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Measurement and Modeling of Solute Diffusion Coefficients in Unsaturated Soils

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Soil and Water Sciences

by

Hsin-Yi Chou

December 2010

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Measurement and Modeling of Solute Diffusion Coefficients in Unsaturated Soils

by

Hsin-Yi Chou

Doctor of Philosophy, Graduate Program in Soil and Water Sciences
University of California, Riverside, December 2010
Dr. Laosheng Wu, Chairperson

Solute diffusion in unsaturated soils refers to the transport of dissolved constituents in liquid phase from a higher to a lower concentration point. Several empirical and conceptual models were proposed to predict the solute diffusion coefficients in unsaturated soils, but they were not systematically tested and evaluated under the same conditions using soils of different textures. Our experimental data showed that there is no perfect model that can depict the behavior of solute diffusion coefficient in soil at ranging soil-water contents across soil textures. Therefore, we proposed a new model using matric potential as the variable. The new model combines the two-region linear relationship of the soil-water content versus logarithm tortuosity with the Campbell soil-water retention model. It has compatible predictive capability with previous empirical models while reduces the uncertainty of constants estimation. Also, the use of matric
potential instead of soil-water content as the independent variable directly incorporates the soil pore structural properties, and consequently the diffusive pathway, in the solute diffusion coefficient prediction. Moreover, the new model is applicable to soils of different textures and degrees of aggregation.

Although solute diffusion in soil has been widely examined under the influence of both soil-water content and matric potential, little information is available about the impact of soil-water content/matric potential hysteresis on solute diffusion. Our research shows that the unequal soil-water content at a given matric potential when a soil is subjected to drying or wetting process has substantial impact on solute diffusion. The measured solute diffusion coefficients of drying were greater than those of wetting in certain soil-water content range. When fitted the solute diffusion coefficients of drying and wetting limbs by proposed predictive models, the drying limb is better described by a power function of soil-water content with empirical constants estimated by particle-size distribution and bulk density; while the wetting limb is better described by a conceptual model which assumes the solute diffusive pathway is comprised of the serial arrangement of pore water and film water. This research concluded that the behavior of solute diffusion in unsaturated soils is essentially determined by the liquid phase distribution.
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Chapter 1

Evaluation of Tortuosity Factor Models for Describing the Solute Diffusion Behavior in Unsaturated Soils

1.1 Literature Review

Solute diffusion refers to the transport of a dissolved constituent in aqueous media from a higher to a lower concentration point. In unsaturated soil when convection flux is insignificant, diffusion becomes the key transport mechanism. This concentration-gradient driven process determines the rate of nutrients and potentially harmful constituents transport from soil to plant roots zone or to the groundwater aquifer.

Solute diffusion refers to the transport of a dissolved constituent in aqueous media from a higher to a lower concentration point. In unsaturated soil when convection flux is insignificant, diffusion becomes the key transport mechanism. This concentration-gradient driven process determines the rate of nutrients and potentially harmful constituents transport from soil to plant roots zone or to the groundwater aquifer.

Solutes diffuse at much slower rates through the pores of an unsaturated soil than in a water body. Because some cross-sectional area for diffusion occupied by solid particles makes the pathway for solute diffusion in soil more tortuous. To account for this reduction of solute diffusion in soil, a tortuosity factor, \( \xi \), was introduced to Fick’s law of diffusion to describe the solute diffusion flux, \( J \), in soil [Jury et al., 1991].

\[
J = -\xi D_0 \frac{\partial C}{\partial z} = -D_s \frac{\partial C}{\partial z} \quad (1.1)
\]
where \( D_0 \) is the solute diffusion coefficient in water, \( D_s \) is the solute diffusion coefficient in soil, \( C \) denotes solute concentration, \( \partial C/\partial z \) denotes solute concentration gradient along the flux direction \( z \).

When diffusion takes place, the mass exchange can influence the solute concentration meters away from the source [Helmke et al., 2004]. Therefore, an accurate estimation of solute diffusion fluxes in soil is imperative. At present, tortuosity factor cannot be directly measured. Instead, it is calculated from the ratio of solute diffusion coefficient in soil to that in water that is experimentally determined [Millington and Quirk, 1961]. Direct measurement of solute diffusion coefficient in soil is a comprehensive testing procedure, which is time and labor consuming [Dane and Topp, 2002]. Moreover, experimental measurement of \( D_0 \) is not a common practice for people from broader subjects [Shackelford and Daniel, 1991]. Therefore, a number of tortuosity factor models have been proposed to predict solute diffusion coefficient in soil to reduce time-consuming laboratory works [Moldrup et al., 1996; Moldrup et al., 2001; Moldrup et al., 2007; Olesen et al., 2001a].

The tortuosity factor is thought to be affected by soil attributes such as soil-water content, matric potential, texture, bulk density, and particle-size distribution [Lim et al., 1998; Phillips and Brown, 1965; So and Nye, 1989]. Accordingly, the proposed empirical tortuosity factor models are based on these relatively accessible soil physical characteristics. Furthermore, studies of solute diffusion in soil have been brought to microscopic scales. For example, the average soil-water content is specified by the liquid
phase distribution in soil to define the diffusive pathway [Conca and Wright, 1992; Phillips and Brown, 1965; So and Nye, 1989]. Hu and Wang [2003] used laser ablation-inductively coupled plasma-mass spectrometry technique to study diffusion in porous media. They found that at different soil-water content stages, the liquid phase is structured in different forms and geometric arrangements. At higher volumetric soil-water content (0.05 - 0.5 cm$^3$ cm$^{-3}$), the liquid phase mainly distributes between continuously connected pores. As soil-water content reduced (0.005 - 0.05 cm$^3$ cm$^{-3}$), liquid phase is held in pendular form that results in a less continuous diffusive pathway. The transition of liquid phase distribution from continuously connected pores form to pendular form caused a sudden decline in solute diffusion coefficient. Lim et al. [1998] also proposed a conceptual model to predict the diffusion coefficient from the microscopic prospects.

The following is a summary of the solute diffusion tortuosity factor models:

1.1.1 Empirical Tortuosity Factor Models

The existing empirical tortuosity factor models can be classified into four mathematical forms: (1) exponential function, (2) power function, (3) quadratic function, and (4) linear function. Researches attempted to improve the model predictive capability by adding more measurable soil properties; however, more parameters in a model require more measurements. Therefore, a cross evaluation is pivotal to verify the best predictive function and necessity of additional parameters.
(1) Exponential function

The tortuosity factors were widely recognized as affected by soil-water contents. Olsen and Kemper [1968] proposed an exponential function tortuosity factor model relates to soil-water content:

$$\xi = \Omega \cdot \exp(\lambda \theta)$$ (1.2)

where $\Omega$ and $\lambda$ are empirical constants, and $\theta$ is the volumetric soil-water content (cm$^3$ cm$^{-3}$). This model is only applicable to soils of at matric potential from -33 to -1500 kPa. van Rees [1989] fitted their experimental data of a loamy soil to this exponential tortuosity factor model, and found that $\Omega = 3.13$, and $\lambda = 1.92$ best described the data.

Hamamoto et al. [2009] concluded that $\log (\xi)$ linearly increases with $\theta$. This $\log (\xi)$-$\theta$ linear relation implies a mathematical agreement to the above exponential function with the base 10 instead of $e = 2.7321$. In addition, their result showed a two-region linear log $(\xi)$-$\theta$ relationship: $\log (\xi)$ -$\theta$ has a steeper slope at lower soil-water contents while a more moderate slope at higher soil-water contents. This finding is in agreement with Hu and Wang’s [2003] microscopic investigation of solute diffusive pathway in soil: the liquid phase distribution at relatively lower soil-water contents is different from that at higher soil-water contents.

(2) Power function

Papendick and Campbell [1981] proposed a power function tortuosity factor model in the form of:
where $c$ is an empirical constant for matrix factor, and $\varepsilon$ is an empirical constant to account for the influence of smaller cross sectional area available for diffusion. They found that $c = 2.8$ and $\varepsilon = 3.0$ best describe the experimental data of their soils. Mehta et al. [1995] further examined this power function tortuosity factor model using a dune sand and a loamy soil. They found that this power function only described the behavior of the dune sand but failed to describe the behavior of the loamy soil. For the loamy soil, they imputed the model inaccuracy to the neglect of the soil-water content status. Therefore, Mehta et al. [1995] modified this model by using giving different values of $c$ and $\varepsilon$ to different soil-water content status, namely, below the residual, above saturation, and between residual and saturation soil-water content.

The measurement of gas diffusion is far more concise as it is more controllable and less time consuming. Based on the successes in predicting gas diffusion, Millington and Quirk [1961] modified the gas diffusion tortuosity factor model to form a solute diffusion tortuosity factor model by replacing the volumetric air fraction in soil with volumetric soil-water content:

\[
\xi = \frac{\gamma \theta^n}{\phi^m}
\]  

(1.4)

where $\gamma$, $n$, and $m$ are empirical constants, and $\phi$ is the total porosity ($\text{cm}^3 \text{ cm}^{-3}$). Values of $\gamma$, $n$, and $m$ all followed the results of their gas diffusion study, which are $\gamma = 1$, $n = 10/3$, \[ \text{cm}^3 \text{ cm}^{-3} \].
and $m = 2$ for all soil types. The model has been widely applied for its simplicity, yet the outcomes have been challenged for its representation.

Olesen et al. [1996] modified the above Millington and Quirk’s [1961] solute diffusion tortuosity factor model [Eq. (1.4)] by defining the empirical constants with measurable parameters. The soil-water retention parameter, $b$, in the Campbell soil-water retention model was included in this model to account for the particle-size distribution effect:

$$
\xi = \xi^* \theta \left( \frac{\theta}{\phi} \right)^{k_1 + k_2 b}
$$

(1.5)

where $\xi^*$ represents the tortuosity factor at 100% soil-water saturation, $k_1$ and $k_2$ are empirical constants. The term $(k_1 + k_2 b)$ accounts for the water film thickness, water film disconnection, ion exclusion, and dead-end pores. $b$ is the soil-water retention parameter based on the Campbell soil-water retention model, which is the slope of the soil water retention curve on a semi-log coordinate system. Williams et al. [1992] proposed two $b$ value predicting models according to their multiple regressions of 400 intact Australia soil cores to simplified the model. The first $b$ value predicting model is based on soil texture:

$$
b_i = (0.403 - 0.0871 \cdot (\ln(CL)) - 0.0014 \cdot (CS) + 0.00077 \cdot (FS))^{-1}
$$

(1.6)
where CL is the mass fraction (g g$^{-1}$) of clay (< 0.002 mm), CS is the mass fraction (g g$^{-1}$) of coarse sand (0.2 - 2 mm), and FS is the mass fraction (g g$^{-1}$) of fine sand (0.02 - 0.2 mm). Subscript $t$ denotes the texture-based prediction.

The second $b$ value predicting model is based on the soil texture and bulk density:

$$b_{tb} = (0.303 - 0.093 \cdot (\ln(\rho)) - 0.0565 \cdot (\ln(CL)) + 0.00003 \cdot (FS)^2)^{-1}$$  \hspace{1cm} (1.7)$$

where $\rho$ is the bulk density (g cm$^3$), and subscript $tb$ denotes the texture and bulk density based prediction.

(3) Quadratic function

Mehta et al. [1995] noted the same phenomenon as Mullins and Sommer [1986] did: The tortuosity factor increases with the increasing soil-water content to a maximum and then decreases in the same manner as soil-water content continues to rise. A quadratic function of soil-water content tortuosity factor model was proposed to describe this constrained increasing of tortuosity factor with soil-water content:

$$\xi = \delta \theta^2 + \mu \theta$$  \hspace{1cm} (1.8)$$

where $\delta$ and $\mu$ are empirical constants, and $\mu$ is always a negative number to account for the constrained increasing trend.

Olesen et al. [1996] further defined the constants in Eq. (1.8) by the tortuosity factor at water saturation, $\xi^*$, and a threshold soil-water content, $\theta_{th}$. The concept of $\theta_{th}$ was
brought by presuming that the constrained increasing trend of tortuosity factor is due to
the unavailable diffusive pathway caused by poorly connected pores and anion exclusion
at lower soil-water contents. The solute diffusion rate approaches zero when soil-water
content is lower than the $\theta_{th}$.

$$\xi = \xi^* \cdot \theta \cdot \left( \frac{\theta - \theta_{th}}{\phi - \theta_{th}} \right)$$  \hspace{1cm} (1.9)

Olesen et al. [2000; 2001b] concluded that the threshold soil-water content can be
accurately predicted from soil texture and bulk density:

$$\theta_{th} = 0.81(CL) - 0.90(CL)^2 - 0.07(SF) - 0.6(\rho) + 0.22(\rho)^2 + 0.42$$  \hspace{1cm} (1.10)

or by including soil water retention parameter $b$ in the model:

$$\theta_{th} = 0.035b - 0.0010b^2 - 0.063(CL) - 0.023(SF) + 0.51\rho - 0.25\rho^2 - 0.26$$  \hspace{1cm} (1.11)

where $SF$ is the mass fraction (g g$^{-1}$) of silt (0.002 - 0.02 mm). If the soil water retention
parameter, $b$, is not attainable from direct measurement, it can be predicted by Eq. (1.6)
and (1.7) (Williams et al. [1992]).

