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Field estimation of soil hydraulic and chemical transport properties

Salem Ali Matar Al-Jabri

Iowa State University

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Field estimation of soil hydraulic and chemical transport properties

by

Salem Ali Matar Al-Jabri

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

Major: Water Resources
Major Professor: Robert Horton

Iowa State University
Ames, Iowa
2001
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This is to certify that the Doctoral dissertation of

Salem Ali Matar Al-Jabri

has met the dissertation requirements of Iowa State University
DEDICATION

To my mom, who is wondering when I’ll be done with my studies
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ABSTRACT

Managing soil and groundwater resources requires characterization of the hydraulic and chemical transport properties. The determination of such properties on field scales requires conducting extensive numbers of measurements to well represent the spatial distribution and variability of field properties. However, extensive measurements of properties in the field is hampered by the long time-frame required by most of current field procedures.

This study introduces a setup and procedure by which the hydraulic and chemical transport properties can be rapidly estimated at multiple locations. The setup consists of a multiple dripper permeameter, where drippers serve as point sources. The hydraulic properties include saturated hydraulic conductivity ($K_s$) and macroscopic capillary length ($\lambda_c$). The hydraulic properties were estimated by measuring a sequence of steady-state water flux densities on the soil surface. The chemical transport properties include immobile water content ($\theta_{im}$), mass exchange coefficient ($\alpha$) and dispersion coefficient in the mobile domain ($D_m$). These chemical transport properties were determined by applying a sequence of conservative tracers into the soil (ST method).

The setup and the procedure were evaluated on six sites on a greenhouse soil pit and tested under actual field conditions with a total of 50 sites. The hydraulic and chemical transport properties were found to be representative when compared with previously reported results for nearby locations and similar soils. A field procedure for determining the chemical transport properties, based on using time domain reflectometry (TDR), was also presented. Breakthrough curves of 38 field locations were obtained from real-
time TDR-measurements of soil bulk electrical conductivity. The transport parameters \((\theta_{im}, \alpha, D_m)\) from the BTCs were found to be comparable with the parameters produced by the ST-method conducted on the same field location.

The overall results of this study show that the setup and procedure presented here facilitate rapid measurements of surface hydraulic and chemical transport properties at multiple field locations. Such procedures are ideal for management studies that require conducting extensive measurements to better characterize transport processes through the vadose zone.
1.1 Introduction

The vadose zone is that portion of the geologic profile beneath the earth’s surface and above the first principal water-bearing zone (Cullen et al., 1993). Water flow in the vadose zone is characterized by periods of unsaturated flow interrupted by periods of nonequilibrium flow events, such as preferential flow. In the last three decades, the vadose zone became a major interest for soil and environmental scientists as a result of increased concerns, by the general public and federal agencies, about the quality of drinking water. Water and dissolved chemicals move through interconnected pore spaces and reach groundwater resources. The quality of groundwater could be easily deteriorated from land-applied chemicals. The potential contamination of groundwater resources could be minimized by monitoring the movement of water and chemicals through the vadose zone. Soil hydraulic (hydraulic conductivity and water retention) and chemical transport properties are considered the major inputs in the transport models to predict the movement of water and chemicals through the vadose zone.

Understanding the mechanisms by which water and chemicals move through the vadose zone helps in developing management programs to protect soil and water resources. Thus, field and laboratory studies have been conducted for the last three decades to study water and chemical movement through the vadose zone. Such initiatives have provided a conceptual understanding on the processes that control such movement. However, the complexity associated with transport mechanisms necessitates the need for further re-
search exploration, especially for nonequilibrium flow mechanisms. Most field methods, unfortunately, require extensive allocations of time and labor resources. They are confined to a single measurement from a single observation site in a given time period. Such constraints limit the extent of conducting field studies. As a result, current advancement in field studies have lagged behind advancement in theoretical concepts and simulation transport models (Ward et al., 1995).

The overall objectives of this research work were: (1) to present a field setup and procedure that facilitate conducting rapid measurements of the hydraulic and chemical transport properties at multiple field locations, and (2) to study the spatial distribution of those properties across a field. This chapter briefly describes the theory behind the processes by which water and chemicals move through the vadose zone. It also reviews the experimental work conducted to study flow mechanisms with special emphasis on characterization of preferential flow.

### 1.2 Water Movement

Water movement into the soil is governed by the interaction of water-source geometry, the hydraulic conductivity, \( K \), and the sorptivity, \( S \) (Philip, 1969). The sorptivity is a soil-water parameter that gives information about the soil water pressure potential, \( h \), the hydraulic conductivity, \( K = K(h) \), and the soil water diffusivity function, \( D(\theta) \). It represents the capillary forces of the soil. The hydraulic conductivity, \( K \), reflects the effects of gravitational forces on water flow through the soil. These parameters are used in predicting and quantifying the distribution of water and chemicals in the vadose zone.

Water flow in the vadose zone can be described by Richards (1931) equation. For three dimensional flow of water into rigid, isothermal, unsaturated soils, the Richards equation can be written as:

\[
\frac{\partial \theta}{\partial t} = \nabla \cdot (K \nabla H)
\]  

(1.1)
where \( \theta \) is the soil water content (L\(^3\) L\(^{-3}\)), \( K \) is the hydraulic conductivity (L T\(^{-1}\)), \( H = h + x \) is the total pressure head (L), \( h \) is the soil pressure head (L), \( x \) is the gravitational-head component (L), \( t \) is the time (T), and \( \nabla \) is the vector gradient operator (L\(^{-1}\)). The steady-state form, i.e. \( \partial \theta / \partial t = 0 \), of Eq. 1.1 can be written as (Philip, 1969):

\[
\frac{\partial K}{\partial z} = \nabla \cdot (D \nabla \theta) 
\]  

(1.2)

where \( D = K(dh/d\theta) \) is the soil water diffusivity (L\(^2\) T\(^{-1}\)), and \( z \) is soil depth (L). Both \( K \) and \( D \) are a function of \( \theta \) and the soil water pressure head, \( h \) (Scotter et al., 1982). Equation 1.2 can be linearized using the following transform (Gardner, 1958):

\[
\phi(\theta) = \int_{\theta_i}^{\theta} D(\theta) \, d\theta = \int_{h_i}^{h} K(h) \, dh 
\]  

(1.3)

where \( \phi \) is the matric flux potential (L\(^2\) T\(^{-1}\)), \( \theta_i \) and \( \theta \) are the dry (initial) and wet (final) water contents that correspond to \( h_i \) and \( h \); the dry and wet soil pressure heads (L). This linearization often assumes the Gardner (1958) exponential function:

\[
K(h) = K_s \exp(h/\lambda_c)  
\]  

(1.4)

where \( K_s \) is the saturated hydraulic conductivity (L T\(^{-1}\)), and \( \lambda_c \) is a soil parameter called the macroscopic capillary length (L). The \( \lambda_c \) parameter quantifies the importance of capillary forces relative to gravity forces (Philip, 1969). In other words, it predicts the lateral movement of water from a source relative to its vertical penetration deep into the soil. It is large in fine-textured soils, while small in coarse-textured soils. Any discrepancies in the trend of \( \lambda_c \) is attributed to the presence of preferential flow paths (White and Sully, 1992). Following the above linearization procedure, Eq. 1.2 can be written in a linearized form as:

\[
\nabla^2 \phi = (1/\lambda_c) \, \partial \phi / \partial z 
\]  

(1.5)

Wooding (1968) provided the first analytical solution for the flow equation from a source at steady-state conditions. He assumed that soil was uniform, homogenous,
nonswelling, and followed the hydraulic conductivity function described by Eq. 1.4. He
proposed a quasi-analytical solution for infiltration of water per unit area, $q$, from a
circular source of radius $r_o$ on the soil surface as:

$$q = \frac{Q}{\pi r_o^2} = K(h) + \frac{4}{\pi r_o} \phi(h)$$  \hspace{1cm} (1.6)

where $Q$ is the volumetric flux rate from the source ($L^3 T^{-1}$). If the pressure-head
boundary of the source is known, i.e. a device where the applied pressure head is known
or controlled, then Eq. 1.6 becomes:

$$q = K_s \exp \left( \frac{h}{\lambda_c} \right) \left( 1 + \frac{4\lambda_c}{\pi r_o} \right), \quad K(h_i) \ll K(h)$$  \hspace{1cm} (1.7)

Equation 1.7 has been used to determine the hydraulic properties ($K(h)$, $\lambda_c$) from
ponded and tension infiltrometers (disc sources) with one or more supply pressure heads
(Ankeny et al., 1988, 1991; Reynolds and Elrick, 1991; Prieksat et al., 1992; Logsdon and
Jaynes, 1993; Hussen and Warrick, 1993). For water application from a point source,
Wooding (1968) assumed $h \approx 0$ for $r < r_o$ and $q \approx 0$ for $r > r_o$. Using those boundary
conditions, Wooding (1968) presented a solution for water flow from a shallow circular
pond of radius $r_o$ on the soil surface so that Eq. 1.7 can be written as:

$$q = K_s \left( 1 + \frac{4\lambda_c}{\pi r_o} \right), \quad r_o/\lambda_c \leq 10$$  \hspace{1cm} (1.8)

Water flow from a source is three-dimensional. This is because of gravity forces
acting downward and capillary forces acting in all directions. Water application from a
point source usually creates a circular saturated zone (shallow pond) on the soil surface.
The ponded area is created due to the infiltration rate at the soil surface (below the
source) is being lower than the discharge rate from the source. A wetted area, i.e. less
than saturation, is created around the saturated front on the soil surface. The lateral
movement of the saturated front (on the soil surface) will continue until gravitational
forces (acting downward) predominate the infiltration process. The saturated area, over
the soil surface, will then reach a constant size (Bresler, 1978) and steady-state conditions and their solutions can then be implemented (Shani et al., 1987). Wooding’s solution for water application from a point source (Eq. 1.8) implies that applying increasing flow rates from a source (on the same soil location) would yield ponded areas of increasing diameters (at steady-state conditions). Regressing the different values of $q$ versus their corresponding $1/r_0$ results in a linear relationship with a positive slope and intercept (Eq. 1.8). The $K_s$ is equivalent to the intercept, and the $\lambda_c$ parameter can be determined from the slope, $4K_s\lambda_c/\pi$. A wide range of discharge rates is desirable for better estimation of the hydraulic parameters (Shani et al., 1987).

Several studies have used the point source method and Wooding’s (1968) solution to quantify soil’s hydraulic properties. Merrill et al. (1978) observed good agreement between measured and predicted pressure heads in an undisturbed column during steady-state infiltration from a point source. Hydraulic parameters and pressure head-water content relations in the field were studied by Shani et al. (1987) using the point source method. The estimates for parameters produced by the point source method were in good agreement with those produced from ring infiltrometers. A similar comparison study was conducted by Yitayew et al. (1998). They conclude that the method is practical and can be used under varying conditions. Water flow and chemical transport from a point source were studied on sand columns by Ward et al. (1995) using time domain reflectometry (TDR). Ward et al. (1995) reported that the estimates of macroscopic capillary length, $\lambda_c$, were comparable to independently determined values (for a given soil). They suggested that this method is practical in predicting $\lambda_c$ and chemical travel times, which are used to investigate the migration of contaminants from point sources and design of drip irrigation systems.

The variability of the pressure potential of the soil, average pore velocity, and water content around point sources yield a complex relationship between soil properties and chemical transport. Numerous temporal and spatial studies are required to prop-
erly characterize this relationship. However, conducting such studies is hampered by shortage of instrumentation and soil variability, which makes such investigations almost impossible for validating analytical or numerical models for three-dimensional flow using field experiments (Ward et al., 1995). Moreover, field methods are confined to a single output for each observation site in a given time period. Thus, most field methods require extensive time and labor resources, which make them not feasible for conducting extensive spatial and temporal measurements. Recently, Or (1996) presented a field setup that utilizes the point source method so that hydraulic properties can be rapidly measured with minimum labor requirements. He was able to determine the field distribution of hydraulic properties within a short time period. Perhaps, his setup can be a foundation for simultaneous estimation of the hydraulic and chemical transport properties across fields. This would increase understanding of the mechanisms by which water and chemicals move and the interactions between different transport parameters and the hydraulic properties for a given soil condition and time.

1.3 Chemical Transport

Chemical transport within soils is governed by three mechanisms, namely convection or mass flow, diffusion, and dispersion. Convection of chemicals refers to the passive movement of dissolved chemicals along with flowing water. For one-dimensional transport, the convective movement of chemicals, \( J_m \), is described as:

\[
J_m = qC
\]  

where \( q \) is the Darcy’s flux or flux density (L T\(^{-1}\)), and \( C \) is the solution concentration (M L\(^{-3}\)). Diffusive movement, \( J_d \), refers to the thermal movement of dissolved ions and molecules. Thus, it can be described by Fick’s law of diffusion as:

\[
J_d = -\theta D_d \frac{\partial C}{\partial z}
\]
where $D_d$ is the soil diffusion coefficient (L² T⁻¹). Diffusion of chemicals in soil or any porous media is always less than that in water. This is because of the tortuosity effects in soil and other porous media. The tortuosity is a result of variable pore geometry, i.e., size and distribution. Different sizes, shapes, and orientation of pores result in different pore velocity, $v$. The pore velocity also varies within each pore from maximum at the center of the pore to minimum at the pore boundaries.

The mechanical spreading of $v$ is called mechanical dispersion. Dispersive transport, $J_h$, can be described by the following equation:

$$J_h = -\theta D_h \frac{\partial C}{\partial z}$$  \hspace{1cm} (1.11)$$

where $D_h = \gamma v$ is the mechanical dispersion coefficient (L T⁻²), and $\gamma$ is the soil dispersivity (L). The coefficients $D_d$ and $D_h$ are usually combined to produce the longitudinal hydrodynamic dispersion, $D$ (van Genuchten and Wierenga, 1986).

Combining Equations 1.9, 1.10, and 1.11 produces the flux of chemicals, $J_s$, in soil and other porous media as:

$$J_s = -\theta D \frac{\partial C}{\partial z} + qC$$  \hspace{1cm} (1.12)$$

Combining Eq. 1.12 with the continuity equation for one-dimension transport of chemicals yields the general chemical transport equation, which is often called convective-dispersive equation (CDE). For one dimensional transport of nonsorbing chemicals, the CDE can be represented as:

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial z} \left[ \left( \theta D \frac{\partial C}{\partial z} \right) - qC \right]$$  \hspace{1cm} (1.13)$$

For sorbing chemicals the CDE becomes:

$$\frac{\partial C}{\partial t} = \frac{D \frac{\partial^2 C}{\partial z^2}}{R} - \frac{v}{R} \frac{\partial C}{\partial z}$$  \hspace{1cm} (1.14)$$

where $R$ is the retardation factor (M L⁻³) that can be described as:

$$R = 1 + \frac{\rho_b K_f}{\theta}$$  \hspace{1cm} (1.15)$$
where \( \rho_b \) is the soil bulk density \( (M \, L^{-3}) \), and \( K_f \) is the first-order Freundlich partition coefficient. The \( R \) parameter represents the relative movement of chemicals through pore spaces. Except for negatively charged ions, the \( R \)-value is usually \( \geq 1 \).

A retardation factor greater than 1 means a delay in the downward movement of chemicals. This results in the delay of chemical front behind the wetting front of water. The effects of dispersivity, \( \gamma \), is less pronounced. It affects the concentration/depth distribution, but does not affect the depth of maximum concentration. During a rainfall or irrigation event, chemical transport depends on the initial water content of the soil. During the early stages of infiltration, chemicals move with flowing water, i.e. convective movement, into the unsaturated zone. During water redistribution, diffusion is considered the most dominant mechanism by which chemicals move through the soil. Moreover, transport of chemicals at field conditions is a function of the heterogeneity of soil properties and preferential flow.

### 1.4 Preferential Flow

In structured soils that contain large pores, such as root and worm holes and cracks, water and chemicals may move preferentially through these pores. This phenomena is variously called macropore flow, bypassing, short-circuiting, partial displacement, preferential flow, or transport within “mobile” and “immobile” domains (Brusseau and Rao, 1990). It can be defined as the rapid movement of water and/or chemicals through a fraction of the total pore space available for flow (Radcliffe and Rasmussen, 1999). The movement of chemicals through a fraction of the pore space results in increasing the pore velocity in this fraction and, thus, water and chemicals reach great depths within a short time. This results in water bypassing a fraction of pore spaces in the soil matrix. Preferential flow has been documented by many research studies, such as Biggar and Nielsen (1962); Ehlers (1975); Kanwar et al. (1985); Rice et al. (1986); Bond and
Wierenga (1990). Such nonequilibrium movement causes asymmetry, which is the early arrival of chemicals and long tailing in the breakthrough curves, BTCs (Khan and Jury, 1990). The early arrival of chemicals is attributed to the rapid transport of chemicals through the macropores (between the aggregates). The long tailing is attributed to the gradual release of chemicals (through molecular diffusion) from small pores in the aggregates and "dead-end" pores back into the main stream of flow (van Genuchten and Wierenga, 1976).

