady flow conditions (Wraith et al., 1993), quantitative comparison of TDR σ_w to effluent fraction BTCs is not straightforward. Although TDR σ_w and effluent BTCs were qualitatively similar in most cases, an appropriate quantitative method to evaluate similarity in transient flow BTCs needs to be developed for rigorous comparative purposes. The CDE fits symmetrical curves to all BTCs, creating uncertainty in estimated transport parameters. Less biased estimations of v and D are generated by time-moment analysis, but statistical comparisons among BTCs cannot be made. Additional work will be required before this methodology may be applied as a practical alternative to related steady flow techniques using TDR, but this simplified approach appears promising for estimation of TDR σ_w BTCs.

CHAPTER THREE

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

Introduction

Prediction and monitoring of solute movement through soils are critical aspects of soils research and management. The fate of soil-applied fertilizers, pesticides, and other chemicals needs to be known to facilitate development of preventative and remedial water quality procedures and policies. It is difficult to monitor or predict chemical movement under field conditions where varying soil types, water contents, and other transport conditions place high demands on sensors or theoretical predictions. When reliable transport parameters are determined for a particular soil, the ability to accurately predict solute movement may help to minimize groundwater contamination by delineating areas and conditions susceptible to rapid chemical movement.

Current field techniques for monitoring chemical transport are often destructive and time-consuming. The common technique of collecting resident soil solution using porous solution samplers is limited to high levels of soil wetness (Nagpal, 1982) and restricted by the cost of the solution samplers plus analysis of acquired samples (Ward et al., 1994). Sample variability also makes the use of porous solution samplers problematic (Hansen and Harris, 1975; Lord and Shepherd, 1993). However, few alternative methods are available.

Time domain reflectometry (TDR) has been recognized as a reliable method of

simultaneously and non-invasively measuring volume water content (θ_v) and bulk electrical conductivity (σ_a) in soils (Dalton et al., 1984; Topp et al., 1988, Zegelin et al., 1989). A few recent investigations have applied TDR to monitoring the transport of ionic solutes through soils under steady water flow conditions. These studies were all conducted, in part, to avoid the limitations of solution samplers and other measurement techniques. Kachanoski et al. (1992) were able to characterize Cl⁻ mass breakthrough curves (BTCs) in a field soil by monitoring σ_a using vertical TDR probes. TDR σ_a values were compared to effluent samples following a Cl⁻ pulse application. Wraith et al. (1993) compared TDR σ_a measurements for horizontal probes in intact soil columns to effluent fraction Br⁻ concentration (ion chromatograph) and soil solution electrical conductivity (σ_w) (conductivity bridge). Dispersion coefficient (D) and retardation factor (R_f) parameters estimated by fitting TDR σ_a BTCs to the convective-dispersive equation (CDE) were not different from those estimated using effluent samples. Ward et al. (1994) monitored Cl⁻ transport through intact soil columns during steady flow by relating TDR measures of σ_a to resident Cl⁻ concentration (C_R). Their measured BTC closely matched the BTC fitted using the CDE, with only slight underestimation of C_R by the CDE near the end of the BTC.

The ability to monitor σ_a under steady flow conditions using TDR thus presents a practical alternative for monitoring *in situ* ionic solute transport, and for estimating model transport parameters from measured BTCs. Extending these techniques to transient water flow conditions is highly desirable for monitoring chemical transport under field conditions. Development of effective procedures to measure or estimate time- and space-

dependent concentrations of ionic solutes in field soil profiles would substantially benefit many research and management applications.

The objectives of this study were to investigate the potential to exploit a simplified soil-specific relationship for estimating σ_w based on θ_v and σ_a , and to apply this concept to monitoring transport of an ionic chemical using TDR under imposed transient flow conditions in a field soil. A field study was conducted near Bozeman, MT, with vacuum extracted soil solution samples compared to results of the proposed TDR methodology.

Materials and Methods

Theory

Soil reactions of importance to the fate and transport of soluble chemicals 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)

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

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 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 from linearity in 12 soils of varying texture until σ_w became less than about 1 dS m^{-1} .

Given the ability to simultaneously monitor θ_v and σ_a during successive soil wetting and drying at constant known σ_w , T and σ_s may be determined from eq. [1] by linear regression of σ_a against $(\sigma_w \cdot \theta_v)$. With T and σ_s known (i.e., calibrated), eq. [1] may be rearranged as

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

for estimation of unknown σ_w during transient water and chemical flow.