Olesen et al. [2001b] observed a linear relationship of impedance factor ($f = \xi / \theta$)
vs. $\theta$, which implies the same mathematical form as the quadratic function model.
Moldrup et al. [2007] combined the finding of Olesen et al. [2001b] plus the concept of
threshold soil-water content (Olesen et al. [1996]) to develop a new tortuosity factor
predictive model:
\[ f = \frac{\xi}{\theta} = H(\theta - \theta_{th}) \text{ or } \xi = H \cdot \theta(\theta - \theta_{th}) \text{ for } \theta > \theta_{th} \]

\[ f = 0 \text{ or } \xi = 0 \text{ for } \theta \leq \theta_{th} \quad (1.12) \]

\[ \theta_{th} = \varpi \cdot FC_{vol} = \varpi \cdot \rho \left( \frac{CL}{d_{cl}} + \frac{OMF}{d_{om}} \right) \quad (1.13) \]

where \( OMF \) represents the organic matter fraction (g g\(^{-1}\)); \( d_{cl} \) is the density of clay particle, which equals to 2.7 g cm\(^{-3}\), and \( d_{om} \) is the density of organic matter that is 1.0 g cm\(^{-3}\); \( \varpi \) is a fraction constant that is thought to be 1.0 for compacted or aggregated soils and 0.8 for non-aggregated and non-compacted soils with clay fraction between 5 ~ 40\% (g g\(^{-1}\)). For soils with similar total porosity (0.45 - 0.47 cm\(^3\) cm\(^{-3}\)), Moldrup et al. [2007] found a strong linear relation of the \( \theta_{th} \) with the soil-water retention parameter \( b \) for the finer textured soils, which is:

\[ \theta_{th} = 0.02b \quad (1.14) \]

Hamamoto et al. [2009] found that the threshold soil-water content, \( \theta_{th} \), is not only influenced by bulk density, volumetric content of fine particles and the soil-water retention parameter, but also by the volumetric soil surface area and soil structure. However, the effect of silt fraction on \( \theta_{th} \) was found not significant.

Moldrup et al. [2007] were inspired by Olesen et al. [2001b] and linked Eq. (1.12) with the Campbell soil-water retention model to present a LIFE-Campbell model for
solute diffusion in soil. The model directly links the tortuosity factor with various soil-water saturation statuses and the corresponding soil-water matric potentials:

\[ \tilde{\xi} = H(\theta_s)^2 \left[ \left( \frac{\psi_e}{\psi} \right)^k - \left( \frac{\psi_e}{\theta_i} \right)^k \right] \text{ for } \psi_i < \psi < \psi_e \]

\[ \tilde{\xi} = H(\theta_s)^2 \left[ 1 - \left( \frac{\theta_i}{\theta_s} \right) \right] \text{ for } \psi_e < \psi < 0 \]

\[ \tilde{\xi} = 0 \text{ for } \psi < \psi_i \]

(1.15)

where \( \theta_i \) is the intercept on the x axis of the \( f-\theta \) relation; \( \theta_i \) represents the saturated soil-water content, which is assumed equal to the soil total porosity; \( \psi \) represents the soil-water matric potential (cm-H\(_2\)O), \( \psi_e \) is the matric potential at air entry, and \( \psi_i \) is the threshold soil-water matric potential below which the solute diffusion is constrained.

There were limited number of studies that have been conducted to relate the tortuosity factor with soil-water matric potential. Mehta et al. [1995] found that there is a turning point on the log (\( \xi \)) vs. \( \theta \) curve at the corresponding pF of around 2.8 and 3.0 (pF is the logarithm of the negative matric potential in cm-H\(_2\)O) for their volcanic ash and dune sand soil, respectively. They also found that \( f-pF \) exhibits a linear relationship at pF 1.7 to 4.2. Olesen et al. [2001a] found that the threshold soil-water content, where the solute diffusion ceased, occurs at pF 4.0 to 6.0 depending on the soil type.
(4) Linear function

So and Nye [1989] proposed that tortuosity factor is a linear function of soil bulk density and soil-water content:

\[ \xi = \alpha + \beta \theta + \omega \rho \] (1.16)

where \( \alpha, \beta, \) and \( \omega \) are empirical constants. \( \omega \) is set to be a negative number because the increase in bulk density was found to result in a decrease in tortuosity factor (So and Nye [1989]). This means that a more compacted soil creates a more tortuous pathway for solute diffusion.

Hamamoto et al. [2009] found that the increase in bulk density only reduces the tortuosity factor at higher soil-water contents; while at lower soil-water contents, the increase in bulk density increases the tortuosity factor. The dividing soil-water content is found at around 0.3 cm\(^3\) cm\(^{-3}\) for the test volcanic ash soil in three different bulk densities. Their results indicated that, at higher soil-water contents, increase in soil bulk density disconnects the continuous diffusive pathway that results in a reduction in tortuosity factor; while at lower soil-water content, increase in bulk density enhances the connection of the solute distributed in pores, resulting in an increase in tortuosity factor.

1.1.2 Conceptual model

Lim et al. [1998] conceptualized the liquid phase distribution in soil and generated a solute diffusion coefficient predictive model. They proposed that the liquid phase in soil
stays in two major regions: water-filled pores and water films along the particle-air boundaries. A set of tortuosity models was generated based on the arrangements of these two liquid phase forms: (I) solute diffuses through parallel arranged water-filled pores and water films [Eq. (1.17)]; (II) the diffusive pathway is connected by serially arranged water-filled pores and water films [Eq. (1.19)]; and (III) the diffusive pathway is connected by a proportion of parallel arrangement and serial arrangement [Eq. (1.20)] (Figure 1-1). They concluded that Model (III) with a 0.5 parallel to 0.5 series proportion best fitted their experimental data.

Figure 1-1. Schematic illustration of the parallel and series conceptual models [Lim et al., 1998].

Model I. Independently parallel model

\[
D(S) = D^* \left[ 1 - \frac{v_r S_r(1-S_r)}{S} \right] S + (1-S_r)R \tag{1.17}
\]

\[
R = (1 - \frac{a}{r})^2 \left[ 1 - 2.1\left(\frac{a}{r}\right) + 2.09\left(\frac{a}{r}\right)^3 - 0.95\left(\frac{a}{r}\right)^5 \right] \tag{1.18}
\]
Model II. Series model

\[ D(S) = \left( \frac{D^*}{1 - \nu \cdot S_r} \right) \cdot \left( \frac{1}{S} + \frac{(1 - S)^2}{R(1 - S_e)} \right) \]  

(1.19)

Model III. Combined parallel and series model

\[ D(S) = \left[ \eta \cdot D^* \cdot \left( \frac{1}{S} + \frac{(1 - S)^2}{R(1 - S_e)} \right) \right] + \left[ (1 - \eta) \cdot \left( \frac{1}{1 - \nu \cdot S_r \cdot (1 - S_e) / S} + \frac{(1 - S)^2}{R(1 - S_e)} \right) \right] \]  

(1.20)

where \( D(S) \) is the solute diffusion coefficient at any given degree of saturation \( S \) (%), equal to the volumetric water content divided by total porosity); \( D^* \) is the solute diffusion coefficient at \( S = 100 \% \); \( \nu \) is the fraction of soil-water contained in water film form that can be calculated based on the total surface area of the soil particles and an assumed water film thickness; \( S_r \) is the residual degree of saturation; \( S_e \) is the effective degree of saturation that is equal to \( (S - S_r)/(1 - S_r) \) [Brooks and Corey, 1966]; \( R \) is a factor that includes both the entrance effect and the effects of increasing viscosity and ionic interaction along small pores; \( a/r \) is the ratio of the radius of the hydrated ion to the radius of the pore that is set equal to 0.5 for all soil textures [Lim et al., 1998]; \( \eta \) is the proportion of diffusion along the independently parallel model, and \( 1 - \eta \) is the proportion of diffusion along the series model.

The predictive models if validated may simplify the estimation of the solute diffusion coefficient. However, these models were not systematically tested and
evaluated under the same experimental conditions using soils of different textures. The objectives of this research is to measure solute diffusion coefficients of three soils of varying textures at various soil-water contents to (1) evaluate the predictive capabilities of the proposed tortuosity factor models on an equal basis using soils of different textures and under the same experimental conditions; to (2) assess the strength and weakness of the models in terms of predictive capabilities, range of applicability, and requirements of input parameters; and to (3) illustrate the solute diffusion behavior in unsaturated soils.

1.2 Materials and Methods

1.2.1 Sample preparation

Three soils, a sand, a sandy clay loam and a clay, were used in this study (Table 1-1). The sand was obtained from Weist Rentals and Sales® Masonry Material Supplies in Riverside, California. The sandy clay loam and clay soils were obtained from the Imperial Valley of California. Collected samples were air dried and sieved with 2 mm openings. Aliquots of prepared experimental materials were packed into cylindrical acrylic Tempe® diffusion cells (Figure 1-2) to the predetermined bulk densities (Table 1-1). The cell consists of a high-flow porous ceramic plate at the bottom and connected to a tubing, from which the soil-water can flow out.

Prior to the diffusion experiment, prepared diffusion cells were first saturated with 0.01 M potassium bromide solution and then placed into a pressure chamber to apply the prescribed pressures. The corresponding volumetric soil-water contents after pressure
applications were recorded. The cell was then transfer to a 25 °C, vapor saturated humidity chamber to equilibrate for another 7 days for the diffusion experiments. The diffusion experiment employed Bromide as tracer because it is a non-reactive and conservative element and it presents negligible quantities in natural soils.

Table 1-1. Physical properties of the soils used in diffusion experiments.

<table>
<thead>
<tr>
<th>Texture</th>
<th>Particle size distribution (%)</th>
<th>Bulk density (g cm$^{-3}$)</th>
<th>Porosity (cm$^{3}$ cm$^{-3}$)</th>
<th>Specific area (m$^{2}$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coarse sand (0.2 - 2.0 mm)</td>
<td>Fine sand (0.02 - 0.2 mm)</td>
<td>Silt (0.002 - 0.02 mm)</td>
<td>Clay (&lt;0.002 mm)</td>
</tr>
<tr>
<td>Sand</td>
<td>16.1</td>
<td>71.2</td>
<td>10.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Sandy clay loam</td>
<td>0.6</td>
<td>65.3</td>
<td>12.6</td>
<td>21.5</td>
</tr>
<tr>
<td>Clay</td>
<td>0.2</td>
<td>5.5</td>
<td>36.4</td>
<td>57.9</td>
</tr>
</tbody>
</table>

Figure 1-2. Schematic illustration of the diffusion Tempe cell.

1.2.2 Solute diffusion coefficient measurements

The diffusion experiments were also conducted in the 25 °C vapor saturated humidity chamber. At time 0, a Cl$^-$ saturated polythelsulfone/copolymer anion-exchange
membrane (PALL, SB-6407) was placed in contact with the exposed soil surface to act as the sink for the diffusing Br\(^-\) [Tinker, 1969]. To minimize the convection flow between the membrane and the soil, the anion-exchange membrane was pre-equilibrated to the same matric potential along with the soil samples. A flat glass lid was laid on the top of membrane to exclude trapped air pockets and to ensure a good contact between the membrane and the soil surface. Based on the membrane’s exchange capacity, the diffusion period was set to be 81 minutes. At higher water contents, double or triple layers of membrane were laid to maintain a near-zero Br\(^-\) concentration at the soil-membrane boundary.

At time \(t\), the membranes were removed, rinsed with deionized water, and then dried. The bromide in the membrane was extracted by 50 ml of 0.5 M HNO\(_3\). The bromide concentration in the extracts is determined by the spectrophotometric method [Chiu and Eubanks, 1989].

The solute diffusion coefficient in soil is then calculated by the measured quantity and time:

\[
D_s = \frac{M^2\pi}{4\theta^2C^2t} \tag{1.21}
\]

where \(M\) is the amount of bromide per unit surface area that diffused into the anion-exchange membrane (g cm\(^{-2}\)) in time \(t\) (sec), \(C\) is the initial concentration of Br\(^-\) in the soil solution (g cm\(^{-3}\)), and \(\pi = 3.14\).
1.2.3 Model evaluation

The existing tortuosity factor models are evaluated using the diffusion data measured from the cores. The goodness of the models fit to the experimental data were measured by the Root Mean Square Error (RMSE) [Olesen et al., 1996].

\[
RMSE = \sqrt{\frac{1}{\kappa} \sum_{i=1}^{\kappa} d_i^2}
\]  

(1.22)

where \(d_i\) is the difference between the estimated and measured values, and \(\kappa\) is the number of measured values. The RMSE quantifies the difference between an estimated and a measured value. A RMSE = 0 indicates a perfect prediction capability.