Many studies showed that the CDE (Eq. 1.13) cannot describe the preferential flow events in the BTCs (Jaynes and Horton, 1998). A two-region model, often called the mobile-immobile model (MIM), has proven to better describe the asymmetry in the BTCs (Griffioen et al., 1998). This model was first introduced by Coats and Smith (1964) in the field of petroleum engineering and later used by van Genuchten and Wierenga (1976) to describe chemical transport in soils. This model has been used to describe transport of chemicals in saturated and unsaturated soils. In its simplest form, it divides the water-filled pore space ($\theta$) into two domains: a mobile water domain ($\theta_m$) where water and chemicals move by advection, and immobile water domain ($\theta_{im}$) where water is stagnant (relative to $\theta_m$) and chemicals move by diffusion only. For one dimensional transport of a conservative nonsorbing chemical, the MIM can be written as (van Genuchten and Wierenga, 1976):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - q \frac{\partial C_m}{\partial z}$$

(1.16)

where $C_m$ and $C_{im}$ are the chemical concentrations in the mobile and immobile domains (M L$^{-3}$) and $D_m$ is the dispersion coefficient (L$^2$ T$^{-1}$) in the mobile domain. The transfer of chemicals between the two domains is proportional to the concentration difference between the two domains and is described as a first-order process (van Genuchten and Wierenga, 1976):

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

(1.17)
where $\alpha$ is a first-order mass exchange coefficient ($T^{-1}$).

Many studies have used the MIM model as a basis for predicting chemical transport parameters. The preferential flow parameters, $\theta_m$ and $\alpha$, are affected by average pore velocity, $v$, water content, and aggregate size (van Genuchten and Wierenga, 1977; Gaudet et al., 1977; Nkedi-Kizza et al., 1983; Kookana et al., 1993). The mobile water content was found to fluctuate with variations in total water content ($\theta$) and increases with increasing pressure head of flowing water (Angulo-Jaramillo et al., 1996; Casey et al., 1998). The mobile water content was found to vary from 0 (Cassel, 1971) to 35-55% (Smettem, 1984; Gvirtzman and Magaritz, 1986) to 75% in tropical soil (Seyfried and Rao, 1987) and massive desert soil (Jaynes et al., 1988). The $\alpha$ parameter was found to be a function of the pore velocity, even though they are not dependent on each other (see Eq. 1.17). Positive correlations between $q$ and $\alpha$ have been reported by many studies, such as van Genuchten and Wierenga (1977), Kookana et al. (1993), and Casey et al. (1997).

The MIM parameters $(\theta_m, \alpha, D_m)$ are usually found by inverse methods, where the transport parameters are fitted to observed BTCs (Parker and van Genuchten, 1984). However, BTCs are difficult to obtain in the field. Alternatively, Clothier et al. (1992) proposed a field procedure to estimate $\theta_m$ from field studies. They used tension infiltrometers to infiltrate $Br^-$ into soil under unsaturated conditions. Assuming negligible $\alpha$ and $D_m$ in the sampling zone, and concentration in the mobile domain ($C_m$) equal to the input concentration ($C_0$), Clothier et al. (1992) solved Eq. 1.17 for finding $\theta_m$ as:

$$
\theta_m = \theta \left( \frac{C}{C_0} \right) 
$$

(1.18)

where $C$ is the tracer concentration in the soil sample ($M L^{-3}$).

Jaynes et al. (1995) extended the solution of Clothier et al. (1992) to further estimate $\alpha$. Assuming piston displacement in the mobile domain ($C_m = C_0$), negligible $D_m$ within the sampling zone, and no tracers in the soil prior to any tracer application, Jaynes et al.
(1995) presented the following solution to Eq. 1.17 as:
\[
\ln \left(1 - \frac{C}{C_0}\right) = \ln \left(\frac{\theta_{im}}{\theta}\right) - \frac{\alpha}{\theta_{im}} t^*
\]  
(1.19)
for sequential application of conservative tracers. The term \(t^*\) represents the time required for solution-front to pass the sampling depth, \(z'\), as determined by \(t^* = t - z'/v\).

As shown by Eq. 1.19, regressing \(\ln(1 - C/C_0)\) versus \(t^*\) would yield both \(\theta_{im}\) and \(\alpha\) from the resulting intercept and slope, respectively. Jaynes et al. (1995) used fluorobenzoic acids as their conservative tracers. Those tracers were found to have similar transport properties in many soils (Jaynes, 1994) and similar diffusion coefficients (Bowman and Gibbens, 1992; Benson and Bowman, 1994).

The solution presented by Jaynes et al. (1995) was tested in the laboratory by Lee et al. (2000b) using undisturbed columns. They compared it with parameters determined from effluent BTC data by using inverse fitting procedures. They found that 70% of transport parameters produced by Eq. 1.19 were within the 95% confidence interval of parameters produced by the fitting output. They concluded that the sequential tracer solution (Eq. 1.19) was successful in predicting the transport parameters. Casey et al. (1997) used tension infiltrometers to infiltrate a sequence of fluorobenzoate tracers on 47 sites along a transect at a ridge-tilled corn field. They found that immobile water fraction \(\left(\theta_{im}/\theta\right)\) ranged from 0.39 to .95 and \(\alpha\) ranged from 0.014 to 0.29 h\(^{-1}\). These estimates were within the magnitude reported by other investigators.

### 1.5 Use of TDR to estimate Chemical Transport Properties

Time domain reflectometry (TDR) for simultaneous estimation of the total water content \(\theta\) and the bulk electrical conductivity of soil \(\sigma_a\) was introduced by Dalton et al. (1984). Since then, several studies have provided the basis for theory and procedures for using the TDR for measuring \(\theta\) and \(\sigma_a\) (Zegelin et al., 1989; Nadler et al., 1991; Ward et al., 1994). Measurements of \(\sigma_a\) using the TDR are related to chemical
concentrations in soil pores, which is related to the total concentration of chemicals surrounding the TDR probes (Kachanoski et al., 1994). The soil bulk electrical conductivity is inversely related to the impedance load, $Z$ (Ω), of the TDR (Nadler et al., 1991):

$$\sigma_a = \kappa Z^{-1} \quad (1.20)$$

where $\kappa$ is a cell constant that depends on the probe geometry. The impedance load from the TDR is affected by the total water content, $\theta$, and the electrical conductivity of surrounding solution, $\sigma_w$. These effects take place in the region of influence of the TDR probes. At steady state conditions ($\partial\theta/\partial t = 0$), a linear relationship is observed between $\sigma_a$ and $\sigma_w$ (Rhoades et al., 1976). This assumption is valid for practical levels of $\sigma_w$ of 4.0 to 50.0 dS m$^{-1}$ (Ward et al., 1994). For a similar range of $\sigma_w$, a linear relation was also observed between the concentration of ions, $C$, and $\sigma_w$. At constant $\theta$, therefore, there exists a linear relationship between $C$ and $\sigma_a$ as (Ward et al., 1994):

$$C = \delta + \xi \sigma_a \quad (1.21)$$

where $\delta$ and $\xi$ are calibration constants. Substituting the $\sigma_a$ of Eq. 1.20 into Eq. 1.21 yields:

$$C = \beta_0 Z^{-1} + \beta_1 \quad (1.22)$$

where $\beta_0$ and $\beta_1$ are calibration constants. In leaching experiments, thus, one can determine the change in relative concentration at any time, $\mathcal{C}(t)$, from TDR-measured $Z$ using Eq. 1.22 as:

$$\mathcal{C}(t) = \frac{C(t) - C_i}{C_o - C_i} = \frac{Z_i^{-1}(t) - Z_i^{-1}}{Z_o^{-1} - Z_i^{-1}} \quad (1.23)$$

where $C_i$ is the background chemical concentration (M L$^{-3}$), $Z_i$ is the TDR impedance load for $C_i$, and $Z_o$ is the impedance load for $C_o$. Because of the linear relationship between $C$ and $Z$ (see Eq. 1.21), the calibration constants in Eq. 1.22 need not be determined for estimating $\mathcal{C}(t)$. 
The term $C/C_0$ in Eq. 1.19 represents the relative resident concentration in the soil. Similarly, the term $\bar{C}(t)$ from Eq. 1.23 also represents the relative resident concentration in the soil. Thus, one can use the $\bar{C}(t)$, as measured by the TDR-technique, to determine the chemical transport parameters ($\theta_{im}$ and $\alpha$) from the solution proposed by Jaynes et al. (1995). Lee et al. (2000a) used this concept to determine the chemical transport parameters ($\theta_{im}$, $\alpha$) from a column-leaching study. They used horizontal TDR-probes (installed at an angle for a vertical depth of 2 cm from the soil surface) to determine the transport parameters from the TDR-measured $Z$. They found that estimated parameters from the TDR technique were similar to those estimated from the method of sequential application of tracers proposed by Jaynes et al. (1995).

The $Z_i$ term in Eq. 1.23 can be directly determined from the known concentration of the tracer in background solution. However, the $Z_o$ term is difficult to determine. Ward et al. (1994) and Mallants et al. (1996) suggested applying a long pulse of step solution to determine $Z_o$. Their assumption was that application of the step solution for a long time yields a uniform distribution of the tracer in the soil matrix, and that $Z_o$ was then assumed to be the TDR-reading at the end of the experiment, i.e. at final time step ($t_f$). If, however, $\theta_{im} > 0$, then the concentration of the tracer applied in the soil matrix is less than that in the input solution (Jaynes and Horton, 1998). This has been verified by Lee et al. (2000a) with leaching experiments using intact soil columns. To overcome such difficulty, Lee et al. (2000a) suggested sampling the soil around the TDR probes and analyzing it for the tracer concentration at $t_f$. The $\bar{C}(t_f)$ and the final TDR reading, $Z(t_f)$, can be substituted in Eq. 1.23 to determine $Z_o$. Relative concentration at any given time, $\bar{C}(t)$, can then be determined from Eq. 1.23 using the TDR readings of $Z(t)$.

The impedance load, $Z$, can be determined from the TDR waveforms using the simplified procedure described by Wraith et al. (1993). Wraith et al. (1993) introduced a simplified analysis of TDR waveform for automated monitoring of chemical transport
using TDR. Wraith et al. (1993) stated that the impedance load, \( Z \), can be determined from:

\[
Z = Z_{\text{ref}} \frac{(1 + \rho)}{(1 - \rho)}
\]

(1.24)

where \( Z_{\text{ref}} \) is the reference impedance load from the cable tester (50 \( \Omega \) for Tektronix 1502B/C), and \( \rho \) is the reflection coefficient of the TDR waveform. Detailed analysis on how to determine \( Z \) from the TDR-waveform can be found in Wraith et al. (1993).

The above procedure, that involves using the TDR, can be utilized to determine chemical breakthrough curves (BTCs) from field measured \( \bar{C}(t) \). Besides using the solution developed by Jaynes et al. (1995) to estimate \( \theta_{im} \) and \( \alpha \), all transport parameters (\( \theta_{im}, \alpha, D_m \)) can be estimated from the real-time measurements of \( \bar{C}(t) \). This can be achieved by fitting those parameters on measured BTCs. The CXTFIT fitting package (Toride et al., 1995) can be used to process the fitting procedure. Obtaining BTCs from field studies can be a difficult task. This TDR technique provides a simple means for obtaining BTCs from field measurements, allowing for more data collection, and thus, more accurate prediction of transport of chemicals can be achieved.

1.6 Dissertation Organization

This dissertation is organized into three technical articles, which are intended to be or have been submitted to professional scientific journals for publication. The first article (Chapter 2) represents an evaluation study, in which a point source setup was evaluated for coupled determination of the hydraulic and chemical transport properties. The study was conducted on six observation sites in a greenhouse soil pit. The estimated parameters produced by the point source method were compared with those produced by the ponded and tension infiltrometers. The point source method produced representative estimates for both sets of properties and with minimum set of variability. The results from the evaluation study are the basis for the second article (Chapter 3), where 50
field locations were simultaneously evaluated for the hydraulic and chemical transport properties. The spatial distribution of properties across the field was also investigated. A procedure to estimate the chemical transport properties from real-time measurements of change in chemical concentration is presented in the third article (Chapter 4). Time domain reflectometry (TDR) was used to measure the chemical concentration in soil over time at multiple field locations. All transport parameters (immobile water content, mass exchange coefficient, and dispersion coefficient) were determined from the TDR-technique by fitting them on observed breakthrough curves from field measurements. Chapter 5 summarizes the general conclusions of this research work and future research opportunities.

References


CHAPTER 2  A POINT SOURCE METHOD FOR RAPID ESTIMATION OF HYDRAULIC AND CHEMICAL TRANSPORT PROPERTIES

A paper submitted to Soil Science Society of America Journal

Salem A. Al-Jabri¹, Robert Horton², and Dan B. Jaynes³

2.1 Abstract

Hydraulic and chemical transport properties are needed for accurate prediction of water and chemical movement through the vadose zone. Field methods used to estimate such properties are often hampered by extensive labor and time constraints. One of the objectives of this study was to develop an experimental setup for a point source method that facilitates rapid and simultaneous measurements of soil hydraulic and chemical transport properties at multiple locations. Another objective was to evaluate the point source method by comparing the parameters with those produced by ponded and tension infiltrometers. The experimental setup consisted of three dripper lines equipped with pressure-compensating drippers. The setup was evaluated on a greenhouse soil pit. Determined hydraulic properties were saturated hydraulic conductivity \((K_s)\) and macroscopic capillary length \((\lambda_c)\). Hydraulic properties from the point source method were

¹Dept. of Soil and Water Sciences, Sultan Qaboos University, Muscat, Sultanate of Oman
²Dept. of Agronomy, Iowa State University, Ames, Iowa
³USDA-ARS, National Soil Tilth Laboratory, Ames, Iowa
determined by applying four consecutive discharge rates on the soil surface and measuring their corresponding steady-state saturated areas. Determined chemical transport parameters were immobile water fraction ($\theta_{im}/\theta$) and mass exchange coefficient ($\alpha$). They were determined by applying a sequence of three conservative fluorobenzoate tracers. The point source method gave consistent estimates for both sets of properties with minimum set of variability. Except for $\alpha$, there was no significant difference between the two procedures (point source vs. infiltrometers) in determining both sets of properties. The study showed that the point source setup could be utilized for rapid and simultaneous estimation of soil hydraulic and chemical transport properties at multiple locations with minimum labor requirements.

2.2 Introduction

Determining hydraulic and chemical transport properties of field soils is a fundamental requirement for managing soil and water resources. Hydraulic properties (hydraulic conductivity and water retention) are needed to predict the movement of water and chemicals through the vadose zone towards groundwater resources. Characterizing hydraulic and chemical transport properties helps in developing best management practices that minimize potential contamination of natural resources. Hydraulic and chemical transport properties are also needed for efficient management of different irrigation systems.

Adequate evaluation of field hydraulic and chemical transport properties requires a large number of measurements to reflect their spatial and temporal variability across the field. Despite the availability of mathematical analysis and models describing the steady flow of water (Philip, 1969; Warrick, 1974, 1985) and transport of chemicals (Gelhar and Collins, 1971; van Genuchten and Wierenga, 1976; Clothier et al., 1992; Jaynes et al., 1995), there have been only a few studies conducted in the field. One reason for a lack of
field studies is that field procedures require extensive time and labor resources. Current field methods are confined to a single measurement at a single field location. For example, tension infiltrometers are widely used to characterize field hydraulic properties. However, it requires a relatively long time to use them with management studies, especially where spatial and temporal measurements are needed. Moreover, different field methods result in different estimations of properties. Therefore, field methods should be evaluated and compared for their applicability in determining soil properties (Reynolds et al., 2000). In general, simple and reliable methods are needed to characterize hydraulic and chemical transport properties at field conditions.

A point source method has been developed for measuring in situ hydraulic properties (Shani et al., 1987; Revol et al., 1991, 1997; Yitayew et al., 1998) and chemical transport parameters under controlled environments (O’Brien et al., 1994; Ward et al., 1994, 1995). The simplicity of this method makes it ideal for rapid and repeatable measurements of field hydraulic properties (Yitayew et al., 1998). Recently, Or (1996) introduced an experimental setup for determining hydraulic properties using the point source method. His setup consisted of a multiple-dripper permeameter that facilitated determining the properties with minimum labor requirements.

Jaynes et al. (1995) proposed a procedure to determine chemical transport properties in the field. They used tension infiltrometers to apply a sequence of conservative tracers to the soil. By measuring the resident concentration in soil samples, they were able to determine the immobile water fraction, \( \theta_{im}/\theta \), and the mass exchange coefficient of chemicals, \( \alpha \). Casey et al. (1998) used tension infiltrometers to estimate hydraulic and chemical transport properties across a field. They estimated hydraulic properties using the multiple tension method (Logsdon and Jaynes, 1993), and chemical transport properties using the sequential tracer method proposed by Jaynes et al. (1995). Their study, however, required extensive labor allocations and was time consuming (about 4 weeks). Thus, there exists a need for a method that facilitate rapid determination of
field hydraulic and chemical transport properties.

One objective of this study was to develop and evaluate an experimental setup and a procedure, that utilizes a point source method, to rapidly and simultaneously determine soil hydraulic and chemical transport properties with minimum labor requirements. Another objective was to evaluate the point source method for coupled estimation of hydraulic and chemical transport properties. This was achieved by comparing the estimates of hydraulic and chemical transport properties produced from the point source method with those produced by the ponded and tension infiltrometers. Determined hydraulic properties were saturated hydraulic conductivity ($K_s$) and macroscopic capillary length ($\lambda_c$). Wooding's (1968) solution was used to estimate $K_s$ and $\lambda_c$. Chemical transport properties were immobile water content (expressed as immobile water fraction, $\theta_{im}/\theta$) and mass exchange coefficient ($\alpha$). The sequential tracer method proposed by Jaynes et al. (1995) was used to estimate $\theta_{im}/\theta$ and $\alpha$. Estimated parameters from the point source method were compared with the estimates produced by ponded and tension infiltrometers.

