Models and calibration approaches for soil solution electrical conductivity using time domain reflectometry
by Michael Christopher Mullin

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Resources and Environmental Sciences
Montana State University

Abstract:
Monitoring ionic solutes in soils is necessary to understand transport processes and to enable effective managerial decisions regarding application and remediation of soil applied chemicals. Soil solution electrical conductivity (ςw) is directly related to ionic solute concentration (Cr) and thus is useful as a surrogate measurement. Time domain reflectometry (TDR) has shown promise for assessing ionic solute distributions and has a number of advantages over other established methods; however, calibration models must be invoked to estimate ςw using TDR. Three models and four calibration approaches to obtain soil-specific model coefficients were investigated in this study for their efficacy to infer ςw based on TDR measurements of bulk soil electrical conductivity (ςa) and volumetric soil water content (θ). Two types of laboratory experiments were performed: a static (no flow) soil column factorial matrix, and miscible displacement through soil columns under steady and transient water flow conditions. Model parameters were determined from laboratory experiments in conjunction with the various calibration methods by optimization of model estimated ςw against measured ςw from soil solution extracts or effluent fractions. Model parameters that were determined from laboratory experiments for a Flathead sandy loam soil were then used to generate predictions of ςw under field conditions and results were compared with measurements obtained from soil solution extracts. Some calibration model/method combinations resulted in excellent agreement with independently measured ςw, although different combinations of . optimized model parameters (i.e. non-unique solutions) provided substantially different agreement with independent measurements for both laboratory and field trials. An apparent relationship was found between procedures used to acquire baseline . measurements (field, laboratory) and for model calibration (laboratory). Results of this study are potentially useful for those considering use of TDR for research or management applications.

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Michael Christopher Mullin

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APPROVAL

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Michael Christopher Mullin

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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TABLE OF CONTENTS

Page

LIST OF TABLES

Table Page

Chapter 2

Chapter 3

LIST OF TABLES continued

LIST OF FIGURES

Figure Page

Chapter 2

Chapter 3

LIST OF FIGURES continued

ABSTRACT

Monitoring ionic solutes in soils is necessary to understand transport processes and to enable effective managerial decisions regarding application and remediation of soil applied chemicals. Soil solution electrical conductivity (σ_w) is directly related to ionic solute concentration (C_r) and thus is useful as a surrogate measurement. Time domain reflectometry (TDR) has shown promise for assessing ionic solute distributions and has a number of advantages over other established methods; however, calibration models must be invoked to estimate σ_w using TDR. Three models and four calibration approaches to obtain soil-specific model coefficients were investigated in this study for their efficacy to infer σ_w based on TDR measurements of bulk soil electrical conductivity (σ_a) and volumetric soil water content (θ). Two types of laboratory experiments were performed: a static (no flow) soil column factorial matrix, and miscible displacement through soil columns under steady and transient water flow conditions. Model parameters were determined from laboratory experiments in conjunction with the various calibration methods by optimization of model estimated σ_w against measured σ_w from soil solution extracts or effluent fractions. Model parameters that were determined from laboratory experiments for a Flathead sandy loam soil were then used to generate predictions of σ_w under field conditions and results were compared with measurements obtained from soil solution extracts. Some calibration model/method combinations resulted in excellent agreement with independently measured σ_w, although different combinations of optimized model parameters (i.e. non-unique solutions) provided substantially different agreement with independent measurements for both laboratory and field trials. An apparent relationship was found between procedures used to acquire baseline measurements (field, laboratory) and for model calibration (laboratory). Results of this study are potentially useful for those considering use of TDR for research or management applications.

CHAPTER 1

INTRODUCTION

The effects of agricultural and other land use practices on surface and groundwater quality is a major concern, regionally and nationally. Accurate measurements of soil physical attributes such as water content (θ) and electrical conductivity (σ) are critical to monitoring the fate and transport of soil-applied chemicals such as fertilizer salts. As an index of salinity, σ can be used to detect the presence and magnitude of ionic solutes. A technique known as time domain reflectometry (TDR) has made possible the unattended, simultaneous measurement of *in situ* θ and bulk electrical conductivity (σ_a) within the same sample volume (Dalton, 1992). This unique ability of TDR provides an attractive alternative to convential time-consuming and often destructive procedures.

Many important chemical and physical processes in soil-water systems, such as transport and bioavailability of chemicals, are characterized more accurately by soil solution electrical conductivity (σ_w) or resident solute concentrations in the soil solution (C_r) than by measurements of the bulk soil (e.g. σ_a). The response of plants to salinity effects are also more strongly correlated to σ_w than σ_a. Substantial effort has gone towards identifying relationships between σ_a and σ_w or C_r in soil-water systems (Gupta and Hanks, 1972; Rhoades et al., 1976; Shainberg et al., 1980; Nadler and Frenkel, 1980; Bohn et al., 1982, Rhoades et al., 1989; Nadler, 1982; Nadler, 1997). Extending the solute measurement capabilities of TDR will require reliable means of relating measured

σ_a to σ_w or C_r, and this has been an active area of research (e.g. Ward et al., 1994; Vanclooster et al., 1994; Mallants et al., 1996; Risler et al., 1996; Persson, 1997; Vogeler et al., 1997; Persson and Berndtsson, 1998; Wraith and Das, 1998; Das et al., 1999). Finding a universal calibration technique that will work well for all types of soils under variable water flow regimes would constitute a definite advancement. Whether or not a universal calibration technique for all applications may be found, evaluation of alternative approaches under different soil and experimental conditions will advance our knowledge and abilities in this area.

Electrical Conductivity in Soils

The electrical conductivity associated with dissolved ions in the pore water (σ_w) accounts for the primary contribution to σ_a for most soils. The remaining contribution is attributed to ions adsorbed to clay and other solid surfaces (σ_s). Bohn et al. (1982) and others have reported that σ_w is proportional to the sum of moles of ion charge:

$$\sigma_w = k\sum_{i=1}^{n}\lambda_i M_i|V_i| \qquad [1]$$

where k is the cell constant of the electrode, λ_i is the molar-limiting ion conductivity (can be obtained from tabled values), M_i is the ion molar concentration, V_i is the value of the ion charge, and i denotes ionic species. While it is known that the magnitude of σ_s is dependent upon the amount and type(s) of clay present (Cremers and Laudelout, 1966), there is no direct (non-destructive) technique available for σ_s measurement. Rhoades et al. (1976) suggested that σ_s could be determined from extrapolation of the σ_w-σ_a curve to

$\sigma_w = 0$, and later (Rhoades et al., 1989) presented an empirical relation based on clay content. Other methods for obtaining σ_s based on physical/empirical relationships exist and are presented in Nadler and Frenkel (1980). Rhoades et al. (1989) believe that a continuous conductance pathway along solid surfaces is unrealistic; instead, they indicated that σ_s is coupled in series with an electrical conductance element associated with water-filled pores that bridge adjacent particle surfaces. The magnitude of electrical current flow through the continuous pore water pathway is dependent upon σ_w and a geometry factor (F_g) related to the tortuous nature of flow paths (e.g. Rhoades et al., 1976; Bohn et al., 1982). F_g is known to be a function of θ but has been described in various ways (Archie, 1942; Rhoades et al., 1976; Mualem and Friedman, 1991).

There are a number of techniques available for *in situ* σ_a measurement (TDR, 4-electrode sensors, electromagnetic induction sensors); however, there currently appear to be no reliable methods available to directly measure σ_w *in situ.* Thus, the electrical conductivity of a solution extract obtained from a saturated soil paste is the standard measurement used for appraising soil salinity (USDA-ARS, 1954; Slavich and Petterson, 1990). For a large number of samples, this is a time consuming process relative to other estimates, such as obtaining extracts at higher θ ratios, or inferring σ_w from TDR measurements of σ_a and θ. A limitation of using 1:1 or 1:5 extracts is that the measured value of σ_w may not be representative of σ_w under field moisture conditions. Reitemeier (1946) reported that for five of six loam soils of arid or semi-arid origins, total dissolved salts, which are linearly related to σ_w (Tanji and Biggar, 1972; Griffin and Jurinak, 1973;

Marion and Babcock, 1976), increased 2- to 9-fold upon dilution from field-moist to 500% wetness. The increase in TDS upon dilution for the five soils was attributed primarily to dissolution of sparingly soluble salts (Reitemeier, 1946).

Overview of Time Domain Reflectometry

TDR is essentially a form of 'cable radar', as discontinuities along a transmission line can be detected by analysis of a reflected electromagnetic signal. The TDR technique has been historically associated with mining, construction, and telecommunications industries and was first adapted for use in soil science for measuring θ about two decades ago (Davis and Annan, 1977; Topp et al., 1980). Topp et al. (1980) obtained an empirical third order polynomial relationship between θ and the soil apparent dielectric constant (ε) which is measured by TDR travel time analysis:

$$\theta = -5.3X10^{-2} + 2.9X10^{-2}\varepsilon - 5.5X10^{-4}\varepsilon^2 + 4.3X10^{-6}\varepsilon^3 \qquad [1]$$

Dalton et al. (1984) later demonstrated that σ_a could be determined using TDR based on the attenuation of the TDR pulse by the medium of interest, using the same probes.

A thin-section approach credited to Giese and Tiemann (1975) is commonly used to determine σ_a using TDR and has been shown to produce excellent results (e.g. Topp et al., 1988; Nadler et al., 1991). The Giese and Tiemann equation as reported by Topp et al. (1988) can be written as:

$$\sigma_a = \left(\frac{\varepsilon_0 c Z_0}{L Z_u}\right)\left(\frac{2V_0}{V_f} - 1\right) \qquad [2]$$

where the constants ε_0 and c are the permittivity of free space ($8.854 \ X \ 10^{-12}$ F m^{-1}) and the velocity of electromagnetic waves in free space (2.997×10^8 m s^{-1}), L is length (m) of the TDR probe, and Z_o and Z_u are the characteristic probe impedance (Ω) and output impedance from the TDR cable tester (usually 50 Ω). V_o and V_f are the initial and final (after multiple signal reflections have died out) signal voltages, which may be determined from the cable tester output signal. The ratio V_0/V_f is directly proportional to the TDR signal attenuation across the embedded probe, which is the basis for measurement of σ_a by the TDR technique. The product $\varepsilon_0 c$ is equivalent to $(120\pi)^{-1}$ and has units of Ω^{-1}. Thus Eq. [2] can be written as:

$$\sigma_a = \left(\frac{Z_0}{120\pi L Z_u}\right)\left(\frac{2V_0}{V_f} - 1\right); \qquad [3]$$

or more commonly as:

$$\sigma_a = \frac{Z_0}{120\pi L Z_L} \qquad [4]$$

where $Z_L = Z_u/[(2V_0/V_f) - 1]$ is the measured resistive impedance load (Ω) across the embedded TDR probe. The term $Z_0/(120\pi L)$ can be equated to a probe constant (K_c) related to TDR probe geometry and impedance (Heimovaara, 1992; Baker and Spaans, 1993). K_c is normally determined by immersing the TDR probe in one or more solutions of known σ:

$$K_c = \frac{\sigma_{ref} Z_L}{f_T} \qquad [5]$$

where σ_{ref} is the known σ of a reference solution, and f_T is a temperature correction coefficient used to normalize the reference solution measurement to a standard temperature (often 25°C). An empirical, salt specific relationship can be used to calculate f_T:

$$f_T = \frac{1}{1+\beta(T - T_s)} \quad [6]$$

with the measurement (T) and standard (T_s) temperatures in °C and β about 0.02 for many common salts.

TDR has excellent spatial and temporal measurement resolution, and is an essentially non-destructive sampling technique. Other advantages of the TDR technique include the capability for automated measurement and for multiplexing sensors; that is, obtaining measurements from multiple probes at multiple locations with a single TDR instrument. Currently, the initial cost of obtaining a TDR system appears to be the major limitiation to a more widespread use of this technology (Noborio et al., 1994). However, Ward (1994) noted that for certain applications, when costs such as sample analyses associated with conventional techniques are accounted for, TDR may be less expensive in the long-run. There are potential disadvantages of using TDR in certain situations. For example, it is difficult to obtain θ at very high salinity (σ_w) levels [greater than about 14 to 20 dS m^{-1}, depending on θ (Dalton, 1992)] due to extensive attenuation of the TDR signal. However, σ_w would be expected to reach this magnitude only under highly saline conditions. Accurate TDR measurement of θ in soils that exhibit cracking can be problematic due to the possibility of air gaps forming between the probe and soil (Annan, 1977; Zegelin et al., 1992). In a limited number of situations (soils very high in ash, organic matter, or clay) it may become necessary to determine a soil-specific calibration relationship in order to accurately determine θ (Zegelin et al., 1992; Bridge et al., 1996). This is not a difficult process, but is somewhat time-consuming. Temperature effects should be corrected for when σ_a is measured at temperatures other than the standard reference (25°C). Heimovaara (1995) and Persson and Berndtsson (1998) reported σ_a temperature dependence similar to that for pure solutions. There is some debate as to the need to correct for cable resistance (R_{cable}) influences on TDR σ_a measurements. Heimovaara (1995) found that if R_{cable} was unaccounted for, TDR significantly underestimated σ_a above 2.5 dS m^{-1} when using a 3 m coaxial cable. Because R_{cable} increases as cable length increases and diameter decreases, there may be a need to account for R_{cable} under certain conditions.

Most salinity research to date has been conducted using methods other than TDR - primarily the four-electrode probe. While this technology is still in use, Nadler et al. (1991), and others have advocated the use of TDR for σ_a measurement because of its many advantages. For example, the four-electrode probe is quite sensitive to quality of contact with the soil, while the attenuation of the TDR signal is considered less sensitive to soil-probe contact (Nadler et al., 1991).

Due to the soil specific nature of the relationship between θ, σ_a, and σ_w, relating TDR measurements (σ_a and θ) to σ_w requires calibration. Many physical/conceptual calibration models have been proposed along with numerous methods for obtaining the necessary model coefficients.

Thesis Objective

The primary objective of this study was to compare three models to describe the relationships between σ_a and σ_w under variable θ in soils, and four calibration approaches to obtain the required soil-specific model parameters. Two popular conductor-based conceptual calibration models were evaluated and results presented in Chapter 2. Experiments and calibration techniques were designed to test these models under a diverse set of conditions, with the primary objective to further elucidate their utility in estimating σ_w for transient soil wetness conditions. Model parameters determined from each calibration technique were compared relative to their abilities to provide estimates in agreement with independently measured laboratory breakthrough curves (BTCs) for KCl solutions. These miscible displacement BTCs were measured under steady and non-steady (transient) water flow conditions. Chapter 3 contains an analysis of a soil hydraulic property-based calibration model using the same experiments and procedures as described in Chapter 2. In addition, coefficients determined for all three physical/ conceptual models were applied to predict σ_w in the root zone of an agricultural crop (peppermint: *Mentha piperita* L.), using θ and σ_a measured at multiple locations with TDR. Based on the experiments performed, recommendations are provided regarding the potential utility of specific models and calibration procedures under different combinations of soil and transport conditions.