Regression analysis was also applied to obtain the best-fit constants for our three test soils by each tortuosity factor model. The derived constants were compared with those in the published literature if the soils in the literature were classified as the same textures as our test soils or the particle-size distribution are within ± 5 % gravimetric percentage of sand, silt and clay respectively. The model predictive capabilities with empirical constants obtained by both regression analysis and literature were examined by the experimental data and evaluated by RMSE. Although the diffusion experiments in the published literature were conducted by different means from our experimental method, we assumed it to have a minimum effect on outcomes of the evaluation.
1.3 Results

1.3.1 Exponential function

Experimental data of the three test soils fitted by the non-linear regression of the exponential tortuosity factor model [Eq. (1.2)] are shown in Figure 1-3. The $\Omega$ and $\lambda$ values derived from the regressions are shown in Table 1-2. While exponential tortuosity factor model [Eq. (1.2)] fitted the data well, the mathematical relationships were entirely empirical, i.e., no pattern was observed among the soils.

The plotted log ($\xi$) vs. $\theta$ (Figure 1-4) shows the two-region linear behavior, which also implies that there exists a logarithm function relationship between $\xi$ and $\theta$. For all three test soils, log ($\xi$) - $\theta$ has a steeper slope at lower soil-water contents (Slope 1) and a moderate slope at higher soil-water contents (Slope 2) (Table 1-3). The slopes change abruptly at the inflection water contents (Figure 1-4, and Table 1-3), which represents the separation of dominant diffusive pathway form intra-aggregate to inter-aggregate pore space regions [Hu and Wang, 2003]. However, the factor that influences the slope is not clear, because it does not show a significant dependence on soil texture (Table 1-3) or bulk density (Table1-1 and 1-3).
Table 1-2. Values of $\Omega$ and $\lambda$ of exponential tortuosity factor model [Eq. (1.2)] [Olsen and Kemper, 1968] derived by nonlinear regression method; and the statistical analysis of RMSE.

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Sandy clay loam</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega$</td>
<td>0.0003</td>
<td>0.0001</td>
<td>0.0014</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>11.09</td>
<td>19.35</td>
<td>6.77</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.0030</td>
<td>0.0280</td>
<td>0.0020</td>
</tr>
</tbody>
</table>

Figure 1-3. Experimental data and the non-linear regression fitted lines of Olsen and Kemper’s [1968] exponential tortuosity factor model [Eq. (1.2)] for the three test soils.

Table 1-3. The two-region linear behavior of $\log (\xi)$ vs. $\theta$ relation.

<table>
<thead>
<tr>
<th>Texture</th>
<th>Sand</th>
<th>Sandy clay loam</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope 1</td>
<td>4.46</td>
<td>8.97</td>
<td>7.09</td>
</tr>
<tr>
<td>Slope 2</td>
<td>1.78</td>
<td>4.13</td>
<td>1.17</td>
</tr>
<tr>
<td>$R^2_{1}$</td>
<td>0.90</td>
<td>0.94</td>
<td>0.98</td>
</tr>
<tr>
<td>$R^2_{2}$</td>
<td>0.84</td>
<td>0.97</td>
<td>0.68</td>
</tr>
<tr>
<td>Inflection $\theta$</td>
<td>0.28</td>
<td>0.31</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Subscript 1: water content below the inflection point, 2: above the inflection point
1.3.2 Power function

We tested the predictive capability of the power function tortuosity factor model [Eq. (1.3)] with constants derived from Papendick and Campbell [1981], Mehta et al. [1995], and from the non-linear regression (Figure 1-5). In the case of Papendick and Campbell [1981], $c = 2.8$ and $\varepsilon = 3.0$ were used to test the model’s fitness for all three experimental soils. In the case of Metha et al. [1995], the values of $c$ and $\varepsilon$ are texture and volumetric soil-water content dependent, and their values were correspondingly compared with the soils of the same texture (sand and the sandy clay loam) in our experiment (Table 1-4).

The power function constants adopted from Papendick and Campbell [1981] overestimated the tortuosity factor of all three test soils (Figure 1-5); while Mehta et al.’s [1995] overestimated the measured tortuosity factors of the test sand soil at $\theta \geq 0.0464$ cm$^3$ cm$^{-3}$. For the sandy clay loam soil, the power function model fitted the experimental data well for $\theta \leq 0.396$ but not for $\theta \geq 0.396$ cm$^3$ cm$^{-3}$. The experimental data for the
sandy clay loam soil appear to exhibit what Mehta et al. [1995] elaborated that the increase of tortuosity factor with soil-water content approaches an upper limit. This observation also confirms the result of Hamamoto et al. [2009] that \( \log (\xi) \) vs. \( \theta \) exhibits a two-region behavior.

Millington and Quirk’s [1961] solute tortuosity factor model [Eq. (1.4)] used their empirical constants of gas tortuosity factor model (Table 1-5). Sadeghi et al. [1989] modified the model constants based on the outcomes obtained from seven soils with different textures and bulk densities (Table 1-5). They found that the constants of Millington and Quirk [1959; 1961] overestimated the tortuosity factors for three of their experimental soils at any given soil-water content. We fitted our experimental data using Sadeghi et al.’s [1989] constants and found that their constants well predicted the tortuosity factor of our sandy clay loam soil but failed to provide a compatible estimation of the sand and clay soils. The best-fit constants to our experimental data generated by regression are shown in Table 1-5. It showed that the power function model can describe the experimental data well; however, the fitted constants vary with soil types (Table 1-5).

The tortuosity factor model [Eq. (1.5)] proposed by Olesen et al. [1996] requires the inputs of particle-size distribution, bulk density, and soil-water retention parameter \( (b) \). The measured water retention curves of our three test soils are shown in Figure 1-7 and the corresponding measured water retention parameter \( (b_m) \) by linear regression are shown in Table 1-6. The subscript of \( m \) denotes the parameter derived from
measurement. The water retention parameters \( b \) estimated from Eq. (1.6) and Eq. (1.7) are listed in Table 1-6.

Since the soil types used in this study do not exactly match those used by Olesen et al. [1996], we compare the sand, sandy clay loam, and clay soils of our experiment correspondingly with their sand, sandy loam and silty clay soils to test the general pattern of the predictive capability of Olesen’s power function tortuosity factor model [Eq. (1.5)]. When soil texture (sandy clay loam vs. sandy loam) and bulk density (1.45 vs. 1.40 g cm\(^{-3}\)) are comparable, the best fitted \( \xi^* \) obtained from the experimental data are in close agreement (0.43 and 0.48 vs. 0.45) with Olesen et al.’s [1996] (Table 1-6). Besides, by comparing all \( \xi^* \) in Table 1-6, it shows a dependency of \( \xi^* \) on bulk density. For the sand soil, the derived \( k_2 = 0 \) from both regression and Olesen et al. [1996] affirms that the tortuosity factor of sand is independent of bulk density and soil texture (Table 1-6).

Olesen’s power function tortuosity factor model is an amended form of Millington and Quirk’s [1961] two-variable power function tortuosity factor model [Eq. (1.4)]. RMSEs show that Olesen’s power function tortuosity factor model improves the predictive capability of Millington and Quirk’s [1961] model if the constants from the literature are applied to the model ([Millington and Quirk, 1959; 1961; Olesen et al., 1996; Sadeghi et al., 1989]) (Table 1-5 and 1-6). However, if constants obtained from the best-fit of experimental data are applied, the extra parameters in this model only reduce the \( RMSE \) of our test sandy clay loam soil, but not the sand and clay soils (Table 1-5 and 1-6).
Table 1-4. Values of $c$ and $\varepsilon$ of the power function tortuosity factor model [Eq. (1.3)] derived from Papendick and Campbell [1981], Mehta et al. [1995], and from the nonlinear regression for the three test soils; and the statistics of $RMSE$.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sand</td>
<td>Clay</td>
<td></td>
</tr>
<tr>
<td>$\theta$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$c$</td>
<td>2.8</td>
<td>2.8</td>
<td>0.7</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>3</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>$RMSE$</td>
<td>0.0736</td>
<td>0.1127</td>
<td>0.2581</td>
</tr>
</tbody>
</table>

|                | Sandy clay loam               | Clay                 |            |
| $\theta$       | -                             | -                    | -          |
| $c$            | 2.8                           | 2.8                  | 0.7        |
| $\varepsilon$  | 3                             | 3                    | 0.8        |
| $RMSE$         | 0.0352                        | 0.0161               | 0.005      |


Figure 1-5. Experimental data and the non-linear regression fitted lines of power function tortuosity factor model [Eq. (1.3)] for the three test soils, and the predicted lines with $c$ and $\varepsilon$ values adopted from Papendick and Campbell [1981] and Mehta et al. [1995].
Figure 1-6. Experimental data and the non-linear regression fitted lines of the two-variable power function tortuosity factor model [Eq. (1.4)] for the three test soils, and the predicted lines with $\gamma$, $n$, and $m$ values adopted from Millington and Quirk [1961] and Sadeghi et al. [1989].
Figure 1-7. Water retention curves of the experiment soils. The soil-water retention parameter \( b \) is the slope of the pF vs. \( \theta \) curve, which are 2.6, 2.1, and 4.5, respectively, for the test sand, sandy clay loam, and clay soils.
Table 1-5. Values of $\gamma$, $n$ and $m$ of the two-variable power function tortuosity factor model [Eq. (1.4)] from Millington and Quirk [1959; 1961], Sadeghi et al. [1989] and from regression analysis of the experimental data; and the statistics of $RMSE$.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture</td>
<td>All</td>
<td>All</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sandy clay loam</td>
<td>Clay</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$n$</td>
<td>3.33</td>
<td>3.33</td>
<td>3.33</td>
</tr>
<tr>
<td>$m$</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$RMSE$</td>
<td>0.1258</td>
<td>0.0600</td>
<td>0.1218</td>
</tr>
</tbody>
</table>

Table 1-6. Tortuosity factor at saturation ($\xi^*$) are obtained from measurement and from Olesen et al. [1996]; $k_1$ and $k_2$ values are derived from Olesen et al. [1996] or from fitting the model [Eq. (1.5)] to the experimental data. The soil-water retention parameter $b$ is obtained from three independent means: measured, $b_m$; predicted by Eq. (1.6), $b_t$; and by Eq.(1.7), $b_{tb}$; and the statistics of $RMSE$.

<table>
<thead>
<tr>
<th>Source</th>
<th>Olesen et al. [1996]</th>
<th>Regression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture</td>
<td>Sand</td>
<td>Sandy clay loam</td>
</tr>
<tr>
<td>Bulk density (g cm$^{-3}$)</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>$\xi^*$</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>$k_1$</td>
<td>1.8</td>
<td>0</td>
</tr>
<tr>
<td>$k_2$</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>$b$</td>
<td>Measured $b_m$</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>[Eq.(1.6)] $b_t$</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>[Eq.(1.7)] $b_{tb}$</td>
<td>5.1</td>
</tr>
<tr>
<td>$RMSE$</td>
<td>$b_m$</td>
<td>0.0775</td>
</tr>
<tr>
<td></td>
<td>$b_t$</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>$b_{tb}$</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 1-8. Experimental data and the non-linear regression fitted lines of Olesen’s power function tortuosity factor model [Eq. (1.5)] for the three test soils, and the predicted lines with $k_1$ and $k_2$ values adopted from Olesen et al. [1996]. The soil-water retention parameters ($b$) were obtained from three independent means: measured, $b_m$; predicted by Eq. (1.6), $b_t$; and by Eq. (1.7): $b_{tb}$. 

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1.3.3 Quadratic function

The quadratic function tortuosity factor model [Eq. (1.8)] fitted the experimental data well as indicated by the RMSEs (Table 1-7). Different model constants of $\delta$ and $\mu$ were derived from regression of soils with different textures (Table 1-7). Mullins and Sommer [1986] reported that $\delta = 1.6$, and $\mu = -0.172$ best described the tortuosity factor of a sandy clay loam soil. When these values are applied to predict the tortuosity factor of the sandy clay loam soil used in the experiment, it overestimates the measured tortuosity factor for almost the entire test range of soil-water contents (Figure 1-9).

The quadratic function tortuosity factor model [Eq. (1.8)] generated a stationary point where the tortuosity factor equals to zero. The corresponding soil-water contents fall on the zero tortuosity factor are 0.10, 0.18, and 0.12 $\text{cm}^3 \text{ cm}^{-3}$, respectively, for our test sand, sandy clay loam and clay soils. Based on the derived best-fit equations, the model application should be limited to the soil-water content greater than the zero tortuosity factor, or it will result in an error of generating negative tortuosity factor value.