2.3 Theory

Water flow into soils can be described using Richards (1931) equation. For one dimensional water flow into rigid, isothermal soils, Richards equation can be written as:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[ K(h) \left( \frac{\partial h}{\partial z} + 1 \right) \right]$$

(2.1)

where $\theta$ is the soil water content (L$^3$ L$^{-3}$), $K(h)$ is the hydraulic conductivity (L T$^{-1}$), $h$ is the soil-water pressure head (L), $t$ is time (T), and $z$ is depth (L). Solving Eq. 2.1 for steady state conditions often requires a linearization procedure using the matrix flux potential, $\phi$, (Philip, 1968):

$$\phi(h) = \int_{h_i}^{h} K(h) \, dh$$

(2.2)
where $h_i$ and $h$ are the dry and wet soil-water pressure heads (L). Wooding (1968) presented an approximate solution to Eq. 2.1 for steady-state flow per unit area, $q$, from a shallow saturated pond on the soil surface as:

$$q = \frac{Q}{\pi r_o^2} = K_s \left(1 + \frac{4\lambda_c}{\pi r_o}\right), \quad r_o/\lambda_c \leq 10 \quad (2.3)$$

where $Q$ is the discharge rate of the source (L$^3$ T$^{-1}$), $K_s$ is the saturated hydraulic conductivity (L T$^{-1}$), $r_o$ is the steady-state pond radius (L), and $\lambda_c$ is a scaling parameter (L). The $\lambda_c$ parameter quantifies the importance of capillary forces relative to gravity forces (Philip, 1969). Wooding (1968) assumes that the soil is uniform, homogenous, nonswelling and has an exponential hydraulic conductivity function (Gardner, 1958):

$$K(h) = K_s \exp\left(\frac{h}{\lambda_c}\right) \quad (2.4)$$

The first term on the right side of Eq. 2.3 represents the contribution of gravity to the flow, and the second term represents the contribution of capillarity and geometry of the source. If a disc source is used, such as ponded or tension infiltrometers, the same principle applies (Ankeny et al., 1991). Using the definition of the matric flux potential (Eq. 2.2) and substituting the hydraulic-conductivity function (Eq. 2.4) for $K(h)$, Wooding’s solution (Eq. 2.3) can be rewritten to describe water flow from disc sources as:

$$q = K_s \exp\left(\frac{h}{\lambda_c}\right) \left(1 + \frac{4\lambda_c}{\pi r_o}\right), \quad K(h_t) \ll K(h) \quad (2.5)$$

where $r_o$ is the disc radius (L). Equation 2.5 has been widely used to determine the hydraulic parameters ($K(h), \lambda_c$) from steady infiltration data produced by ponded and tension infiltrometers (Ankeny et al., 1988, 1991; Reynolds and Elrick, 1991; Prieksat et al., 1992; Logsdon and Jaynes, 1993; Hussen and Warrick, 1993).

Applying water to the soil surface from a point source produces a circular (or nearly circular) saturated area on the soil surface. This occurs when the discharge rate is higher than the infiltration rate of the soil. When a constant flux of water is applied to
the soil from a source the saturated area increases with time, but eventually reaches a constant size (Bresler, 1978), where steady-state conditions prevail. Once steady-state conditions occur, Wooding’s solution can be applied (Shani et al., 1987). Warrick (1985) introduced another solution for hydraulic properties from a point source at steady-state conditions. The surface boundary-condition used by Warrick (1985) was constant flux rate, whereas Wooding (1968) used constant head for his solution. Warrick’s solution produces estimates about 20% higher than Wooding’s solution. Thus, it is not necessary to compare the output of the two solutions as Yitayew et al. (1998) did. In this study, we used Wooding’s solution in our analysis to determine $K_s$ and $A_c$. Applying increasing discharge rates ($Q$) from a point source at the soil surface would yield ponded areas of increasing $r_a$. Following Eq. 2.3, plotting the values of $q$ versus the corresponding $1/r_o$ results in a straight line with an intercept equivalent to $K_s$, and $A_c$ can be determined from the resulting slope, $4K_s \lambda_c / \pi$.

Chemical movement through soils is often described by the convection-dispersion equation (CDE). However, many studies have reported the occurrence of preferential flow, which often cannot be described by the classical CDE (Jaynes and Horton, 1998). Preferential flow can be described as the rapid movement of water and chemicals through large pores, such as cracks or pores made by earthworms and plant roots. Thus, a small quantity of water is needed for chemicals to reach great depths in the soil. A two domain model was proposed by Coats and Smith (1964) and later extended by van Genuchten and Wierenga (1977) to better describe preferential flow into structured soils. This model suggests that wetted pore volume is a combination of mobile and immobile domains. For one dimensional movement of nonsorbing chemicals, the CDE can be written in the form of the two domains as (Coats and Smith, 1964):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - q \frac{\partial C_m}{\partial z}$$

(2.6)

where $\theta_m$ and $\theta_{im}$ are the water contents of mobile and immobile domains ($L^3 L^{-3}$), $C_m$
and \( C_{\text{im}} \) are the chemical concentrations in the mobile and immobile domains (M L\(^{-3}\)), and \( D_m \) is the dispersion coefficient (L\(^2\) T\(^{-1}\)), active in the mobile domain only. The movement of chemicals between the two domains is described as a first-order diffusion process (van Genuchten and Wierenga, 1976):

\[
\theta_{\text{im}} \frac{\partial C_{\text{im}}}{\partial t} = \alpha (C_m - C_{\text{im}}) \tag{2.7}
\]

where \( \alpha \) is a first-order mass exchange coefficient (T\(^{-1}\)).

Jaynes et al. (1995) provided a simple procedure to estimate \( \theta_{\text{im}} \) and \( \alpha \) parameters of the "mobile-immobile" model without the need for extensive breakthrough experiments. Their method involves using a sequence of conservative tracers having similar transport characteristics. Assuming piston movement of chemicals in the mobile domain of the soil, Jaynes et al. (1995) integrated Eq. 2.7 to give:

\[
\ln \left(1 - \frac{C}{C_o}\right) = \ln \left(\frac{\theta_{\text{im}}}{\theta}\right) - \left(\frac{\alpha}{\theta_{\text{im}}}\right)t^*
\]

where \( C \) is the chemical concentration of soil solution, \( C_o \) is the chemical concentration of input solution, \( \theta \) is total water content, \( t^* = t - z'/v \) is the time required for the tracer front to reach sampling depth, \( z' \), and \( v \) is the average pore velocity (L T\(^{-1}\)) in the mobile domain. Jaynes et al. (1995) assumed no prior concentration of chemicals in the soil, chemical concentration in the mobile domain equal to \( C_o \), negligible \( D_m \) within the sampling zone, and \( C \) as a combination of chemicals in the mobile and immobile domains. Based on Eq. 2.8, plotting \( \ln(1 - C/C_o) \) versus \( t^* \) results in a straight line with a negative slope. Immobile water fraction can be determined from the resulting intercept, and \( \alpha \) can be computed from the slope.

### 2.4 Materials and Methods

A greenhouse soil pit was used in this study. The soil in the pit was disturbed having a loam texture (0.344 sand, 0.416 silt, and 0.240 clay mass fraction), a bulk density of
Figure 2.1  The experimental setup for the point source method.

1.20 Mg m$^{-3}$, and a particle density of 2.63 Mg m$^{-3}$. The soil pit was about 60 cm deep, underlain by sawdust and undisturbed soil (Jaynes et al., 1995), and was continuously cropped for the past 15 years.

A dripper line setup was constructed on a transect 7 m long on the soil surface (Fig. 2.1). The setup consisted of three dripper lines mounted on the soil surface. The three dripper lines were connected to a PVC manifold with a separate control valve for each line. Water was pumped from a reservoir to the system through a PVC pipe, which had a prime access to facilitate priming the pump. Each dripper line was equipped with drippers that could deliver a designed discharge rate within an applied pressure range (pressure-compensating drippers). Drippers used were designed to deliver discharge rates of 2, 4, and 8 L h$^{-1}$ (Hooks Point, Stratford, IA). A pressure gauge was installed in the system to monitor the applied pressure. A release valve was installed at the far end of the setup to facilitate quick flushing of the system from different applied chemical solutions. This setup allowed application of water or chemical solutions to the soil surface at multiple locations for the same time period. Different discharge rates could be applied at the same location, which minimizes effects of spatial variability. The drippers were
1 m apart. Thus, a total of six observation sites, i.e., six tests, were conducted. The local soil surface at each observation site was leveled with minimal surface disturbance. Experimental work was started by applying water at the soil surface at a discharge rate of 2 L h\(^{-1}\). Discharge rate of each observation site was measured and recorded. Dripers among sites had small variability and their coefficient of variability (CV) ranged from 0.68 to 2.86\%. Water application was continued until steady-state conditions prevailed, i.e., when ponded areas reached a constant size. Steady-state conditions were reached after about 30-40 min of water application. The diameter of the ponded area (at steady-state conditions) of each observation site was measured from different axes, and the average was taken to infer equivalent pond radius. This procedure was followed to minimize any error due to shape distortion (i.e., non-circularity) of the ponded area. A variation in the level of the microrelief could result in shape distortion of the ponded area. After recording the steady-state area of all six observation sites, the next higher discharge rate (4 L h\(^{-1}\)) was applied on the same location. Switching between different \(Q\) was achieved by opening and closing the valves of the corresponding dripper lines. This procedure was repeated for the other applied discharge rates, which were 8 and 12 L h\(^{-1}\). The discharge rate of 12 L h\(^{-1}\) was achieved by opening the valves for the 4 and 8 L h\(^{-1}\) dripper lines. Thus, a total of four discharge rates (2, 4, 8, and 12 L h\(^{-1}\)) were applied on the soil surface of each site. A minimum application of two discharge rates would satisfy Wooding's solution (1968) for determining the hydraulic parameters, \(K_s\) and \(\lambda_c\). However, a wide range of discharge rates is desired for better estimation of parameters. Application of different discharge rates on the same site minimizes errors due to spatial variability (assuming a uniform soil in the area beneath drippers).

Chemical properties were determined by applying a sequence of three conservative tracers. Tracers applied were different fluorobenzoic acids\(^1\). These conservative tracers

\(^1\)Fluorobenzoic acids used were \(\alpha\)-trifluoromethylbenzoic, pentafluorobenzoic, and tri fluorobenzoic acids.
have been reported to have similar transport properties in many soils (Benson and Bowman, 1994; Jaynes, 1994). After recording the steady-state ponded area produced from the highest discharge rate, three consecutive solutions containing multiple fluorobenzoate tracers were sequentially injected through the system. Chemical solutions were applied using the highest discharge rate; i.e., 12 L h⁻¹. The first solution (Solution 1) consisted of 1 mmol L⁻¹ (0.001 M) of Tracer 1. Solution 1 was applied for enough time so that the solution-front was estimated to have passed the intended sampling depth of 1.5 cm. Estimation of application time was based on the computed pore velocity, \( v \). This was followed by applying Solution 2, which consisted of 1 mmol L⁻¹ of Tracer 1 and 1 mmol L⁻¹ of Tracer 2. Again, application time for Solution 2 was long enough for the solution to have passed the sampling depth. This procedure was followed by applying the third solution, which consisted of 1 mmol L⁻¹ each of Tracers 1, 2 and 3. With this procedure, Tracer 1 was applied for the longest time and Tracer 3 for the least time. A soil sample, 1.5 cm deep, was taken from each observation site immediately after the application of the third solution had ceased. Rings used for collecting samples had a 7.6 cm inside diameter and a 1.5 cm depth. Samples were taken from the center of the ponded area (after the ponded water had disappeared from the soil surface). Soil samples were put into plastic bags and stored in a cold environment until chemical analysis and water content determination occurred. In the laboratory, soil samples were thoroughly mixed and a soil subsample was taken from each sample for water content determination. Water content was determined gravimetrically by oven-drying samples for 24 h at 105 °C. Each remaining soil sample was extracted with distilled water at about 2:1 water-mass to soil-water ratio. The extracts and input solutions were analyzed for tracers using an ion chromatograph. Detailed procedures for chemical analysis can be found in Bowman and Gibbens (1992) and Jaynes et al. (1995).

Soil samples obtained from sampling rings had relatively small soil volumes, which led to highly variable bulk densities (\( \rho_b \)). Accurate \( \rho_b \) is needed to determine \( \theta_m \), which is
used to compute the $\alpha$ parameter from Eq. 2.8. Thus, a large error could be introduced in estimating $\alpha$ from using $\rho_b$ of the soil samples to determine the volumetric water content ($\theta_v$). Therefore, instead of using $\rho_b$ of soil samples, we assumed the soil samples to be saturated (sampling was done quickly after water application had ceased) and $\theta_v$ could be determined from the known mass water content ($\theta_g$) and soil particle density ($\rho_s$) using the following relationship:

$$\theta_v = \frac{\theta_g \rho_s}{\theta_g \rho_s + 1} \quad (2.9)$$

Equation 2.9 does not use the $\rho_b$ term. Thus, it removes any possible error in estimating chemical transport properties from miscalculated $\theta_v$ of soil samples.

Another set of experiments was conducted for comparison purposes. Hydraulic properties were determined from infiltration experiments using automated ponded and disc tension infiltrometers. Ponded and tension infiltrometers had disc radii of 7.6 cm. Containment rings (1 cm height, 7.6 cm i.d.) were inserted into the soil to a depth of 5 mm. Ponded infiltrometers were first used to supply water at a pressure head of 5 mm of water. The infiltrometers were equipped with pressure transducers installed at the top and bottom of the water reservoir. The transducers were connected to a data logger to record the change in the water pressure in the reservoir, which was used to determine the infiltration rates. The details of the procedure followed can be found at Prieksat et al. (1992). Water infiltration from ponded infiltrometers was continued until steady-state conditions prevailed; i.e., a constant infiltration rate was reached. The ponded infiltrometers were then removed and containment rings were filled with a thin layer of fine sand to establish a good hydraulic contact between the soil surface and the discs of tension infiltrometers. Tension infiltrometers were then placed on the same locations. Water was infiltrated using a sequence of supply pressure heads of -30, -60, and -150 mm of water. Infiltration rates produced by each supply pressure head were measured using pressure transducers. Details of this procedure can be found in Ankeny et al. (1988).
Six sites were evaluated for hydraulic properties with ponded and tension infiltrometers. The sites tested by infiltrometers were within 1 m of the point source transect. Hydraulic properties were determined by taking the log-linear form of Eq. 2.5 and regressing steady infiltration rates, ln(q), versus applied pressure heads. The $\lambda_c$ parameter was the slope of the regression line, and $K_s$ was determined from the resulting intercept.

Chemical transport properties were evaluated using ponded infiltrometers by sequentially applying three solutions containing a multiple of the three fluorobenzoic tracers. Solutions were applied using a supply pressure head of 5 mm. The application scheme of solutions for ponded infiltrometers was the same one followed for the point source experiments. A soil sample was taken from beneath each infiltrometer immediately after the application of the last solution had ceased. Rings used for collecting samples had 4.5 cm inside diameters and were 2.0 cm deep. Because we had a limited supplies of tracer solutions, only five observation sites were evaluated for chemical transport properties from ponded infiltrometers. Chemical analysis and water content were determined following the same procedure described with the point source method. A test of significance (t-test at 5% probability level) was conducted to study the variability between the two sets of methods (point source vs. infiltrometers) in determining the hydraulic and chemical properties of the soil pit.

2.5 Results and Discussions

2.5.1 Hydraulic properties

Figure 2.2 depicts the relationship of flux densities, $q$, versus the reciprocal of steady state radii, $1/r_a$, produced by the point source method for all observation sites. A wide range of discharge rates is useful and helps to minimize any error for better estimation of hydraulic parameters (Shani et al., 1987). Increasing discharge rates from the drippers resulted in increasing the size of the ponded area and decreasing the flux density (Fig.
2.2). Based on the Wooding's solution, saturated hydraulic conductivity and the $\lambda_c$ parameter can be determined from the regression output of $q$ versus $1/r_o$. Test 3 (Fig. 2.2) resulted in a near-perfect relationship, but the other tests showed some deviation from linearity due to the natural variability of the soil. The fitting procedure of all sites produced a mean value for the coefficient of determination, $r^2$, of 0.95.

Determined values of $K_s$ and $\lambda_c$ from the point source method and ponded/tension infiltrometers are presented in Table 2.1. For the point source method, $K_s$-values ranged from 8.7 to 15.0 cm h\(^{-1}\) with an average of 12.1 cm h\(^{-1}\) (±2.4). The $\lambda_c$ parameter ranged from 2.3 to 7.3 cm with an average of 5.0 cm (± 1.9). Measured $K_s$ from ponded/tension infiltrometers ranged from 2.1 to 22.8 cm h\(^{-1}\) with an average of 11.2 cm h\(^{-1}\) (± 7.5). The $\lambda_c$ parameter ranged from 4.0 to 8.5 cm with an average of 5.4 cm (± 1.6). The average value of $K_s$ produced by the point source method was larger than that produced by infiltrometers, but with no significant difference between the means as indicated in Table 2.1. However, the average value for $\lambda_c$ produced by the point source method was less, though not significantly different, than that of the infiltrometers. With the point source method, $K_s$ is used to determine the $\lambda_c$-parameter. Thus, computed $\lambda_c$ would be expected to have greater variability than computed $K_s$. This is clearly indicated by their coefficient of variability (CV) values.