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CHAPTER 2

APPLICATION OF TWO CONDUCTOR-BASED MODELS FOR SOIL SOLUTION ELECTRICAL CONDUCTIVITY

Introduction

Soil monitoring of common ionic solutes such as fertilizer salts has become an increasingly important issue as dictated by environmental and economic concern. Accurate information regarding soil water status and field solute distributions is needed so land managers can make informed decisions about quantity and timing of irrigation waters and applied chemicals. An increasing number of studies during the past few years have investigated use of time domain reflectometry (TDR) to estimate ionic solute status of soils, in the laboratory or field. TDR measures volumetric soil water content (θ) (Topp et al., 1980) and bulk soil electrical conductivity (σ_a) (Dalton et al., 1984) accurately and rapidly, using the same probes.

Ionic solute concentration is directly related to the electrical conductivity of the soil solution (σ_w). Aqueous soil extracts are a well accepted means of determining σ_w, although many difficulties involved in collecting extracts with conventional techniques have been identified (e.g., van der Ploeg and Beese, 1977; Lord and Shepherd, 1993). Direct soil sampling also provides a viable means of obtaining solution extract; however, the destructive nature (in particular) and cost considerations again make this an unattractive technique for many applications. Because σ_w is a more useful index of solute concentration than is σ_a (which is directly measured by TDR), a considerable amount of attention has been devoted to characterizing the complex relationships between σ_a, θ, and σ_w in soil-water systems (e.g., Rhoades et al., 1976; Shainberg et al., 1980; Nadler and Frenkel, 1980; Bohn et al., 1982; Rhoades et al., 1989; Mualem and Friedman, 1991). To facilitate research and management applications, it is desirable to employ relationships that are based on easily measurable (or easily calibrated) properties.

Rhoades et al. (1976) developed a simple conceptual model with empirical coefficients (designated R76) describing the dependence of σ_a on two soil conductors acting in parallel. A bulk liquid phase conductance element (itself dependent upon θ) and a surface conductance (σ_s) component are considered in this model. Following the approach of Sauer et al. (1955), Rhoades et al. (1989) later incorporated a third parallel electrical conducting pathway accounting for the interaction between liquid and solid phases in series into a modified version of the R76 model. This model is designated R89.

Previous studies (e.g., Risler et al., 1996; Mallants et al., 1996; Persson, 1997) have investigated the R76 and/or R89 model(s) combined with various calibration techniques. The present study provides an assessment of these two models under a more diverse set of experimental conditions than has been previously reported. The objective of this study was to evaluate the abilities of the R76 and R89 models to estimate σ_w based on TDR θ and σ_a measurements under conditions of concurrent variable soil wetness and ionic concentrations. In addition, some practical and conceptual issues associated with the models were explored, including ease of parameter determination, non-unique sets of calibrated model parameters, applicability of parameters derived under one type of experimental condition to estimate σ_w under a separate set of conditions, and whether a particular model may be better suited for certain soil conditions. Two types of laboratory column experiments were undertaken on repacked and intact soils: a static matrix-type factorial (multiple combinations of θ and σ_w), and miscible displacement of solutes under steady and transient flow conditions. From these experiments, four different methods were used to determine R76 and R89 model parameters. Results obtained using different combinations of calibration models and parameter estimation methods were compared with independent measurements of σ_w from soil solution extracts and column effluent fractions.

Materials and Methods

Two-Conductors Calibration Models

Soil bulk electrical conductivity (σ_a) is influenced by three primary factors: conductance arising from ions in the bulk soil solution (σ_w); surface conductance (σ_s) primarily due to ions adsorbed on clay minerals; and tortuosity of the electrical flow path through the soil matrix (Rhoades et al., 1976). The R76 model is a simple two-conductors approach whereby the liquid and solid phases in the bulk soil are treated as two macroscopic and parallel conductors contributing to σ_a:

$$\sigma_a = \sigma_w \theta T(\theta) + \sigma_s \qquad [1]$$

where T(θ) is interpreted as a soil-specific transmission coefficient accounting for changes in the tortuosity of electrical current flow caused by changes in soil wetness. The transmission coefficient has traditionally been characterized as a linear function of θ (Rhoades et al., 1976):

$$T(\theta) = a\theta + b \qquad [2]$$

with empirical soil-specific constants *a* and *b*.

Nadler and Frenkel (1980) and Shainberg et al. (1980) found that the σ_a-σ_W relationship may become curvilinear at $\sigma_W < \sim 3.5$ dS m^{-1}. Rhoades et al. (1989) reported that this nonlinearity was not significant at σ_W values $> \sim 1.0$ dS m^{-1}. Equation [1] is unable to describe this nonlinearity, and this was addressed by Rhoades et al. (1989). In the R89 model, a continuous solid pathway is neglected based on its relative lack of contribution to the overall σ_a (Rhoades et al., 1989), resulting in the following two parallel conductors formula:

$$\sigma_a = \left[\frac{(\theta_{ss} + \theta_{ws})^2 \sigma_{ws} \sigma_s'}{\theta_{ss} \sigma_{ws} + \theta_{ws} \sigma_s'} \right] + \theta_{wc} \sigma_{wc} \qquad [3]$$

where σ_{ws} and σ_{wc} are the soil solution electrical conductivities of the solid/liquid series-coupled pathway ('micropores') and the continuous liquid pathway ('macropores'), and θ_{ws} and θ_{wc} are the corresponding volumetric soil water contents. The conductance of the soil particles in the series-coupled pathway is denoted σ_s'. Similar to $T(\theta)$ in the R76 model, Rhoades et al. (1989) described θ_{ws} as a linear function of θ:

$$\theta_{ws} = \alpha\theta + \beta \qquad [4]$$

with $\theta_{wc} = \theta - \theta_{ws}$. The volumetric soil solid content in the solid/liquid series-coupled pathway, θ_{ss}, is determined as:

$$\theta_{ss} = \rho_b/\rho_s \qquad [5]$$

with ρ_b and ρ_s the densities of the bulk soil and the solid particles. The assumption $\sigma_w = \sigma_{ws} = \sigma_{wc}$ is required in order to solve Eq. [3] for σ_w. This assumption may be valid only under conditions of diffusional equilibrium, which is not expected during many solute breakthrough experiments (Kim et al., 1998).

Determination of Model Coefficients

Four methods were used to obtain the coefficients for the two models (R76, R89) evaluated in this study. Method 1 is a salinity and wetness factorial matrix approach and has been used previously (e.g. Rhoades et al., 1976; Bohn et al., 1982; Nadler, 1982; Ward et al., 1994; Mallants et al., 1996; Vogeler et al., 1996; Persson, 1997). This procedure allows direct determination of the θ-σ_a-σ_w relationship by generating a family of σ_w vs. σ_a curves at different levels of θ. Generally the relationship is determined by adding different amounts of solutions having variable ionic strengths to discrete soil columns. This produces a range in both σ and θ. After an appropriate equilibration period, σ_a and θ of each sample are measured (or assumed). The measured θ and σ_a can then be used to calibrate various models to estimate σ_w for these soils. In some previous studies that used this method (e.g., Rhoades et al., 1976; Mallants et al., 1996; Persson, 1997) an assumption was made that σ_w of the soil columns was equal to σ of the solution added to the soils. For this study, σ_w was measured from soil solution extracts for each column, similar to the method of Nadler (1982), Dalton et al. (1984), and Vogeler et al.

(1996).

Method 2 combines TDR measurements of θ and σ_a with σ_w determined from sampling techniques such as porous solution samplers, soil cores, or soil column effluent fractions. This type of calibration approach has previously been used in laboratory soil column experiments under steady (e.g., Kachanoski et al., 1992; Risler et al., 1996) and transient water flow (Risler et al., 1996; Persson and Berndtsson, 1998), as well as for field conditions (Noborio et al., 1994; Heimovaara et al., 1995; Wraith and Das, 1998; Nissen et al., 1998; Das et al., 1999). Method 1 and Method 2 are similar in that TDR measurements of θ and σ_a are combined with independently measured σ_w to determine (optimize) model parameters. However, Method 1 uses discrete σ_a-θ samples, while Method 2 covers a 'continuous' (at least potentially) range in one or both of these attributes at the same probe location.

The third parameterization method is based on mass conservation of an applied solute pulse having duration t_0 and electrical conductivity σ_0. Total mass density of laboratory or field solute BTCs [i.e., Σ ($\sigma_w t$)] are equated to the total mass of the applied pulse ($\sigma_0 t_0$). This type of procedure was performed by Ward et al. (1994) and Mallants et al. (1996) where TDR measured σ_a and θ were paired with values of resident solute concentration (C_r) to obtain a θ-σ_a-C_r relationship for a particular solute. In the approach of Ward et al. (1994) and Mallants et al. (1996), C_r was determined from a solute-specific calibration that requires conditions of constant θ. In this study we used a procedure similar to that of Das et al. (1999) where constant θ is unnecessary. TDR-measured σ_a

and θ were used in the two calibration models and the model parameters optimized by equating mass recovery calculated from predicted (model) σ_w to that from σ_w measured from effluent fractions.

Method 4 requires conditions of constant σ_w. If a sufficient quantity of ionic solution is leached through a soil, σ_w will eventually become constant once the solutes have been distributed uniformly. After steady σ_w is achieved, simultaneous TDR measurements of σ_a and θ under variable wetness allows determination of the θ-σ_a-σ_w relationship. This approach was used by Risler et al. (1996), Persson (1997), and Das et al. (1999). A benefit of this approach is that no independent paired measurements of σ_w are required. The four methods to determine soil-specific model parameters are summarized in Table 1.

Table 1. Calibration methods used for determination of R76 and R89 model coefficients.

Method	Description
1	Factorial soil column matrix (discrete σ_w-θ combinations)
2	Optimize TDR θ and σ_a to independently measured σ_w
3	Mass conservation of solute pulse
4	Constant σ_w, continuously variable θ and σ_a during soil wetting and drying

Laboratory Calibration Experiments

All θ determinations were made using the Topp et al. (1980) TDR calibration equation, which had been previously confirmed for the two soils used. TDR measurements of σ_a were based on the Giese and Tiemann (1975) relationship using:

$$\sigma_a = \frac{Z_0}{120\pi L Z_L} \qquad [6]$$

where the probe impedance (Z_0, Ω) was determined by immersion in deionized water (Heimovaara, 1992; Baker and Spaans, 1993), L is probe length (m), and Z_L is the measured resistive impedance load (Ω) across the TDR probe.

Soil Column Matrix. Column matrix calibration experiments were carried out in polyvinyl chloride (PVC) tubing sealed at one end with acrylic discs. A σ_a-θ-σ_w relationship was determined for three soils: a repacked Flathead sandy loam (coarse-loamy, mixed Pachic Udic Haploboroll) obtained at the Northwest Agricultural Research Center near Creston, MT; and repacked and intact Amsterdam silty clay loam soils (fine-silty, mixed Typic Haploboroll) taken from the Arthur H. Post Experimental Station near Bozeman, MT (Table 2). All soil materials were collected from the surface (Ap) horizons.

Table 2. Primary particle size fractions for Flathead SL and Amsterdam SiCL soils.

Size fraction	Flathead sandy loam	Amsterdam silty clay loam
Sand (%)	75	11
Silt (%)	18	60
Clay (%)	7	29

Repacked soils were dried and sieved through 2 mm mesh screen and packed to a height of 0.20 m in PVC columns having 0.05 m diameter and 0.23 m height. Packing was accomplished in two steps: after columns were packed to 0.10 m depth, one-half the solution was added; once the solution had imbibed, the remainder of the soils then solution were added. All repacked columns were packed to a bulk density of 1.25 Mg m^{-3}. After all the soil and solution had been added, the columns were sealed at the top with two layers of parafilm, laid on their sides, and allowed to equilibrate for 30 (Flathead) or 60 d (Amsterdam). All columns were rotated regularly to facilitate uniform dispersion of solution within the soils.

Intact 0.20 m length Amsterdam soil cores were collected in 0.23 m length by 0.04 m diameter PVC tubing using a hydraulic core sampler. Based on additional replicate samples collected at the same time, cores had mean θ of 0.26 m^3m^{-3} (SEM = 0.0037) and mean ρ_b of 1.37 Mg m^{-3} (SEM = 0.075). After oven drying at 55°C for 10 d, the intact cores had mean θ of 0.12 m^3m^{-3} (SEM = 0.0034). Solution was added to the top surface of the cores, and in addition, small holes were drilled in the side of the columns at 0.07 and 0.14 m from the bottom to facilitate addition and redistribution of the remainder of the solution. Parafilm was again placed over the top of the columns and silicone sealant was applied to the small holes. As with the repacked Amsterdam columns, the intact cores were allowed to equilibrate for 60 d. There were a total of 40 columns for each of the Amsterdam soils: five different concentrations of KCl solution (0, 0.27, 1.08, 4.06, and 7.62 dS m^{-1}), four target θ levels (0.20, 0.30, 0.40, 0.50 m^3 m^{-3}), and two replicates for each σ-θ combination. The Flathead soil column matrix comprised four concentrations of KCl solution (0.25, 1.0, 3.6, and 7.2 dS m^{-1}), three target θ levels (0.22, 0.32, 0.42 m^3 m^{-3}), and two replicates of each σ-θ combination for a total of 24 columns. A second soil column matrix experiment was subsequently undertaken using repacked Flathead soil. Five KCl concentrations were used (0, 0.25, 1.0, 3.6, and 7.2 dS m^{-1}) along with three target θ levels (0.10, 0.20, 0.30 m^3 m^{-3}) resulting in a total of thirty columns.

After the equilibration period (30 or 60 d), a three-rod TDR probe (0.198 m rod length, 1.5 mm rod diameter, 10 mm rod spacing) was used to measure θ and σ_a in each column. We used a TDR cable tester (1502C, Tektronix, Beaverton, OR) and a computer which controlled the cable tester through serial interface. Five different waveforms obtained from the same embedded probe were analyzed using a program modified from Spaans and Baker (1993) to ascertain θ and σ_a. Means of the five measured values were used in the σ_a-θ-σ_w calibration relationship; measurement standard errors for each column were exceedingly small. After the TDR analysis was completed, the contents of the columns were carefully removed onto a tray where the cores were sectioned into top and bottom halves. One lateral half of each (top, bottom) sample was allotted for mass water content (θ_m) measurement by oven drying, and the other was used for soil solution extraction. Soil solution extract was obtained by first adding sufficient distilled deionized (DI) water to the sample to obtain approximately 1:1 [kg:kg] soil-water ratio, followed by 45 minutes of shaking (Eberbach Corp., Ann Arbor, MI) and 20 minutes of centrifugation (RC-5B, Du Pont Company, Newtown, CT) at 10,000 rpm. Centrifuged samples were decanted and the conductivity of the extracted solution (σ_e) determined using a conductivity meter (Accumet Model 50, Denver Instrument Co., Arvada, CO with Model 3403 electrode, YSI Inc., Yellow Springs, OH). A circulating water bath (RTE-220D, Neslab Instruments Inc., Newington, NH) maintained the extracted samples at 25°C prior to analysis. The gravimetric (θ_m) core sample halves along with known mass of DI water added allowed calculation of a dilution factor which was then multiplied by σ_e to give σ_w at initial sample wetness. The calculated σ_w representing the top and bottom of each column were averaged, then combined with corresponding TDR-measured σ_a and θ to complete the σ_a-θ-σ_w suite.