Although the linear impedance factor ($f$) vs. $\theta$ relationship is another form of the quadratic function tortuosity factor model [Eq. (1.8)], only the sandy clay loam followed the linear relationship among the three test soils (Figure 1-10). Furthermore, our result does not support Olesen et al.’s [2001a] observation that the slope of $f$-$\theta$ is independent of soil types.

Olesen’s threshold soil-water content tortuosity factor model [Eq. (1.9)] required an immeasurable parameter of threshold water content, $\theta_{th}$. They estimated this parameter by
soil particle-size distribution and bulk density [Eq. (1.10)], or by the addition of soil-water retention parameter, \( b \), [Eq. (1.11)] as introduced in Olesen’s power function tortuosity factor model (Table 1-6). As a result, there were four permutations of \( \theta_{th} \) generated (Table 1-8) to test Olesen’s threshold water content tortuosity factor model [Eq. (1.9)]. In addition, we also applied non-linear regression to generate the best-fit constants to this model.

Table 1-7. Values of \( \delta \) and \( \mu \) of the quadratic function tortuosity factor model [Eq. (1.8)] derived from Mullins and Sommer [1986] and from the multiple regression of the experimental data; and the statistics of \( RMSE \).

<table>
<thead>
<tr>
<th>Source</th>
<th>Mullins and Sommer [1986]</th>
<th>Regression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture</td>
<td>Sandy clay loam</td>
<td>Sand</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sandy clay loam</td>
</tr>
<tr>
<td>( \delta )</td>
<td>1.6</td>
<td>0.18</td>
</tr>
<tr>
<td>( \mu )</td>
<td>-0.17</td>
<td>-0.02</td>
</tr>
<tr>
<td>( RMSE )</td>
<td>0.0440</td>
<td>0.0019</td>
</tr>
</tbody>
</table>

Figure 1-9. Experimental data and the multiple regression fitted lines of the quadratic function tortuosity factor model [Eq. (1.8)] for the three test soils, and the predicted lines generated with \( \delta \) and \( \mu \) values adopt from Mullins and Sommers’ [1986] sandy clay loam soil.
Equation (1.9) is a modification of the quadratic function tortuosity factor model of Eq. (1.8) by defining the empirical constants with soil properties. The incorporation of soil-water retention parameter $b$ in the Eq. (1.8) improved the $RMSE$ only for the test clay soil, but not for the test sand and sandy clay loam soils (Table 1-7 and 1-8). However, even with the incorporation of $b$, the clay soil is still better described by the power function rather than the quadratic function model.

Olesen’s threshold soil-water content tortuosity factor model [Eq. (1.9)] does not improve the predictive capability to the test sandy clay loam and clay soils from Olesen’s power function tortuosity factor model [Eq. (1.5)] (Table 1-6 and 1-8), but it improves the predictive capability of the tortuosity factor of the test sand soil from Eq. (1.5). This supports the observation that the sandy soil is best described by a quadratic function [Eq. (1.3)]. Again, $\theta_{th} = 0$ of the sand soil from Eq. (1.11) (Table 1-8) demonstrates that the
incorporation of soil structure is not necessary to describe the tortuosity factor behavior of a sandy soil.

The sandy clay loam soil is best described by Olesen’s power function tortuosity factor model [Eq. (1.5)] with $b_t$ derived from Eq. (1.6). Although fitting the experimental data by Olesen’s models [Eq. (1.5) and (1.9)] did not obtain the lowest RMSEs for all three test soils, they all provided a reasonable predictive capability (Table 1-5 and 1-8). The $b$ values estimated by the texture give an overall best prediction. The soil-water retention parameter $b$ derived from direct measurement does not show an advantage in improving the model predictive capability.

The required parameters to calculate the $\theta_{th}$ in Moldrup et al.’s linear impedance factor model [Eq. (1.12) and (1.13)] are shown in Table 1-1. The slope ($H$) of the linear relationship of impedance factor ($f$) vs. water content ($\theta$) is shown in Figure 1-10. For a clay soil, Moldrup et al. [2007] introduced another relation between $\theta_{th}$ and $b$ [Eq. (1.14)], which could be derived from three different means i.e. $b_{th}$, $b_t$, $b_{tb}$ (Table 1-6). However, it was found that the derived $b_t$ and $b_{th}$ did not result in a reasonable estimation of $\theta_{th}$ values (0.37 and 0.65 cm$^3$ cm$^{-3}$ respectively).

These three threshold water content tortuosity factor models all generate a stationary water content below which the tortuosity factor is equal to zero. However, we observed that the stationary water contents for our three test soils are different. Moldrup et al.’s model [Eq. (1.12)] is a rectified form of the quadratic function tortuosity factor model [Eq. (1.8)] and Olesen’s threshold water content model [Eq. (1.9)]. However, the RMSEs
showed that it is incapable to improve the predictive capability of the tortuosity factor of the three test soils (Table 1-9).

Despite that Moldrup et al.’s [2007] linear impedance factor model [Eq. (1.12)] did not have the capability to satisfactorily predict the tortuosity factor, the $H$ values we obtained supported the findings reported by Hamamoto et al. [2009]. Firstly, $H$ is highly correlated with the uniformity of particle size distribution. We obtained $H = 0.11$ and $0.08$ for the test sand and clay soils, respectively, which are considered to be more uniform in particle-size distribution; while the test sandy clay loam soil, which is thought to be less uniform in particle-size distribution, has a much greater value of $H = 1.08$. A greater $H$ value represents a steeper increase of tortuosity factor with increasing soil-water content (Figure 1-10). Secondly, the increase in bulk density causes the decrease in $H$. Altogether, a uniform particle size distribution and a higher bulk density reduces the dependence of tortuosity factor on soil-water content.

Table 1-8. Evaluation of Olesen’s threshold water content model [Eq. (1.9)] with $\theta_{th}$ calculated from Eqs. (1.10) and (1.11), and with $b$ values derived from direct measurement or estimated by three means; and the statistics of RMSE.
Figure 1-11. Experimental data and the multiple regression fitted lines of Olesen’s threshold water content model [Eq. (1.9)] for the three test soils; and predicted lines with parameters adopted from Olesen et al. [1996].
We encountered two problems to acquire $\theta_{th}$ from the intercepts on the x-axis of the $f-\theta$ linear regression (Figure 1-10). Firstly, $r^2$ showed that only the test sandy clay loam soil has a significant linear $f-\theta$ relationship. Secondly, the x-intercepts of the test sand and clay soils fell on negative soil-water contents, which are unreasonable values. Therefore, in order to evaluate the LIFE-Campbell model [Eq. (1.15)], we set the $\theta_{th}$ of the test sand and clay soils as 0. The slope of the $f-\theta$ linear regression, $H$, is shown in Figure 1-10. The saturated soil-water content, $\theta_s$, is assumed equal to the total porosity as listed in Table 1-1. The measured matric potential at air entry, $\psi_e$, are listed in Table 1-10. The soil-water retention parameter $b$ from measurement and models [Eq. (1.6) and (1.7)] are listed in Table 1-6.

The LIFE-Campbell model [Eq. (1.15)] is a modification of the Moldrup et al’s linear impedance factor model [Eq. (1.12)]. This approach incorporates the matric potential vs. soil-water content relation (or refers to the pore sizes distribution) at each measured soil-water content into the model, thus the model predicted lines are not smooth (Figure 1-13). Although more parameters are used in this model, the relatively high RMSEs demonstrate the poor predictive capability of the model to the tortuosity factor (Table 1-10). The model with the soil-water retention parameter $b$ derived by three means all showed relatively high RMSEs (Table 1-10). The poor predictive capability might due to the non-significant linear relation of $f-\theta$ and the uncertainty in $\theta_{th}$. 

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Table 1-9. Values of $\theta_{th}$ derived from Eq. (1.13) for all the three test soils and from Eq. (1.14) for the clay soil; and the evaluation of Moldrup et al’s linear impedance factor model [Eq. (1.12)] by $RMSE$.

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Sandy clay loam</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{th}$ [Eq. (1.13)]</td>
<td>0.01</td>
<td>0.12</td>
<td>0.34</td>
</tr>
<tr>
<td>$\theta_{th}$ [Eq. (1.14)]</td>
<td>--</td>
<td>--</td>
<td>0.09</td>
</tr>
<tr>
<td>$RMSE$</td>
<td>0.0031</td>
<td>0.0179</td>
<td>0.0110 0.0063</td>
</tr>
</tbody>
</table>

Figure 1-12. Experimental data fitted by Moldrup et al’s linear impedance factor model [Eq. (1.12)] for the three test soils, and the predicted lines for the clay soils with $\theta_{th}$ values derived from Eqs. (1.13) and (1.14).

Figure 1-13. Experimental data fitted by the LIFE-Campbell’s model [Eq. (1.15)].
Table 1-10. Values of $\theta_{th}$ derived from $f$-$\theta$ linear regression; $\psi_e$ and $b_m$ from soil-water retention measurements; and $b_t$, $b_{tb}$ from model estimation [Eq. (1.6) and (1.7)], and $RMSE$s for the LIFE-Campbell model [Eq. (1.15)].

<table>
<thead>
<tr>
<th>Texture</th>
<th>Sand</th>
<th>Sandy clay loam</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{th}$</td>
<td>0</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>$\psi_e$ (cm-H$_2$O)</td>
<td>-40</td>
<td>-600</td>
<td>-2040</td>
</tr>
<tr>
<td>$b_m$ [Eq. (1.6)]</td>
<td>0.0037</td>
<td>0.0355</td>
<td>0.0039</td>
</tr>
<tr>
<td>$b_{tb}$ [Eq. (1.7)]</td>
<td>0.0038</td>
<td>0.0510</td>
<td>0.0033</td>
</tr>
<tr>
<td>$RMSE$</td>
<td>$b_t$ [Eq. (1.6)]</td>
<td>0.0038</td>
<td>0.0436</td>
</tr>
<tr>
<td></td>
<td>$b_{tb}$ [Eq. (1.7)]</td>
<td>0.0001</td>
<td>0.0259</td>
</tr>
</tbody>
</table>

The three test soils showed a linear $\xi$-pF relationship but non-linear $f$-pF relationship (Figure 1-14 and 1-15), which is contrary to Mehta et al.’s [1995] conclusion. Different from their findings, our test sand soil showed a log ($\xi$) vs $\theta$ linear relationship with slope shifting at pF = 2.0 instead of 2.8 (Figure 1-4). The slopes of log ($\xi$) vs $\theta$ linear relationship shifted at pF = 3.3 and 4.0 for our test sandy clay loam and clay soils respectively (Figure 1-4).

The solute diffusion ceased ($\xi = 0$) at pF 2.4, 3.6 and 4.5 for the test sand, sandy clay loam and clay soils respectively (Figure 1-15). We found the same fact as observed by Olesen et al.[2001a] that the threshold pF is soil type dependent. However, our data does not agree with their found threshold pF occurred at 4 to 6.
1.3.4 Linear function

So and Nye [1989] used multiple regression to relate the tortuosity factor with bulk density and volumetric soil-water content [Eq. (1.16)]. Although the textures of our test soils do not match the soils used in their study, a comparison between our results with their soils of similar textures is still meaningful. We compared their sandy loam and silty clay soils to our test sandy clay loam and clay soils respectively. Their model constants
and the constants obtained from multiple regressions of our experimental data are shown in Table 1-11. For comparable soils, the model constants obtained from our experiment are considerably different from those reported by So and Nye [1989]. Our multiple regressions obtained zero, positive and negative values of $\omega$, respectively, for the test sand, sandy clay loam and clay soils (Table 1-11), which is different from the all negative values reported by So and Nye [1989]. The zero $\omega$ value of the sand soil indicates that its tortuosity factor is not significantly dependent on bulk density. The positive $\omega$ value of our sandy clay loam soil indicates that the tortuosity factor at whole soil-water content range is benefited by its lower bulk density; while, the negative $\omega$ value of the test clay soil shows that a higher bulk density reduces the tortuosity factor.

The influence of bulk density and soil-water content on tortuosity factor is also illustrated in the $f$ vs. $\theta$ linear regression lines (Figure 1-6). The impedance factor linear regression lines cross each other at soil-water content of about 0.17 cm$^3$ cm$^{-3}$ for the three test soils in two bulk densities (Table 1-1). At soil-water content below 0.17 cm$^3$ cm$^{-3}$, the impedance factor of bulk density 1.60 g cm$^{-3}$ is greater than that of bulk density 1.45 g cm$^{-3}$. The opposite relationship was found when soil-water contents are above 0.17 cm$^3$ cm$^{-3}$. Therefore, the obtained $\omega$ values supported the conclusion made by Hamamoto et al. [2009] that a higher bulk density facilitates the tortuosity factor increase at lower water contents, while a lower bulk density enhances the tortuosity factor increase at higher water contents.
Table 1-11. Values of $\alpha$, $\beta$, and $\omega$ of the two-variable linear tortuosity factor model [Eq. (1.16)] proposed by So and Nye [1989] and derived from multiple regressions; and the statistics of $RMSE$.