The point source method gave consistent estimates for hydraulic parameters among the tests as indicated by their relatively low CV. Compared with the point source method, estimated $K_s$ among the tests from the infiltrometers was highly variable. However, estimated $\lambda_c$ from infiltrometer experiments was less variable than the values produced by the point source method. Contact sand, used with tension infiltrometers, might have introduced flow impedance (Reynolds and Zebchuk, 1996) and resulted in higher variability in estimated $K_s$. Small variability among the tests was expected, because complete mixing of the soil in the pit should have produced a somewhat uniform soil.
Figure 2.2  Flux density versus $1/r_o$ for all observation sites from the point source method. The points and solid lines are the measured and fitted values, respectively.
Table 2.1  Estimated hydraulic properties from the point source method and ponded/tension infiltrometers.

<table>
<thead>
<tr>
<th>Test</th>
<th>Point source</th>
<th>Infiltrometers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ks (cm h⁻¹)</td>
<td>λc (cm)</td>
</tr>
<tr>
<td>1</td>
<td>9.9</td>
<td>6.6</td>
</tr>
<tr>
<td>2</td>
<td>8.7</td>
<td>7.3</td>
</tr>
<tr>
<td>3</td>
<td>12.1</td>
<td>5.8</td>
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<tr>
<td>4</td>
<td>14.2</td>
<td>3.5</td>
</tr>
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<td>12.7</td>
<td>4.2</td>
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<tr>
<td>6</td>
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<td>2.3</td>
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<tr>
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<td>5.0</td>
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<tr>
<td>SD</td>
<td>2.4</td>
<td>1.9</td>
</tr>
<tr>
<td>CV(%)</td>
<td>20.1</td>
<td>38.8</td>
</tr>
</tbody>
</table>

a,b insignificant at P < 0.05.

2.5.2 Chemical properties

Figure 2.3 shows normalized resident concentration, ln(1 − C/C₀), versus application time, t*, and their fitted regression lines produced by the point source method for all observation sites. All tests produced a linear relationship between the resident concentration and application time. Differences between the measured and predicted transport behavior is attributed to some experimental limitations, such as difficulty in measuring the small differences in tracer concentration (Jaynes et al., 1995). Linear regression lines for all tests produced a good fit of the measured data (mean r² = 0.99), suggesting that the multiple application of tracers from the point source method produced a good linearity and can be well described using Eq. 2.8.

Total water content (θ), estimated θₘₐₓ/θ and α from the point source method, and ponded infiltrometers are presented in Table 2.2. The point source method produced consistent total water content among the tests and ranged from 0.52 to 0.56 m³ m⁻³ with an average of 0.55 m³ m⁻³ (± 0.01). Immobile water fraction ranged from 0.51 to 0.70 with an average of 0.57 (± 0.07). The mass exchange coefficient ranged from 0.058
Figure 2.3  Resident concentrations vs. application times for all observation sites from the point source method. The points and solid lines are the measured and fitted values, respectively.
Table 2.2  Total water content, $\theta_{im}/\theta$, and $\alpha$ estimates from the point source method (six test sites) and ponded infiltrometers (five test sites).

| Test | Point source | | Ponded infiltrometer | |
|------|--------------|-----------------|-------------------------|
|      | $\theta$  ($m^3/m^3$) | $\theta_{im}/\theta$ | $\alpha$ ($h^{-1}$) | $\theta$  ($m^3/m^3$) | $\theta_{im}/\theta$ | $\alpha$ ($h^{-1}$) |
| 1    | 0.56         | 0.51            | 0.058                   | 0.48         | 0.75            | 0.108                   |
| 2    | 0.55         | 0.53            | 0.088                   | 0.54         | 0.57            | 0.003                   |
| 3    | 0.55         | 0.54            | 0.069                   | 0.51         | 0.46            | 0.002                   |
| 4    | 0.52         | 0.60            | 0.086                   | 0.52         | 0.46            | 0.016                   |
| 5    | 0.54         | 0.56            | 0.073                   | 0.53         | 0.30            | 0.016                   |
| 6    | 0.55         | 0.70            | 0.129                   | -            | -               | -                       |
| Mean | 0.55$^a$     | 0.57$^b$        | 0.084$^c$               | 0.52$^a$     | 0.51$^b$        | 0.029$^c$               |
| SD   | 0.01         | 0.07            | 0.025                   | 0.03         | 0.17            | 0.044                   |
| CV (%) | 1.8         | 12.1            | 29.8                   | 5.9          | 33.3            | 119.0                   |

$^a$, $^b$, $^c$ significant at $P < 0.05$.
$^b$ insignificant at $P < 0.05$.

to 0.129 $h^{-1}$ with an average of 0.084 $h^{-1}$ (± 0.025). Estimated chemical parameters produced by the ponded infiltrometers were, in general, lower than the estimates of the point source method. Total water content ranged from 0.48 to 0.54 $m^3/m^3$ with an average of 0.52 (± 0.03). Immobile water fraction ranged from 0.30 to 0.75 with an average of 0.51 (± 0.17). Estimated $\alpha$ ranged from 0.002 to 0.108 $h^{-1}$ with an average of 0.029 $h^{-1}$ (± 0.044). For all parameters determined, ponded infiltrometers produced more variable values than those produced by the point source method as indicated by higher CV-values (Table 2.2).

In general, the point source method produced larger values for $\theta$, $\theta_{im}/\theta$, and $\alpha$ than those produced by ponded infiltrometers. Larger $\theta_{im}/\theta$ from the point source method was associated with larger $\theta$. The average $\theta$ values produced by the two methods were significantly different as shown in Table 2.2. However, there was no significant difference between the two methods in estimating $\theta_{im}/\theta$. Jaynes et al. (1995) reported an average of $\theta_{im}/\theta$ of 0.61 for the same soil pit. Their average value of $\theta_{im}/\theta$ was associated with lower $\theta$. Similar fluctuations of $\theta_{im}/\theta$ with $\theta$ were also reported by Angulo-Jaramillo.
et al. (1996) and Casey et al. (1998).

The average value of $\alpha$ produced by the point source method was larger than that produced by the ponded infiltrometers. The $\alpha$-values produced by the point source method were significantly different from those produced by ponded infiltrometers (Table 2.2). Compared with the average-value produced by the ponded infiltrometers, the point source method produced larger average $\theta_{im}/\theta$, which meant smaller $\theta_m$. Moreover, the point source method produced larger average $K_s$ value than that produced by the ponded infiltrometers (Table 2.1). The combination of larger $K_s$ and smaller $\theta_m$ for the point source method yielded larger pore velocity ($v$) in the mobile domain than the ponded infiltrometers. Previous studies, as summarized by Griffioen et al. (1998), reported larger $\alpha$ associated with larger $v$. Thus, our $\alpha$ results are consistent with the Griffioen et al. (1998) findings. Both sets of methods, the point source method and the infiltrometers, produced greater average values for $\alpha$ than that reported by Jaynes et al. (1995) for the same soil pit. Jaynes et al. (1995) applied the tracers from tension infiltrometers with a supply tension of -30 mm of water; i.e., unsaturated conditions. Thus, the reported average $\alpha$ value (0.01 h$^{-1}$) reported by Jaynes et al. (1995) was associated with smaller flux densities than the flux densities in this study. The data from both of our methods (point source and ponded infiltrometers) were consistent with the Jaynes et al. (1995) results.

2.6 Conclusion

We developed and evaluated an experimental setup for estimating hydraulic and chemical transport properties using the point source method and compared the method with ponded and tension infiltrometers. The point source method showed a consistency in estimating hydraulic and chemical properties. It produced the minimum variability for determination of both sets of properties. Except for $\alpha$, there was no significant difference
between the two procedures in estimating hydraulic and chemical transport properties. Compared with the values reported by a previous study conducted on the same soil pit, the point source method produced reasonable estimates for measured parameters of the chemical transport properties. From the results of this study, it can be concluded that the point source method is reliable in estimating not only hydraulic properties, but also chemical transport properties (in conjunction with the sequential tracers procedure).

The experimental setup has the advantage of simultaneous estimation of both hydraulic and chemical transport properties at multiple locations within a short time. Another advantage of this setup is that both sets of soil properties can be evaluated on the same location, which minimizes errors due to spatial variability. Moreover, the setup allows rapid and multiple measurements with minimum labor and energy requirements. This enables the conduction of multiple measurements, which provides a better evaluation of distribution of soil properties. Evaluation of the setup and procedure with natural field conditions, such as tillage practices and crop rotations, is required for further establishment of this method.

2.7 Acknowledgments

We thank Dr. Logsdon of the National Soil Tilth Laboratory for loaning infiltrometers to us, and we thank Gavin Simmons for helping with infiltration experiments.

References


CHAPTER 3  FIELD DETERMINATION OF SOIL HYDRAULIC AND CHEMICAL TRANSPORT PROPERTIES

A paper submitted to Soil Science Society of America Journal

Salem A. Al-Jabri\textsuperscript{1}, Robert Horton\textsuperscript{2}, and Dan B. Jaynes\textsuperscript{3}

3.1 Abstract

Hydraulic and chemical transport properties are the major inputs in predictive models that simulate the movement of water and chemicals through the vadose zone. Due to the limitations of field methods to make multiple measurements on different locations, there is a lack of field measurements of such properties to verify models describing water and chemical movement through soil. One of the objectives of this study was to use a point source method to simultaneously determine the hydraulic and chemical transport properties at multiple field locations. Another objective was to determine the spatial distribution of such properties across a field. A total of 50 field locations within a 7 x 15-m area were rapidly and simultaneously evaluated for such properties. The hydraulic properties were saturated hydraulic conductivity ($K_s$) and macroscopic capillary length ($\lambda_c$). The chemical transport properties were immobile water content, expressed as a

\begin{flushleft}
\textsuperscript{1}Dept. of Soil and Water Sciences, Sultan Qaboos University, Muscat, Sultanate of Oman
\textsuperscript{2}Dept. of Agronomy, Iowa State University, Ames, Iowa
\textsuperscript{3}USDA-ARS, National Soil Tilth Laboratory, Ames, Iowa
\end{flushleft}
fraction of water content ($\theta_{im}/\theta$), and mass exchange coefficient ($\alpha$). A set of irrigation drippers was used to achieve the study objectives. The hydraulic properties were determined from applying three discharge rates from the drippers and measuring the resultant steady-state flux densities at the soil surface beneath each dripper. The chemical transport properties were determined from applying a sequence of three conservative tracers at a steady-state infiltration rate and measuring their resident concentration in the soil. The $K_s$ values ranged from 7.5 to 79.0 cm h$^{-1}$ with a median of 27.4 cm h$^{-1}$ ($\pm$ 16.8). The $\lambda_c$ values ranged from 0.03 to 13.1 cm with a median of 2.6 cm ($\pm$ 3.6). The $\theta_{im}/\theta$ values ranged from 0.41 to 0.91 with a median of 0.65 ($\pm$ 0.08). The $\alpha$ values ranged from 0.0004 to 0.12 h$^{-1}$ with a median of 0.04 h$^{-1}$ ($\pm$ 0.03). The values of the hydraulic and chemical transport parameters were found comparable with values reported by studies conducted on nearby field locations or similar soil. Compared with the time of weeks required by other field methods, this study required only 2 days to collect data for the properties from 50 field locations. Therefore, the method presented by this study is ideal for studies that require extensive field measurements of the hydraulic and chemical transport properties.

3.2 Introduction

Concerns about the quality of drinking water have increased in the general public. Such concerns were raised due to published reports (e.g., United States Environmental Agency (USEPA), 1989) about contamination of groundwater resources by agricultural and industrial chemicals. In Iowa, for example, field application of fertilizers and pesticides has resulted in contamination by some chemicals exceeding the USEPA advisory levels (Jayachandran et al., 1994). Thus, there exists a need to protect water resources from land-applied chemicals.

Hydraulic and chemical transport properties are considered to be the major inputs
in predictive models to simulate movement of water and chemicals through the vadose zone. Moreover, screening models would better predict the movement of chemicals toward groundwater resources if such properties were used to describe preferential flow patterns (USEPA, 1992). Therefore, evaluating the hydraulic and chemical transport properties under field conditions is considered an important step in developing management practices to protect our groundwater resources.

Many studies have shown that water and chemicals often move through the vadose zone along some preferred pathways (Biggar and Nielsen, 1962; Ehlers, 1975; van Genuchten and Wierenga, 1977; Priebe and Blackmer, 1989; McKay et al., 1993). Preferred pathways may include large cracks, macropores, root channels, or worm holes. Preferential flow is the rapid movement of water and chemicals through the large openings in the soil. Thus, water and chemicals can reach great depths in a relatively short time, which increases the risk of groundwater contamination. Studies with structured soil columns, e.g. Khan and Jury (1990), showed that preferential flow causes asymmetry (i.e., early breakthrough and distinct tailing) in the effluent breakthrough curves (BTCs). The early arrival of chemicals is often attributed to the preferential movement of water and chemicals through larger pores between soil aggregates. The long tailing of chemicals is often attributed to the diffusion of chemicals from smaller pores and "dead-end" pores back into the main-stream flow.

Such nonequilibrium movement of chemicals often cannot be described using the convective-dispersive equation (van Genuchten and Wierenga, 1976). Alternatively, a two-domain model introduced by Coats and Smith (1964) was used to better describe the asymmetry in BTCs (van Genuchten and Wierenga, 1977). The model, often called the mobile-immobile model (MIM), divides soil water (θ) into two domains: a mobile water domain (θ_m) where water and chemicals move with mean pore velocity (v), and an immobile water domain (θ_{im}) where water (relative to θ_m) is stagnant and chemicals move by diffusion only. Dispersion of chemicals take place in the mobile domain and is
similar to that in the convective-dispersive equation (CDE). The water in the immobile domain acts like a source or sink for chemicals to the mobile domain. Thus, the CDE can be written in the form of the two-region model as (van Genuchten and Wierenga, 1976):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - q \frac{\partial C_m}{\partial z} \tag{3.1}$$

where $C_m$ and $C_{im}$ are the concentrations of chemicals in the mobile and immobile domains ($\text{M L}^{-3}$), $D_m$ is the dispersion coefficient ($\text{L}^2 \text{T}^{-1}$) in the mobile domain, $q$ is the flux density ($\text{L T}^{-1}$), $t$ is time ($\text{T}$), and $z$ is depth ($\text{L}$). Chemical transfer between the two domains is proportional to the concentration difference between the two domains and is described as a first-order process (van Genuchten and Wierenga, 1976):

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \tag{3.2}$$

where $\alpha$ is a first-order mass exchange coefficient ($\text{T}^{-1}$).

The transport parameters of the MIM are usually found by inverse methods, where solutions to Eqs. 3.1 and 3.2 are fitted to observed BTCs (van Genuchten and Wagenet, 1989). However, BTCs are difficult to obtain in the field. As an alternative to BTCs in the field, Clothier et al. (1992) provided a solution to Eq. 3.2 to estimate $\theta_m$ from field studies. Their approach involves applying a single conservative tracer into the soil from a tension infiltrometer. Assuming negligible $D_m$ and $\alpha$ within the sampling zone, Clothier et al. (1992) determined $\theta_m$ from the product of the water content and concentration of the tracer in the soil sample. Jaynes et al. (1995) extended the solution of Clothier et al. (1992) to further estimate $\alpha$. They applied a sequence of conservative tracers from a tension infiltrometer into the soil. Assuming piston displacement of tracers in the soil, Jaynes et al. (1995) gave the following solution to Eq. 3.2:

$$\ln \left(1 - \frac{C}{C_o}\right) = \ln \left(\frac{\theta_{im}}{\theta_m}\right) - \left(\frac{\alpha}{\theta_{im}}\right) t^* \tag{3.3}$$

where $C$ is the concentration of tracers in the soil sample, $C_o$ is the concentration of tracers in the input solutions, and $t^* = t - z'/v$ is the time required for the solution front
to pass the sampling depth \((z')\). Jaynes et al. (1995) assumed negligible tracer concentration in the soil prior to any tracer application, tracer concentration within the mobile domain \((C_m)\) to be equal to the input concentration \((C_o)\), and dispersion to be negligible within the sampling depth. They used multiple fluorobenzoate tracers to conduct their procedure. Fluorobenzoate tracers were found to have nearly identical transport properties in many soils (Jaynes, 1994) and similar diffusion coefficients (Bowman and Gibbens, 1992; Benson and Bowman, 1994). As given by Eq. 3.3, the results reported by Jaynes et al. (1995) showed good linearity between resident concentrations of tracers in the soil, \((1-C/C_o)\), and the application time, \(t^*\). As shown by Eq. 3.3, the immobile water content \((\theta_{im})\) and the mass exchange coefficient \((\alpha)\) can be computed from the resulting intercept and slope.