The following relationships were used to determine best-fit model parameters from nonlinear least squares regression (Wraith and Or, 1998) against measured σ_w. For the R76 model, combining [1] and [2]:

$$\sigma_w = \frac{\sigma_a - \sigma_s}{(a\theta + b)\theta} \; ; \qquad [7]$$

for the R89 model:

$$\sigma_w = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad [8]$$

where $a = -(\theta_{ss})(\theta - \theta_{ws})$, $b = [(\theta_{ss}\sigma_a) - (\theta_{ss} + \theta_{ws})^2(\sigma_s') - (\theta - \theta_{ws})(\theta_{ws}\sigma_s')]$, and $c = (\theta_{ws}\sigma_s'\sigma_a)$ (Rhoades et al., 1989).

Steady Flow Experiments. A peristaltic pump (Wiz, Isco Inc., Lincoln, NE) was used to deliver eluent to the top of soil columns at a constant rate. Columns were initially conditioned with a weak KCl solution. Once a constant background concentration (σ_w) was reached, based on electrode analyses of the column effluent, eluent was switched to a higher KCl pulse concentration (Table 3). Effluent collection was accomplished using a setup similar to that of Langner et al. (1998). In this system, advancement of tubes in the fraction collector (Retriever, Isco Inc., Lincoln, NE) causes 2 three-way solenoid valves (at top and bottom of an intermediary effluent collector) to switch to a sampling position for approximately 10 s allowing effluent to drain into a test tube in the fraction collector. The valves are then returned to the closed sample accumulation position. Unsaturated conditions were maintained by supplying negative pressure to the column outlet. A vacuum line was connected to a regulator (Model 44-20, Moore Products Co., Spring House, PA) and the top solenoid valve, while the bottom solenoid valve was connected to the column outlet by polyurethane tubing. Columns were affixed to a vacuum chamber apparatus (Soil Measurement Systems, Tucson, AZ) and suction at the column outlet was maintained at -20 kPa throughout all column flow experiments, with the exception of the 10 s sampling periods when position of the solenoid valves were switched to allow sample drainage. Soil columns were wrapped with polyurethane tubing and maintained at 25°C by circulating water through the tubing.

Table 3. Selected flow and salinity attributes for steady flow soil column experiments.

	Input Solution σ Background	Input Solution σ Pulse	Pulse Duration	Application Rate	Pore Water Velocity
	dS m^{-1}	dS m^{-1}	pore volumes	cm^3 h^{-1}	cm h^{-1}
Amsterdam Repacked	0.5	4.0	1.1	15	0.2
Flathead Repacked	0.1	1.7	1.3	80	1.2
Flathead Intact	0.5	4.0	1.2	40	0.6

Components of the TDR system were the same as described for the column matrix experiments, except that WinTDR98 software (Utah State Univ. (1998). Logan, UT. Revision available: http://psb.usu.edu/wintdr99/) was used for TDR control, acquisition, and analyses. The basic θ and σ_a relationships were the same as for the program modified from Spaans and Baker (1993). Electrical conductivity of effluent samples was measured using the conductivity meter while θ and σ_a were continuously monitored (30-min interval) using automated TDR. Model parameters were again determined from optimization against σ_w measured in effluent fractions, allowing for calculation of model predicted σ_w using Eq. [7] and [8].

Transient Flow Experiments. The experimental setup was similar to that given for the steady flow columns with the exception of eluent application. Eluent was applied via a precision low-flow syringe pump (Soil Measurement Systems, Tucson, AZ) controlled by a datalogger (21X, Campbell Scientific, Logan, UT). Some of the transient flow experimental conditions are shown in Table 4. Solution was applied at 15 min intervals for 24 h, followed by 48 h were no application took place. During the first 24 h of the cycle, increasing amounts of solution were applied every 15 min until the 12th h, followed by 12 h of decreasing solution application. This resulted in a quasi-sinusoidal pattern of wetting and drying similar to that described in Risler et al. (1996). The 48 h no-addition interval facilitated soil column drainage, resulting in a wider range in θ. Effluent samples were collected in a fraction collector and analyzed using the same procedure described for steady flow conditions. Parameters for all models were determined as previously described with the exception of calibration Method 4 (where σ_w is held constant under variable θ and hence σ_a). Several wetting and drying cycles were

Table 4. Selected flow and salinity attributes for transient wetness soil column experiments.

	Solution σ		Soil Water Content†		Application
	Background	Pulse	Min.	Max.	Rate‡
	dS m^{-1}		m^3 m^{-3}		cm^3 h^{-1}
Amsterdam Repacked	0.5	1.9	0.21	0.38	5.2
Flathead Intact	0.5	4.0	0.27	0.34	4.6

† measured at TDR probe location

‡ mean rate based on effluent fractions collected during several wetting and drying cycles

applied to produce constant σ_w prior to the pulse application. Once steady σ_w was achieved, based on measured column effluent samples, concurrent TDR measurements of σ_a and θ were made while θ continued to vary. This allowed (Method 4) determination of model parameters from optimization of predicted vs. measured σ_a using Eq. [1] and [3].

Results and Discussion

Results from both repacked Flathead soil factorial matrix experiments were combined and are discussed in aggregate. Findings from all our column matrix calibrations are similar to those reported in Nadler (1982) who observed an increase in σ_w measured from solution extracts compared to σ_w of the input solution. Conversely, Vogeler et al. (1996) noted a 63 to 82% decrease in σ_w measured from solution extracts relative to σ_w of the input KCl solutions. Possible explanations given by Vogeler et al. (1996) were cation exchange (replacement of Ca^{2+} by K^+), Cl^- adsorption, and changes in the diffuse double-layer. The SiL soil used by Vogeler et el. (1996) was high in organic matter and contained a high proportion of volcanic ash which is reflected in low ρ_b of 0.84 Mg m^{-3}. For the Flathead SL and Amsterdam SiCL soils, values 1.25 to 40, and 1.1 to 18 times higher respectively were measured for σ_w compared to σ of the added KCl solutions. Similar to the trend observed in Nadler (1982), the magnitude of the differences decreased with increased soil θ. Part of the discrepancy between σ of the input solutions and extracts is probably due to concentration of salts resulting from oven drying the soils during their initial processing. After the soils were re-wetted, the salts left behind during oven drying would then be available to augment the σ attributed to the input solution. Based on a subsequent experiment using the Amsterdam soil where we compared oven dried vs. ambient wetness initial soil conditions, we did confirm this phenomenon, though it was relatively insubstantial in comparison to the differences noted above. In addition, we assumed a linear relationship between θ and σ_w from our dilutions. This may be a precarious assumption (e.g. Reitemeier, 1946; Nadler 1997) as the general tendency of dilution is to increase total dissolved ions (e.g. Khasawneh and Adams, 1967; Ulrich and Khanna, 1972; Fotovat et al., 1997). A number of potential mechanisms that could explain an increase in the total amount of electrolytes upon dilution are described in Fotovat et al. (1997) and include: cation desorption from exchange sites; dissolution of sparingly soluble salts; hydrolysis of exchangeable cations; and a double-layer effect. Experimental evidence is not conclusive according to Reitemeier (1946), who indicated that several studies reported that total ions dissolved in solution remained constant upon dilution for a wide range in θ. Unfortunately our experiments were not designed to discern the effect of dilution on total dissolved ions; therefore, without further intensive experimentation it is uncertain whether the σ_a-θ-σ_w relationships we established based on our soil matrix experiments and experimental techniques might be substantially different were a different method used to obtain $\sigma_{w.}$

Unlike the approach of Mallants et al. (1996) who fitted a different value of σ_s (R76) for each θ series, a single soil-specific value of σ_s (Table 5) was determined from each factorial matrix calibration experiment. It is apparent (Figs. 1, 2) that the approach of Mallants et al. (1996) would have resulted in better R76 model fits for each separate θ

series. However, our results indicated that singular values for a, b, and σ_s adequately described the σ_a-θ-σ_w relationship over a wide range in θ (Table 5). This is in conceptual agreement with the model itself, and avoids the necessity to interpolate between discrete sets of model coefficients as soil wetness changes. Inclusion of σ_a and σ_w measurements from the lowest θ series for each column matrix experiment did not allow a reasonable fit to the R76 model ($r^2 < 0.60$ for all soils), so these were not used. However, data generated from the Flathead and Amsterdam low θ series are in accordance with Mallants et al. (1996) (reported by Nadler, 1998) who for a similar calibration study using a sandy loam soil extrapolated a value of $\sigma_s = 0.04$ dS m^{-1} for a low (0.12) θ series.

Table 5. Best fit parameters for factorial soil column matrix experiments using R76 and R89 models for soil solution electrical conductivity in Flathead SL and Amsterdam SiCL soils.

	Flathead	Amsterdam	
	Repacked	Repacked	Intact
	R76 Model†		
a	1.27	1.95	1.95
b	0.006	-0.18	-0.22
σ_s	0.021	0.48	0.50
r^2	0.95	0.91	0.87
	R89 Model†		
α	0.45	0.11	-0.16‡
β	0.050	0.14	0.25‡
σ_s'	0.019	0.62	0.63
r^2	0.95	0.93	0.90

† lowest θ series not used in determination of model parameters

‡ optimized values do not result in physically realistic θ_{ws} in the context of R89 model

Because σ_a is affected by the tortuosity of electrical flow paths through the soil matrix, T(θ) is presumably an indicator of soil structural development and resultant pore size distribution. Contrary to our expectations, nearly identical model coefficients were determined for the repacked and intact Amsterdam soils (Table 5). The intact cores were taken from an agricultural field, and therefore it is possible that there were no substantial differences in pore size distribution between the intact and repacked soils as a result of annual tillage operations. However, Nadler (1991) reported similar results for four soil types and attributed similar σ_a-σ_w relationships for disturbed and undisturbed soils to recovery of the macroaggregate structure upon wetting and drying. Microaggregate structure was assumed to have not changed upon disturbance to the soil (Nadler, 1991).

Equation [8] (R89) described the measured column matrix σ_a-θ-σ_w relationship similarly to Eq. [7] (R76). As with the R76 model, inclusion of measurements from the lowest θ series for each matrix experiment precluded a reasonable fit to the model, thus they were not used in the fitting procedures. Rhoades et al. (1989) indicated that model parameters α and β (used to describe the dependence of θ_{ws} on θ) were essentially independent of soil type and reported values of $\alpha = 0.468$ and $\beta = 0.064$ from laboratory measurements on field soil cores, and $\alpha = 0.639$ and $\beta = 0.011$ from *in situ* field determinations. Best fit α and β values (Table 5) for the Flathead SL were more similar to those reported by Rhoades et al. (1989) than were those for Amsterdam SiCL repacked and intact soils. This difference is not entirely unexpected. Up to a certain threshold θ value, only pores sizes corresponding to θ_{ws} ('micropores') contain soil solution. Above

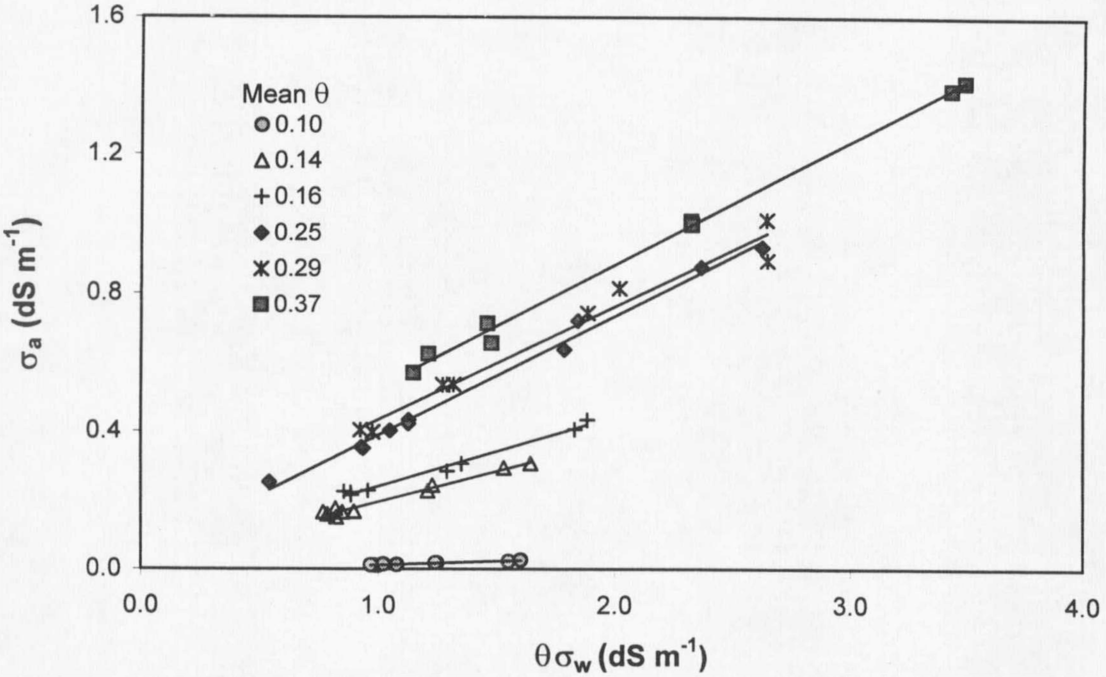

Figure 1. Measured results for repacked Flathead soil column matrix calibration experiment. Linear fit for each θ series shown for illustrative purposes only, as a single value of R76 and R89 model parameters were determined for the entire data set.

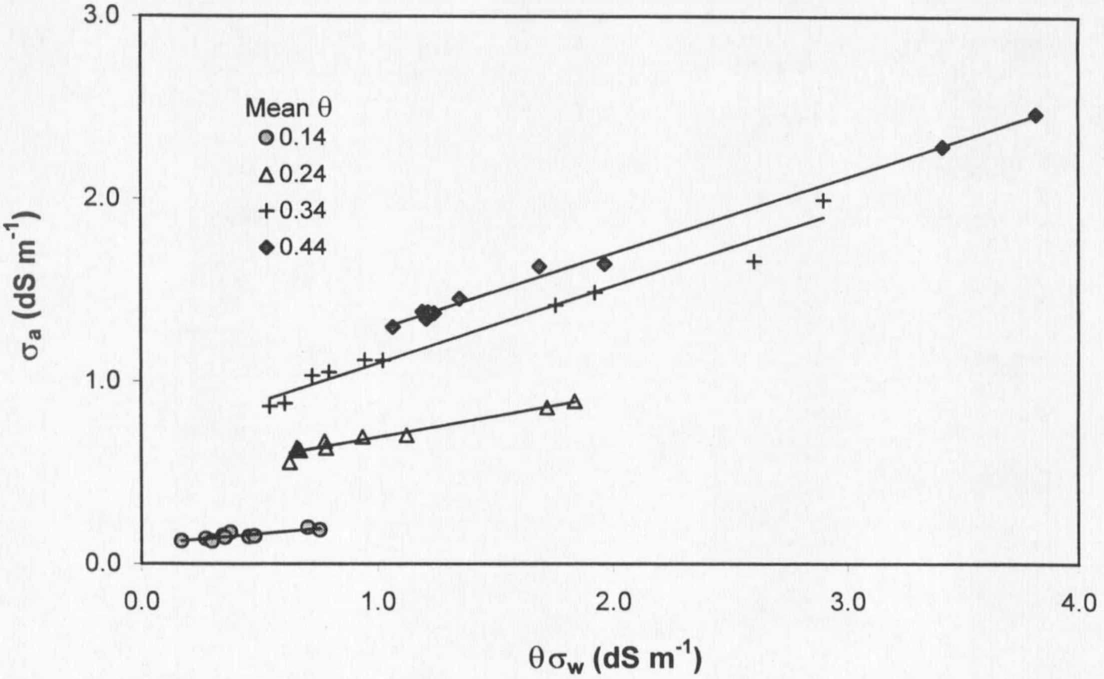

Figure 2. Measured results for repacked Amsterdam soil column matrix calibration experiment. Linear fit for each θ series shown for illustrative purposes only, as a single value of R76 and R89 model parameters were determined for the entire data set.

this level, pores corresponding to θ_{wc} ('macropores') begin to fill and their volume increases linearly as θ increases (Rhoades et al., 1989). According to our fitted results, threshold values of θ where this transition occurred were 0.09 (Flathead repacked) and 0.15 m^3m^{-3} (Amsterdam repacked). This is in relative accordance with expectations based on textural differences (Table 2). The finer Amsterdam SiCL soil likely has a higher proportion of 'micropores' relative to the Flathead SL soil. Below each soil's threshold θ value (i.e. the point where $\theta_{ws} = \theta$) the model is incapable of describing the σ_a-θ-σ_w relationship. When this occurs, the value of θ_{ws} becomes greater than θ which is physically impossible. It could be logically assumed that $\theta = \theta_{ws}$ in this range; however, doing so renders the model unusable as the denominator in [8] goes to zero. Attempts to apply calibration data having $\theta < \theta_{wc}$ thus result in poor optimization outcomes.