<table>
<thead>
<tr>
<th></th>
<th>So and Nye [1989]</th>
<th>Regression</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sandy loam</td>
<td>Silty clay</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.0086</td>
<td>-0.065</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.20</td>
<td>0.78</td>
</tr>
<tr>
<td>$\omega$</td>
<td>-0.125</td>
<td>-0.105</td>
</tr>
<tr>
<td>$RMSE$</td>
<td>0.1432</td>
<td>0.0198</td>
</tr>
</tbody>
</table>

Figure 1-16. Experimental data and the multiple regression fitted lines of the two-variable linear tortuosity factor model [Eq. (1.16)] for the three test soils, and the predicted lines for the sandy clay loam and clay soils with $\alpha$ and $\beta$ values adopted from So and Nye [1989].

1.3.5 Conceptual model

The measured solute diffusion coefficients at 100% degree of saturation ($D'$) are equal to $4.20 \times 10^{-8}$, $44.15 \times 10^{-8}$, $3.75 \times 10^{-8}$ cm$^2$ s$^{-1}$, respectively, for the test sand, sandy clay loam, and clay. Lim et al. [1998] assumed the fraction of soil-water contained in water film form ($\nu$) is related to the ratio of the total surface area of the soil particles. They set $\nu = 0.1$ for the coarse sandy soil. Accordingly, we set $\nu = 0.1$, 0.3, and 0.6,
respectively, for the test sand, sandy clay loam, and clay soils (according to the specific area measured, Table 1-1). The residual degree of saturation (Sr) were measured as 5 %, 15 %, and 35 % for the sand, sandy clay loam, and clay soils, respectively at 1500 kPa. In Lim’s model, solute diffusion coefficient is treated as a function of saturation degree (S) rather than the soil-water content; therefore, the RMSE is not applied to compare this model with other models in this study.

For the combined parallel-series model [Eq. (1.19)], the proportion of diffusion in parallel arrangement, η, and in series arrangement, 1-η, is obtained by the trial and error method. We obtained η = 0.9, 0.5, and 0.7, and thus 1-η = 0.1, 0.5, and 0.3, respectively, for the test sand, sandy clay loam and clay soils.

The parallel model [Eq. (1.17)] poorly describes the normalized diffusion coefficients [D(S) / D(S=1)] for the three test soils (Figure 1-17). Since the parallel model generated a linear relationship between degree of saturation and normalized diffusion coefficient, it could not fit the nonlinear experimental data well (Figure 1-17). On the other hand, the series model [Eq. (1.18)] and the combined model [Eq. (1.19)] generated nonlinear relationships between degree of saturation and normalized diffusion coefficient that were more in agreement with the experimental data (Figure 1-17). Overall, the series model better predicted the normalized diffusion coefficients at lower degree of saturation (∼ S < 50–60 %); while the combined model better predicted the normalized diffusion coefficients at higher degree of saturation (∼ S > 50-60 %) (Figure 1-17).
Figure 1-17. The experimental data and the predicted lines of Lim et al.’s Parallel [Eq. (1.17)], Series [Eq. (1.18)], and Combined [Eq. (1.19)] models.
Despite that Lim’s conceptual models fails to predict the normalized diffusion coefficients at the whole range of degree of saturation, it demonstrates the transition of the diffusive pathway at various degree of saturation. At lower soil-water contents, liquid phase is in the form of water films connecting to water pores or vice versa so that the series model best predicts the diffusion coefficients [Eq. (1.18)]. At higher soil-water contents, solute diffuses through the continuous diffusive pathways made of parallel-arranged continuous water films or water in pores; so that the combined parallel-series model with a proportion \( \eta > 0.5 \) best predicts the solute diffusion coefficient [Eq. (1.19)].

1.4 Conclusion

By comparing all the RMSEs derived from regression, we conclude that the solute diffusion tortuosity factor (and consequently, the solute diffusion coefficient) of the sand soil is best described by a quadratic function of soil-water content. The addition of the bulk density and particle-size distribution into the models has limited contribution to improve the model predictive capability to a sandy soil. For the test sandy clay loam and clay soils, the widely used Millington and Quirk power function model of soil-water content and porosity provided a good descriptive form for the tortuosity factor changes with soil-water content. Inclusion of the extra parameter of bulk density improves the predictive capability of the models to the test sandy clay loam and clay soils. The conceptual approach does not predict tortuosity factors as well as the quadratic function tortuosity factor model and Olesen’s power function tortuosity factor model. However, it
can be modified by applying the series model at lower soil-water content and the parallel-series combined model at higher soil-water content for future application.

The power function model was improved by Olesen et al. by defining the empirical constants with the soil-water retention parameter estimated from texture information. According to the experimental data, we conclude that \( k_2 = 0 \) for the sand soil, and \( k_1 = 0 \) for the other two soils in Olesen et al.’s power function model [Eq. (1.5)]. Furthermore, instead of a fixed \( \xi^* \) value for all soil types in various bulk densities, \( \xi^* \) is thought to be bulk density and texture dependent. Nevertheless, further study is needed to further understand the values of \( \xi^* \), \( k_1 \), and \( k_2 \) in this model.

The two-region linear behavior of \( \log(\xi) \) vs. \( \theta \) and the models constants proposed by Mehta et al. [1995] demonstrated the shift of diffusive pathway from meniscus form (water film) to tortuous capillary tubes (water in pores). Ideally, the tortuosity factor versus \( \theta \) relationship should be predicted by two different functions relating to the different soil-water form present. The intercept of \( f \) vs. \( \theta \) relationship and the \( \omega \) values derived from So and Nye’s [1989] linear function provided the evidence that bulk density contributes to the two-region behavior. Moreover, Lim et al.’s conceptual model also confirms the two-region behavior. Similar to the empirical models, Lim et al.’s conceptual model needs further study in recognizing the transition zone between the lower soil-water content range and high soil-water content range. Moreover, the examination of the parameters, such as \( a/r, S_r \), and \( \nu \) in this model may have the potential to improve the model predictive capability.
The tortuosity factor was found not only depends on bulk density but also on soil texture and particle packing. The tortuosity factor of homogeneous materials (as our test sand and clay soils) is more likely to follow a simple relation with soil-water content, while heterogeneous material (as our test sandy clay loam soil) tends to exhibit a region-wise relation with soil-water content. We attribute this to the more uniform arranged particles and pores that may form a more orderly liquid phase distribution and result in a more consistent behavior of tortuosity factor with soil-water content. However, the orderly arrangement of homogeneous porous material constrained the increase of tortuosity factor with the increase in bulk density. On the other hand, the heterogeneity of porous media enhances the contact of each particle at higher bulk density so that the increase in bulk density enhances the increase of tortuosity factor with soil-water content. This point of view is also supported by the obtained $\omega$ values of So and Nye’s [1989] linear function and $H$ values of the $f-\theta$ relationship. This means that the increase of tortuosity factor is suppressed by the uniform distribution of particle size.

At present, there is no perfect tortuosity factor model that can represent the behavior of tortuosity factor at ranging soil-water contents for soils of different textures. This study evaluated the predictive capability of the current models and identified the key soil and water parameters that influence the tortuosity factor prediction. Incorporation of the findings from this study will greatly improve the predictive capability of future new models.
1.5 References


Chapter 2

Impact of Soil-Water Retention Hysteresis on Solute Diffusion in Unsaturated Soils

2.1 Introduction

Hysteresis is a significant phenomenon exhibited in the soil-water content and matric potential relationship. It refers to the unequal matric potential at a given soil-water content (or vice versa) when a soil is subjected to wetting or drying process. At a given soil-water content when the soil is undergoing drying process, the matric potential is less negative than that undergoing wetting [Jury et al., 1991]. Hysteresis has been proved to have impacts on soil properties such as hydraulic conductivity [Poulavassilis and Tzimas, 1975], gas diffusion [Horgan and Ball, 2005], and solute movement [Naasz et al., 2005]. The neglect of hysteresis may over estimate the rate of solute moving in soil [Jones and Watson, 1987]. The disregard of hysteresis in 1D Mualem simulation resulted errors in predicting solute movement and dispersion [Vereecken et al., 1995].

The release of the dissolved chemicals from soils through the soil liquid phase has been widely examined under the influence of both soil-water content and matric potential. The soil-water content indicates the amount of liquid phase available for solute
diffusion and the matric potential implies the arrangement of the diffusive pathway. At the same matric potential, the amount of water held under the wetting condition is less than that under the drying condition for a soil exhibiting hysteresis. Because the sequence of water intruding into the soil (wetting) does not follow the same sequence of water flow out from the soil (drying) [Reeves and Celia, 1996]. Accordingly, solute diffusion through diffusive pathway formed by soil pore-water is thought to be under the influence of hysteresis. However, at present, there were very few studies directly examined the impact of hysteresis on solute diffusion.

Philips and Brown [1965] derived different solute diffusion coefficients ($D_s$) from different means of bringing the soil-water content to a degree, because the geometry of soil-water distribution in the pores and around the particles are different during wetting and drying. Barraclough and Tinker [1982] confirmed that the method of soil-water intrusion has an impact on $D_s$; and further observed that $D_s$ of drying is greater than that of wetting for soil specimen of the same texture, packed to the same bulk density, and equilibrated to the same soil-water content. However, this finding was not conclusive because the courses of experiments were not conducted for examining this purpose and there were limited data points.

On the other hand, the influence of hysteresis on solute transport in soil has been verified. Solute transported in a slower rate when both the drying and wetting conditions are incorporated in the solute transport simulation than only incorporated the drying limb [Vereecken et al., 1995]. Mitchell and Mayer [1998] drew the same conclusion after they
simulated the solute transport under both hysteretic and non-hysteretic conditions by the finite-element and Eulerian-Lagrangian solute transport model. Hysteresis had shown the importance in solute transport simulations.

Furthermore, hysteresis showed its impact on soil gas diffusion. Goddard [1965] found that the hexane diffusion flux in the wetting soil was greater than that in the drying soil at the same soil-water content. They inferred that hysteresis actually reflects the variation of soil-water distribution; therefore, the gas diffusion flux in partially saturated soil reveals the variance. Although a later study of Shearer et al. [1966a] did not find the effect of hysteresis on oxygen diffusion in soil, they found that both liquid and gas permeability are in relation with hysteresis. Lai et al. [1976] obtained different carbon dioxide diffusion coefficients from wetting condition to drying condition of field soils. Steele and Nieber [1994a] applied a network model to simulate gas diffusion in a porous media and demonstrated that gas diffusion coefficients under wetting is greater than that under drying at the same air-filled porosity.

With only limited data in the literature, it is uncertain about how and to what extent hysteresis would affect the solute diffusion in unsaturated soil. The objective of this study is to examine the impact of hysteresis on solute diffusion in three soils of different textures and to fit the derived tortuosity factors from both drying and wetting methods by proposed predictive models.
2.2 Materials and Methods

Properties of the three test soils are listed in chapter 1 (Table 1-1). Soil specimen preparation methods prior to the solute intrusion all followed the same procedures as our previous study (Section 1.2.1).

After the sieved soils were packed to the designated bulk density in the diffusion Tempe cell, the predetermined soil-water content was reached through either wetting or drying methods. In this experiment, we only considered the extreme wetting and drying conditions, which means the scanning curves within the primary (boundary) soil-water retention curve were not investigated.

2.2.1 Wetting process

Fixed soil-water contents were reached through wetting method by injecting designed volume of 0.01 M KBr solutions into the bottom port of the diffusion Tempe cell. A partial vacuum was applied to accelerate the equilibration [Jury et al., 1991]. After reached the equilibrium, the sample cells were then placed into a humidity-saturated chamber at 20 °C for 24 hours before solute diffusion coefficient measurement.

2.2.2 Drying process

Drying condition was conducted by first saturating soil specimens with 0.01 M KBr solutions for 7 days to uniformly saturate soil-pores with bromide ions. Afterward, saturated soil specimens were placed into a pressure chamber to reach the predetermined matric potential and the corresponding soil-water content. Before diffusion coefficient
measurement, soil samples were kept in a humidity-saturated chamber at 20 °C for 24 hours.

2.2.3 Diffusion coefficient measurements

Solute diffusion coefficients in soil \( (D_s) \) were measured through ion-exchange membrane methods [Vaidyanathan and Nye, 1966]. Details were described in chapter 1 (Section 1.2.2).