Few studies have been performed under field conditions to determine soil surface hydraulic properties (Or, 1996; Casey et al., 1998; Yitayew et al., 1998) and chemical transport properties (Clothier et al., 1992; Angulo-Jaramillo et al., 1996; Casey et al., 1997, 1998). Field methods for determining such properties are time and energy consuming. In other words, they are limited to a single measurement on a single observation site for a given time period. Due in part to such a limitation, the advancements in field studies have lagged behind the advancements in theoretical concepts and simulation-transport models (Ward et al., 1995). Therefore, there exists a need for methods that allow conducting field measurements of such properties at multiple field locations in a short period of time.

A point source method has been developed to estimate the soil hydraulic properties in situ (Shani et al., 1987; Revol et al., 1991; Or, 1996; Revol et al., 1997; Yitayew et al., 1998). Wooding (1968) presented an approximate solution for water flow, at steady-state flow conditions, from a shallow circular pond on the soil surface (point source) as:

\[
q = \frac{Q}{\pi r_o^2} = K_s \left( 1 + \frac{4 \lambda_c}{\pi r_o} \right)
\]  

(3.4)
where $Q$ is the discharge rate from a source ($L^3 \, T^{-1}$), $q$ is the steady flux density ($L \, T^{-1}$), $r_o$ is the pond radius (L), $K_s$ is the saturated hydraulic conductivity ($L \, T^{-1}$), and $\lambda_c$ is the macroscopic capillary length (L). The scaling parameter, $\lambda_c$, quantifies the importance of capillary forces, i.e., the attraction of water to dry soil, relative to gravity forces on water movement (Philip, 1969). It is large for fine-textured soils and small for coarse-textured soils. Thus, water flow from a point source into a fine-textured soil will have a more lateral flow than into a coarse-textured soil. According to Wooding’s solution, applying water from a point source results in a circular (or near circular) saturated ponded area beneath the source on the soil surface. The size of the ponded area increases with time, but eventually reaches a constant size (Bresler, 1978) where steady-state conditions are assumed (Shani et al., 1987). Based on Eq. 3.4, regressing different flux densities (produced from applying different $Q$) versus corresponding $1/r_o$ yields $K_s$ as the intercept, and $\lambda_c$ can be determined from the resulting slope, $4K_s\lambda_c/\pi$.

Or (1996) introduced an experimental setup that utilized the point source method to determine the hydraulic properties in the field. His setup allowed estimating the hydraulic properties with minimum labor requirements. Al-Jabri et al. (2001) further developed and extended the setup that was introduced by Or (1996). They presented a procedure for estimation of both hydraulic and chemical transport parameters from the point source method at multiple locations. Al-Jabri et al. (2001) reported that the setup and procedure showed the capability to rapidly and simultaneously determine both sets of properties. Moreover, the point source method worked well with the procedure of sequential application of tracers developed by Jaynes et al. (1995). Compared with the estimates produced by ponded and tension infiltrometers, the point source method showed a consistency (i.e., less variability) in estimating the hydraulic and chemical transport properties.

Al-Jabri et al. (2001) evaluated the setup and the procedure on a disturbed soil pit under greenhouse conditions. They conducted their experimental work on six obser-
vation sites. The point source method of Al-Jabri et al. (2001) has not been used to determine hydraulic and chemical transport properties of natural field soil nor has it been used at more than six observation sites. As a follow-up to the results reported by Al-Jabri et al. (2001), the point source method should be tested on actual field conditions to determine the hydraulic and chemical transport properties. Therefore, one of the objectives of this study was to apply the point source method for determination of the hydraulic and chemical transport properties at multiple field locations. Another objective was to study the spatial distribution of such properties across the field. A total of 50 field locations were simultaneously evaluated for both sets of properties. The hydraulic properties included the saturated hydraulic conductivity ($K_s$), and the macroscopic capillary length ($\lambda_c$). The chemical transport properties were the immobile water content, expressed as a fraction of total water content ($\theta_{im}/\theta$), and the mass exchange coefficient ($\alpha$).

### 3.3 Materials and Methods

The study took place in a no-till corn (Zea Mays L.) field at the Agronomy and Agricultural Engineering Research Center, Iowa State University, Ames, IA. The soil at the research site is predominantly Nicollet loam (0.389 sand, 0.366 silt, 0.245 clay mass fraction) with an average bulk density of 1.43 Mg m$^{-3}$ for the top 10 cm. The soil is classified as fine loamy, mixed, mesic Aquic Hapludoll and is characterized as being moderately permeable and poorly drained. The soil is derived from a glacial till and has a slope of about 1-3%. The study was conducted on plant rows. Corn plants were cut, and plant residues and weeds were removed from rows with minimal disturbance to the soil surface. Moreover, the soil surface at each location was carefully hand-leveled with minimum disturbance to the surface.

Five parallel transects, on plant rows, were chosen on a 7 by 15 m rectangular grid
Figure 3.1 The experimental setup for the point source method at the field.
(Fig. 3.1). Each transect was 15 m long, and transects were 1.5 m apart. A drip irrigation system, consisting of three dripper lines (irrigation tubes), was positioned on the five transects. Dripper lines of all transects were interconnected with each other so that all lines could be operated simultaneously. Each dripper line (on each transect) was equipped with one type of pressure-compensating dripper (point source). Such drippers were designed to deliver steady discharge rate, $Q$, for a given pressure range. Drippers were designed to deliver discharge rates of 2, 4, or 8 L h$^{-1}$ (Hooks Point, Stratford, IA). The drippers were installed at an interval of 1.5 m on each transect. Thus, a total of 50 sites could be simultaneously evaluated for the hydraulic and chemical transport properties. The dripper lines, at both ends of the system, were connected to PVC manifolds with a separate valve for each line. Using a different valve for the dripper line enabled us to apply water into any line and, thus, maintain the same discharge rate at all sites. A pump was installed at one end of the system to deliver water from a water reservoir into the dripper lines. A pressure gauge was installed at the other end of the system to monitor the applied pressure through the dripper lines. A release valve was installed at the far end of the system to facilitate quick flush of the system from different applied chemical solutions. With this setup, it was possible to simultaneously apply water or different chemical solutions at the 50 sites at controlled discharge rates.

The experimental work began by first determining the hydraulic parameters. This was achieved by applying multiple discharge rates to the soil surface. We first applied water at a discharge rate of 2 L h$^{-1}$). The discharge rate from each dripper (i.e., at each site, was measured and recorded. Water application at each site was continued until steady-state condition prevailed (i.e., the ponded area at each site reached a constant size). The steady-state conditions for all sites were reached after 30-45 min of water application. Since the soil surface was nearly level, the resultant ponded areas were nearly circular in shape. To determine the effective size of the ponded area at each site, the diameter of the pond was measured from three different axes. This procedure
was conducted to reduce any error due to shape irregularity. The average value of the measured diameters was used to infer the effective circular ponded area. After recording the diameters of ponded area produced by the first $Q$, the next higher discharge rate (4 L h$^{-1}$) was then applied. This was achieved by closing the valve of the 2 L h$^{-1}$ discharge rate and opening the valve of the 4 L h$^{-1}$ discharge rate. The same procedure as with the first $Q$ was followed for the second discharge rate. This procedure was also followed for the last $Q$, which was 8 L h$^{-1}$. Thus, a total of three discharge rates were applied. The drippers, among sites, produced some variability in maintaining the desired discharge rate with a coefficient of variability (CV) value of about 7.0% for all discharge rates applied. The experimental work for the first day (for determining hydraulic properties) was ceased after recording the steady-state areas produced by the last discharge rate.

Field experimentation for determining the chemical transport properties was resumed the next day. The procedure of sequential application of tracers, as described by Jaynes et al. (1995), was followed to determine $\theta_{im}/\theta$ and $\alpha$. We used fluorobenzoate tracers to determine the transport parameters. Tracers used were 2,6-difluorobenzoate (DFBA), o-trifluoromethylbenzoate (TFMBA), and pentafluorobenzoate (PFBA) acids. We started the experiment by applying water at a discharge rate of 4 L h$^{-1}$. The discharge rate and steady pond diameter at each site were measured and recorded. Solution 1 was then introduced to the system, which had 0.001 $M$ (1 $mM$) of DFBA. Application time was chosen to allow the wetting front of the solution to pass a sampling depth of 2.0 cm. This was followed by applying Solution 2, which consisted of 1 $mM$ of DFBA and 1 $mM$ of TFMBA. Again, Solution 2 was applied for a long-period of time enough for the solution front to pass the sampling depth. Finally, Solution 3 was applied, which consisted of 1 $mM$ of each of DFBA, TFMBA, and PFBA. With this procedure, Tracer 1 was applied for the longest time, and Tracer 3 was applied for the least time. A soil sample from each site was taken immediately after the ponded water on the surface had disappeared. Each soil sample was taken from the center of the area beneath the dripper.
Soil samples were taken using stainless steel rings, which had an inside diameter of 5.1 cm and a height of 2.0 cm. Soil samples were placed in sealed, labelled plastic containers and stored in a cold environment at 2 °C. In the laboratory, soil samples were thoroughly mixed, and a soil subsample was taken from each sample for gravimetric determination of water content. Distilled water was added to the rest of each sample at a ratio of approximately 1:2 soil-water to water-mass ratio. Samples were shaken for about 5 min and extracted using No. 11 filter paper. The input and sample solutions were analyzed for tracers using an ion chromatograph. Detailed procedures for tracer analysis can be found in Bowman and Gibbens (1992) and Jaynes et al. (1995).

Soil samples obtained from sampling rings had relatively small soil volumes, which led to highly variable bulk densities ($\rho_b$). Accurate $\rho_b$ is needed to determine $\theta_{im}$, which is used to compute the $\alpha$ parameter from Eq. 3.3. Thus, a large error could be introduced in estimating $\alpha$ from using $\rho_b$ of the soil samples to determine the volumetric water content ($\theta_v$). Therefore, instead of using $\rho_b$ of soil samples, we assumed the soil samples to be saturated (sampling was done quickly after water application had ceased) and $\theta_v$ could be determined from the known mass water content ($\theta_g$) and soil particle density ($\rho_s$) using the following relationship:

$$\theta_v = \frac{\theta_g \rho_s}{\theta_g \rho_s + 1} \quad (3.5)$$

Equation 3.5 does not use the $\rho_b$ term. Thus, it removes any possible error in estimating chemical transport properties from miscalculated $\theta_v$ of soil samples.

Histograms for the estimated hydraulic and chemical transport parameters were constructed and tested for normality (i.e., normal distribution test; Neter et al., 1996) at normal and log-normal scales. The data were first transformed into log-values before conducting the normality tests under log-normal scale. Normality tests were conducted by determining the correlation coefficient ($r$) between the error-residual values of the estimated parameters and their expected values under normality. The values of $r$ were
matched with the critical value of Pearson's $r$-value at 5% probability level. It should be noted that the normality test with log-transformed data was conducted only if the data were not normally distributed at normal scale.

To study the spatial variability of the hydraulic and chemical properties, a non-directional semivariogram test (Davis, 1973) was conducted for each parameter for all measured values in the field. The spatial variability of all computed parameters were tested over the 6 x 15 m grid at 1.5 m lag intervals and 0.75 as a lag search interval (lag tolerance). The calculated semivariograms have a directional angle of 90° (from the x-axis) and a tolerance angle of 90°. Semivariogram-values (for each estimated parameter) with number of couples (NC) of less than 30 were excluded from the analysis of the spatial correlation test. Moreover, the semivariograms were cut at about half of the transect distance, i.e., any points beyond the half of transect-distance were excluded from the analysis of the spatial correlation.

After the sequential application of tracers had ceased, undisturbed soil cores (7.6 cm x 7.7 cm i.d.) were taken from all transects (between sites). A core sampler was used to collect a total of 50 undisturbed soil cores. Soil cores were taken along the transects. In the laboratory, the soil cores were saturated from the bottom with 5 mM CaCl$_2$. The saturated hydraulic conductivity of each soil core was then determined using the constant-head method described by Klute and Dirksen (1986). The bulk density of each soil core was also determined.

3.4 Results and Discussions

3.4.1 Hydraulic Properties

Examples of measured flux densities, $q$, versus the inverse of the pond radius, $1/r_o$, for some selected sites are shown in Fig. 3.2. Those sites were shown to present the trend of goodness of the linear fitting among the sites. The points and solid lines in Fig. 3.2
represent the measured and predicted (fitted) values of flux densities, respectively. The hydraulic properties were determined from the regression output (slope and intercept) of \( q \) versus \( 1/r_a \). Six sites were excluded from analysis for the hydraulic properties, because drippers at those sites had clogging problems. Thus, the hydraulic properties of 44 sites are reported in this study. The fitting procedure of \( q \) versus \( 1/r_a \) produced some variability among the sites. We excluded the differences in the discharge rates, \( Q \), among the sites as a source of variability because of their low CV value (\( \approx 7\% \)). The degree of such variability is considered to be marginal when compared with the variability produced by the natural heterogeneity of the soil (Or, 1996). The fitting procedure produced a median value for the coefficient of determination (\( r^2 \)) of 0.89. A possible source of error in the measurements could be due to the presence of macropores (vented macropores were visible). The presence of the macropores causes water to move preferentially into them leading to a smaller ponded area and, thus, the linear relationship presented by the Wooding’s solution is not satisfied. Wu et al. (1997) reported that the presence of the macropores yielded unreasonable values for \( K_s \) (negative values) from the borehole permeameter. Thus, macropores can have a major role in the variability of the hydraulic properties.

The hydraulic properties (\( K_s, \lambda_c \)) for the 44 sites are presented in Table 3.1. Measured values of the saturated hydraulic conductivity (\( K_s \)) ranged from 7.5 to 79.0 cm h\(^{-1}\) with an average value of 31.2 cm h\(^{-1}\) (\( \pm 16.8 \)) and a median of 27.4 cm h\(^{-1}\). The values of measured \( K_s \) among sites produced some variability with a CV of 54\%. Measured values of the macroscopic capillary length (\( \lambda_c \)) ranged from 0.03 to 13.1 cm with an average value of 4.0 cm (\( \pm 3.6 \)) and a median of 2.6 cm. The CV for \( \lambda_c \) values was 90\%. Large variability associated with \( \lambda_c \) is expected, because it is affected by the level of variability of the corresponding \( K_s \)-value (see Eq. 3.4). Because of the effects of \( K_s \)-variability, the degree of variability in estimating \( \lambda_c \) is nearly doubled. The large values of \( K_s \) are attributed to the presence of macropores. The measurements were taken on plant rows
Figure 3.2  Examples of flux densities versus $1/r_o$ of some selected sites. The points and solid lines are the measured and predicted (fitted) values, respectively.
Table 3.1 Hydraulic parameters as determined from the point source method.

<table>
<thead>
<tr>
<th></th>
<th>(K_s) (cm h(^{-1}))</th>
<th>(\lambda_c) (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>Mean</td>
<td>31.2</td>
<td>4.0</td>
</tr>
<tr>
<td>Median</td>
<td>27.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Min.</td>
<td>7.5</td>
<td>0.03</td>
</tr>
<tr>
<td>Max.</td>
<td>79.0</td>
<td>13.1</td>
</tr>
<tr>
<td>SD</td>
<td>16.8</td>
<td>3.6</td>
</tr>
<tr>
<td>C.V. (%)</td>
<td>53.8</td>
<td>89.8</td>
</tr>
<tr>
<td>C.I. (95%)</td>
<td>5.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

at the end of the growing season, where the macropores are common to exist due to fully-developed rooting system (Prieksat et al., 1994).

The constant-head method applied to the soil cores produced \(K_s\) values ranging from 0.7 to 62.4 cm h\(^{-1}\) with an average of 15.9 cm h\(^{-1}\) (± 13.7) and a median of 12.4 cm h\(^{-1}\). These values were, in general, smaller than those produced by the point source method in the field. Smaller \(K_s\)-values obtained from the constant-head method could be due to slight compaction of soil and/or surface smearing of cores during sampling. Mohanty et al. (1994) reported that wheel-trafficked (surface-compacted) soils have the lowest values of hydraulic conductivity when compared with values from plant and no-track field soils. The t-test (Neter et al., 1996) indicated that the \(K_s\)-values produced in the field were significantly different from those produced by the constant-head method at the 5% probability level.

Figure 3.3 represents a map-figure of the distribution of the measured \(K_s\)-values across the grid and their corresponding histogram. The five columns (from the east side) represent the transects, where measurements were taken. The missing places along the transects represent the discarded data due to the clogging of the drippers. The map figure shows some trend in the distribution of measured \(K_s\). However, there is no overriding (strong) pattern in the distribution within each transect. Most of measured \(K_s\)
Figure 3.3 Spatial distribution of measured $K_s$-values across the research site and their corresponding histogram.
values (about 77%) fall between 20 and 40 cm h\(^{-1}\). The test of normality indicated that the \(K_s\) histogram is skewed and not normally distributed but normally distributed on the log-normal scale. The distribution of \(K_s\) measured on the soil cores showed similar distribution to that of the field measurements (figure not shown). The large \(K_s\)-values might have caused the skewness in the distribution on the normal scale.

Figure 3.4 represents a map-figure of the distribution of the measured \(\lambda_c\)-values across the grid and their corresponding histogram. The map figure shows that there is no obvious pattern in the distribution of \(\lambda_c\) across the field. The histogram of measured \(\lambda_c\) indicates that about 55% of \(\lambda_c\) values were in the range of 0 to 5 cm. The test of normality showed that the distribution of \(\lambda_c\) values is skewed and not normally distributed at the normal or log-normal scales.