A negative value for the intact Amsterdam soil R89 parameter α (e.g., Table 5) indicates a decrease in θ_{ws} with increasing θ. This is both physically unrealistic (in the context of the conceptual model) and contrary to results of Rhoades (1989), who reported that both θ_{wc} and θ_{ws} increased with increasing θ. However, if optimized α and β parameters determined from the *repacked* Amsterdam soil (which are consistent with the pattern expressed by Rhoades (1989)) are applied to the *intact* Amsterdam soil core data, the goodness of fit between measured and predicted σ_w decreases only insignificantly from r^2 of 0.87 to 0.86. This is a potential indication of obtaining non-unique best-fit model coefficients, as will be addressed below.

Mallants et al. (1996) and Persson (1997) found poor agreement between R76 model predictions from soil column matrix experiments as applied to steady and transient flow experiments respectively. Application of model (R76, R89) parameters determined from our factorial matrix experiments to TDR measurements of σ_a and θ from flow experiments (and vice versa) also resulted in poor agreement with measured effluent σ_w ($r^2 < 0.50$ in all cases). There are a number of potential reasons for the disparity: matrix experimental technique may have led to an anomalous σ_a-θ-σ_w relationship as mentioned previously; inability of the model(s) to accurately describe the σ_a-θ-σ_w relationship under certain experimental conditions, and; differences could exist in the σ_a-θ-σ_w relationship determined from TDR measurements in experiments where diffusional equilibrium has or has not occurred (Kim et al. 1998). The R89 model assumption that $\sigma_w = \sigma_{wc} = \sigma_{ws}$ was discussed previously. In addition, TDR and soil solution extracts measure resident solute concentrations while effluent fractions are considered to represent flux-averaged concentrations (Parker and van Genuchten, 1984). Resident and flux-averaged concentrations are likely to be different unless diffusional equilibrium is reached. This criteria is not expected to occur during solute breakthrough experiments, especially under transient wetness.

A timing mismatch between TDR and effluent breakthrough curve (BTC) measurements resulted from placement of TDR probes 3.0 to 3.5 cm above the soil column outlets. To account for the spatial separation of TDR and effluent measurements, all effluent-generated σ_w BTCs were shifted back in time. For steady flow experiments, effluent BTCs were shifted by the pore volume fraction within the total soil volume that was below the TDR probe. Because variable wetness did not allow determination of a unique water-filled pore volume, transient flow BTCs based on effluent fractions were shifted in time based on visual observation to correspond with TDR BTCs.

Model parameters determined by calibration Methods 2, 3, and 4 for all flow experiments are summarized in Table 6. As expected, all calibration experiments showed σ_s (R76) and σ_s' (R89) were much higher for the SiCL than for the SL soil, presumably due to differences in clay content (Table 2) and perhaps clay mineralogy (which was not investigated). Neither set of optimized model parameters for the intact Flathead soil (steady flow) is physically/conceptually realistic within the constraints of the R76 and R89 models, yet both provide excellent agreement with measured effluent σ_w. In fact, a number of model parameter combinations provided equally good fit (r^2 as criterion) to measured σ_w, a possible result of the rather small variation in θ for this soil. For example, values of $a = 1.95$, $b = 0.050$, and $\sigma_s = 0.059$ (R76 model) also produce in an r^2 of 0.98 when calibrated to the effluent σ_w. However, when these two sets of parameters are applied to the intact Flathead soil transient flow experiment, the subsequent agreements with effluent σ_w are very different (RMSE of 1.32 dS m^{-1} compared to 0.20 dS m^{-1}). Caution should therefore be exercised if R76 and R89 model coefficients determined from steady flow experiments are to be used to predict σ_w under conditions of variable wetness.

Similar to steady flow experiments, we also encountered the potential to obtain non-unique model parameters for calibration Method 4 (Fig. 3). In this case, the problem may be exacerbated by a lack of variance (range) in σ_w rather than θ. While multiple sets of optimized parameters for the Amsterdam SiCL (e.g. $a = 5.43$, $b = -0.48$, $\sigma_s = 0.29$;

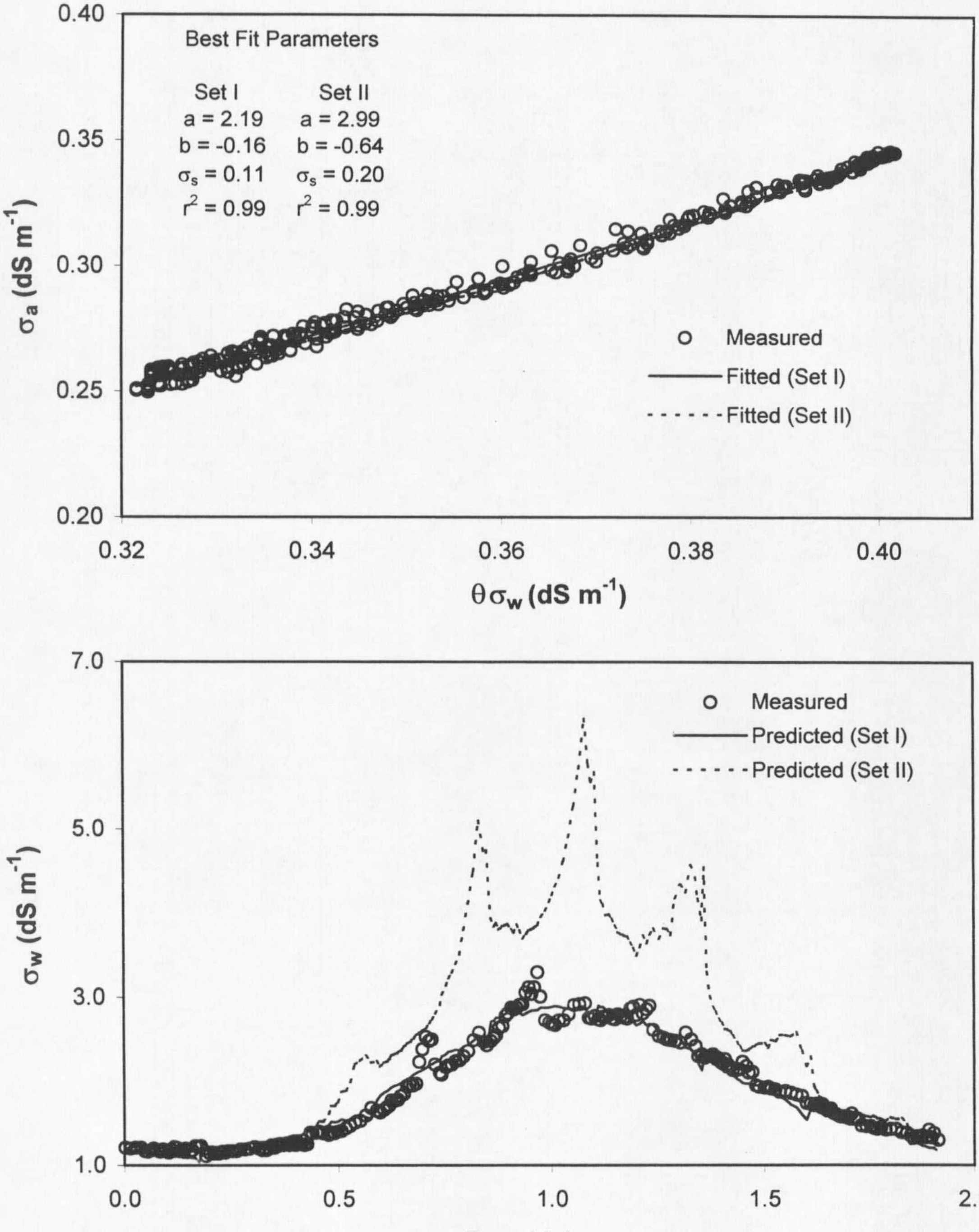

Figure 3. Top: Two parameter sets obtained using calibration Method 4 for the intact Flathead soil with the R76 model. Bottom: Predicted σ_w for the intact Flathead soil (transient flow BTC) based on the two sets of best fit R76 model parameters in top panel.

Table 6. Best fit R76 and R89 model parameters from soil column flow experiments for Flathead SL and Amsterdam SiCL soils.

	Flathead SL							Amsterdam SiCL				
	Intact					Repacked		Repacked				
	Steady Flow		Transient Flow			Steady Flow		Steady Flow		Transient Flow		
	Calibration Method†											
	2	3	2	3	4	2	3	2	3	2	3	4
	R76 Model											
a	-18.27	1.91	1.52	1.90	2.19	5.64	1.40	-2.54	2.99	4.33	4.40	5.43
b	7.50	-0.02	0.082	-0.03	-0.16	-1.50	-0.02	1.45	-0.035	-0.29	-0.30	-0.48
σ_s	0.092	0.11	0.094	0.09	0.11	0.056	0.060	0.37	0.35	0.29	0.29	0.29
r^2	0.98	0.96	0.96	0.96	0.99	0.99	0.98	0.97	0.92	0.90	0.89	0.99
	R89 Model											
α	7.82‡	7.82‡	-0.007‡	-0.007‡	-0.21‡	-1.56‡	-1.56‡	1.93‡	1.92‡	-2.64‡	-2.65‡	-2.25‡
β	-2.80‡	-2.80‡	0.14‡	0.14‡	0.19‡	0.74‡	0.74‡	-0.46‡	-0.47‡	0.66‡	0.64‡	0.31‡
σ_s'	0.12	0.12	0.12	0.12	0.11	0.064	0.065	0.63	0.64	0.49	0.50	0.34
r^2	0.99	0.99	0.96	0.96	0.99	0.99	0.99	0.97	0.95	0.80	0.78	0.99

† Method 2 involves optimizing parameters based on the goodness of fit with a measured σ_w BTC (from effluent fractions); Method 3 is a mass-balance approach where parameters are optimized by equating the mass density of the solute BTCs with model predicted BTCs; Method 4 requires steady σ_w while θ and σ_a vary which allows for parameter estimation without independently measured σ_w data.

‡ values do not result in physically realistic θ_{ws} in the context of the R89 model

a = 1.50, *b* = 1.88, $\sigma_s = 0.0022$) produce an r^2 of 0.99 using calibration Method 4, the RMSE generated from the respective parameter sets when applied to the Amsterdam SiCL transient σ_w BTC more than doubles from 0.16 to 0.33 dS m^{-1}.

We found that some R76 and R89 model parameters had very high degree of cross-correlation (Table 7), especially between *a* and *b* (R76) and α and β (R89), which potentially indicates over-parameterization of the models, thus increasing the probability of obtaining non-unique parameter sets. A single set of values suggested by Rhoades et al. (1989) could be used for α and β thus reducing the number of fitted parameters for the R89 model. However, based on our results and those of Vanclooster et al. (1994), it appears more realistic to assume that α and β are soil specific. Substitution of alternative functional forms for T(θ) in R76 and $\theta_{ws}(\theta)$ in R89 may provide more robust (unique) model parameter sets.

Table 7. Correlation coefficients (r)† for R76 and R89 parameter values reported in Tables 5 and 6.

	R76 Model			R89 Model		
	a:b	$a:\sigma_s$	$b:\sigma_s$	α:β	$\alpha:\sigma_s'$	$\beta:\sigma_s'$
Flathead Repacked (Matrix)	-0.860	0.486	-0.837	-0.729	0.420	0.278
Flathead Intact (Steady Flow)‡	-0.999	-0.406	0.396	-0.999	0.452	-0.445
Flathead Intact (Transient Flow)‡	-0.975	0.168	-0.372	-0.973	0.066	0.152
Amsterdam Repacked (Matrix)	-0.894	0.374	-0.706	-0.922	0.073	0.270
Amsterdam Repacked (Steady Flow)‡	-0.991	-0.290	0.170	-0.998	0.286	-0.242
Amsterdam Repacked (Transient Flow)‡	-0.893	0.514	-0.833	-0.964	-0.626	0.782

† PROC NLIN, SAS Institute Inc. 1991.

‡ Calibration Method 2 used for flow experiments.

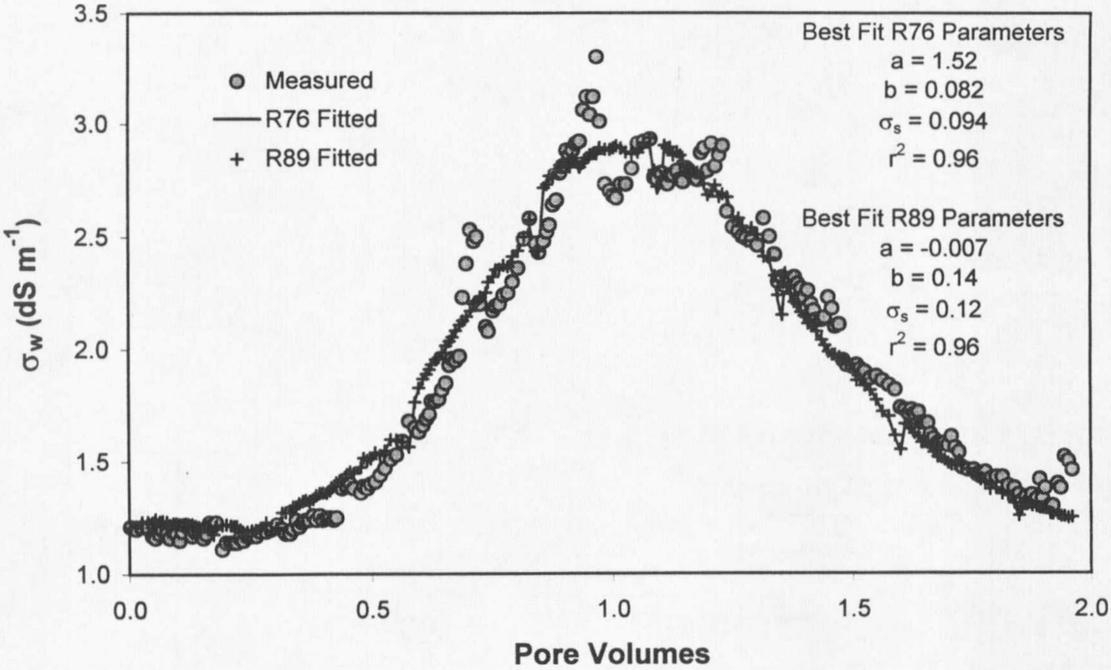

Figure 4. Fitted (optimized) σ_w for transient flow BTC using best fit Method 2 parameters from R76 and R89 models for intact Flathead soil.