2.2.4 Water retention curves

The drying limb of the soil-water retention curve was obtained by recording the applied matric potentials and the corresponding equilibrium soil-water contents. The wetting limb of the soil-water retention curve was obtained through the hanging column method by measuring the established matric potential after the soil specimen reached the equilibrium soil-water content. The accuracy of the matric potential was brought to 1.0 cm-H\(_2\)O. The van Genuchten and Mualem model was applied to fit the derived drying and wetting limb data.

\[
S = [1 + (\alpha \psi)^n]^{-m} \tag{2.1}
\]

where \( S = (\theta - \theta_r) / (\theta_s - \theta_r) \) is the soil-water saturation degree (%); \( \theta, \theta_s, \) and \( \theta_r \) are volumetric, saturated, and residual soil-water content, respectively; \( \alpha, n, m \) are fitting constants that best describe the curve.
2.2.5 Tortuosity factor models

Derived bromide diffusion coefficients in soil \((D_s)\) were divided by the bromide diffusion coefficient in free water \((D_0 = 2.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})\) to obtain the tortuosity factors. An empirical [Olesen et al., 1996] model and a conceptual [Lim et al., 1998] tortuosity factor model were applied to fit the tortuosity factors derived from both drying and wetting methods. Details about these two models are depicted in chapter 1 and summarized in the following.

Olesen et al. [1996] empirical model:

\[
\xi = \xi^* \cdot \theta \cdot \left(\frac{\theta}{\phi}\right)^{k_1 + k_2 b}
\]  

(1.5)

where \(\xi^*\) represents the tortuosity factor at 100% soil-water saturation, \(k_1\) and \(k_2\) are empirical constants, \(b\) is the soil-water retention parameter based on the Campbell soil-water retention model. \(b\) can also be estimated by bulk density, clay and sand mass fraction [Williams et al., 1992]:

\[
b_{wb} = (0.303 - 0.093 \cdot \ln(\rho)) - 0.0565 \cdot (\ln(CL)) + 0.00003 \cdot (FS)^2 \]  

(1.7)

where \(\rho\) is the bulk density (g cm\(^{-3}\)); \(CL\) and \(FS\) are the mass fraction (g g\(^{-1}\)) of clay and fine sand respectively.
Lim et al. [1998] conceptual model:

Three tortuosity factor models based on the arrangements of the diffusive pathway formed by the distribution of the interconnected soil-water filled pores and films are as follows:

I. Solute diffuses through soil-water filled pores and films independently

\[ \xi(S) = \xi^* \cdot \left[ 1 - \frac{\nu \cdot S_r (1 - S_r)}{S} \right] \cdot S + (1 - S_r) \cdot R \]  \hspace{1cm} (1.17)

\[ R = (1 - \frac{a}{r})^3 \left[ 1 - 2.1(\frac{a}{r}) + 2.09(\frac{a}{r})^3 - 0.95(\frac{a}{r})^5 \right] \]  \hspace{1cm} (1.18)

where \( \xi(S) \) is the tortuosity factor at a given saturation degree \( S \) (\%)(volumetric water content/total porosity), \( \xi^* \) is the tortuosity factor at 100\% saturation, \( \nu \) is the fraction of liquid phase contained in the films, which is estimated through the total surface area of the soil particles and an assumed liquid phase film thickness (here we assumed \( \nu = 0.1, 0.3, \) and 0.6 for the sand, sandy clay loam and clay soils respectively based on the measured particle specific surface area of 0.61, 19.73, and 37.19 m\(^2\)g\(^{-1}\), respectively), \( S_r \) is the residual saturation degree, \( S_e \) is the effective saturation degree which equals to \( (S - S_r)/(1 - S_r) \) [Brooks and Corey, 1966], \( R \) is a factor that includes the entrance constriction, viscosity and ionic interaction along small pores, and \( a/r \) is the ratio of the hydrated ion radius to the soil pore radius (here we assumed \( a/r = 0.5 \) for all three soils).
II. Solute diffuses through series connected water filled pores and films

\[ \xi(S) = \frac{\xi^*}{1 - \nu \cdot S_s(1 - S_e)/S} + \frac{(1 - S)^2}{R(1 - S_e)} \] (1.19)

III. Solute diffuses proportionally through parallel and series arrangements

\[ \xi(S) = \left\{ \eta \cdot \xi^* \cdot \left[ 1 - \nu \cdot S_s(1 - S_e)/S \right] \cdot S + (1 - S_e)R \right\} + \left\{ \eta \cdot \xi^* \cdot \left[ 1 - \nu \cdot S_s(1 - S_e)/S \right] + \frac{(1 - S)^2}{R(1 - S_e)} \right\} \] (1.20)

where \( \eta \) is the proportion of diffusion along the independently parallel water-filled pores and water films, and \( 1 - \eta \) is the proportion of diffusion along the series water-filled pores and water films.

2.3 Results and Discussions

2.3.1 Soil-water retention curves

The three test soils all exhibited soil-water retention hysteresis (Figure 2-1), which means water intrusion through wetting and drying sustained different amount of soil-water in the soil-pores even when the same matric potential was obtained. The derived experimental data were fitted to van Genuchten and Mualem soil-water retention model [Eq. (2.1)] with best fit constants of \( \alpha \), \( n \), and \( m \) listed in Table 2-1. Wetting and drying curves exhibit a generally acknowledged relationship of \( \alpha_w = 2 \alpha_d \) [Mitchell and Mayer, 1998]. The subscripts of \( w \) and \( d \) denote wetting and drying respectively.
Table 2-1. Constants obtained from the best fitting of experimental data to van Genuchten and Mualem water retention model [Eq. (2.1)].

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Sandy clay loam</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_d$</td>
<td>0.1</td>
<td>0.05</td>
<td>0.0025</td>
</tr>
<tr>
<td>$n$</td>
<td>1.3</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>$m$</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$\alpha_w$</td>
<td>0.2</td>
<td>0.01</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Figure 2-1. Measured wetting and drying soil-water retention data (points), and the predicted lines generated by the van Genuchten and Mualem soil-water retention model [Eq. (2.1)] for the primary drying and first wetting curves.
2.3.2 Solute diffusion hysteresis

Experimental data showed non-unique solute diffusion coefficient to soil-water content and to matric potential relationship (Figure 2-2). At the same soil-water content or fixed matric potential, solute diffusion coefficients at drying limb \( (D_d) \) are greater than those at wetting limb \( (D_w) \), which is consistent with the finding of Barraclough and Tinker [1982]. The difference can be explained by the microscale investigation of the soil-water distribution in soil [Mitchell and Mayer, 1998; Shearer et al., 1966a; Steele and Nieber, 1994a]. Steele and Nieber [1994b] found that during drying process, the once saturated soil pores were drained out evenly and then formed dichotomous form of soil-water in soil pores, which means a more continuous soil-water distribution by relatively low volume of soil-water in pores. During wetting process, the soil-water saturated the smaller pores first and then filled larger pores nearby; therefore, it reaches the equivalent continuous diffusive pathway at a relatively high volume of soil-water [Mitchell and Mayer, 1998]. Accordingly, higher solute diffusion coefficients were observed from the drying method due to its efficient diffusive pathway distribution.

The solute effective diffusion coefficients at drying limb showed a dramatic drop from higher soil-water contents to lower soil-water contents (Figure 2-2); while at wetting limb they exhibited a moderate decreasing trend with decreasing soil-water content. This is due to that when the soil-water is drained by drying process to a degree and formed a dichotomous form, it will subject to a suddenly empty at a critical point and causes the diminishes of the thin but continuous pathway [Shearer et al., 1966b; Steele and Nieber, 1994a]. On the other hand, when the soil-water is brought in by wetting
process, some small but not relatively smallest pores are isolated during soil-water invasion process, so they might remain dry while the larger pores are filled. This reduces the diffusive transport through the system until the linear continuous bundles of small pores are sequentially filled. This unequal solute diffusion coefficient to soil-water content relationship continues from high soil-water contents to low soil-water contents until the sharp drop of solute diffusion coefficient at drying limb intermittent (Figure 2-2). We attribute this to that the soil-water is held in smallest pores regardless of drying or wetting at this stage.

Research on the interfacial area, between air-water interfaces, supported our results and explained the variations in Figure 2-2. At comparable soil-water content, a higher interfacial area refers to a less continuous form of soil-water clusters [Reeves and Celia, 1996] (which are thought to be the media for solute diffusion in soil pores). The solute diffusion coefficients of drying separated from wetting at the soil-water content where the interfacial area reaches the climax. Above this soil-water content, the interfacial area of wetting limb is greater than that of drying limb. Below this soil-water content, the interfacial area of drying limb is greater than that of wetting limb. Below the separation soil-water content, the soil-water distribution in the soil pores is very scattered due to the limited amount of available soil-water volume. It demonstrates that the solute diffusive pathways of drying and wetting at comparatively low soil-water content are all limited by the available soil-water volume, so that the solute diffusion coefficients did not show too much in difference. After the interfacial area reaches the maximum, different soil-water distribution patterns induced by drying and wetting processes caused the difference in
solute diffusion coefficients. Furthermore, Reeves and Celia [1996] found that the interfacial area of the drying process has a steeper rise and fall, while the wetting process has a relatively moderate change. This corresponds to our finding that the solute diffusion coefficients of drying exhibited a much more dramatic change with soil-water content than those of wetting.

Gvirtzman and Roberts’s [1991] pore scale investigation of two immiscible fluids demonstrated that the soil-water spreads in the porous media starting from the stage of pendular form, funicular form, and then insular form. At about 20 % to 60 % saturation degree, the pendular form of soil-water starts to meet each other. After pendular rings meet together (the saturation degree is greater than 20 to 60%), the difference of soil-water distribution between drying and wetting becomes more apparent. Before pendular rings merges, there is a limited range of positions where a relatively stable interface may occupy. After pendular rings merge, the wetting process tends to form a uniform water plume, while drying process to form thin films. Culligan et al. [2004] used synchrotron based X-ray micro-tomography to obtain three-dimensional images of the soil-water distribution under drying and wetting processes. The high-resolution images of interfacial areas of unsaturated glass beads in column showed that the highest interfacial area occurs in a narrow range of saturation degrees, from 20 % to 35 %. In Figure 2-2, the solute diffusion coefficients of drying and wetting separated at 0.08 to 0.14 cm$^3$ cm$^{-3}$ soil-water contents, which are between 20 % to 35 % saturation degrees.
The moderate increasing trend of solute diffusion coefficients with soil-water content of wetting limb breaks at soil-water content around 0.4 cm$^3$ cm$^{-3}$ (Figure 2-2 b and c). This breaking point might be referred to the “ink-bottle” effect that accounts for the hysteresis of water in the soil. Horgan and Ball [2005] reported that when the soil-water content exceeds 0.4 cm$^3$ cm$^{-3}$, the bottles of the “ink-bottle” are almost filled with water and the adjacent necks are filled next, which results in a quick continuously connection of the diffusive pathway in a small increase of soil-water content. Accordingly, the solute diffusion coefficient above this soil-water content exhibits a steeper increasing trend.

The test sand and clay soils were categorized as homogeneous soils and the test sandy clay loam as heterogeneous soil (details in chapter 1), and all the soil materials exhibit hysteresis in solute diffusion coefficient; but the heterogeneous material has higher solute diffusion coefficients than homogeneous materials at a given soil-water content (Fig. 2-2). This is in agreement with Vereecken et al. [1995] and Naumov et al.’s [2007] numerical simulations that heterogeneities result in different fluid dynamical properties in soils. This point of view also supported by Ewing and Horton [2002] that when the pore-size distribution widens the solute diffusion coefficients increase.
2.3.3 Experimental data fitted by tortuosity factor models

Olesen et al. [1996] empirical model

Figure 2-3 shows the solute diffusion coefficients of drying limb fitted by Olesen’ et al.’s model [Eq. (1.5)] with constants derived from chapter 1 (Table 1-6). At present, there is no model exist to describe the solute diffusion coefficients of the wetting limb; therefore, we applied a try and error method to fit the wetting limb by Olesen et al.’s model. However, Olesen et al.’s model has limited capability to generate a curve close enough to the wetting data.

Out of expectation, we observed an interesting relationship between drying limb and wetting limb. The solute diffusion coefficient of wetting at a given soil-water content could be predicted by that of drying times the given soil-water content (Figure 2-3).

\[ D_{w,\theta} = \theta \cdot D_{d,\theta} \]  \hspace{1cm} (2.2)

where \( D_{d,\theta} \) is the solute diffusion coefficient derived from drying at a given soil-water content \( \theta \), and \( D_{w,\theta} \) is the solute diffusion coefficient derived from wetting at the same soil-water content \( \theta \).