The effects of the saturated hydraulic conductivity on measured \(\lambda_c\) are shown in Fig. 3.5. The two parameters are correlated (see Eq. 3.4). This is expected, because both parameters are related to soil pore geometry (White and Sully, 1992). For a specific pore size, the general trend of the data suggests an inverse relationship; as \(K_s\) increases, the \(\lambda_c\) parameter gets smaller. Any discrepancy in this trend is attributed to occurrence of macropores, i.e., a texture-controlled condition (Or, 1996). In other words, the presence of the macropores causes the contribution of capillary-flow to be marginal, because water mainly flows through the macropores. A similar trend between \(\lambda_c\) and \(K_s\) was also reported by Or (1996).

### 3.4.1.1 Spatial analysis of the hydraulic properties

The non-directional semivariograms of calculated for \(K_s\) and \(\lambda_c\) are shown in Fig. 3.6(a) and 3.6(b), respectively. The \(K_s\)-semivariogram shows almost a pure nugget effect (i.e., no spatial correlation between sites) with perhaps minor spatial correlation between the nearest sites for the measured-\(K_s\). However, the \(\lambda_c\)-semivariogram shows only a nugget relationship for the measured-\(\lambda_c\). There is no obvious spatial trend of
Figure 3.4  Spatial distribution of measured $\lambda_c$-values across the research site and their corresponding histogram.
distribution of $K_s$ and $\lambda_c$ that can be deduced along the corn-rows (at distances > 1.5 m) under no-till conditions.

### 3.4.1.2 Comparison of hydraulic properties with previously reported values

The reported values from this study can be compared with those reported in previous studies. Mohanty et al. (1994) measured $K_s$ and $\lambda_c$ of a nearby no-till corn field plants. They used ponded and tension infiltrometers to determine the hydraulic properties. Their reported values for $K_s$ ranged from 1.0 to 260.4 cm h$^{-1}$ with an average of 39.9 cm h$^{-1}$ (± 36.4) and a CV of 91%. The average of this study, 31.2 cm h$^{-1}$, was comparable to their average. However, our study produced less variable $K_s$ values than their study with a CV of 51%. Their measured values of $\lambda_c$ ranged from 7.8 to 55.6 cm.
Figure 3.6 Calculated non-directional semivariograms (2D) for (a) $K_s$, and (b) $\lambda_c$. 
with an average of 24.4 cm (± 55.5). Their average value of $\lambda_c$ was much larger than the average of this study. Their CV from estimating $\lambda_c$ was about 44% (compared with 90% of our study). Differences in the values reported in this study and the study of Mohanty et al. (1994) are due in part to the natural spatial and temporal variability of the soil. However, different fitting procedures to determine $K_s$ and $\lambda_c$ used by the two studies can also be considered as a source of variability for values reported. We used simple linear regression between the flux density and the inverse of the steady-state pond radius with negligible head over the soil surface. Mohanty et al. (1994) used the piece-wise linear fitting procedure developed by Ankeny et al. (1991) with known (i.e., controlled) pressure heads over the soil surface as their boundary conditions. The semivariograms presented by Mohanty et al. (1994) study are similar to the semivariograms reported in this study.

### 3.4.2 Chemical transport properties

Figure 3.7 shows some examples for the normalized resident concentration, $\ln(1 - C/C_0)$, versus the application time of tracers, $t^*$. The sites shown in Fig. 3.7 are those ones shown in the section of the hydraulic properties. The chemical transport properties are determined from the regression output of $\ln(1 - C/C_0)$ versus $t^*$. The sequential tracer method developed by Jaynes et al. (1995) worked well with the point source method at field conditions. This is indicated by high median $r^2$ of 0.926 for the linear fitting procedure. The good linearity of the fitted lines indicates that Eq. 3.3 well describes the physical processes occurring in the soil (Jaynes et al., 1995).

The measured chemical transport parameters, immobile water fraction ($\theta_{im}/\theta$) and mass exchange coefficient ($\alpha$), are presented in Table 3.2. The measured soil water content ($\theta$) from the study was consistent and ranged from 0.41 to 0.52 m$^3$ m$^{-3}$ with a median of 0.51 m$^3$ m$^{-3}$ (± 0.02). Consistent values of $\theta$ can be attributed to the soil being uniform along the corn rows. Uniformity of the soil in the plant rows is indicated by uniform values of bulk density ($\rho_b$) as measured from soil cores. Measured $\rho_b$ along
Figure 3.7 Examples of normalized resident concentration versus application time of some selected sites. The points and solid lines are the measured and predicted (fitted) values, respectively.
Table 3.2 Chemical transport properties as determined from the point source method.

<table>
<thead>
<tr>
<th></th>
<th>$\theta_{im}/\theta$</th>
<th>$\alpha$ (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Mean</td>
<td>0.65</td>
<td>0.04</td>
</tr>
<tr>
<td>Median</td>
<td>0.65</td>
<td>0.04</td>
</tr>
<tr>
<td>Min.</td>
<td>0.41</td>
<td>0.0004</td>
</tr>
<tr>
<td>Max.</td>
<td>0.91</td>
<td>0.11</td>
</tr>
<tr>
<td>SD</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>C.V. (%)</td>
<td>12.3</td>
<td>63.0</td>
</tr>
<tr>
<td>C.I. (95%)</td>
<td>0.02</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Plant rows had a CV-value of only 7%. Therefore, a uniform distribution of water content could be expected with uniform distribution of $\rho_b$.

The estimated immobile water fraction ($\theta_{im}/\theta$) ranged from 0.41 to 0.91 with an average and a median of 0.65 (± 0.08). The consistency and uniformity of $\theta_{im}/\theta$ is indicated by a low CV value of about 12%. Estimated values for the mass exchange coefficient ranged from $4 \times 10^{-4}$ to 0.12 h$^{-1}$ with a median of 0.04 h$^{-1}$ (± 0.02). Estimated values of $\alpha$ were highly variable (as compared with $\theta_{im}/\theta$) with a CV-value of 50%. This is expected, because estimated $\alpha$ is affected by the degree of variability of corresponding $\theta_{im}/\theta$.

Figure 3.8 represents a map-figure of the distribution of the estimated $\theta_{im}/\theta$-values across the research grid and their corresponding histogram. The map-figure represents the $\theta_{im}/\theta$-values for all 50 sites in the field. The map figure shows that the first two transects have some spatial pattern in estimated immobile water content (similar values of $\theta_{im}/\theta$ are close to each other). However, the trend is not obvious within the rest of transects; i.e., there is no obvious spatial pattern in estimated $\theta_{im}$ within each transect. The histogram figure of $\theta_{im}/\theta$ indicates that about 80% of the estimated $\theta_{im}/\theta$-values were in the range of 0.4 to 0.7, which means that most of the estimated $\theta_{im}/\theta$-values were concentrated toward the middle-range of possible values. The test of normality.
Figure 3.8 Spatial distribution of measured $\theta_{im}/\theta$-values across the research site and their corresponding histogram.
(\(P = 0.05\)) indicated that the \(\theta_{im}/\theta\) distribution was not normally distributed at either normal or log-normal scales.

Figure 3.9 presents estimated \(\alpha\)-values across the research grid and their corresponding histogram. The map-figure of estimated \(\alpha\) shows more spatial pattern than that of the estimated \(\theta_{im}/\theta\) (similar values in the range are closer to each other). As shown by its histogram, about 72\% of the estimated \(\alpha\) values were in the range of 0.02 to 0.08 h\(^{-1}\). The distribution of \(\alpha\) is skewed toward the left and found to be not normally distributed at either normal or log-normal scales.

The effects of estimated immobile water fraction (\(\theta_{im}/\theta\)) on estimated mass exchange coefficient (\(\alpha\)) are shown in Fig. 3.10. It is shown that the estimated \(\alpha\) parameter is proportional to \(\theta_{im}/\theta\). Skopp et al. (1981) and Casey et al. (1997) also reported such a relationship. Large immobile water contents yield large contact regions between the mobile and immobile domains. Consequently, more chemical transfer is expected to occur between the two domains and, thus, large \(\alpha\) is observed. The linear relationship shown by Fig. 3.10 can also be observed from Eq. 3.3. The estimated \(\alpha\) parameter is the product of the estimated \(\theta_{im}\) (as determined from the intercept) and the slope of the regression line. Thus, large \(\theta_{im}\) yields large \(\alpha\). This means that the degree of variability in estimated \(\alpha\) is expected to be higher than that of the estimated \(\theta_{im}\). The degree of variability (in terms of CV) is shown in Table 3.2.

### 3.4.2.1 Spatial analysis of the chemical properties

Figure 3.11(a) and 3.11(b) represent the semivariograms calculated for \(\theta_{im}/\theta\) and \(\alpha\), respectively. Both semivariograms show a pure nugget relationship, which means that there is no obvious spatial correlation in the distribution of those parameters along the corn rows (at distances > 1.5 m) under notill conditions.
Figure 3.9 Spatial distribution of measured $\alpha$-values across the research site and their corresponding histogram.
3.4.2.2 Comparison of chemical properties with previously reported values

The results obtained from this study can be compared with results from previous studies. Casey et al. (1997) used tension infiltrometers to estimate chemical transport properties ($\theta_{im}/\theta$, $\alpha$) on a loam soil (a nearby field location to our study). They applied multiple conservative tracers from infiltrometers to the soil using a supply pressure head of -30 mm of water. They reported a median of 0.64 for $\theta_{im}/\theta$, with extremes ranging from 0.44 to 0.97. Our study produced a median of 0.65, which is very comparable to their computed median. Angulo-Jaramillo et al. (1996) reported an average $\theta_{im}/\theta$-value of 0.63 for a loamy soil, which is also very comparable to the average obtained from this study. For the $\alpha$ parameter, Casey et al. (1997) reported a median of 0.074 h$^{-1}$, with extremes ranging from 0.014 to 0.289 h$^{-1}$. Our study yielded a median of 0.04 h$^{-1}$,
Figure 3.11 Calculated non-directional semivariogram (2D) for (a) $\theta_{im}/\theta$, and (b) $\alpha$. 
which is 90% lower than that of Casey et al. (1997). The results obtained from this study showed a linear relationship between the $\alpha$ parameter and the pore velocity (figure is not shown). Moreover, a nonparametric correlation test (Pearson coefficient test, Neter et al. (1996)) showed that there is a positive correlation, though not significant ($r = 0.361$), between the flux density ($q$) and the $\alpha$ parameter. Previous studies, as compiled by Griffioen et al. (1998), showed that there is a positive relationship between the flux density and the $\alpha$ parameter. This indicates that the $\alpha$ values obtained from this study were consistent with the general trend of the $\alpha$ values reported by previous studies. The semivariogram tests reported by Casey et al. (1997) showed similar nugget relationship as reported by this study. In general, the measured values of the transport parameters ($\theta_{im}/\theta$, $\alpha$) were found to fall within the ranges reported by other studies (Kookana et al., 1993; Griffioen et al., 1998).

3.5 Conclusion

This study presents measurements of soil hydraulic and chemical transport properties at multiple field locations. A total of 50 field locations were simultaneously evaluated for $K_s$, $\lambda_c$, $\theta_{im}/\theta$, and $\alpha$ within a 2-day period with minimum labor requirements. The values of the estimated parameters presented by this study were comparable with those of previously reported studies conducted on nearby field locations with similar soil type and tillage system. Moreover, the spatial correlation tests conducted by this study showed similar trends in distributions of properties as reported by previous studies. Compared with the number of observations that other field methods can produce for the same time period, the setup and procedure presented by this study allow for conducting extensive measurements of the hydraulic and chemical transport properties. This should provide the needed data for better understanding of the mechanisms by which water and chemicals move through the vadose zone.
References


CHAPTER 4 A TDR-BASED METHOD FOR FIELD DETERMINATION OF CHEMICAL TRANSPORT PROPERTIES

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

Salem A. Al-Jabri\textsuperscript{1}, Jaehoon Lee\textsuperscript{2}, Robert Horton\textsuperscript{2}, and Dan B. Jaynes\textsuperscript{3}

4.1 Abstract

Field determination of chemical transport properties helps in protecting groundwater resources from land-applied chemicals. Most field methods to determine the chemical transport properties are either time and energy consuming and/or they provide a single measurement for a given time period. In this study, we present a field method that allows conducting real-time measurements of chemical transport properties at multiple field locations within a short time period. The chemical transport properties are immobile water content, expressed as a fraction of total water content \(\theta_{im}/\theta\), mass exchange coefficient \(\alpha\), and dispersion coefficient \(D_m\). Multiple dripper lines were built over five transects in the field. Background and step solutions were applied from the point sources at 38 field locations. Time domain reflectometry (TDR) was used to measure the bulk electrical conductivity of the soil at steady state flow of solutions. Breakthrough

\textsuperscript{1}Dept. of Soil and Water Sciences, Sultan Qaboos University, Muscat, Sultanate of Oman
\textsuperscript{2}Dept. of Agronomy, Iowa State University, Ames, Iowa
\textsuperscript{3}USDA-ARS, National Soil Tilth Laboratory, Ames, Iowa
curves (BTCs) for all sites were determined from the TDR measurements. Two fitting procedures, log-linear and nonlinear fitting, were followed to estimate the transport parameters from observed BTCs. The nonlinear fitting procedure produced estimates for $\theta_{im}/\theta$ ranging from 0.18 to 0.63 with a median value of 0.43 ($\pm$ 0.10). For the $\alpha$ parameter, the estimates ranged from 0.00 to 0.30 h$^{-1}$ with a median value of 0.015 h$^{-1}$ ($\pm$ 0.054 h$^{-1}$). The $D_m$ ranged from 200 to 6380 cm$^2$ h$^{-1}$ with a median value of 1860 cm$^2$ h$^{-1}$ ($\pm$ 1600 cm$^2$ h$^{-1}$). The estimated values of transport parameters were found to fall within the range reported by previous studies conducted on nearby field locations. The setup presented in this study is fully automated so that it is simple to operate and require minimum labor requirements. Moreover, the procedure requires applying only one single conservative tracer. When compared with the time and energy constraints of other field methods, the setup and procedure presented in this study are ideal for rapid estimation of surface transport properties at multiple field locations with minimum labor requirements.

4.2 Introduction

Chemical transport through soils has been intensively studied for the last two decades due to increased environmental concerns about the quality of drinking water. Chemical transport properties help in predicting transport of land-applied chemicals through the vadose zone and, thus, help in protecting groundwater resources. Water and dissolved chemicals may move in the soil through a small fraction of pore space available for flow, which causes water and dissolved constituents to reach great depths in a relatively short time (Rice et al., 1986). This nonequilibrium flow phenomenon is known as preferential flow. One cause of preferential flow in soil is the occurrence of macropores, such as cracks, worm holes, and dead plant roots. In laboratory studies, such as Khan and Jury (1990), preferential flow can cause asymmetry in breakthrough curves (BTCs), i.e., early
breakthrough of chemicals and distinctive tailing.

Coats and Smith (1964) introduced a model to describe the preferential flow of chemicals through the porous media. The model, often called the mobile-immobile model (MIM), was found to better describe preferential flow events in structured soils than the classical convective-dispersive equation (van Genuchten and Wierenga, 1976). The concept of the MIM is that it partitions the water-filled pore space ($\theta$) into two domains: a mobile domain ($\theta_m$) where water and chemicals move by advection, and an immobile domain ($\theta_{im}$) where water is stagnant and chemicals move by diffusion only. The chemical dispersion in the mobile domain is similar to that in the convective-dispersive equation (CDE). For one dimensional movement of conservative chemicals, the MIM can be written as (van Genuchten and Wierenga, 1976):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - q \frac{\partial C_m}{\partial z}$$  \hspace{1cm} (4.1)

where $C_m$ and $C_{im}$ are the concentrations of chemicals in the mobile and immobile domains (M L$^{-3}$), $q$ is flux density (L T$^{-1}$), $D_m$ is the dispersion coefficient (L$^2$ T$^{-1}$) in the mobile domain, $t$ is time (T), and $z$ is depth (L). The water in the immobile domain ($\theta_{im}$) acts like a source or sink for the dissolved chemicals in the mobile domain. Chemical transfer between the two domains is a function of the concentration difference between the domains and is described as a first-order rate of diffusion process (van Genuchten and Wierenga, 1976):

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im})$$  \hspace{1cm} (4.2)

where $\alpha$ is a first-order mass exchange coefficient (T$^{-1}$).