Experimentation

A field transport study was conducted at the Arthur H. Post Experimental Station near Bozeman, MT. The soil at this site is an Amsterdam silt loam (fine-silty, mixed Typic Haploboroll) having < 1 percent slope. A 76 cm square by 28 cm high metal frame was inserted about 5 cm into a fallowed (1 year) area, following which a 45 cm wide by 35 cm deep trench was dug along one side of the frame, and the trench wall facing the frame was lined with plastic sheeting. Two porous ceramic solution samplers, two TDR waveguides, and two thermocouples were then inserted at each of three depths (10, 20, and 30 cm) below the soil surface. Each of these devices was installed into the face of the trench and extending beneath the undisturbed area enclosed by the frame. Three-rod TDR

waveguides were constructed using 29 cm (length) by 3.175 mm (diameter) rods spaced 4 cm apart (center-to-center). A guide was used to maintain parallel rod spacing upon insertion of the waveguides into the soil. A metallic TDR cable tester (1502C, Tektronix, Beaverton, OR¹) was controlled by microcomputer (Wraith et al., 1993), with a coaxial multiplexer (SDMX50, Campbell Scientific, Inc., Logan, UT) employed to monitor σ_a and θ_v for the 6 TDR probes using the single cable tester. Soil temperature was monitored using copper-constantan thermocouples attached to an electronic datalogger (21X, Campbell Scientific, Inc., Logan, UT). All electronics were housed in a portable trailer, and powered by 12V marine batteries.

Solution samplers were installed at a slight downward angle by first removing a soil core of equal dimension and injecting a slurry of silica flour into the cavity to ensure adequate soil contact. Short lengths of small diameter tubing were used for removal of extracted solution from ceramics to the soil surface. After all equipment was installed, the trench was carefully refilled and covered with plastic sheeting.

The soil within the frame was conditioned by flushing with 4.0 mM (1.2 dS m⁻¹) CaCl₂ to attain a constant σ_w . The metal frame was fitted with a float valve to control flow of CaCl₂ solution from a covered plastic trough which served as a reservoir. After conditioning, cyclic wetting and drying was accomplished by periodic manual application of the CaCl₂ solution in order to estimate T and σ_s using eq. [1] during transient flow at constant σ_w (Chapter 2).

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

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

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

with the probe impedance (Z_o) determined by immersing each probe in deionized water 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 of Wraith et al. (1993), and L being the length (m) of the TDR probe. TDR σ_a measurements (eq. [3]) were corrected for soil temperature using the linear relationship of Dalton et al. (1990) (i.e., a 2% compensation per °C).

BTCs were monitored at each sensor location following the addition of a 13 cm depth, 32.0 mM (4.0 dS m⁻¹) KBr pulse. This was manually applied in three increments over six days to impose transient flow conditions, and was followed by subsequent periodic applications of CaCl₂ solution. σ_a , θ_v , and soil temperature were measured every half hour. Collection of soil solution samples was attempted twice daily, with ~1 ml of solution collected and discarded before sampling to prevent contamination. σ_w estimates based on eq. [2] were compared with analyses of vacuum extraction samples. Br⁻ concentration was analyzed using a Dionex 4000i ion chromatograph with Dionex AS4A column (Dionex Corp., Sunnyvale, CA), and σ_w measurements were determined at 25°C using a conductivity bridge (Model 4010, Jenway Ltd., Essex, England). 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 time-moment analysis (Jury and Sposito, 1985; Valocchi, 1985)

$$M_n = \frac{\int_0^{\infty} t^n \bar{C}(t) dt}{\int_0^{\infty} \bar{C}(t) dt} \quad [4]$$

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 thus the mean travel time to the measurement depth, and M_2 is the variance of the distribution. From these time-moments, CDE transport parameters D and pore water velocity (v) were calculated as

$$D = \frac{Z^2}{2} \frac{(M_2 - M_1^2)}{M_1^3} \quad [5]$$

and

$$v = \frac{Z}{M_1} \quad [6]$$

for comparison among TDR σ_w and effluent fraction BTCs.

Results and Discussion

Collection of Soil Solution

Soil solution samples were collected in less than 1 h with a maximum of 10 ml collected to minimize impacts on resident soil solution, but sample collection was difficult, if not impossible, at all depths during periods of low soil wetness. At the 10 cm depth, only a few solution samples were obtained. This may have been a result of poor contact between soil and ceramic, or largely a result of the heavy silt loam texture in this layer. Due to the insufficient number of samples available for comparison to TDR σ_w estimates, results from the 10 cm depth will not be presented.

Calculated T and σ_s

Measured changes in σ_a corresponded to fluctuating θ_v during cyclic wetting and drying as expected (Fig. 8), because of the excellent electrical conducting properties of water. Table 6 displays estimates of T and σ_s from these transient flow cycles by linear regression using eq. [1]. The calculated values of T were different from one another at the 20 cm depth (Table 6), and the generated σ_s values were negative. Low coefficients of determination (r^2) indicate poor fit of the linear model to measured data. This resulted from a high degree of scatter in the field data.