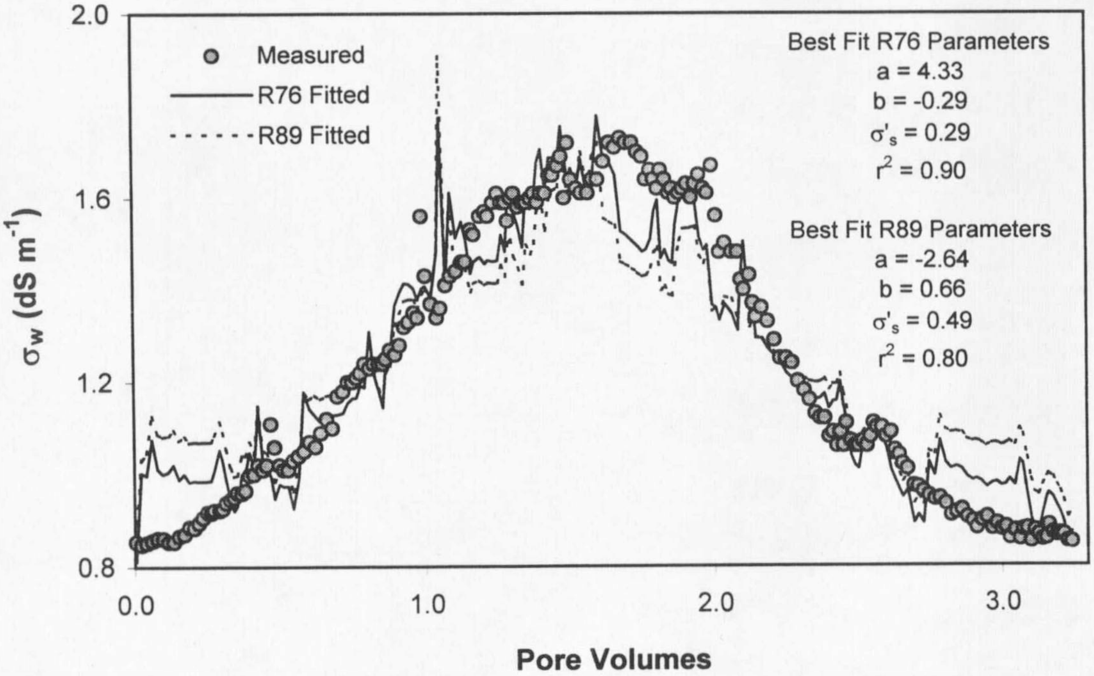

Figure 5. Fitted (optimized) σ_w for transient flow BTC using best fit Method 2 parameters from R76 and R89 models for repacked Amsterdam soil.

Results (Table 6) indicate little substantial difference (r^2) in the capability of the two models to describe the σ_a-θ-σ_w relationship for the transient flow experiments and any combination of calibration methods used in this study, with the exception of Methods 2 and 3 for the Amsterdam soil. Figures 4 and 5 show the best fit of both calibration models to transient flow BTCs for both soils. Both sets (Flathead and Amsterdam) of α and β parameters determined from the R89 model not only differ substantially from those suggested by Rhoades et al. (1989), but are physically unrealistic according to the model. Our results along with those of Kim et al. (1998) indicate that the R89 model may not be appropriate to use under strongly transient wetness conditions. σ_{wc} may not have been equal to σ_{ws} for our miscible displacement experiments, with the possible exception of (partial) periods when there was no solution application. Because of the greater range in θ for the Amsterdam soil (Table 4), it is likely that differences between σ_{wc} and σ_{ws} occurred more often than, and were more pronounced than for the Flathead soil. This may partially explain the poorer fit of the R89 relative to the R76 model for the Amsterdam soil.

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CHAPTER 3

PREDICTING SOIL SOLUTION ELECTRICAL CONDUCTIVITY UNDER LABORATORY AND FIELD CONDITIONS

Introduction

Maintaining, and in some instances improving soil and water quality is a priority among land stewards and scientists alike. Soils and water bodies are sinks for many pollutants including those generated from common agricultural practices. Many solutes derived from fertilizer salts become potential groundwater contaminants once leached through the upper soil profile. Aside from environmental concerns, monetary considerations increasingly advocate efficient use of soil-applied chemicals. Increasingly intensive farming practices require land managers to make informed decisions regarding the quantity and location of chemical inputs. Rapid and reliable measurement techniques that are able to assess ionic solute distributions (e.g., fertilizer salts) in soils could provide farmers with a potentially useful management tool. In addition, ionic contaminant monitoring and rehabilitation of contaminated soils could be expedited by such techniques.

Time domain reflectometry (TDR) is an established method for measuring volumetric soil water content (θ), is robust in terms of low sensitivity to local soil conditions, and has high spatial and temporal resolution (Topp et al., 1980; Wraith and

Baker, 1991). TDR can also measure bulk electrical conductivity (σ_a) in the same soil volume using the same probes (Dalton et al. 1984). Because of this unique ability, TDR has shown promise to monitor ionic solute distributions under transient soil wetness conditions (Risler et al., 1996; Persson, 1997; Hart and Lowery, 1998; Das et al., 1999).

Resident solute concentrations (C_r) can be estimated from σ_a measurements by invoking explicit or implied calibration models. Other available techniques to determine C_r *in situ* such as solution samplers and soil cores also have inherent advantages and limitations but do not have the potential of TDR to provide fast, real-time estimates. Soil solution electrical conductivity (σ_w) is directly related to C_r and thus is a more useful index of soil salinity than is σ_a. An appreciable effort has already been put forth to elucidate and model the complex relationships between σ_a, θ, and σ_w in soil-water systems (e.g., Sauer et al., 1955; Gupta and Hanks, 1972; Rhoades et al., 1976; Shainberg et al., 1980; Nadler and Frenkel, 1980; Bohn et al., 1982; Rhoades et al., 1989; Mualem and Friedman, 1991). Additional efforts, particularly in field settings, are needed to investigate the effectiveness of various models and calibration methods to estimate σ_w *in situ.*

This combined laboratory and field study was undertaken to help define the utility of three physical/conceptual models to predict σ_w under diverse experimental conditions. Two categories of laboratory column experiments were completed using repacked and intact soils: a static soil matrix factorial (multiple combinations of θ and σ_w); and ionic solute miscible displacement under steady and transient flow conditions. These experiments were combined with four different calibration methods to optimize soil-specific model parameters. Predictions of σ_w obtained using the Mualem and Friedman (1991) model were compared with independent measurements of σ_w from soil solution extracts and soil column effluent fractions. The efficacy of applying model parameters determined in a laboratory setting to predict σ_w under field conditions was then examined. Best-fit parameters from the MF model, as well as those obtained for the Rhoades et al. (1976; R76) and Rhoades et al. (1989; R89) models (Chapter 2) were combined with TDR measurements of θ and σ_a to estimate σ_w in the root zone of a peppermint (*Mentha piperita* L.) field. TDR σ_w estimates were compared with independently measured σ_w from soil core solution extracts obtained concurrently from the same field areas. Some results from the field study have been reported previously (Das et al., 1999). However, this paper builds upon the work of Das et al. (1999) by evaluating an additional model (R89) and two additional calibration techniques, using new calibration data.

Materials and Methods

Theoretical Background

Many relationships have been proposed between σ_a and σ_w in porous media. Mualem and Friedman (1991) developed one such conceptual model based on assumed similarity between electrical and water flow lines for a given hydraulic gradient:

$$\sigma_a = \sigma_w(\theta - \theta_r)F_g \qquad [1]$$

where θ_r is residual water content, θ-θ_r is the mobile pore water content or effective water content (θ_{eff}), and F_g is a θ-dependent geometry (flow tortuosity) function. Mualem and Friedman (1991) proposed F_g as the ratio of the hydraulic conductivity of the soil to that of a bundle of straight capillaries having the same effective pore diameter distribution. Their F_g is commonly expressed as:

$$F_g = \theta_{eff}^{\beta} \frac{\left[\int_0^{\Theta} \frac{1}{h(x)} dx\right]^2}{\int_0^{\Theta} \frac{1}{h(x)^2} dx} \qquad [2]$$

where Θ is relative saturation $[(\theta - \theta_r)/(\theta_s - \theta_r)]$, θ_s is saturated water content, h(x) is the soil water retention function subjected to integration and β is an empirical parameter that can be determined from known σ_a and σ_w at two or more θ. Combining Eq. [2] with [1] yields

$$\sigma_a = \sigma_w \theta_{eff}^{\beta+1} \frac{\left[\int_0^{\Theta} \frac{1}{h(x)} dx\right]^2}{\int_0^{\Theta} \frac{1}{h(x)^2} dx} \qquad [3]$$

Using the van Genuchten (VG) (1980) water retention function Heimovaara et al. (1995) obtained a closed form solution to Eq. [3]:

$$\sigma_a = \sigma_w \theta_{eff}^{\beta+1} \frac{\left[1-(1-\Theta^{1/m})^m\right]^2}{1-(1-\Theta^{1/q})^q} \qquad [4]$$

where m = 1-1/n and q = 1-2/p are empirical parameters describing the shape of $h(\theta)$, and may be estimated using a two step optimization process (Heimovaara et al., 1995). Other water retention models are available and some have been adapted for use with the MF model (Weerts et al., 1999; Das and Wraith, in review) but were not considered here.

The R76 approach is a simple two-conductors model whereby the liquid and solid phases in the bulk soil are treated as two parallel conductors contributing to σ_a:

$$\sigma_a = \sigma_w T(\theta)\theta + \sigma_s \qquad [5]$$

where σ_s is the electrical conductivity attributed to exchangeable ions along the surfaces of soil solids, and $T(\theta)$ is interpreted as a soil-specific transmission coefficient accounting for changes in the tortuosity of electrical current flow caused by changes in soil wetness. T has traditionally been characterized as a linear function of θ (Rhoades et al., 1976):

$$T(\theta) = a\theta + b \qquad [6]$$

with empirical soil-specific constants *a* and *b*.

Rhoades et al. (1989) developed a more complex conductor-based model (R89), in part to address the issue of curvilinearity between σ_a and σ_w at low σ_w as discussed by Nadler and Frenkel (1980), Shainberg et al. (1980), and others. A continuous solids conductance pathway is neglected in the R89 model based on its relative lack of contribution to the overall σ_a (Rhoades et al., 1989), resulting in the commonly utilized two parallel conductors formula:

$$\sigma_a = \left[\frac{(\theta_{ss} + \theta_{ws})^2 \sigma_{ws}\sigma'_s}{\theta_{ss}\sigma_{ws} + \theta_{ws}\sigma'_s}\right] + \theta_{wc}\sigma_{wc} \qquad [7]$$

with σ_{ws} and σ_{wc} the soil solution electrical conductivities of the solid/liquid series-coupled pathway (‘micropores’) and the continuous liquid pathway (‘macropores’), and

θ_{ws} and θ_{wc} the corresponding volumetric soil water contents. The surface conductance element in the solid/liquid series pathway is denoted σ_s'. Similar to $T(\theta)$ in the R76 model, Rhoades et al. (1989) described the magnitude of θ_{ws} in the solid/liquid series pathway as a linear function of θ:

$$\theta_{ws} = \alpha\theta + \beta \qquad [8]$$

with $\theta_{wc} = \theta - \theta_{ws}$.

The Topp et al. (1980) TDR calibration equation, previously confirmed for these soils, was used to determine θ under laboratory and field conditions. TDR σ_a measurements were based on the Giese and Tiemann (1975) relationship using:

$$\sigma_a = \frac{Z_0}{120\pi L Z_L} \qquad [9]$$

where the probe impedance (Z_0, Ω) was determined by immersion of probes in deionized water (Heimovaara, 1992; Baker and Spaans, 1993), L is TDR probe length (m), and Z_L is the measured resistive impedance load (Ω) across the embedded probes.

Laboratory Calibration Experiments

The soil water retention relationship [$\theta(h)$] required for F_g [2] in the MF model was determined for two soils: Flathead sandy loam (coarse-loamy, mixed Pachic Udic Haploboroll) obtained at the Northwest Agricultural Research Center near Creston, MT, and Amsterdam silty clay loam (fine-silty, mixed Typic Haploboroll) taken from the Arthur H. Post Experimental Station near Bozeman, MT (Table 1). For both Flathead and Amsterdam soils, $\theta(h)$ was obtained with a pressure plate apparatus (Klute, 1986).

Data were collected in the range 0 to -80 kPa for the Flathead soil (Das et al., 1999) and 0 to -1300 kPa for the Amsterdam soil. VG model parameters (α, n, m, p, q in Eq. [4]) were determined by fitting to measured water retention data using nonlinear least-squares optimization (Wraith and Or, 1998). Unlike Heimovaara et al. (1995), we did not fix α at the value obtained during the first step in the optimization process (m,n) during the second (p,q) step. Following the approach of Das et al. (1999), we fit α separately in both optimization steps, avoiding a mathematical inconsistency inherent in the method used by Heimovaara et al. (1995).

Table 1. Primary particle size fractions for Flathead SL and Amsterdam SiCL soils.

Size fraction	Flathead sandy loam	Amsterdam silty clay loam
Sand (%)	75	11
Silt (%)	18	60
Clay (%)	7	29

Two categories of laboratory soil column experiments were performed and are described in greater detail in Chapter 2. They included a soil salinity and wetness factorial matrix (different combinations of θ and σ_w), and ionic solute breakthrough under steady (Table 2) and transient (Table 3) flow conditions. Analogous to methods reported in Chapter 2 where laboratory experiments were combined with four different calibration approaches to provide parameter sets for the R76 and R89 models, we optimized the MF model β parameter using:

$$\sigma_w = \frac{\sigma_a\left[1-(1-\Theta^{1/q})^q\right]}{\theta_{eff}^{\beta+1}\left[1-(1-\Theta^{1/m})^m\right]^2} \qquad [10]$$

for the same soils under the same experimental conditions.

Calibration Method 1 (Table 2) was used in conjunction with the soil matrix factorial experiments and allowed estimation of model parameters from measurements of discrete σ_w-θ samples. Calibration Methods 2 and 3 were used with both transient and steady flow ionic solute breakthrough experiments. Method 2 is similar to Method 1 in that model parameters were estimated based on agreement with independently measured σ_w. However, Method 1 uses discrete σ_w-θ samples, while Method 2 covers a 'continuous' (at least potentially) range in one or both of these attributes at the same probe location. Method 3 is a mass-balance approach where model parameters were determined (optimized) by equating mass recovery calculated from predicted (model) σ_w to that from σ_w measured in the column effluent fractions. Method 4 was used only with the transient flow experiments. Conditions of constant σ_w are necessary for this method and were accomplished by leaching sufficient solution through the soil column.