According to the study of Hillel [1980] regarding pore number, pore neck sizes and the interconnection of pores of different widths to relate the diffusive flow to the number of narrow “necks” present in the soil. A medium at a given pore volume composed of numerous small pores is likely to have a higher pore connectivity; while composed of larger pores is likely to have a lower connectivity. Geometrically, the number of pore
connections, \( N \), across any porous plane is inversely related to the cross-sectional area of the pores, i.e., \( N \propto 1/r^2 \), where \( r \) is the pore radius. According to Poiseuille’s law, the flow rate \( Q \) through each pore is proportional to the forth power of the radius, i.e., \( Q \propto r^4 \). The water diffusivity is equal to the product of diffusive flow rate and the number of pore connections, so that \( QN \propto r^2 \). Lim et al. [1998] applied this assumption in the study of hydraulic conductivity to the solute diffusive pathway simulation in order to predict the solute diffusion coefficients in soil. The diffusive pathway of wetting is mainly comprised of the connectivity of the infinite cluster; therefore, the fraction of continuous water-filled pores during wetting at any given saturation degree is assumed proportional to the square of pore radius \( r^2 \). Based on this, they speculated that the fraction of continuous water-filled pores at any given saturation degree is proportional to that saturation degree. Followed by these speculations, the diffusive pathway of wetting is presumed proportional to the saturation degree or soil-water content, which might explain that the ratio of the diffusion coefficient of wetting at a given soil-water content to that of drying is equal to the given soil-water content.
Figure 2-2. Solute diffusion coefficients versus soil-water content (a, b, c) and matric potential (d, e, f) relationships of the three test soils derived from drying and wetting methods.
Lim et al. [1998] conceptual model

Figure 2-4 shows the result of applying Lim et al.’s [1998] conceptual model to predict the solute diffusion coefficients of drying and wetting. Constants from the non-linear curve fitting of the data are listed in Table 2-2. The series arrangement of water-filled pores and films diffusive pathway model [Eq. (1.19)] predicts the diffusion coefficients of wetting well for all the three test soils (Figure 2-4). This confirms to the concept that when water is added to the system (refers to the wetting process), small pores filled first followed by successively larger pores until all pores are filled [Jury et al., 1991]. The series arrangement model exactly simulates this process so that it performs well in predicting the solute diffusion coefficients of wetting.

The combined model [Eq. (1.20)] predicts the diffusion coefficients of drying at higher soil-water contents well but not at lower soil-water contents. The parallel model [Eq. (1.17)] fails to predict the diffusion coefficients for all the three test soils at any soil-water content. The particle distribution of the three test soils is highly variable in size and shape so that the particles interconnect with each other in a variety of ways. Although the drying process refers to the water first fills all pores and then drains from the soil, the process does not always follow the sequence as the pores are filled. Therefore, the soil-water distribution under the drying process neither follows the parallel nor the series diffusive pathway arrangements.
Figure 2-3. Experimental data of the drying limb fitted by Olesen et al.’s [1996] empirical model [Eq. (1.5)], and the wetting limb fitted by Eq. (2.2).
Figure 2-4. Experimental data fitted by Lim et al.’s [1998] model: independently parallel arrangement model Eq. (1.17), series arrangement model Eq. (1.19), and the combined model Eq. (1.20).
Table 2-2. Constants obtained from the best fit of the experimental data for the three test soils to Lim et al.’s [1998] conceptual model.

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Sandy clay loam</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>υ</td>
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<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>a/r</td>
<td>0.5</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Sr</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>η</td>
<td>0.9</td>
<td>0.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

2.3.4 Impact of solute diffusion hysteresis in solute transport

Figure 2-5. The impact of soil-water retention hysteresis on solute diffusion in soil. (c is the concentration, $C_0$ is initial concentration, $t$ denotes time, $x/L$ denotes relative distance)

Figure 2-5 demonstrates the impact of hysteresis on solute diffusion. Diffusion coefficients of the test sandy clay loam soil at 0.4 cm$^3$ cm$^{-3}$ soil-water content were used to generate the simulation ($D_{s,w} = 1.29 \cdot 10^{-7}$ cm$^2$ s$^{-1}$; $D_{s,d} = 2.66 \cdot 10^{-7}$ cm$^2$ s$^{-1}$). Initial condition is set as $c(x, t = 0) = 0$ and boundary conditions as $c(x=0, t) = C_0$, $c(x=\infty, t) = 0$.
(where $c$ is the concentration, $C_0$ is initial concentration, $t$ denotes time, $x$ denotes distance). At a given soil-water content, solute diffusion in soil under wetting condition is much slower than that under drying condition. As time increases, the difference becomes more evident. Therefore, it is important to consider the effect of hysteresis on modeling solute diffusion in soil.

2.4 Conclusion

Soil-water retention hysteresis has been proved to have influence on soil hydraulic conductivity, permeability, and gas diffusion. Our experimental data showed that hysteresis also has impact on solute diffusion in soil. At a given soil-water content, the solute diffusion coefficient of drying is generally greater than that of wetting. But, hysteresis in solute diffusion is not a random phenomenon. Our study shows that diffusion coefficients of wetting at a given soil-water content can be predicted by the diffusion coefficient of drying multiplied by that given soil-water content for the range of our measurement. By fitting the measured diffusion coefficients with conceptual models, it shows that the difference in diffusion coefficients between wetting and drying processes is essentially determined by liquid phase distribution in soil. Comparison of our results with studies in microscale examination of soil-water distribution in soil illustrates the mechanism that causes the difference in solute diffusion coefficients. Overall, the consideration of hysteresis in solute diffusion in soil is essential to improve the simulation accuracy. Presumption of only considering the diffusion coefficients derived from drying process might cause errors in solute transport prediction.
2.5 References


Chapter 3

A New Tortuosity Factor Model for Predicting Solute Diffusion in Unsaturated Soil

3.1 Introduction

Many natural transport processes, such as contaminant release from soil, nutrient transport from soil to plant roots, and environmental remediation, are related to solute diffusion in soil. Accurate estimation of solute diffusion flux in soil is vital for solute movement prediction.

Solute diffusion flux in soil is described by Fick’s law [Eq. (1.1)]. The key parameter in Fick’s law is the tortuosity factor ($\xi = D_s / D_0$, the ratio of the solute diffusion coefficient in soil to that in the free water). The dependency of $\xi$ on volumetric soil-water content ($\theta$) and matric potential ($\psi$) has been well recognized. The volumetric soil-water content indicates the amount of available diffusive pathway for solute diffusion; while the matric potential ($\psi$) reveals the arrangement of the diffusive pathway [Hamamoto et al., 2009; Jury et al., 1991].

However, most of the proposed $\xi$ predictive models only consider the dependency of $\xi$ on $\theta$ but not on $\psi$. Mehta et al. [1995] concluded that the prediction of the tortuosity factor should base on both $\psi$ and $\theta$. Moreover, the $\xi$-$\psi$ relationship is found to be less soil texture dependent (Mehta et al. [1995]).
Matric potential was first incorporated in a $\xi$ prediction model by Olesen et al. [1996] who used the soil-water retention parameter ($b$) of the Campbell model to estimate one of the empirical constants in the $\xi$ predictive model. Recently, Moldrup et al. [2007] directly used $\psi$ as a variable in the prediction of $\xi$. The model combines the linear impedance factor equation (LIFE) versus $\theta$ relationship ($D_s / D_0 \theta$ vs. $\theta$) and the Campbell soil-water retention model. Use of $\psi$ as a variable in the model enables the model to illustrate the effect of pore-size distribution on soil-water distribution and the effect of soil type on pore connection. This attempt successfully bridges the dependence of $\xi$ on $\psi$ and incorporates the soil-water distribution in $\xi$ prediction.

Moreover, the linear $D_s/D_0\theta$ versus $\theta$ relationship was challenged by Mehta et al. [1995]. Instead, a distinct linear two-region log ($\xi$) versus $\theta$ relationship was found in recent studies for soils across the textural types [Hamamoto et al., 2009; Mehta et al., 1995]. The slope of this linear relationship is steeper at lower soil-water contents until it reaches an inflection point. After the inflection point, the slope of log ($\xi$)-$\theta$ linear relationship becomes relatively moderate [Mehta et al., 1995]. Based on this observation, $\xi$ should be represented by two different equations: one for lower soil-water contents and one for higher soil-water contents. Furthermore, the two-region linear log ($\xi$) versus $\theta$ behavior was not only found in non-aggregated (repacked) soils but also in aggregated soils [Hamamoto et al., 2009].

The microscopic exploration of the soil-water distribution supports this two-region linear log ($\xi$) versus $\theta$ behavior. When gamma ray attenuation [Saba et al., 2001], and x-
ray computerized microtomography \cite{Culligan et al., 2004; Hu et al., 2004} methods were applied to examine the solute distribution in the soil, it was found that the liquid phase coats on solid particles transformed from meniscus form to capillary tube form as soil-water content increased. The soil water served for solute diffusive pathway at lower soil-water content is in meniscus form. An incremental decrease in $\theta$ can result in a great disconnection in meniscus. Accordingly, a steeper log ($\xi$) vs. $\theta$ slope can be observed. In addition, the electric diffusive double layer on the solid particle surface restricts the ion diffusion in the thin solute film around the particles and results in the fast decrease of $\xi$ with $\theta$. At higher $\theta$, solute diffuses through continuous inter-particle pore space formed as capillary tubes, which can lessen the impact of decreasing $\theta$, and consequently, a relatively moderate log ($\xi$) vs. $\theta$ slope can be expected in this region.

Relating the soil-water retention curve to the solute diffusion in soil behavior shows a glimpse of the observed log ($\xi$)-$\theta$ relationship. According to Jury et al. \cite{1991}, a continuous soil-water retention curve can be divided into three zones. At the air entry zone (when $\theta$ at around saturation), great change in matric potentials causes unnoticeable change in soil-water content. As soil-water content drops to the capillary zone (after air enters the system), an incremental change in $\psi$ causes a dramatic drop in $\theta$. As soil-water content continues to drops to the adsorption zone (when the soil-water is connected by the inter-particle pores), large changes in $\psi$ caused only small change in $\theta$. Since $\psi$ is more capable to represent the soil-water distribution and mechanic status, the prediction of $\xi$ through $\psi$ will be more responsive to the delicate change in diffusive pathway. On
the other hand, the prediction of $\xi$ based only on $\theta$ may fail in the air entry zone and adsorption zone where solute diffusive pathway undergoes a great shift within small change in $\theta$. Therefore, a $\psi$ related $\xi$ predictive model is desirable to describe the sensitive response of $\xi$ to $\theta$ at near air-entry zone and adsorption zone.

Experimental determination of the solute diffusion coefficient in soil is very time and labor consuming. Developing a reliable model for predicting $\xi$ as a function of soil-water content and matric potential is of great practical importance in modeling solute transport in soil. Inspired by the Moldrup et al.’s [2007] LIFE-Campbell model and based on the distinct two-region log ($\xi$) vs. $\theta$ linear relationship found across soil types [Mehta et al., 1995] and aggregation conditions [Hamamoto et al., 2009], the objectives of this research are to (1) measure $D_s$ in a range of soil-water contents and the corresponding matric potentials in soils of different textures; and to (2) develop and evaluate a two-region $\xi(\psi)$ predictive model, which is based on the two-region log ($\xi$) vs. $\theta$ linear relationship and the Campbell soil-water retention model.

3.2 Model Development

3.2.1 Two-region linear log ($\xi$) vs. $\theta$ relationship

The liquid phase in soil at lower $\theta$ is formed by meniscus while at higher $\theta$ by continuous capillary tubes. These two soil-water forms serve as the solute diffusive pathways, and result in a two-region linear relationship of log ($\xi$) versus $\theta$. Therefore, this predictive model separates $\xi$ into two-regions [Mehta et al., 1995].
Region 1: \[ \log\left(\frac{\xi_{r_1}}{\xi^*}\right) = -\chi_1 (\theta' - \theta_{r_1}) \] when \( \psi_{r_1} < \psi' \) or \( \theta_{r_1} < \theta' \) (3.1)

Region 2: \[ \log\left(\frac{\xi_{r_2}}{\xi^*}\right) = -\chi_2 (\theta_s - \theta_{r_2}) \] when \( \psi' < \psi_{r_2} < 0 \) or \( \theta' \leq \theta_{r_2} < \theta_s \) (3.2)

when \( \psi = 0 \) or \( \theta = \theta_s \) \( \xi = \xi^* \) (3.3)

where \( \xi \) represents the tortuosity factor (dimensionless), \( \theta \) represents the volumetric soil-water content (cm\(^3\) cm\(^{-3}\)), and \( \psi \) represents the soil-water matric potential (cm-H\(_2\)O). The subscripts \( r_1 \) and \( r_2 \) denote region 1 and region 2, respectively; \( \xi^* \) is the \( \xi \) at 100 % saturation degree (when volumetric soil-water content equals porosity), which is derived from dividing the measured solute diffusion coefficient in soil at 100% saturation degree by solute diffusion coefficient in free water. \( \theta' \) is the volumetric soil-water content at the inflection point, below which the log (\( \xi \)) vs. \( \theta \) has a steeper slope (region 1), while above which it has a relative moderate slope (region 2). Accordingly, the matric potential at the inflection point is denoted as \( \psi' \) and tortuosity factor as \( \xi' \). \( \chi_1 \) and \( \chi_2 \) are the slopes of the linear log (\( \xi \)) vs. \( \theta \) relationships at region 1 and region 2, respectively.
Figure 3-1. Demonstration of the two-region log ($\xi$)-$\theta$ relationship.