Jaynes et al. (1995) solved Eq. 4.2 to give estimates for the immobile water content ($\theta_{im}$) and the mass exchange coefficient ($\alpha$). They applied a sequence of conservative tracers into the soil using tension infiltrometers and presented the following solution to
Eq. 4.2:

\[
\ln \left( 1 - \frac{C}{C_0} \right) = \ln \left( \frac{\theta_{im}}{\theta} \right) - \left( \frac{\alpha}{\theta_{im}} \right) t^* \tag{4.3}
\]

where \(C\) and \(C_0\) are the tracer concentrations in the soil and input solutions (M L\(^{-3}\)); respectively, \(t^* = t - z'/v\) is the time needed for the tracer front to pass sampling depth, \(z'\), and \(v\) is the water-pore velocity in the mobile domain (L T\(^{-1}\)). Jaynes et al. (1995) assumed negligible \(D_m\) within the sampling zone. According to Eq. 4.3, plotting the normalized resident concentration in the soil, \(\ln(1 - C/C_0)\), versus the travel time of tracers, \(t^*\), yields a straight line with a negative slope and intercept (from which transport parameters could be determined). Jaynes et al. (1995) suggested using fluorobenzoic acids as conservative tracers in order to determine the transport parameters from Eq. 4.3. Possible errors in estimating transport parameters \(\theta_{im}, \alpha\) from applying such tracers may arise from difficulty in measuring the small differences in tracer concentration and/or nonidentical transport behavior of individual tracers (Jaynes et al., 1995).

As an alternative to applying a sequence of multiple tracers, Lee et al. (2000) applied one single conservative tracer and used time domain reflectometry (TDR) to monitor the change in tracer concentration with respect to time. Lee et al. (2000) used the TDR-technique with probes installed at an angle to estimate the transport parameters from the soil surface (top 2 cm) of intact soil columns. They used the solution of Jaynes et al. (1995) to determine \(\theta_{im}\) and \(\alpha\) from TDR-measured bulk electrical conductivity \(\sigma_a\). Furthermore, they fitted the transport parameters of the MIM \(\theta_{im}, \alpha, D_m\) to observed BTCs from the TDR and effluent data. They reported a good agreement between estimated parameters from the Jaynes et al. (1995) solution and the TDR method. Moreover, their estimated transport parameters from the TDR method were in good agreement with the estimated parameters from the effluent data.

Most of the current field techniques used for measuring the chemical transport properties commonly require extensive labor resources and/or have some limitations. For
example, it took Casey et al. (1997) about 5 weeks to determine $\theta_{im}$ and $\alpha$ of 47 field locations using tension infiltrometers. Other field devices, such as soil coring and solution samplers, are destructive and/or provide a single measurement for a given time, i.e., they only provide a snapshot of parameters at a given time period. Consequently, the degree of advancement of current field techniques have lagged behind the theoretical basis of modeling of chemical transport into soils (Ward et al., 1995). Thus, there is a need for field methods that are low destructive and allow conducting measurements at multiple field locations during the same time period.

The objectives of this study were to extend the method reported by Lee et al. (2000) and present a field procedure for simultaneous measurements of the chemical transport properties at multiple locations. Another objective was to determine the chemical transport of a field soil from TDR-measured data (TDR technique) and study their spatial distribution across the field. The chemical transport properties were the immobile water content, expressed as a fraction of the total water content ($\theta_{im}/\theta$), the mass exchange coefficient ($\alpha$), and the chemical dispersion coefficient ($D_m$). The dripper-line setup presented by Al-Jabri et al. (2001) was utilized by this study to conduct measurements on multiple field locations during the same time period. A total of 38 field locations were simultaneously evaluated for the chemical transport properties. The transport parameters from the Jaynes et al. (1995) solution and field BTCs (from the TDR-data) were evaluated by comparing them with estimates from a nearby field location (which produced by previous studies).

4.3 Theory: Use of TDR to estimate Transport Parameters

Measurement of the soil bulk electrical conductivity, $\sigma_a$, using TDR is related to chemical concentration in soil pores, which is related to the total concentration of chemicals surrounding the TDR probes (Kachanoski et al., 1994). The bulk soil electrical
conductivity is inversely related to the impedance load, \( Z (\Omega) \), of the TDR (Nadler et al., 1991):

\[
\sigma_a = \kappa Z^{-1}
\]  

(4.4)

where \( \kappa \) is a cell constant that depends on the probe geometry. The \( Z \)-parameter (as measured by TDR) is affected by \( \theta \) and the electrical conductivity of surrounding solution, \( \sigma_w \). Rhoades et al. (1989) presented that, at steady-state water flow (\( \partial \theta / \partial t = 0 \)), the \( \sigma_a \) parameter is linearly related to \( \sigma_w \). This is valid for practical levels of \( \sigma_w \) of 4.0 to 20.0 dS m\(^{-1} \) (Ward et al., 1994). For a similar range of \( \sigma_w \), a linear relationship was also observed between chemical concentration, \( C \), and \( \sigma_w \). At constant \( \theta \), therefore, there should be a linear relationship between \( C \) and \( \sigma_a \) as (Ward et al., 1994):

\[
C = \delta + \xi \sigma_a
\]  

(4.5)

where \( \delta \) and \( \xi \) are calibration constants. Substituting the \( \sigma_a \) parameter from Eq. 4.4 into Eq. 4.5 produces:

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

(4.6)

where \( \beta_0 \) and \( \beta_1 \) are calibration constants. For chemical-leaching experiments, the relative concentration at any given time, \( \overline{C}(t) \), can be computed from the TDR-measured \( Z \) as:

\[
\overline{C}(t) = \frac{C(t) - C_i}{C_0 - C_i} = \frac{Z^{-1}(t) - Z_i^{-1}}{Z_0^{-1} - Z_i^{-1}}
\]  

(4.7)

where \( C_i \) is background chemical concentration (M L\(^{-3} \)), \( Z_i (\Omega) \) is TDR impedance load for \( C_i \), and \( Z_0 (\Omega) \) is impedance load for \( C_0 \). Because of the linear relationship between \( C \) and \( Z \), the calibration constants in Eq. 4.7 are not required to be determined for estimating \( \overline{C}(t) \).

The \( Z_i \) parameter can be determined directly from the background solution, because the added mass of the chemical is known. However, determining \( Z_0 \) requires additional work. Ward et al. (1994) and Mallants et al. (1996) suggested applying a long pulse of
step solution in order to determine $Z_o$. Their assumption was that application of the step solution for a long period of time yields a uniform distribution of the solution in the soil matrix. This is true when $\theta_{im} = 0$. If, however, $\theta_{im} > 0$, then the chemical concentration in the soil matrix is less than that of the input solution (Jaynes and Horton, 1998). This has been verified by Lee et al. (2000) with a study involving intact soil columns. To accurately estimate $Z_o$, Lee et al. (2000) suggested taking a soil sample (from the region of the influence of the TDR) after the final measurements of the TDR ($t_f$) and analyze for the resident concentration of the applied tracer. The resident concentration of solution in the soil (at $t_f$) is equivalent to $\bar{C}(t_f)$. Knowing the final impedance load; $Z(t_f)$, from the TDR and $\bar{C}(t_f)$ from the soil sample, the $Z_o$ parameter can be explicitly determined from Eq. 4.7. Lee et al. (2000) reported that using such a calibration procedure to determine $Z_o$ minimizes any error due to nonequilibrium transport of chemicals through the soil. Knowing $Z_i$ and $Z_o$, $\bar{C}(t)$ (at any given time) can be explicitly determined from TDR-measured $Z(t)$ using Eq. 4.7.

The term $(\bar{C}/C_0)$ in Eq. 4.3 represents the relative resident concentration of chemicals in the soil. Similarly, the term $\bar{C}(t)$ in Eq. 4.7 is equivalent to the relative resident concentration of chemicals in the soil. Thus, the immobile water content ($\theta_{im}$) and the mass exchange coefficient ($\alpha$) can be estimated from the TDR-computed $\bar{C}(t)$ using the log-linear solution (Eq. 4.3) developed by Jaynes et al. (1995). Real-time measurements of chemical concentration, $\bar{C}(t)$, from the TDR implies that breakthrough curves (BTCs) from field experiments can be easily determined with minimum labor requirements. Moreover, all transport parameters ($\theta_{im}$, $\alpha$, and $D_m$) can also be estimated by inversely fitting them to observed BTCs measured by the TDR technique. The CXTFIT package (Toride et al., 1995) can be used to run the inverse fitting procedure to estimate all transport parameter from measured BTCs. It should be noted that the transport parameters are fitted to observed BTCs using the analytical solution of the MIM.
4.4 Materials and methods

The study was conducted on a no-till corn field (Zea Mays L.) at the Agronomy-Agricultural Engineering Research Center, Iowa State University, Ames, IA. The soil at the research site is predominantly Nicollet loam (0.389 sand, 0.366 silt, 0.245 clay mass fraction), and classified as fine loamy, mixed, mesic Aquic Hapludolls. The study was conducted on a 6 by 15 m field grid. Five parallel transects were selected on corn rows. Transects were about 15 m long and 1.5 m apart. Dripper lines (irrigation tubes) were built on each transect and equipped with pressure-compensating drippers (Hooks Point, Stratford, IA). More details about the dripper-line setup can be found in Al-Jabri et al. (2001). Selected drippers had a discharge capacity of 4 L h$^{-1}$. The dripper lines on the five transects were interconnected so that all lines can be operated simultaneously.

A total of 38 sites were evaluated for the chemical transport properties using the TDR technique. Before any experimental work has conducted, the soil surface at each site was levelled with a minimum of disturbance.

The TDR-system (Fig. 4.1) consisted of a 1052B Tektronix cable tester (Tektronix, Beaverton, OR)$^{1}$, a multiplexer (Dynamax, Houston, TX), TDR probes, and a computer. The TDR probes (2 rods (5 cm apart), 2-mm diam. by 100 mm long) were connected to the cable tester through the multiplexer. Each TDR probe was connected to the multiplexer with a 50 $\Omega$ coaxial cable (10 m long). The cable tester was connected to the computer, where the TACQ program (Evett, 1998) was used to acquire the data required for measuring $Z(t)$.

The experimental work was started by applying a background solution composed of 0.005 $M$ CaCl$_2$ from the drippers (at each site) on the soil surface. The discharge rate of each dripper was measured and recorded. Applying the solution from the drippers caused water to create a circular (or near-circular) pond on the surface. The ponded area

$^{1}$Company and product names do not imply endorsement.
Figure 4.1 Experimental TDR setup at the field (2 transects are shown).
increases in size with time, but eventually reaches a constant size, where steady-state conditions prevail (Bresler, 1978). The ponded diameter at the steady-state conditions (at each site) was measured and recorded. The diameter of the ponded diameter was measured from three axis and the average value was used to determine the flux density \( q \) at each site. After the steady-state conditions prevailed, a TDR probe (at each site) was carefully installed beneath the ponded area at an angle to a depth equivalent to 20 mm from the soil surface. The installation of each TDR probe was made so that the whole length of the probe was covered by the ponded area. It was assumed that the TDR-probe measures \( \sigma_a \) for the top 20 mm from the soil surface (Lee et al., 2000). The TDR-waveform analysis presented by Wraith et al. (1993) was used to determine \( Z(t) \) as:

\[
Z(t) = Z_{ref} \frac{(1 + \rho)}{(1 - \rho)}
\]  

(4.8)

where \( Z_{ref} \) is the output-impedance load of the cable tester (50 \( \Omega \)), and \( \rho \) is the reflection coefficient of the TDR waveform. The details of the TDR-waveform analysis for the determination of \( Z(t) \) can be found in Wraith et al. (1993). The background solution was used to determine the background impedance load, \( Z_i \). A step solution (composed of 0.2 \( M \) CaCl\(_2\)) was then introduced to the system. The dripper tube was quickly flushed from the background solution by opening the release valve at the end of the system. The increase in the concentration of solution (from 0.005 \( M \) to 0.2 \( M \)) satisfies the required linear relationship between \( Z \) and \( \sigma_a \) (Nadler et al., 1991). We applied the step solution for a time long-enough for the solution front to pass the sampling depth, which is the 20 mm below the soil surface. The time needed for the solution-front to pass the sampling depth was estimated from a pre-assumed pore velocity. After the application of step solution for sufficient time, a soil sample (equivalent to the depth of the TDR probe) was taken from beneath each dripper using a stainless steel ring. The depth at which the TDR probe was located (at each site) was measured during
the sampling. Each soil sample was placed into a sealed plastic bag and kept in a cold environment until water content and chemical analysis occurred. In the laboratory, each sample was thoroughly mixed and a subsample was taken for determining the water content gravimetrically. Distilled water was added to the rest of each sample at a ratio of approximately 1:2 soil-water to water-mass ratio. Samples were shaken for about 5 min and filtered using No. 11 filter paper. Filtered solutions and input solutions were analyzed for \( \text{Cl}^- \) concentration using a chloridimeter.

Soil samples obtained from sampling rings had relatively small soil volumes, which lead to highly variable bulk densities (\( \rho_b \)). Accurate \( \rho_b \) is needed to determine \( \theta_{\text{im}} \), which is used to compute the \( \alpha \) parameter from Eq. 4.3. Thus, a large error could be introduced in estimating \( \alpha \) from using \( \rho_b \) of the soil samples to determine the volumetric water content (\( \theta_v \)). Therefore, instead of using \( \rho_b \) of soil samples, we assumed the soil samples to be saturated (sampling was done quickly after water application had ceased) and \( \theta_v \) could be determined from the known mass water content (\( \theta_g \)) and soil particle density (\( \rho_s \)) using the following relationship:

\[
\theta_v = \frac{\theta_g \rho_s}{\theta_g \rho_s + 1} \quad (4.9)
\]

Equation 4.9 does not use the \( \rho_b \) term. Thus, it removes any possible error in estimating chemical transport properties from miscalculated \( \theta_v \) of soil samples.

### 4.4.1 Estimation of transport parameters

Equation 4.8 was used to determine the impedance load as a function of time, \( Z(t) \). The relative concentration from the TDR-readings, \( \overline{C}(t) \), was determined using Eq. 4.7. The details on how to determine \( \overline{C}(t) \) from the TDR-measured \( Z(t) \) can be found in Lee et al. (2000). Breakthrough curves from the TDR-measured \( \overline{C}(t) \) were constructed for each site.
Equation 4.3 (called the log-linear output hereafter) was used to determine the im-
mobile water content \((\theta_{\text{im}})\) and the mass exchange coefficient \((\alpha)\) using the normalized
resident concentration, \(\ln(1 - \overline{C}(t))\), from the TDR-measured \(\overline{C}(t)\). The transport pa-
rameters were found by fitting the normalized resident concentration versus the applica-
tion time, \(t^*\). It should be noted that only the \(\overline{C}(t)\) data for long application time of
the step solution were used to determine the transport parameters using Eq. 4.3.

All transport parameters \((\theta_{\text{im}}, \alpha, D_m)\) were inversely estimated by fitting them to
observed BTCs. The CXTFIT package (Toride et al., 1995) was used to run the fitting
procedure (called the inverse output hereafter). The soil depth, at which the transport
parameters were fitted, was the middle point of the vertical depth of the TDR probes
(Lee et al., 2000). Initial work with the CXTFIT package revealed a non-uniqueness
problem with our data, whereby the predicted values, \(D_m\) in particular, were sensitive
to initial guesses. The transport parameters produced from the log-linear output \((\theta_m, \alpha)\)
were set as initial guesses in the input files of the CXTFIT package. To assure that
the fitted \(D_m\) values correspond to a global rather a local minimum error sum of squares,
we tested a wide range of initial \(D_m\) values against a range of initial \(\theta_m\) and \(\alpha\) values,
and then chose the initial \(D_m\) value \((100 \text{ cm}^2 \text{ h}^{-1})\), which generally led to a global
minimum. As a result from the above analysis, two data sets of transport parameters
could be generated: one from the log-linear output \((\theta_{\text{im}}\text{ and } \alpha\text{ only})\), and another from
the inverse output \((\theta_{\text{im}}, \alpha, \text{ and } D_m)\).

### 4.4.2 Spatial distribution of transport properties

To study the spatial distribution of the chemical transport properties across the field,
non-directional semivariograms were determined (Davis, 1973) for parameters produced
by the inverse output. The spatial distribution of each transport parameter was tested
over the 6 by 15 m grid at a lag interval of 1.5 m and lag tolerance of 0.75 m. The
directional and tolerance angles of the semivariograms were set at 90° (from the x-axis).
Semivariogram-values (for each estimated parameter) with number of couples (NC) of less than 30 were excluded from the analysis of the spatial correlation test. Moreover, the semivariograms were cut at about half of the transect distance, i.e., any points beyond the half of transect-distance were excluded from the analysis of the spatial correlation.

The histograms of all transport parameter (produced by the inverse output) were constructed and tested for normality (Neter et al., 1996) at normal and log-normal scales. For log-normal tests, the data of estimated parameters were transformed into log-values. Normality tests were conducted by determining the correlation coefficient ($r$) between the error-residual values of the estimated parameters and their expected values under normality. The values of $r$ were matched with the critical $r$-value at 5% significance level. It should be noted that the normality test with log-transformed data was conducted only if the data were not normally-distributed at normal scale.

4.5 Results and Discussions

Examples of observed breakthrough curves (BTCs) of the relative resident concentration ($C(t)$) from the TDR measurements are shown in Fig. 4.2. The points and solid lines in Fig. 4.2 represent the measured and predicted (inverse output) $C(t)$, respectively. Due to an interruption in recording the data (by the computer) for determining $Z(t)$, the BTCs of Sites 17 and 26 show gaps in the measurements. However, the abrupt stoppage of the computer occurred at a time when the wetting-front of the step solution had passed the influence zone of the TDR, so TDR measurements and data recording could be continued with only minimum effects due to the interruption. The CXTFIT-fitting procedure among all sites produced an average coefficient of determination ($r^2$) of 0.977. The differences between measured BTCs is indicative of the natural variability of soil across the field. Most sites produced a maximum relative concentration $C(t)$ of about 70% of the total maximum concentration, which indicates the influence of $\theta_{im}$ on the
Table 4.1 The chemical transport parameters as estimated from the log-linear and inverse fitting outputs.