Preconditioning the soil to a constant σ_w was difficult in the field. Measurements of σ_w (conductivity bridge) from effluent samples collected before pulse application revealed only slight variations in σ_w after a month of conditioning, so a mean σ_w value (over the week prior to pulse application) was used for calculation of T and σ_s . If the soil was not completely preconditioned, changes in σ_w during cyclic wetting and drying may

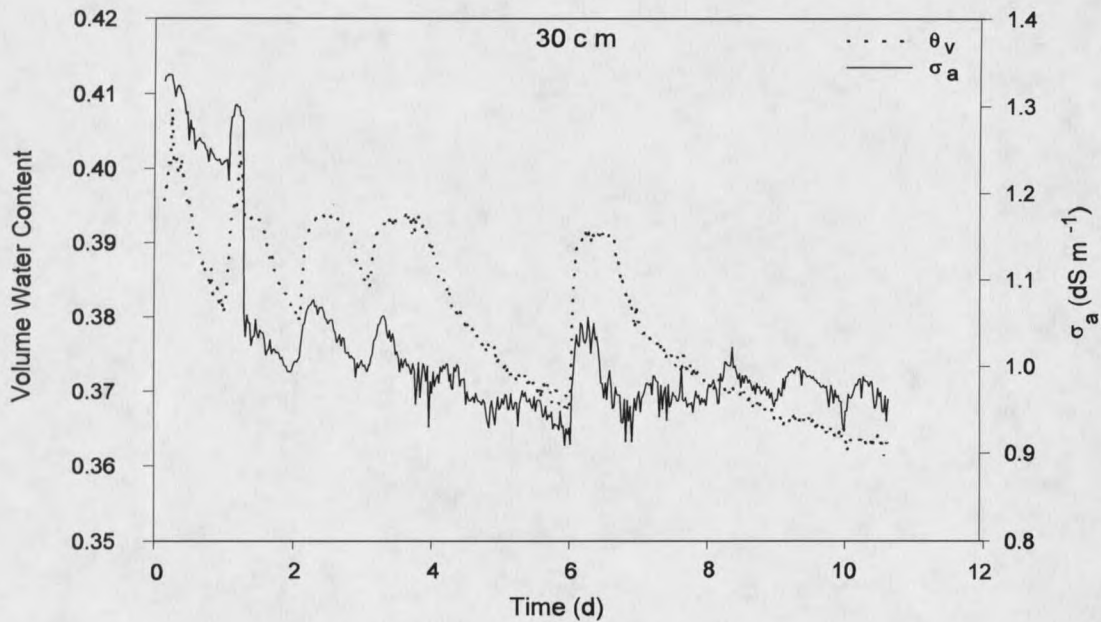


Fig. 8. Measured volume water content (θ_v) and bulk electrical conductivity (σ_a) during cyclic wetting and drying of Amsterdam silt loam soil for estimation of transmission coefficient (T) and surface conductivity (σ_s) at 30 cm depth. Data are from one of two TDR probes at this depth.

have affected estimated T and σ_s values. However, the variations in σ_w measured during soil conditioning may be due in part to the well-documented variability and problems associated with solution samplers (van Der Ploeg and Beese, 1977; Barbee and Brown, 1986).

Because the negative σ_s values obtained from linear regression of eq. [1] are not physically meaningful, a value of 0.025 dS m^{-1} was used based on previous column experiments (Chapter 2) using a soil having similar texture. This value was subsequently used in the determination of σ_w (eq. [2]) at both depths. A mean value for T was attained by averaging the replicate determinations at each depth. Resulting values were $T=2.111$ at 20 cm and $T=3.451$ at 30 cm. Based on these experiments, it is recommended that

Table 6. Comparison of calculated (eq. [1]) transmission coefficient (T) and bulk surface conductivity (σ_s) at 20 cm and 30 cm depths in Amsterdam silt loam soil.

Depth (cm)	TDR Probe	T	T Std Error	σ_s (dS m ⁻¹)	fit r ²
20	1	1.570	0.125	-0.0190	0.243
	2	2.652	0.122	-0.6123	0.490
30	1	3.610	0.203	-1.2055	0.390
	2	3.291	0.291	-0.6436	0.205

intact cores be conditioned in the laboratory under constant temperature to determine appropriate T and σ_s values during cyclic wetting and drying for application to future field studies.