Table 2. Calibration methods used for determination of R76 and R89 model coefficients.

Method	Description
1	Factorial soil column matrix (discrete σ_w-θ combinations)
2	Optimize TDR θ and σ_a to independently measured σ_w
3	Mass conservation of solute pulse
4	Constant σ_w, continuously variable θ and σ_a during soil wetting and drying

Simultaneous TDR measurements of variable σ_a and θ (at constant σ_w) then allowed for optimization of model coefficients (Risler et al., 1996). Further details on the calibration methods used in this study are presented in Chapter 2.

Field Study

A field experiment was performed from 15 April to 6 August, 1996 at the Northwest Agricultural Research Center near Creston, MT. This is the same location (within about 0.25 mi) where the Flathead soil used in the laboratory investigations was collected. The study area comprised four contiguous 21 x 6 m plots within a field under peppermint cultivation. An automated TDR system measured θ and σ_a every 6 h for three soil depths (0.15, 0.45, 0.90 m) at three locations within each plot. Thermocouples were placed near each TDR probe to compensate measured σ_a for ambient temperature. Sprinkler irrigation was applied approximately weekly during the latter half of the growing season. The study site was fertilized the previous October and on day of year (DOY) 99 (9 April). KNO_3 salt was hand-applied to plots I, II, and III at 300, 150, and 75 kg N ha^{-1} respectively on DOY 170 (19 June). Plot IV served as a control, with no added KNO_3. Soil core samples were collected every 1 or 2 weeks at three depth increments (0.10-0.20, 0.35-0.55, 0.80-1.00 m) at five randomly selected locations within each plot at each sample date. σ_w was measured from solution extracts obtained from each soil core using the methods outlined in Chapter 2. Additional details regarding experimental procedures for the field study were reported in Wraith and Das (1998) and Das et al. (1999).

Model parameter estimates obtained for the Flathead SL soil using the MF, R76, and R89 models and the four calibration methods were applied to TDR measurements of field soil θ and σ_a to generate TDR σ_w estimates for comparison with those from soil core solution extracts. The calibrated R76 and R89 parameters were presented in Chapter 2.

Results and Discussion

Laboratory Calibration of Model Parameters

Measured soil column flow attributes are summarized in Tables 3 and 4. Best fit parameters for the VG soil water retention model for both soils are shown in Table 5.

Table 3. Selected flow and salinity attributes for steady flow soil column experiments.

	Input Solution σ		Pulse	Application	Pore Water
	Background	Pulse	Duration	Rate	Velocity
	$dS\ m^{-1}$		pore volumes	$cm^3\ h^{-1}$	$cm\ h^{-1}$
Amsterdam Repacked	0.5	4.0	1.1	15	0.2
Flathead Repacked	0.1	1.7	1.3	80	1.2
Flathead Intact	0.5	4.0	1.2	40	0.6

Table 4. Selected flow and salinity attributes for transient wetness soil column experiments.

	Input Solution σ		Soil Water Content†		Application
	Background	Pulse	Min.	Max.	Rate‡
	$dS\ m^{-1}$		$m^3\ m^{-3}$		$cm^3\ h^{-1}$
Amsterdam Repacked	0.5	1.9	0.21	0.38	5.2
Flathead Intact	0.5	4.0	0.27	0.34	4.6

† measured at TDR probe location

‡ mean rate based on effluent fractions collected during several wetting and drying cycles

Table 5. Measured van Genuchten (1980) soil water retention parameters for Flathead and Amsterdam soils, using a two-step optimization process.

	Step I				Step II			
Soil Type	$\alpha_{m,n}$	n	m†	r^2	$\alpha_{p,q}$	p	q‡	r^2
Flathead SL	0.22	1.37	0.27	0.96	0.33	2.32	0.14	0.98
Amsterdam SiCL	0.092	1.44	0.31	0.98	0.14	2.38	0.16	0.99

† $m = 1 - 1/n$
‡ $q = 1 - 2/p$

MF model prediction agreement with independently measured σ_w was substantially better in experiments using the Flathead SL soil relative to those using Amsterdam SiCL soil. Predictions generated from the transient flow experiment with Amsterdam soil were especially poor compared to those for the Flathead soil. This may be explained in part by the greater magnitude in wetting and drying observed for the Amsterdam soil column relative to that of the Flathead soil (Table 4). In addition, the disparity in model performance between the two soils may be related to soil textural (and perhaps mineralogical) differences. The potential contributions of surface conductance (σ_s) to σ_a is unaccounted for by the MF model. Nadler (1991) emphasized the relative importance of σ_s by reporting that it can comprise a substantial proportion of σ_a depending on θ, minerology, and the concentration of ions in solution. Ions residing on the surfaces of clay minerals constitute the major contributions to σ_s (Nadler and Frenkel, 1980). Considering that the Flathead soil is low in clay (Table 1), σ_s would not be expected to contribute appreciably to σ_a for this soil relative to the Amsterdam soil which has about 29% clay fraction. Results presented here and statements made elsewhere (Mualem and Friedman, 1991; Vanclooster et al., 1994) suggest that the utility of the MF model may be limited primarily to coarse-textured soils.

Substantial variation in the value of optimized β for both soils from different experiments and calibration approaches was observed (Table 6). Analogous results were also reported in Chapter 2, where dissimilar parameters were obtained using the R76 and R89 models under the same experimental conditions as applied to MF here. β ranged from -1.139 for the Amsterdam SiCL transient flow experiment (Method 4) to 0.396 for the Flathead SL soil matrix experiment (Method 1). Other studies (Heimovaara et al., 1995; Leij et al., 1997; Das and Wraith, in review) have also obtained similar values for fitted β. Predicted σ_w for solute breakthrough curves (BTCs) under transient flow conditions using the MF model with different calibrated estimates of β provided inconsistent agreement with σ_w measured in the column effluent (Fig. 1, 2). The curves based on β derived from the soil matrix experiments substantially overpredicted effluent σ_w for both soils. This may be a result of dissimilar techniques used to measure σ_w

Table 6. Best fit MF model parameter β for all experiments and calibration approaches.

Experiment /	Flathead SL		Amsterdam SiCL	
Calibration Approach	Repacked	Intact	Repacked	Intact
	β (r^2)			
Soil Matrix / Method 1	0.396 (0.94)	-	-0.526 (0.65)	-0.575 (0.58)
Steady Flow / Method 2	0.053 (0.91)	-0.134 (0.97)	-0.907 (0.75)	-
Steady Flow / Method 3	-0.089 (0.88)	-0.197 (0.97)	-0.957 (0.71)	-
Transient Flow / Method 2	-	-0.112 (0.92)	-1.030 (0.26)	-
Transient Flow / Method 3	-	-0.125 (0.92)	-1.052 (0.24)	-
Transient Flow / Method 4	-	-0.246 (0.99)	-1.139 (0.62)	-

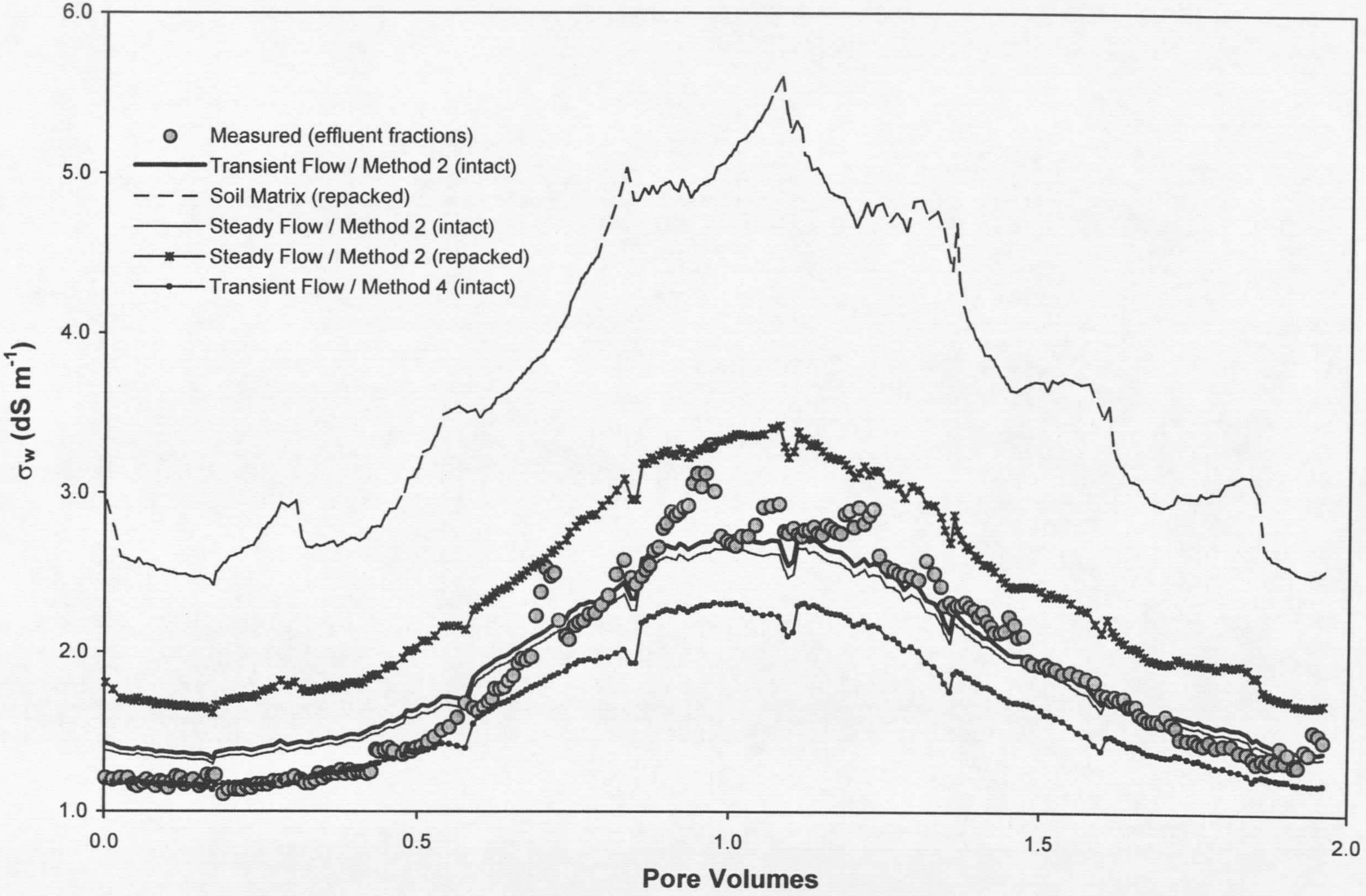

Fig. 1 Predicted σ_w for the intact Flathead SL soil using the MF model with best fit parameters obtained from 5 different experiments. Measured data is from transient flow miscible displacement experiment.

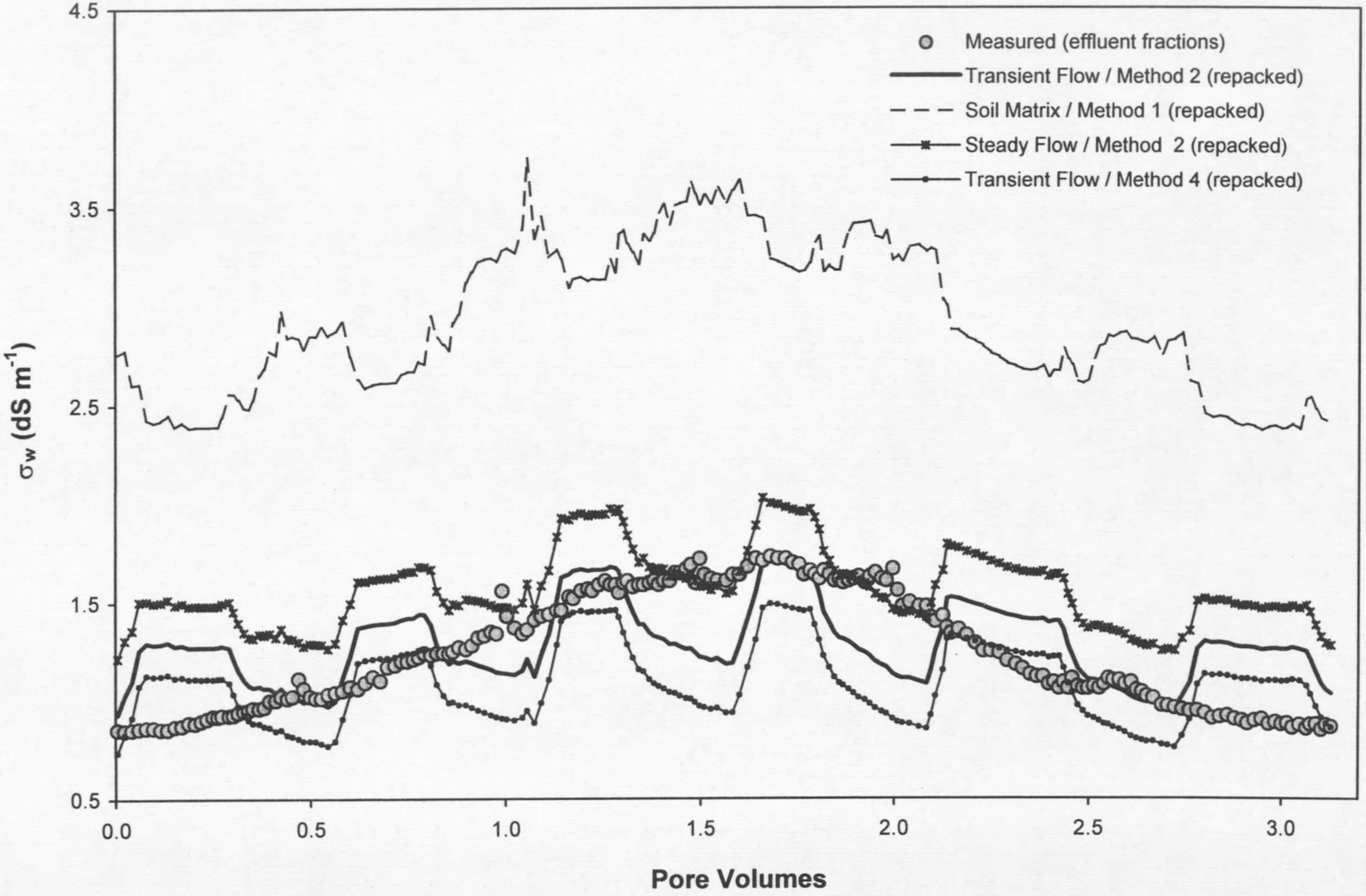

Fig. 2 Predicted σ_w for the repacked Amsterdam SiCL soil using the MF model with best fit parameters obtained from 4 different experiments. Measured data is from transient flow miscible displacement experiment.

among the flow column and soil column matrix experiments (Chapter 2). Nadler (1997) pointed out that for most soils it may be unrealistic to assume σ_w can be reconstructed from aqueous extract salinity (σ_e) by considering dilution only. However, an exact relationship between σ_w and σ_e for a particular soil would be difficult and time-consuming to quantify.