<table>
<thead>
<tr>
<th></th>
<th>Log-linear output</th>
<th>Inverse output</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_{im}/\theta$</td>
<td>$\alpha$ $\theta_{im}/\theta$</td>
</tr>
<tr>
<td>Mean</td>
<td>0.53</td>
<td>0.040</td>
</tr>
<tr>
<td>Median</td>
<td>0.50</td>
<td>0.023</td>
</tr>
<tr>
<td>Min.</td>
<td>0.38</td>
<td>0.002</td>
</tr>
<tr>
<td>Max.</td>
<td>0.85</td>
<td>0.215</td>
</tr>
<tr>
<td>SD</td>
<td>0.11</td>
<td>0.061</td>
</tr>
<tr>
<td>C.I. (95%)</td>
<td>0.03</td>
<td>0.017</td>
</tr>
</tbody>
</table>

distribution of chemicals in the soil matrix.

Table 4.1 presents a summary of the chemical transport parameters estimated from the log-linear and the inverse outputs. Since the log-linear output does not consider $D_m$, only the immobile water content, expressed as a fraction of the total water content ($\theta_{im}/\theta$), and the mass exchange coefficient, $\alpha$, are shown. The inverse output produces estimates for all transport parameters. The measurements of the total water content (data are not shown in Table 4.1) produced a median value of 0.51 m$^3$ m$^{-3}$ with a deviation from the mean of 0.03 m$^3$ m$^{-3}$.

For $\theta_{im}/\theta$, the log-linear output produced estimates ranging from 0.38 to 0.85 with mean and median values of 0.53 and 0.50 (± 0.11). The inverse output produced estimates ranging from 0.18 to 0.63 with mean and median values of 0.42 and 0.43 (± 0.10). Compared with the inverse output, the log-linear output overestimated $\theta_{im}/\theta$ by about 26%. For the $\alpha$ parameter, the log-linear output produced estimates ranging from 0.002 to 0.215 h$^{-1}$ with mean and median values of 0.040 and 0.023 h$^{-1}$ (± 0.061 h$^{-1}$). The inverse output produced $\alpha$-estimates ranging from 0.000 to 0.300 h$^{-1}$ with mean and median values of 0.033 and 0.015 h$^{-1}$ (± 0.054 h$^{-1}$). Compared with the estimates produced by the inverse output, the log-linear output overestimated $\alpha$ by 39%. For the dispersion coefficient, $D_m$, the inverse output produced estimates ranging from 200 to
Figure 4.2 Examples of observed (points) and predicted (solid line) breakthrough curves of the relative resident concentration ($\bar{C}(t)$) from the TDR measurements.
6380 cm² h⁻¹ with mean and median values of 2310 and 1860 cm² h⁻¹ (± 1600 cm² h⁻¹). In terms of confidence interval, the output of the two fitting methods yielded comparable limits for $\theta_{im}/\theta$ and $\alpha$ parameters.

Since the log-linear solution (Eq. 4.3) assumes negligible $D_m$ within the regions behind the solution front, it is expected that the log-linear method overestimates $\alpha$ when compared with the estimates from the inverse output (Table 4.1). This is because the dispersion of the chemicals in $\theta_m$ (with log-linear solution) is assumed to be a function of $\alpha$ alone. Thus, the $\alpha$ parameter in Eq. 4.3 represents the diffusion and dispersion effects of the chemicals in the soil. The inverse fitting procedure, however, splits the dispersion effects of chemicals over $\alpha$ and $D_m$ parameters. Thus, lower $\alpha$ estimates are expected to be produced from the inverse output (as shown in Table 4.1).

Figure 4.3 shows the histograms of the estimated chemical transport parameters produced from the inverse output. Figure 4.3a indicates that about 66% of the estimated $\theta_{im}/\theta$ fall within the range of 0.4-0.5. The test for normality indicates that the $\theta_{im}/\theta$-histogram is normally distributed. About 90% of the estimated values of the $\alpha$ parameter fall within the range of 0-0.05 h⁻¹ (Fig. 4.3b). The estimated $\alpha$-values are not normally distributed at normal or log-normal scales. Figure 4.3c indicates that 66% of the estimated $D_m$ values fall within the range of 0-3000 cm² h⁻¹. The normality test for the $D_m$-histogram shows that it is log-normally distributed.

### 4.5.1 Spatial distribution of chemical transport properties

Figure 4.4 shows the calculated non-directional semivariograms of the chemical transport parameters (estimated from the CXTFIT fitting). The semivariograms of all transport parameters show pure nugget relationship, which means that there is no spatial correlation in the distribution of those parameters along the corn rows (at distances > 1.5 m) under no-till conditions.
Figure 4.3 Histograms for the chemical transport parameters (inverse output); (a) immobile water fraction, (b) mass exchange coefficient, and (c) dispersion coefficient.
Figure 4.4 Calculated non-directional semivariograms for the chemical transport parameters (inverse output); (a) immobile water fraction, (b) mass exchange coefficient, and (c) dispersion coefficient.
4.5.2 Comparison of chemical transport properties with previously reported values

To evaluate our procedure, the results from this study should be compared with results reported by other methods and studies. Al-Jabri et al. (2001) followed the sequential application of multiple tracers suggested by Jaynes et al. (1995) (i.e., the log-linear method) to estimate $\frac{\theta_{im}}{\theta}$ and $\alpha$ of a loam soil of a field (having similar soil, crop, and tillage system) nearby to the field where this study was conducted. Their reported mean-value of estimated $\frac{\theta_{im}}{\theta}$ was 0.65, which is larger than that estimated by the log-linear method of this study by about 23%. Moreover, their reported mean value for $\frac{\theta_{im}}{\theta}$ was larger than that estimated from the CXTFIT fitting by 55%. Angulo-Jaramillo et al. (1996) and Casey et al. (1997) reported mean values of 0.63 and 0.64 for $\frac{\theta_{im}}{\theta}$ for a loam soil using tension infiltrometers. Using ponded infiltrometers, Casey et al. (1998) reported a median $\frac{\theta_{im}}{\theta}$ value of 0.40 for a notill loam soil. This is comparable to the median values obtained from the CXTFIT. Lee et al. (2000), using intact soil columns, reported a mean of 0.31 for $\frac{\theta_{im}}{\theta}$, which is smaller than the means reported in this study.

In general, the estimated values of $\frac{\theta_{im}}{\theta}$ reported in this study were comparable with previous field and laboratory studies (Griffioen et al., 1998). The spatial distribution analysis (semivariograms) of $\frac{\theta_{im}}{\theta}$ shown in this study is similar to that reported by Casey et al. (1997) and Al-Jabri et al. (2001).

For the $\alpha$ parameter, Al-Jabri et al. (2001) reported a mean value of 0.04 h$^{-1}$. Their mean value for $\alpha$ is smaller than that produced by the log-linear method of this study. Moreover, the mean value for $\alpha$ reported by Al-Jabri et al. (2001) is larger than that produced by the CXTFIT output (by about 20%). Casey et al. (1997), using tension infiltrometers, reported a median value of 0.074 h$^{-1}$, which is larger than those reported in this study. A median of 0.59 h$^{-1}$ was reported by Casey et al. (1998) under ponded conditions. This value seems to be extremely large when compared with values reported
by previous field and column studies (Griffioen et al., 1998). The spatial distribution analysis of $\alpha$ shown in this study was similar to that reported by Casey et al. (1997) and Al-Jabri et al. (2001).

For the $D_m$ parameter, Lee et al. (2000) reported a mean value of 245 cm h$^{-1}$ for intact soil columns. The reported mean value for $D_m$ in this study is much larger than that reported by Lee et al. (2001). However, expressing the $D_m$ values from this study in form of dispersivity, $\gamma = D/v$, produces values for $\gamma$ comparable to that reported by Lee et al. (2001). The median value for $\gamma$ obtained in this study is 14 cm. Lee et al. (2001) reported a mean value for $\gamma$ of 10 cm. In general, expressing the $D_m$ values (of this study) in form of $\gamma$ yields values that fall within the typical range of $\gamma$ reported by van Genuchten and Wierenga (1986).

4.6 Conclusion

This study presents a method for rapid estimation of soil chemical transport properties at multiple field locations. All transport parameters ($\theta_m/\theta$, $\alpha$, $D_m$) for 38 field locations could be rapidly estimated from real-time measurements of soil bulk electrical conductivity using the TDR. The field setup presented in this study is fully automated, which means that measurements can be taken with minimum labor requirements. Moreover, the procedure is simple and requires applying and analyzing for only a single tracer. When compared with the sequential-tracer method, the TDR-procedure presented here eliminates any source of error that might arise from nonidentical transport behavior of different tracers. Thus, this TDR-procedure provides accurate estimates for the transport parameters. This study demonstrates that breakthrough curves from field measurements can be easily constructed and, thus, transport parameters can be estimated with reliable fitting techniques. The estimated values for the transport parameters reported in this study fall within the range reported by previous studies conducted on nearby
The simplicity of the setup and procedure make them ideal for rapid estimation of surface transport properties at field scale with minimum time and labor requirements.

References


CHAPTER 5  GENERAL CONCLUSIONS

This study consists of three major parts, which comprise three technical papers that have been, or will be, submitted to professional scientific journals. The overall objectives of this research work were to present a point-source setup and procedure to rapidly estimate the hydraulic and chemical transport properties at field scale, and to study the spatial distribution of properties across a field. The hydraulic properties were the saturated hydraulic conductivity, $K_s$ (L T$^{-1}$), and the macroscopic capillary length, $\lambda_c$ (L). The chemical transport properties were the transport parameters of the mobile/immobile model (MIM). These transport parameters include the immobile water content, expressed as a fraction of the total water content ($\theta_{im}/\theta$), the mass exchange (transfer) coefficient, $\alpha$ (T$^{-1}$), and the dispersion coefficient of the mobile domain, $D_m$ (L$^2$ T$^{-1}$).

The first stage of this research work (Part 1) was the development stage, where a multiple-dripper permeameter was built in order to apply water and chemical solutions at multiple field locations. The drippers served as point sources. The setup was evaluated on a greenhouse soil pit with a total of six experimental sites (i.e., six tests). To evaluate the point source method for simultaneous estimation of the hydraulic and chemical transport parameters, the estimated values from the point source method were compared with those estimated by the ponded and tension infiltrometers. The results showed that the setup allowed conducting measurements at multiple sites for the same time period. The point source method worked well with sequential application of multiple tracers and produced estimates with the minimum set of variability when compared with the
estimates produced by ponded and tension infiltrometers.

Following the results from Part 1, the setup and procedure were tested in field conditions. The objectives of the second part of this research work were to determine the hydraulic and chemical transport properties of a field soil using the point source method and to study the spatial distribution of such properties on a field scale. A total of 50 field locations on a 1.5 by 7 m rectangular grid were evaluated for the hydraulic and chemical transport properties. The results of this study showed that the hydraulic and chemical transport properties could be evaluated on a field scale with minimum time and energy requirements. The results produced by this study were comparable with those reported by previous studies conducted on nearby field locations or on similar soil type. Compared with the other field methods that are used to estimate the hydraulic and chemical transport properties, this study (i.e., setup and procedure) showed that a large number of observation can be tested for such properties within a short period of time (one to two days).

The third part of this study deals with providing a field procedure for real-time measurements of the chemical transport properties using the TDR technique. A total of 38 field locations were evaluated for the chemical transport properties ($\theta_{im}$, $\alpha$, $D_m$). The chemical transport properties were determined from the TDR-measurements of bulk electrical conductivity of soil. Breakthrough curves (BTCs) from field measurements were constructed and the transport parameters were estimated from inverse fitting procedures using the CXTFIT package. The results of this study were comparable to the results produced by the second part of this work and previously reported studies. Moreover, the results showed that the simple procedure presented here can be applied to determine all transport parameters with minimum soil disturbance and labor requirements.

The overall conclusion of this research work is that a setup and procedure for rapid determination of the hydraulic and chemical transport properties of field soils has been developed, evaluated, and used. The measurements of such properties can be made at
multiple field locations at the same time period. This makes the setup and procedure potential tools for studies that require extensive measurements of the hydraulic and chemical transport properties. This would provide means for conducting more field studies to validate the existing transport models, which increases our understanding for different transport mechanisms of water and chemicals through the vadose zone.

5.1 Recommendations for Future Research Work

This results from this study provide the following future research opportunities:

- Study the spatial distribution of the hydraulic and chemical transport properties under different field conditions, such as cropping and tillage systems and different compaction levels.

- Study the temporal variability and distribution of the hydraulic and chemical transport properties for different cropping and tillage systems.

- Study the effects of spatial distribution of the hydraulic and chemical transport properties on the movement of different fertilizers and pesticides across the field (precision agriculture).

- Use of the TDR to study the water and chemical transport under transient flow conditions, such as monitoring and managing salt-affected soils under different irrigation systems and/or scheduling.
**APPENDIX RAW DATA**

Table A.1 shows the raw data that used to estimated the hydraulic properties ($K_s$, $\lambda_c$) in Chapter 3. Table A.2 presents the data used to estimate the chemical transport properties, $\theta_{im}$ and $\alpha$, in Chapter 3 using the Jaynes et al. (1995) solution.

Table A.3 presents the data results for the TDR study (Chapter 4). The data include measured total water content, $\theta$, and the estimated transport parameters: the immobile water fraction; $\theta_{im}/\theta$, mass exchange coefficient; $\alpha$, and dispersion coefficient of the mobile domain; $D_m$ as produced from the inverse fitting procedure using the CXTFIT package.

Table A.1 The flux densities and corresponding saturated ponded radii for each site that used to determine the hydraulic properties in Chapter 3. The $q_n$ and $r_n$ are the flux density (L T$^{-1}$) and corresponding pond radius (L).

<table>
<thead>
<tr>
<th>Site</th>
<th>$q_1$ (cm h$^{-1}$)</th>
<th>$r_1$ (cm)</th>
<th>$q_2$ (cm h$^{-1}$)</th>
<th>$r_2$ (cm)</th>
<th>$q_3$ (cm h$^{-1}$)</th>
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Table A.2  Total water content; $\theta$, tracers concentrations; $C$, and their application times; $t^*$, used to estimate the chemical transport properties in Chapter 3. The average input concentrations, $C_0$, for the tracers applied were 126.3, 151.3, and 148.8 mg L$^{-1}$; respectively.

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Table A.2  (Continued)

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|      |                 | DFBA (mg L$^{-1}$) | $t^*$ (min) | TFMB (mg L$^{-1}$) | $t^*$ (min) | PFBA (mg L$^{-1}$) | $t^*$ (min) |
| 31   | 0.51            | 22.18           | 38.75          | 22.74           | 21.75          | 16.12           | 20.30          |
| 32   | 0.46            | 56.11           | 38.95          | 60.45           | 21.95          | 48.15           | 21.16          |
| 33   | 0.51            | 50.03           | 39.48          | 56.39           | 22.48          | 52.04           | 21.83          |
| 34   | 0.52            | 55.96           | 38.73          | 65.35           | 21.73          | 54.27           | 21.03          |
| 35   | 0.52            | 51.99           | 38.82          | 58.43           | 21.82          | 49.76           | 22.25          |
| 36   | 0.41            | 95.40           | 39.38          | 107.01          | 22.38          | 98.19           | 22.91          |
| 37   | 0.50            | 47.54           | 39.58          | 54.93           | 22.58          | 51.69           | 22.97          |
| 38   | 0.51            | 52.64           | 39.39          | 56.59           | 22.39          | 65.27           | 22.73          |
| 39   | 0.51            | 69.59           | 38.30          | 81.72           | 21.30          | 69.18           | 21.65          |
| 40   | 0.52            | 57.34           | 39.23          | 66.69           | 22.23          | 57.56           | 25.40          |
| 41   | 0.52            | 60.61           | 39.35          | 65.08           | 22.35          | 71.87           | 23.87          |
| 42   | 0.49            | 58.65           | 39.44          | 67.83           | 22.44          | 68.26           | 24.01          |
| 43   | 0.50            | 53.70           | 39.54          | 64.94           | 22.54          | 57.22           | 24.75          |
| 44   | 0.48            | 56.55           | 39.61          | 66.17           | 22.61          | 66.28           | 24.99          |
| 45   | 0.51            | 50.17           | 39.65          | 60.55           | 22.65          | 53.20           | 24.91          |
| 46   | 0.51            | 48.36           | 39.29          | 54.83           | 22.29          | 45.05           | 25.47          |
| 47   | 0.47            | 57.55           | 39.46          | 63.74           | 22.46          | 39.43           | 25.75          |
| 48   | 0.46            | 49.97           | 39.35          | 50.98           | 22.35          | 53.87           | 25.65          |
| 49   | 0.49            | 51.56           | 39.32          | 55.51           | 22.32          | 61.18           | 25.81          |
| 50   | 0.50            | 54.68           | 37.96          | 63.17           | 20.96          | 67.94           | 24.44          |
Table A.3  Total water content; $\theta$, pore velocity; $v$, and the estimated transport parameters for the TDR study (Chapter 4) as estimated from the fitting procedure using the CXTFIT package.

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