TDR and Soil Solution BTCs

Fluctuations in θ_v and temperature were measured throughout the transport experiment (Fig. 9). Changes in θ_v were the result of imposed transient flow conditions. Temperature fluctuations responded to diurnal changes in solar radiation and air temperature. Because the field trial was conducted during the Fall season, soil temperatures during field operations were relatively low (generally 3 to 22°C). θ_v and temperature each affect the magnitude of σ_w and are independently compensated for in the estimation of TDR σ_w BTCs.

Raw transient flow BTCs as measured using TDR (i.e., σ_a vs. time) responded to fluctuating θ_v as expected (Fig. 10). Estimated TDR σ_w and soil solution extract BTCs were neither smooth nor closely matched, but the pulse could be detected with each method (Figs. 11,12). Earlier detection of the pulse at 20 vs. 30 cm depth is not apparent,

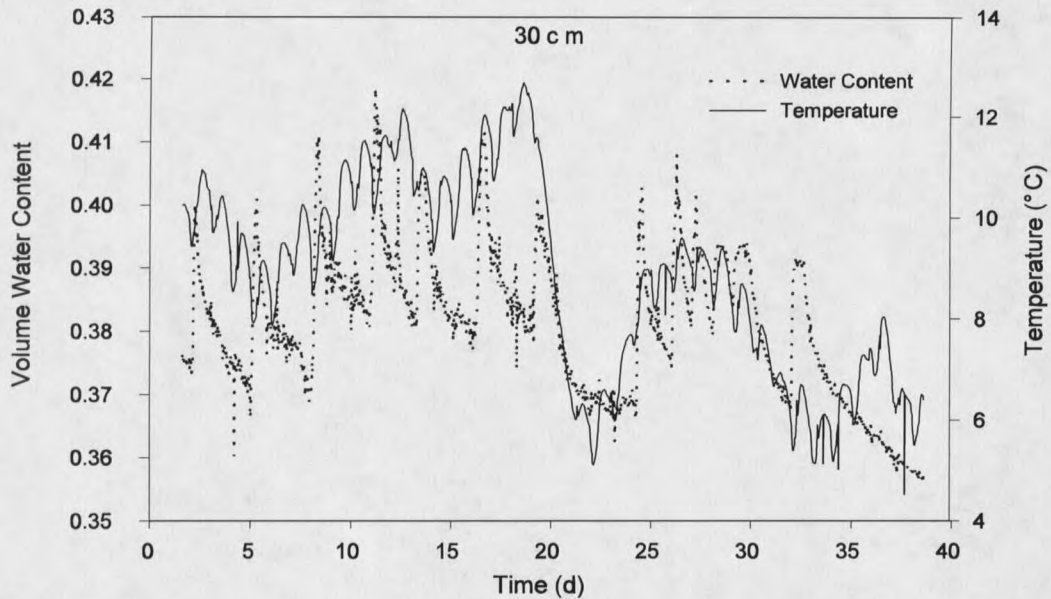


Fig. 9. Measured soil volume water content (θ_v) and temperature at 30 cm depth during imposed transient flow conditions following Br^- pulse application in Amsterdam silt loam soil. Data are from one of two TDR probes at this depth.