Prediction of the *intact* Flathead soil transient BTC based on β optimized from the *repacked* Flathead soil steady flow experiment mimicked the measured BTC in shape but systematically overestimated its magnitude (Fig. 1). For the same soils and experimental conditions, we found the same results with the R76 and R89 models (Chapter 2). This is likely a result of dissimilar experimental conditions that the two soil columns (repacked, intact) were subjected to (Table 2). Because β estimated using Method 2 from steady flow and transient flow experiments for the intact Flathead soil were similar (Table 6), these produced nearly identical predictions for the measured transient flow BTC (Fig. 1). Note that the transient flow β was optimized to measured effluent σ_w shown in Fig. 1, while β from the steady flow experiment was obtained from the same column but a different set of experimental conditions. For the same two experiments (Method 2, steady and transient flow) but with the Amsterdam soil, there was more variation in estimated β (Table 6) which is visually apparent from the model predictions generated from these parameters (Fig. 2). We found that for the transient wetness experiments, β estimated from calibration Method 4 (sequential wetting and drying) for both soils was smaller than from calibration Methods 2 and 3 (Table 5), resulting most noticeably in an underestimation of measured effluent σ_w except near the tails of the BTCs (Fig. 1,2).

Unlike Rhoades et al. (1976), Nadler (1991) suggested that σ_s varies with θ. Calculations using our data (not shown) confirmed that improved model estimates could be obtained by adding a variable surface conductance element to the MF model, especially for the fine-textured Amsterdam SiCL soil. For results presented in Chapter 2, specifying σ_s as a linear $f(\theta)$ for the R76 model showed a similar, although less substantial improvement.

Application of Laboratory Calibration Results to Field Data

Optimized MF model parameters determined from laboratory calibration experiments, in addition to those for the R76 and R89 models (Chapter 2), were applied to the measured field TDR σ_a and θ to generate TDR-predicted σ_w at 0.15 m depth. Spatial mean values of measured σ_a and θ for each time step were determined from TDR probes in three separate locations within each plot, and used to estimate plot-averaged σ_w. The σ_w obtained from soil cores were also calculated as means of measurements from five samples taken at randomly selected locations within each plot at each sample date. A subset of results are presented in Figs. 3 to 7. Magnitude of error bars for soil cores (Fig. 3-7) reflects spatial variance at the field location (Das et al., 1999).

Performance of all three models was best in terms of agreement with soil cores when using parameters determined from soil column matrix experiments. Figures 3 and 6 (R76 model), and 4 and 7 (MF model) illustrate a substantial difference in estimated σ_w generated by two distinct sets of laboratory-measured model parameters. Das et al.

(1999) obtained a similar underestimation of soil core σ_w when applying R76 model parameters independently determined in the laboratory to the same field data described in this study. Both Das et al. (1999) and Heimovaara et al. (1995) observed good agreement of MF model predicted versus field measured σ_w when using $\beta = 0.5$ (Mualem, 1976). Similar to our results, Heimovaara et al. (1995) applied an optimized β value (-0.40) from a laboratory soil column experiment under transient wetness conditions that resulted in an underestimation of field measured σ_w. The discrepancy was thought to be possibly related to differences in the magnitude of observed flux densities between the laboratory and field experiments (Heimovaara et al., 1995). A greater range in soil solution flux densities was observed for the Flathead SL transient wetness soil column experiment relative to the Flathead SL field experiment and thus could have been a contributing factor to the variability in β observed from our experiments. However, based on our results and on those of Das et al. (1999), we believe that similarities in experimental procedure primarily contributed to the result that model parameters generated from the soil column matrix experiments resulted in σ_w predictions closer to those of soil cores, relative to use of parameters determined from solute BTC experiments. Heimovaara et al. (1995) measured σ_w from solution samplers for both laboratory and field experiments. In both our field and soil column matrix experiments σ_w was determined from aqueous extracts, whereas salinity was measured directly from effluent fractions in the miscible displacement experiments. As stated previously (Chapter 2), dilution procedures involved in obtaining sample extracts may have affected the nature of the resulting

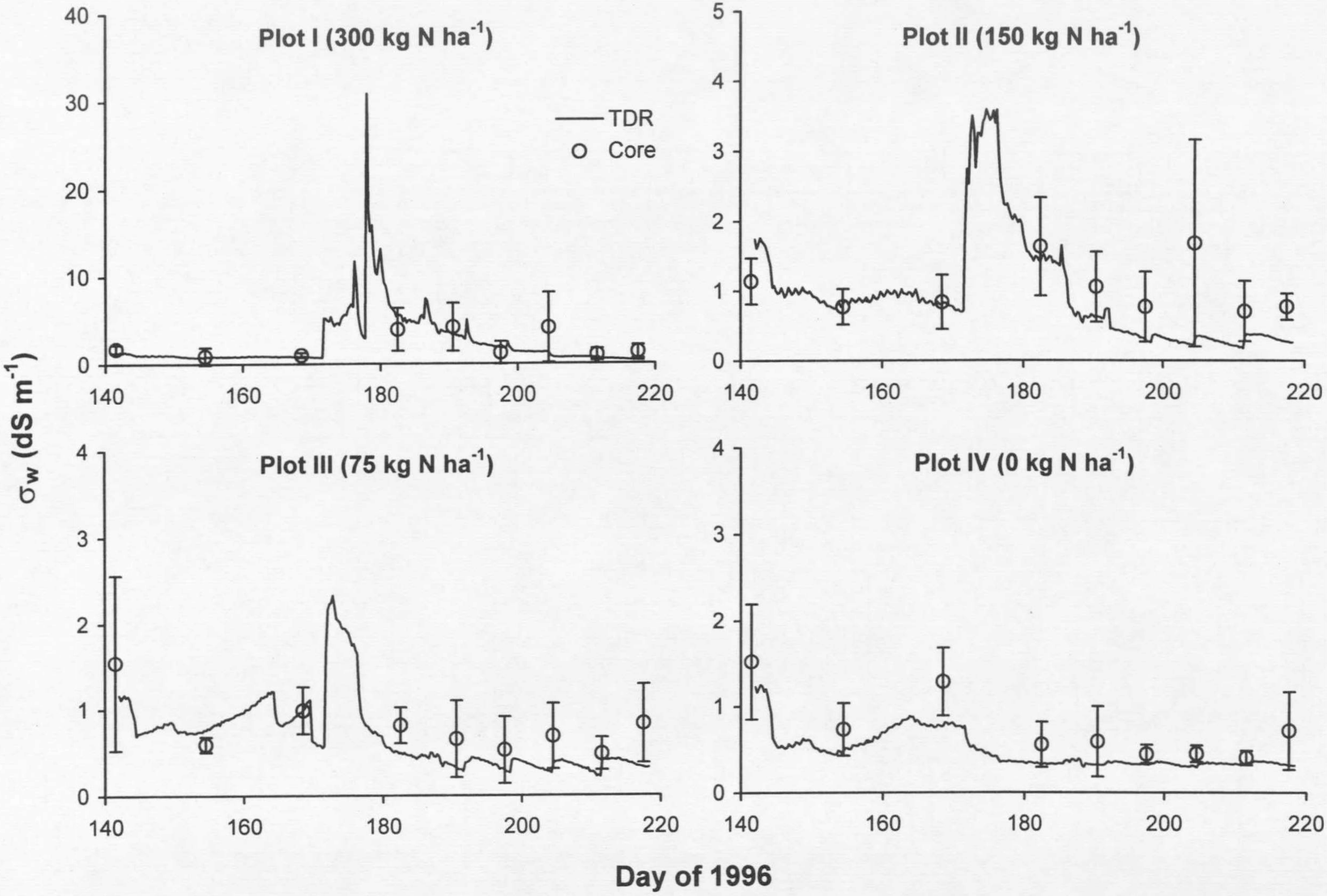

Fig. 3 TDR estimates of σ_w at 0.15 m depth in Flathead SL soil using the R76 model with best fit parameters determined from soil matrix experiments (Method 1). KNO_3 hand-applied on day 170.

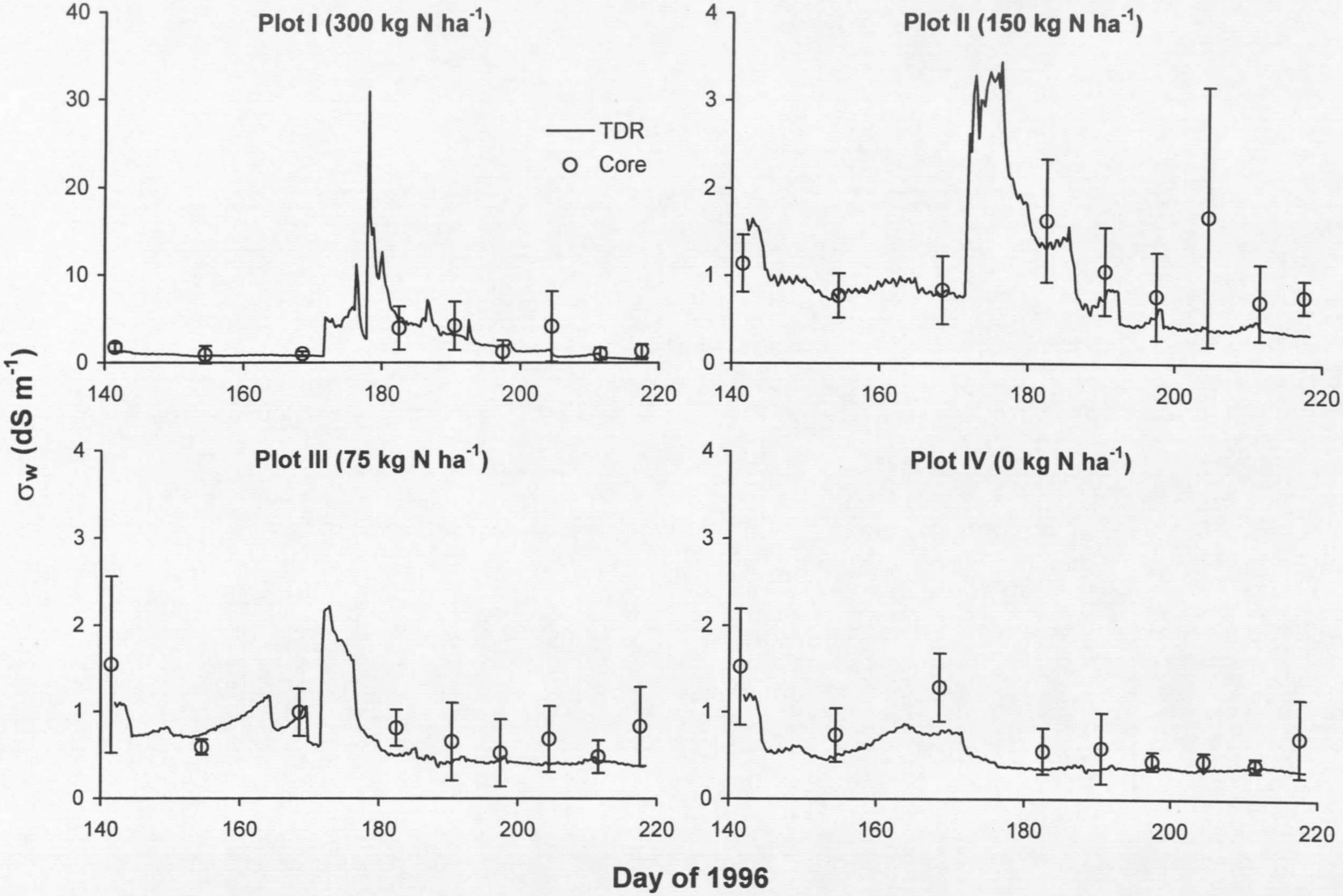

Fig. 4 TDR estimates of σ_w at 0.15 m depth in Flathead SL soil using the R89 model with best fit parameters determined from soil matrix experiments (Method 1). KNO_3 hand-applied on day 170.

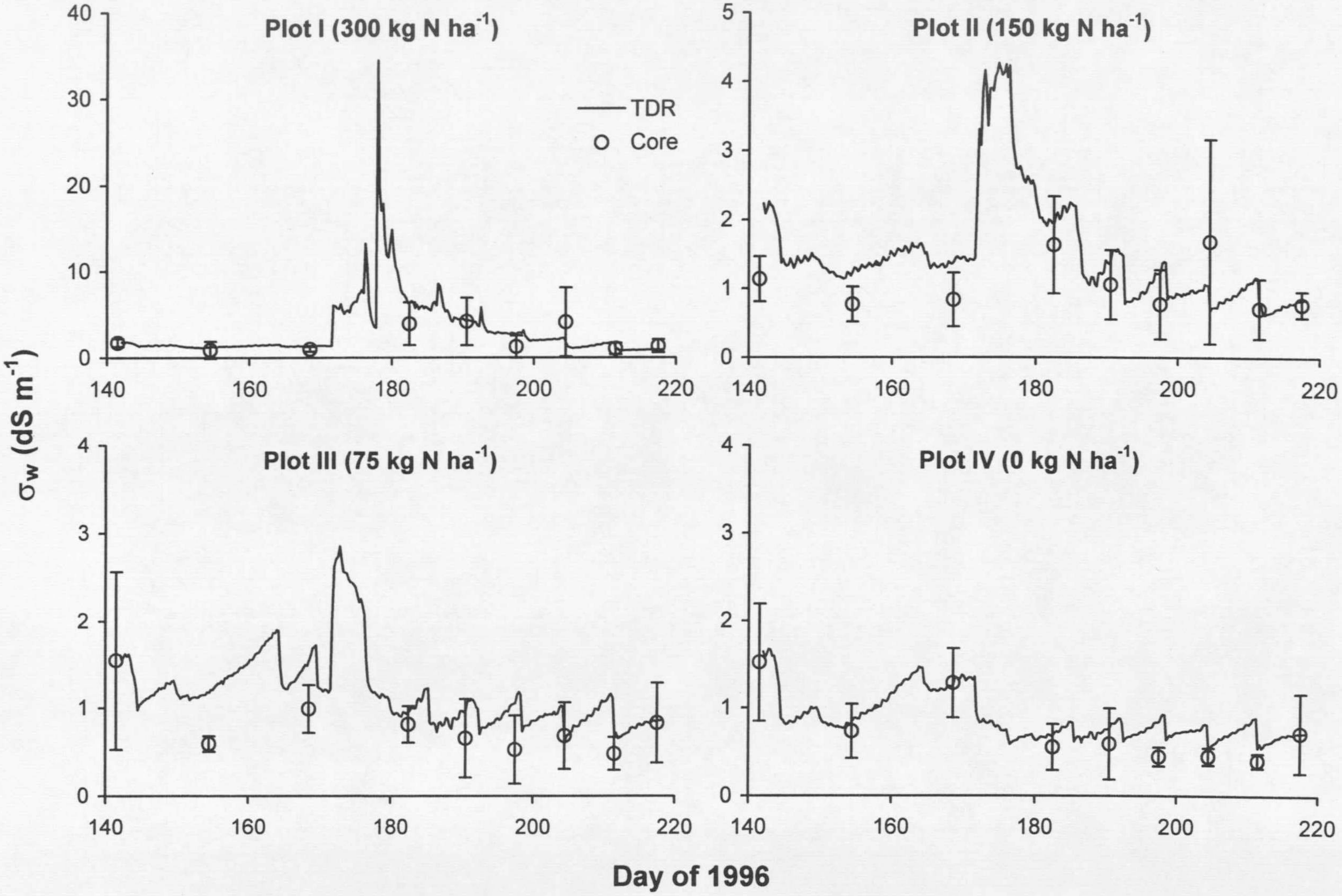

Fig. 5 TDR estimates of σ_w at 0.15 m depth in Flathead SL soil using the MF model with best fit parameters determined from soil matrix experiments (Method 1). KNO_3 hand-applied on day 170.