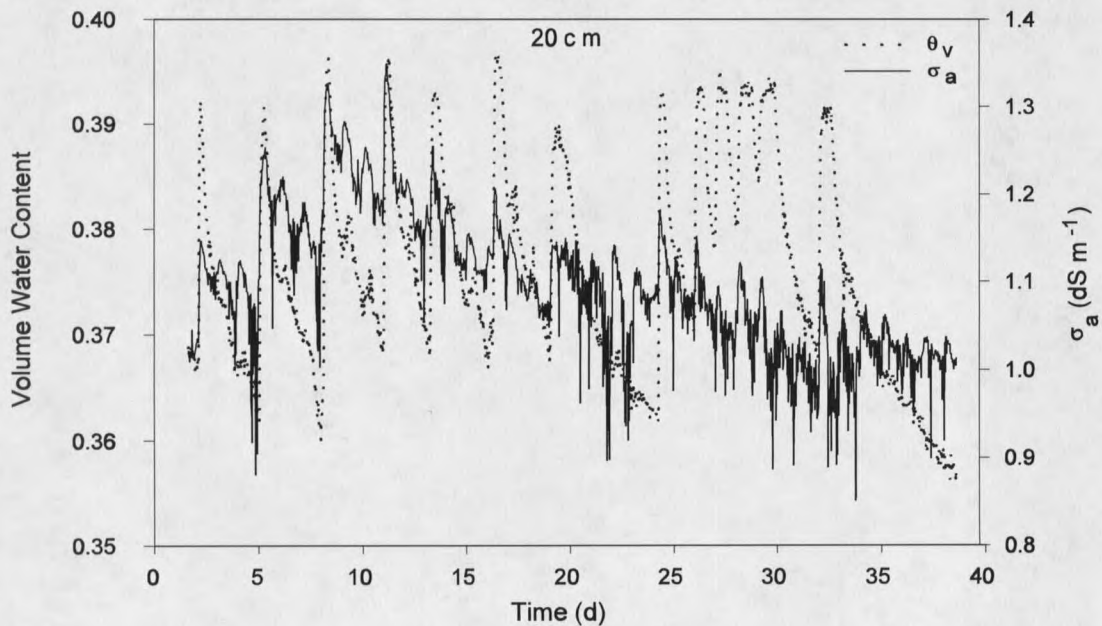


Fig. 10. Measured volume water content (θ_v) and bulk electrical conductivity (σ_a) at 20 cm depth during imposed transient flow conditions following Br^- pulse application in Amsterdam silt loam soil. Data are from one of two TDR probes at this depth.

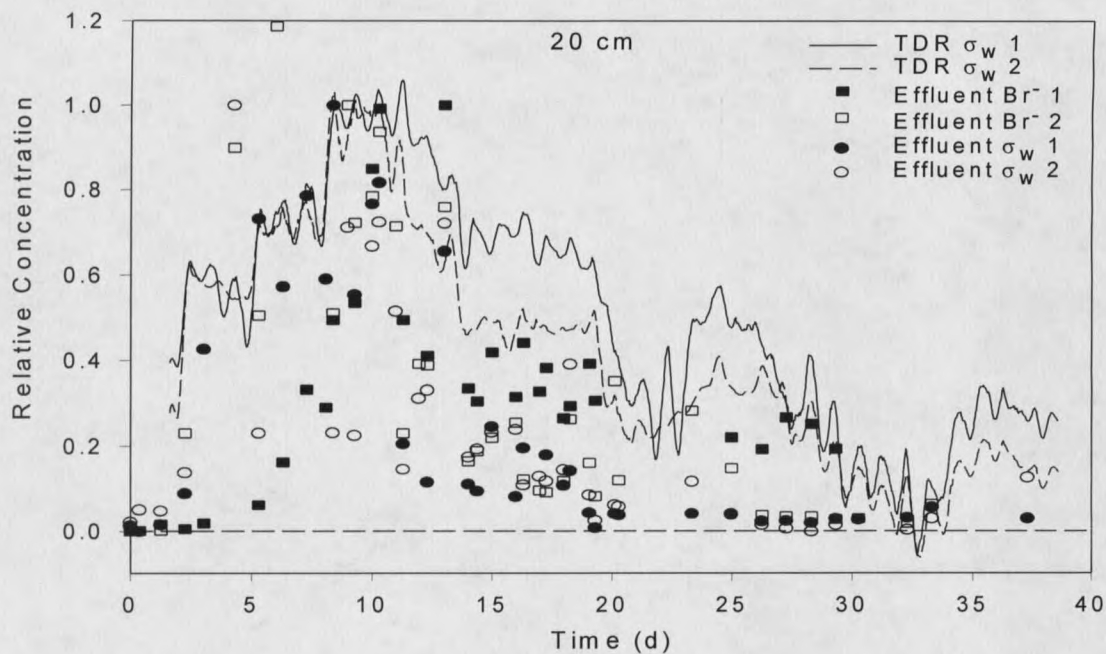


Fig. 11. Measured breakthrough curves for Amsterdam silt loam soil at 20 cm depth following application of KBr solution.

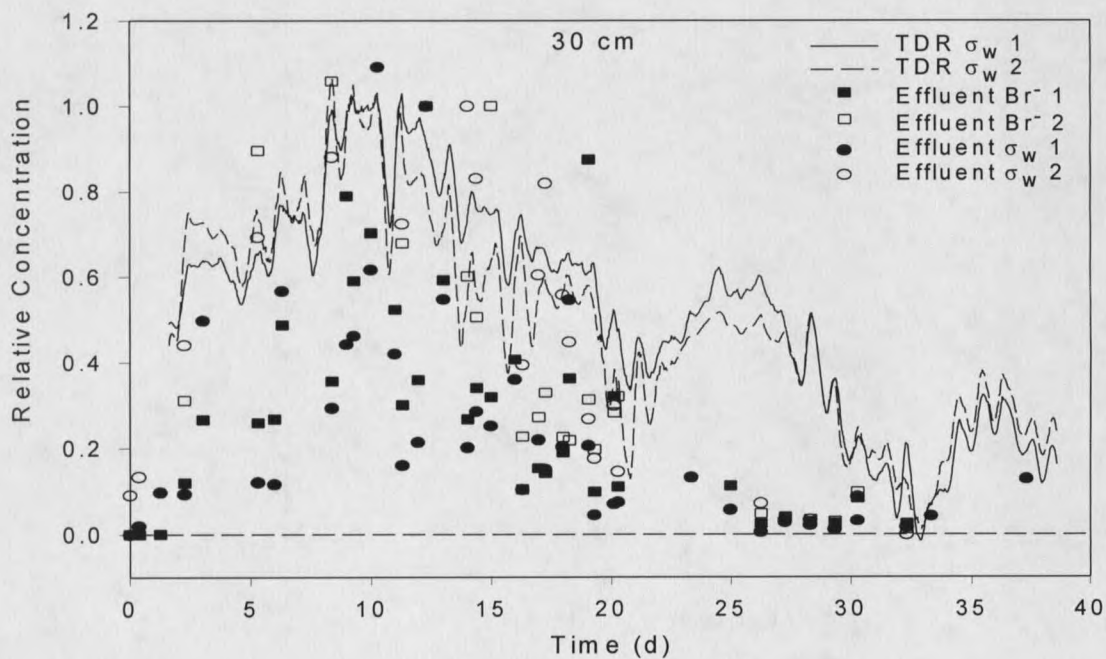


Fig. 12. Measured breakthrough curves for Amsterdam silt loam soil at 30 cm depth following application of KBr solution.

but Br breakthrough is somewhat more defined at the 20 cm depth (Fig. 11). It is possible that resolution of TDR measurements may not be sufficient to discern concentration differences that occurred within the 10 cm depth separating 20 and 30 cm depths. However, soil sampling in an area adjacent to the study location revealed large numbers of vertical macropores below about 20 cm. This could explain the similar Br breakthrough times, along with the more poorly defined BTC at 30 cm.

There is a high degree of scatter in the vacuum extraction data (Figs. 11,12). Variability in porous solution samplers has been reported to be influenced by long sampling intervals, differences in intake rate, plugging, and variable initial vacuum (Hansen and Harris, 1975). In this study, sampling was always completed within one hour, but concentrations may have been affected by plugging or variable intake rates of the ceramic samplers.

The relative paucity of vacuum extraction data points is an inherent limitation of this methodology. Numerous samples are needed to adequately characterize a detailed BTC, with analyses being tedious and time-consuming. TDR has the advantage of being able to instantaneously and continuously monitor total electrolyte concentrations *in situ*. The quantity and quality of effluent sample data obtained in this experiment is deemed inadequate to serve as a baseline measurement of solute concentration for comparison to TDR σ_w . Under steady flow conditions in the field, Kachanoski et al. (1992) were able to collect sufficient effluent samples in a sandy soil for comparison to TDR σ_a .

Fluctuations (noise) throughout the TDR σ_w BTCs appear to result from noise in measured θ_v and from soil temperature changes. In column experiments (Chapter 2) where

temperature was maintained at 25°C, agreement between effluent fraction and TDR σ_w BTCs was affected by low θ_v , possibly due to inherent limitations of eq. [2] in over-compensating for θ_v . In the field, this effect may be coupled with an incomplete temperature compensation. Fluctuations in σ_w tend to follow diurnal changes in temperature (Figs. 9,11,12).

It is difficult to discern between the influences of fluctuating water and temperature in the field. In a steady-state column study, Wraith et al. (1993) were able to successfully compensate TDR σ_a measurements for measured soil temperature changes of 2 to 3°C. Kachanoski et al. (1992) made no reference to any temperature correction of TDR σ_a during their steady flow field trial. The results of this study represent, to my knowledge, the first attempt to simultaneously compensate TDR σ_a estimates for transient soil wetness and temperature.

Transport Parameters

Estimation of transport parameters by fitting the field BTCs to the CDE was not attempted. In previous column experiments (Chapter 2), fitting D and v while fixing R_f to 1.0 produced the most satisfactory results. Estimation of \bar{v} under transient flow conditions requires knowledge of the average fluid application rate, but this was not measured due to the nature of the field trial. However, this information would likely be of little usefulness for quantitative comparisons due to the steady-state assumption of the CDE, with resulting symmetrical curves fitted to the non-symmetric transient flow BTCs. Moment analysis (Jury and Sposito, 1985; Valocchi, 1985) is also poorly suited for quantitative comparative purposes because the lack of confidence intervals for calculated

D and v restricts statistical comparison among BTCs. However, it is better suited to transient flow because it does not fit symmetrical curves to the measured BTCs as CXTFIT does. Table 7 displays parameters determined by time-moment analysis. Paired measurement techniques for TDR σ_w , effluent Br⁻, and effluent σ_w at each depth (Table 7) are independent measures due to the arrangement of sampling equipment and are considered as replicate measurements. Parameters based on extracted soil solution tend to be more variable than those based on TDR σ_w (Table 7). Greatest agreement among BTCs is with M_1 and v parameters. D of effluent σ_w is the most variable of all parameters.