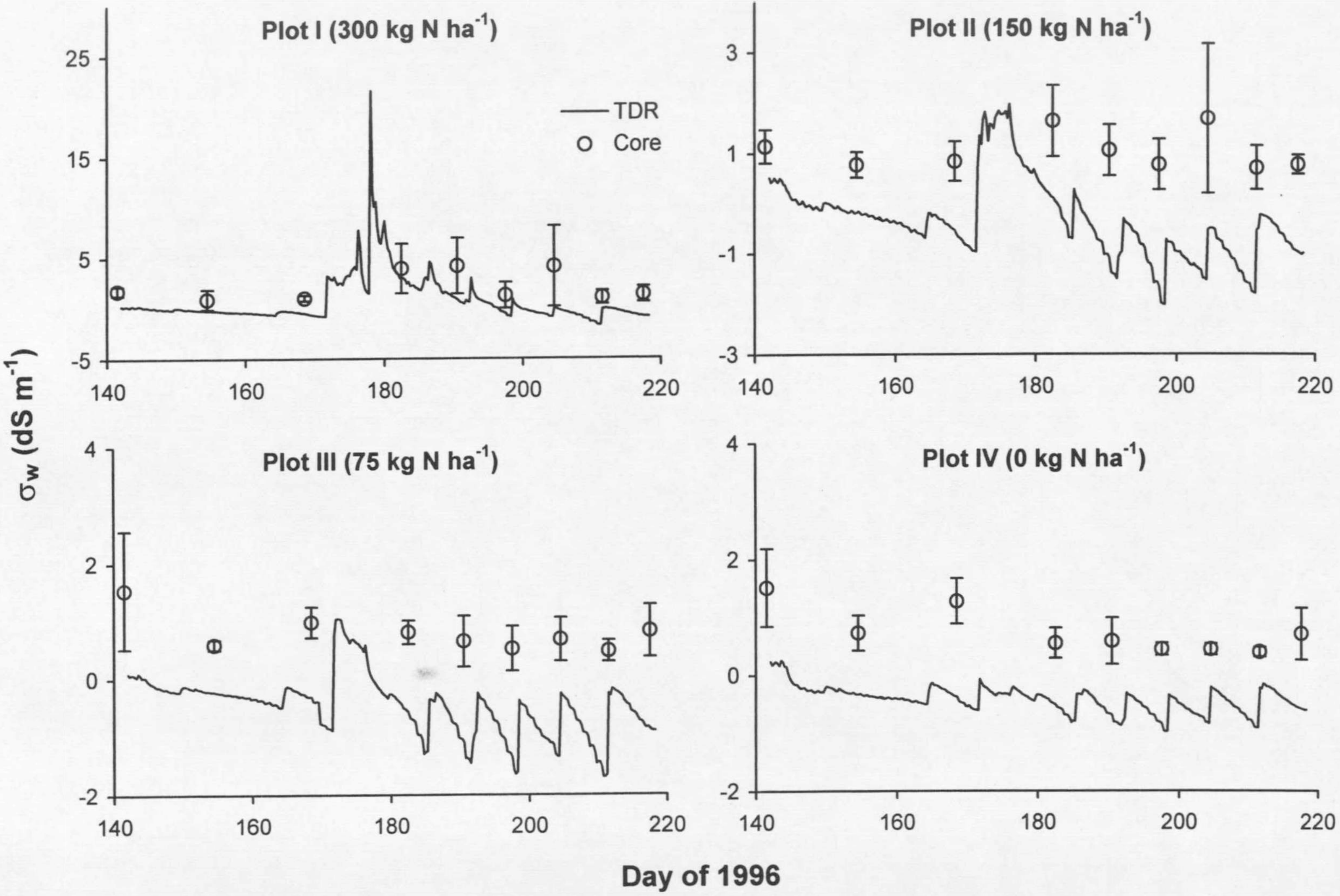

Fig. 6 TDR estimates of σ_w at 0.15 m depth in Flathead SL soil using the R76 model with best fit parameters determined from transient BTC experiment (Method 2). KNO_3 hand-applied on day 170.

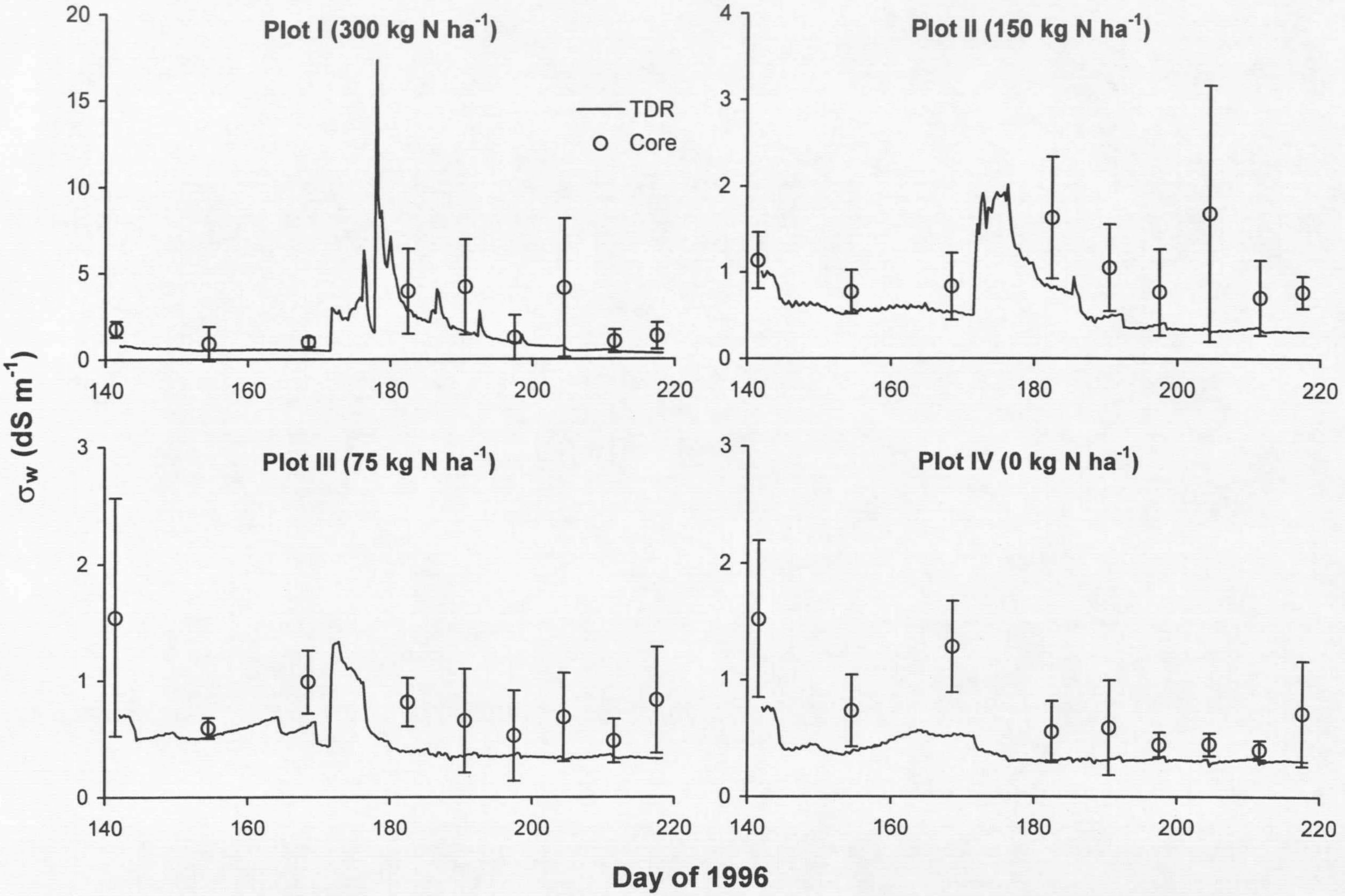

Fig. 7 TDR estimates of σ_w at 0.15 m depth in Flathead SL soil using the MF model with best fit parameters determined from transient BTC experiment (Method 2). KNO_3 hand-applied on day 170.

σ_a-θ-σ_w relationship. Potentially, this is a contributing factor to a systematic underestimation of field-measured σ_w by all parameter sets determined from solute breakthrough experiments (e.g. Fig. 6, 7). Unfortunately, we were unable to obtain soil solution samples from the field by vacuum extraction except for sample dates near the beginning of the field trial. Hence, we were unable to derive a meaningful comparison between σ_w measured from solution samples and soil cores. However, in instances where solution sample was collected by vacuum extraction, measured σ_w was nearly always less than as measured from soil cores in the same plots (Das et al., 1999: Figs. 3, 4).

The MF model parameterized using laboratory soil column solute breakthrough experiments provided better agreement with soil cores than did the R76 and R89 models parameterized using the same experiments (e.g. Figs. 6 and 7). For the MF model, we observed smaller changes in estimated σ_w when testing a range in parameter values, relative to varying parameters for the R76 and R89 models. We varied only β for the MF model, as the retention parameters (α, m, p, θ_r, θ_S) were fitted to measured water retention data for each soil. The lower 'sensitivity' exhibited by the MF model proved a benefit in this case, although in the absence of accurate retention parameters this characteristic might be of little practical value.

Using TDR data from steady flow experiments (obtained prior to the pulse application when σ_a was relatively stable) we found that the standard deviations ($100 < n < 267$) varied from 0.0004 to 0.002 (θ) and from 0.001 to 0.004 dS m^{-1} (σ_a). Thus the maximum uncertainty in θ and σ_a measurements due to repeatability are about

0.002 (θ) and 0.004 dS m^{-1} (σ_a). Using these values, the predicted uncertainty (sensitivity) to changes in σ_w based on measured changes in θ and σ_a should be no more than (Wraith and Baker, 1991) $2^{0.5}(0.002) + 2^{0.5}(0.004) = 0.0085$ dS m^{-1}, and could be as low as $2^{0.5}(0.0004) + 2^{0.5}(0.001) = 0.0020$ dS m^{-1}. Combining these sensitivity estimates with a measured calibration relationship between σ_w (dS m^{-1}) and nitrate-N (ppm) for the Flathead soil (Das et al., 1999) results in a measurement sensitivity of 0.20 to 0.90 ppm for changes in soil nitrate concentration. These results suggest that TDR provides a highly sensitive means to discern small changes in both σ_w and ionic solute concentration, under variable soil wetness. For some practical applications it may be more important to detect changes in σ_w with very high resolution than to (necessarily) estimate σ_w with high absolute accuracy. For example, detection of solute loading near the base of the root zone could allow land managers to schedule water and chemical inputs more efficiently.

The possibility of experimental bias in determining the σ_a-θ-σ_w relationships based on dilution then extraction of solution from soils for Method 1 and for the field study does not detract from the observations made in this study and in Das et al. (1999) regarding the potential utility of TDR for *in situ* field monitoring of ionic solutes. The fact that the pattern and magnitude of some σ_w estimates based on TDR measurements are in good agreement with those based on independently measured σ_w is encouraging. Results from this study and others (Noborio et al., 1994; Das et al., 1999) indicate that useful estimates of σ_w, particularly in coarse-textured homogenous field soils, are achievable using TDR combined with simple conceptual models and calibration methods.

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CHAPTER 4

SUMMARY

Laboratory experiments were conducted to evaluate the efficacy of three calibration models coupled with four calibration approaches to infer σ_w under variably saturated soil conditions. In addition, model coefficients optimized from laboratory procedures were used to estimate σ_w under field conditions and results were compared with σ_w measured from soil core extracts. This study demonstrated the potential to obtain very good estimates of σ_w for laboratory and field conditions, under variable wetness and ionic concentrations, using appropriate TDR models and calibration methods. Optimization of R89 and MF model parameters was more tedious than for the R76 model due to their greater mathematical complexity. While many model/calibration method combinations provided excellent σ_w estimates based on comparisons to independently measured values, dissimilar model parameters were generated for the same soils under different experimental conditions and for different calibration methods. Some of the systematic discrepancy in the σ_a-θ-σ_w relationship determined from flow and soil column matrix experiments is explained by differences in experimental procedures for obtaining measured σ_w. Parameters obtained from transient flow experiments and using calibration Methods 2 (optimization of TDR θ and σ_a to σ_w measured from column effluent fractions) and 3 (mass conservation of a solute pulse) always described the experimental data from Method 4 (which had low variability in σ_w) and from steady flow experiments (having low variability in θ) better than for the converse situation. Therefore it seems prudent to calibrate the σ_a-θ-σ_w relationship under conditions having as wide a range in variability of σ_a, σ_w, and θ as possible. Choosing a calibration method that will provide a reasonable amount of variability in σ_a, θ, and σ_w should also minimize the potential for obtaining non-unique parameters for both the R76 and R89 models. Alternative functional forms for T(θ) in R76 and θ_{ws} in R89 models might also potentially provide a useful means to address the issue of non-unique model parameters.

This study and the related work of Das et al. (1999) indicated that the selection of appropriate calibration techniques is at least as important to obtaining reliable estimates of σ_w with TDR as is the chosen calibration model. The best estimates of σ_w for the Flathead field soil were obtained using model (R76, R89, MF) parameters derived from calibration Method 1 (soil column matrix), presumably due to similar techniques used to measure σ_w in each case. Because of this potential procedural artifact, we are not confident in the universality of our findings that the factorial soil column matrix is the superior laboratory calibration method for application to field measurements. Calibration relationships determined based on agreement with σ_w are useful only if the baseline measurements are accurate. Additional research is needed to evaluate the agreement and accuracy of different techniques used to measure baseline σ_w in soils.

Based on results of the three models analyzed in this study, it seems likely that the conductor-based models (R76, R89) may be better suited to use with heavier textured soils than is the MF model. Adding a surface conductance (σ_s) element to the MF model could potentially improve σ_w estimates for finer textured soils. In accordance with Heimovaara et al. (1995), results indicated that fitting the β parameter in the MF model (rather than assuming $\beta = 0.5$; Mualem 1976) improved TDR σ_w estimates. The MF model is potentially as effective as the conductor based models (R76, R89) for use with coarse textured soils, has only one fitting parameter (other than for the chosen soil water retention model) compared to three for the R76 and R89 models, and σ_w estimates appear to be less sensitive to changes in this (β) parameter than for some of the parameters in the R76 and R89 models.

Preliminary results (not shown) from this study also suggest that specifying σ_s as a variable function of θ should improve model estimates of σ_w, especially for fine-textured soils and under conditions of extreme transient soil wetness. The trade-off between an additional level of empiricism and improved model performance could prove worthwhile. Additional work is needed to help clarify the relationships between σ_s, θ, and σ_w.