Table 7. Pore water velocity (v), dispersion coefficient (D), and dispersivity (λ) parameters determined from analysis of the first (M_1) and second (M_2) time-moments of field breakthrough curves.

Depth		M_1 (d)	M_2 (d ²)	v (cm d ⁻¹)	D (cm ² d ⁻¹)	λ (cm)
20 cm	TDR σ_w 1	14.47	318.7	1.383	7.236	5.23
	TDR σ_w 2	13.44	269.4	1.488	7.304	4.91
	Effluent Br ⁻ 1	15.48	292.7	1.292	2.864	2.22
	Effluent Br ⁻ 2	10.18	146.5	1.965	8.148	4.15
	Effluent σ_w 1	9.811	136.6	2.039	8.552	4.19
	Effluent σ_w 2	7.599	99.3	2.632	18.97	7.21
30 cm	TDR σ_w 1	15.36	331.6	1.953	11.88	6.08
	TDR σ_w 2	14.87	338.7	2.018	16.13	7.99
	Effluent Br ⁻ 1	12.46	194.3	2.407	9.062	3.76
	Effluent Br ⁻ 2	11.21	165.7	2.676	12.81	4.79
	Effluent σ_w 1	10.10	167.2	2.971	28.53	9.60
	Effluent σ_w 2	11.69	170.5	2.567	9.532	3.71

D and v are greater at the 30 cm depth. This is expected due to the increased distance of solute travel and greater spread of the solute at increased measurement depths, but the presence of macropores below about 20 cm would also be a factor. Dispersivity (λ) values are lowest for effluent Br⁻ at both depths, resulting from lower values of v and D ($\lambda = D/v$). Generally, λ falls into the range of 5 to 20 cm which is typical for field soils (Jury et al., 1991).

Under steady flow conditions (Wraith et al., 1993), the CDE can be utilized to quantify agreement between measurement/analysis methods, but quantitative comparison of TDR σ_w to effluent BTCs is not straightforward under transient water flow because of the lack of an appropriate comparative method. Use of deterministic water and chemical transport models in combination with carefully measured top boundary conditions may be useful in future investigations.

Summary and Conclusions

TDR σ_w and soil solution BTCs measured under transient flow conditions in a field soil are in basic agreement with one another. TDR σ_w BTCs have much less scatter, and they provide a continuous record of σ_w compared to vacuum extracted samples. However, TDR measures total ionic concentration and cannot characterize the soil solution constituents. Noise in measured θ_v and/or incomplete temperature correction are apparent causes of fluctuating TDR σ_w . Evaporative losses are negligible in this study and therefore do not alter constant σ_w during calibration of T and σ_s , but this technique should not be used within several cm of the soil surface under normal field conditions.

Additional experimentation performed under controlled conditions in the laboratory

as well as in the field is recommended to evaluate the ability to more completely compensate for changes in θ_v and temperature. Field trials will require a more suitable method for acquisition of baseline data upon which the TDR methodology presented here may be rigorously evaluated. Intensive soil coring is probably the best technique available for this purpose.

Statistical comparison among BTCs is difficult under transient flow due to the lack of an appropriate quantitative method. Estimated M_n , \bar{v} , D , and λ parameters by time-moment analysis provided relative comparisons among analysis methods. Effluent fraction parameters were more variable than those based on TDR σ_w . However, with the appropriate input data, well-calibrated computer models such as LEACHM (Wagenet and Hutson, 1989) may be utilized for quantitative evaluation of BTCs under transient water flow conditions.

Amsterdam silt loam soil was difficult to precondition to a constant σ_w for calculation of T and σ_s . It would be useful to determine whether an intact soil core conditioned in the laboratory at constant temperature would produce appropriate T and σ_s values resulting from cyclic wetting and drying for application to field conditions. If so, this difficult step in the field would be eliminated, but BTCs could still be obtained under natural flow regimes.

This methodology was examined because of its simplicity, whereby specific knowledge of soil physical or chemical properties is not required. The detailed BTCs obtained using automated TDR constitute a significant advantage over time-consuming effluent collection and analyses. The initial field results are quite promising with respect

to continuous monitoring of ionic solutes. However, additional work will be required before applying this procedure as a practical alternative to related steady flow techniques for determination of model transport parameters.

CHAPTER FOUR

SUMMARY

Prediction and monitoring of solute movement through soils are important soil research and management applications. It is difficult to determine the fate of soil-applied fertilizers, pesticides, and other chemicals. Monitoring chemical movement under field conditions is difficult where varying soil types, water contents, and other transport conditions place high demands on sensors or theoretical predictions. Groundwater contamination may be minimized if solute movement can be accurately predicted based on reliable transport parameters by delineating areas and conditions susceptible to rapid chemical movement.

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) (Dalton et al., 1984; Topp et al., 1988; Zegelin et al., 1989). TDR has recently been applied to monitoring of ionic solutes in soils under steady water flow conditions (Kachanoski et al., 1992; Wraith et al., 1993; Ward et al., 1994). These studies compared TDR σ_a measurements to effluent analyses and found TDR to be a practical alternative method of 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 determination of soil solution electrical conductivity (σ_w), and to apply this relationship to monitoring ionic soil solute transport under transient flow conditions using TDR.

The proposed, simplified relationship is that of Rhoades et al. (1976), where the association between σ_a and σ_w takes into account the effect of varying θ_v . A primary advantage of this approach is its relative simplicity, whereby specific knowledge of soil physical/chemical properties (particle size distribution, clay mineralogy, etc) is not required.

This relationship was applied to repacked column and field transport studies conducted under transient flow conditions. TDR σ_w breakthrough curves (BTCs) were compared to BTCs obtained using conventional soil solution collection and analysis procedures. Soil solution was analyzed for Br^- concentration (ion chromatograph or Br^- -specific electrode) and σ_w (conductivity bridge).

The transport studies were conducted using several soils and salinity levels. Obtaining constant σ_w for calibration of the transmission coefficient (T) and bulk surface conductivity (σ_s) at each salinity level in the repacked columns was quite time-consuming. Growth of microorganisms in the columns was also a problem, but 0.1% liquid bleach inhibited growth. Once calibrated, variations in T and σ_s in a given soil column over a range of soil solutions were generally within 22% of the mean value for each soil, and did not notably alter the shape of the resulting TDR σ_w BTCs. Calibration was even more difficult in the field, and this may have resulted in the poor fit of the linear model to the measured data. σ_s values obtained from the field experiment were not physically

meaningful, but using a σ_s value obtained from a previous column experiment on a soil having similar texture resulted in suitable BTCs. It would be useful to determine whether values of T and σ_s obtained from intact soil columns under constant temperature in the laboratory are similar to those calibrated in the field, with the possibility of eliminating this difficult step in field studies. Evaporative losses were negligible in the column and field studies and therefore did not alter constant σ_w during calibration of T and σ_s , but this technique should not be used within several cm of the soil surface under normal field conditions.

TDR σ_w BTCs generally agreed with soil solution BTCs. Regions where they did not match correspond to θ_v extremes during the transient flow cycle. Inherent limitations in the relationship in over-compensating for θ_v is a possible reason for the discrepancies. In the field, this effect may be coupled with an incomplete correction for 25°C temperature. It is difficult to discern between the influences of fluctuating water and temperature in the field, with this study being the first attempt at compensating TDR σ_a estimates for transient soil wetness and temperature.

Some disagreement among BTCs arises from the difficulty of collecting soil solution in the column and field studies. Variations in v throughout column transport studies resulted in minimal volumes of effluent collected by the fraction collector during drying cycles. Analyses of small volumes of effluent are then a problem. In the field, insufficient soil solution collection made comparisons to TDR σ_w difficult. A more suitable method for acquisition of baseline data is needed to evaluate TDR σ_w data in field studies.

Column transport parameters were estimated by fitting the convective-dispersive equation (CDE) to TDR σ_w and effluent BTCs, and by time-moment analysis (Jury and Sposito, 1985; Valocchi, 1985). Transport parameters based on the field data were estimated only by time-moment analysis. The steady-state flow and local equilibrium assumptions of the CDE caused symmetrical curves to be fit to the transient flow BTCs. The appropriateness of the estimated dispersion coefficient (D) and pore water velocity (v) parameters is therefore questionable under the imposed transient conditions. Time-moment analysis provides independent estimates of D and v, but lacks confidence intervals for statistical comparison of calculated parameters. A suitable quantitative method to evaluate similarity in transient flow BTCs needs to be developed for rigorous comparative purposes. Use of deterministic water and chemical transport models in combination with carefully measured top boundary conditions may be useful in future investigations.

The relationship of Rhoades et al. (1976) was successfully manipulated to estimate changes in σ_w based on simultaneous measurement of θ_v and σ_a using TDR during transient Br^- transport through five soils. TDR is able to instantaneously and continuously monitor ionic chemical movement, with detailed TDR σ_w BTCs being an advantage over time-consuming effluent collection and analyses. However, additional investigations will be required before this methodology may be applied as a practical alternative to related steady flow techniques for determination of transport parameters.

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