3.2.2 The Campbell soil-water retention model

Soil-water matric potential $\psi$, instead of $\theta$, has been widely applied as an indicator of soil particle-size distribution (or soil texture) and soil-water energy status (or soil-water characteristics). It has also been recognized to influence solute diffusion. Therefore, a $\xi$ predictive model using $\psi$ as variable may be able to represent the change of $\xi$ with soil-water distribution that serves as the diffusive pathway.

The Campbell soil-water retention model is used to link the transform of $\xi(\theta)$ to $\xi(\psi)$:

\[
\theta =\theta_s \left(\frac{\psi_a}{\psi}\right)^{\frac{1}{b}} \text{ for } \psi < \psi_a 
\]

(3.4)

\[
\theta = \theta_s \text{ for } \psi_a \leq \psi < 0
\]

(3.5)
where $\theta_s$ is the volumetric soil-water content at 100% saturation degree, which is assumed equal to the total porosity. $\psi_a$ is the matric potential at air entry. $b$ is the soil-water retention parameter which can be referred as pore-size distribution parameter (a positive number). The Campbell model is chosen because of its simplicity and it provides reasonable fit to most of the water retention data [Moldrup et al., 2007].

3.2.3 The combination of two-region log ($\zeta$) versus $\theta$ linear relationship with the Campbell soil-water retention model

Our proposed model combines the two-region log ($\zeta$) versus $\theta$ linear behavior Eqs. (3.1-3.3) with the Campbell soil-water retention model Eqs. (3.4-3.5), which yields a two-region $\xi(\psi)$ model.

Region 1: \[ \log \left( \frac{\xi_1}{\psi_a} \right) = -\chi_1 \left( \theta' - \theta_s \left( \frac{\psi_a}{\psi_{r1}} \right)^{\frac{1}{b}} \right) = -\chi_1 \theta_s \left( \frac{\theta'}{\theta_s} \right) - \left( \frac{\psi_a}{\psi_{r1}} \right)^{\frac{1}{b}} \] for $\psi_{r1} < \psi'$

or $\xi_1 = \xi' \cdot 10^{-\chi_1 \theta_s \left( \frac{\theta'}{\theta_s} \right)} \left( \frac{\psi_a}{\psi_{r1}} \right)^{\frac{1}{b}} \] \quad (3.6)

Region 2: \[ \log \left( \frac{\xi_{r2}}{\psi_a} \right) = -\chi_2 \left( \theta_s - \theta \left( \frac{\psi_a}{\psi_{r2}} \right)^{\frac{1}{b}} \right) = -\chi_2 \theta_s \left( 1 - \left( \frac{\psi_a}{\psi_{r2}} \right)^{\frac{1}{b}} \right) \] for $\psi' < \psi_{r2} < 0$

or $\xi_{r2} = \xi' \cdot 10^{-\chi_2 \theta_s \left( 1 - \left( \frac{\psi_a}{\psi_{r2}} \right)^{\frac{1}{b}} \right) \] \quad (3.7)

when $\psi = 0$ \[ \xi = \xi' \] \quad (3.8)
3.3 Materials and Methods

Three test soils, a sand, a sandy clay loam, and a clay soil with bulk densities of 1.60, 1.45, and 1.60 g cm\(^{-3}\), respectively, were used to evaluate the new \(\xi(\psi)\) model. Soil physical properties of these three soils were described in chapter 1 (Table 1-1). The \(\psi-\theta\) relationship of each soil was measured by pressure plate method and fitted by the Campbell soil-water retention model.

The solute diffusion coefficients of these three soils (\(D_s\)) in a range of \(\psi\) and corresponding \(\theta\) were measured by ion-exchange membrane method (detailed experimental method is described in Chapter 1). The tortuosity factor at saturation of the three soils, \(\xi^*\), were calculated in chapter 1 (Table 1-6). The least square regression was applied to fit the derived \(\xi\) data with the \(\xi(\psi)\) model to yield the best fit \(\chi_1\), \(\chi_2\), \(\xi^*\), and \(\psi'\) parameters for the test soils.

The root mean square error (\(RMSE\)) was used to assess the model performance.

\[
RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (d_i)^2} \tag{3.9}
\]

where \(n\) is the number of data points, \(d_i\) is the difference between the data and the model prediction at a given \(\psi\). A lower \(RMSE\) value indicates a better agreement between the experimental data and the model prediction.
3.4 Results and Discussions

The required soil properties and parameters from measurements for the $\xi(\psi)$ model are listed in Table 3-1. Values of $\psi_a$ (matric potential at air entry), and $b$ (the slope of the soil-water retention curve on semi-log coordinate) were derived from the soil-water retention measurements. Best-fit values of $\chi_1$, $\chi_2$, $\xi'$, and $\psi'$ were obtained from the least square regression (Table 3-2).

Figure 3-2. Experimental data fitted by the Campbell soil-water retention model.

Figure 3-3. Experimental data exhibit two-region linear log ($\xi$) vs. $\theta$ behavior.
Figure 3-4. The derived experimental data fitted by the $\xi(\psi)$ model [Eqs. (3.6)-(3.8)] and by the simplified model [Eqs. (3.10)-(3.13)].
Table 3-1. The measured parameters of the three test soils for the $\xi(\psi)$ model.

<table>
<thead>
<tr>
<th>Soil</th>
<th>$\theta_s$ (cm$^3$ cm$^{-3}$)</th>
<th>$\psi_a$ (cm-H$_2$O)</th>
<th>$b$</th>
<th>$\xi^*$</th>
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<tr>
<td>Sand</td>
<td>0.40</td>
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<td>-2040</td>
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</tr>
</tbody>
</table>

Table 3-2. Values of $\chi_1$, $\chi_2$, $\xi^*$, and $\psi'$ and its corresponding $\theta'$ derived from the least square regression; and the RMSEs between model prediction and experimental data for the three test soils.

<table>
<thead>
<tr>
<th>Soil</th>
<th>$\chi_1$</th>
<th>$\chi_2$</th>
<th>$\xi^*$</th>
<th>$\psi'$ (cm-H$_2$O)</th>
<th>$\theta'$ (cm$^3$ cm$^{-3}$)</th>
<th>RMSE</th>
</tr>
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<td>-100</td>
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</tr>
<tr>
<td>Sandy clay loam</td>
<td>2.0</td>
<td>1.8</td>
<td>0.010</td>
<td>-2,000</td>
<td>0.28</td>
<td>0.0121</td>
</tr>
<tr>
<td>Clay</td>
<td>4.0</td>
<td>1.8</td>
<td>0.007</td>
<td>-12,500</td>
<td>0.18</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

3.4.1 Values of $\chi_1$ and $\chi_2$

The $\chi_1$ and $\chi_2$ values derived from the least square regression are listed in Table 3-2. The fitted $\chi_1$ and $\chi_2$ values exhibit similar pattern as shown by Hamamoto et al. [2009]. The slopes of the two-region linear log ($\xi$) vs. $\theta$ relationship are relatively similar for all the three test soils at region 2 ($\chi_2$), while the slopes are very different at region 1 ($\chi_1$).
It is worth of mentioning that one value of $\chi_2 = 1.8$ fits best to all the three test soils. This value is similar to that found in Resurreccion et al.'s [2008] gas diffusion model and Hamamoto et al.’s [2009] solute diffusion coefficient model. Resurreccion et al. [2008] observed that the gas diffusion in unsaturated soil also exhibits a two-region linear log ($\xi$) vs. $\theta$ behavior. At higher $\theta$ (while lower air porosity), the gas tortuosity factor vs. air porosity relationship can be represented by a power function, which is equivalent to the semi-log linear relationship. They concluded that the best fitted power term is 1.8. Since the gas diffusion study has always been taken as a reconnaissance of solute diffusion, this power term of 1.8 at higher $\theta$ is in agreement with our slope at region 2, implying a consistent pattern in this region. Hamamoto et al. [2009] concluded a two-region log ($\xi$) vs. $\theta$ linear behavior of soils in two textures and with various degrees of aggregation. We calculated the average slope of all their test soils and obtained an average slope of 1.75 at higher $\theta$ region, which is very close to 1.8 of our three test soils. The specimens of their soils include different textures as well as degrees of aggregation in a range of bulk densities of 0.62-1.58 g cm$^{-3}$. Therefore, the value of $\chi_2 = 1.8$ seems to be found across soil types.

Since we noticed that $\chi_1$ change with soil type, we tested the $\xi(\psi)$ model sensitivities responding to the change of $\chi_1$. It was found that a smaller $\chi_1$ value is more influential to the $\xi$ changes with relative matric potential ($\psi_a/\psi_r$), while a greater $\chi_1$ value makes a moderate $\xi$ change with ($\psi_a/\psi_r$) (Figure 3-5). In our study, the sandy clay loam has smaller $\chi_1$ value of 2.0, while the sand and clay soils have greater $\chi_1$ values (Table 3-2).
We attribute the $\chi_1$ variation to the soil particle-size heterogeneity. A more heterogeneous soil, such as the sandy clay loam soil, tends to have a smaller $\chi_1$ value; while homogeneous soils, such as the sand and clay soils, have greater $\chi_1$ values. Heterogeneous soils have a wider range of soil particle-size distribution and consequently, pore-size distribution, which can enhance the connection of the meniscus at the lower soil-water content region. Therefore, a lower $\chi_1$ value or more rapid $\xi$ increase with the increase of $\psi_b/\psi_{r1}$ (or $\theta$) can be observed. On the other hand, homogeneous soils have a narrower range of soil particle-size (and thus pore-size) distribution that can hinder the connection of the continuous meniscus. Thus, a higher $\chi_1$ value or a moderate $\xi$ change with $\psi_b/\psi_{r1}$ (or $\theta$) was found. In conclusion, $\chi_1$ value changes with soil texture and is influenced by soil particle-size distribution.

Figure 3-6 shows that $\xi$ responds more sensitively to the incremental change of $\chi_2$ than $\chi_1$. The determined value of $\chi_2 = 1.8$ for all soils of different textures and degrees of aggregation is a great presumption we made in this study.
Figure 3-5. Model sensitivities to the variation of $\chi_1$ at region 1. The simulation is generated under the condition of $\theta' = 0.3$, $\theta_s = 0.4$, $\xi' = 0.01$, and $b = 2.4$.

Figure 3-6. Model sensitivities to the variation of $\chi_2$ at region 2. The simulation is generated under the condition of $\theta_s = 0.4$, $\xi^* = 0.05$, and $b = 2.4$.

3.4.2 Values of $\psi^*$, $\theta'$ and $\xi^*$

The inflection points of the two-region linear log ($\xi$) vs. $\theta$ behavior are at pF 2.0 ($\theta' = 0.26$) for the test sand soil, pF 3.3 ($\theta' = 0.28$) for the test sandy clay loam soil, and pF 4.1 ($\theta' = 0.18$) for the test clay soil. These values are different from those obtained by
Mehta et al. [1995] and Hamamoto et al. [2009]. They found that the inflection points were at pF 2.8 - 3.0 for a sandy soil. We attribute the sudden change in slopes between the higher and lower soil-water content regions to the transition of the soil-water distribution from meniscus form to continuous capillary tubes. However, the inflection point was found not occurring at a fixed $\psi'$ or $\theta'$ value in the two-region linear log ($\xi$) vs. $\theta$ relationship [Mehta et al., 1995; Olesen et al., 2000; Olesen et al., 2001]. Instead, we found the turning points fall on $\xi' \approx 0.01$ (Table 3-2) for all three test soils. This demonstrates that the overall constraint and enhancement from soil physical properties on solute diffusion in soil is not reflected by the total mass ($\theta$) or the energy status ($\psi$) of the soil-water present in the soil but on the overall tortuous status ($\xi$). Therefore, we propose that instead of using a threshold value of $\psi'$ or $\theta'$, the separation of region 1 (lower $\theta$ or more negative $\psi$) from region 2 (higher $\theta$ or less negative $\psi$) should be based on $\xi$, and set $\xi = 0.01$ seems to be a reasonable choice.

Hamatomot et al. [2009] stated that the inflection point falls on a higher $\theta$ as clay fraction increases. However, our result does not show this relationship between $\theta'$ and the clay fraction (Table 3-2). Again, the $\psi'$ or $\theta'$ varies with soil conditions.

3.4.3 The Parameter $b$

We used the $b$ values and the corresponding soil properties derived from Olesen et al. [1999] and from our experimental data to obtain a multiple regression relationship of $b$ with soil properties:
where CL and SD represent clay (< 0.002 mm) and sand (0.02 - 2mm) mass fractions (g g\(^{-1}\)) respectively. This strong correlation of \(b\) with soil properties provides a way to estimate \(b\) without experimental measurements of the soil-water retention.

Eq. (3.10) shows that the soil structure and pore size distribution indicator, \(b\), is mainly determined by the composition of the fine and coarse particles, but not silt fraction and bulk density. This implies that the incorporation of \(\psi\) into \(\xi\) predictive model through the Campbell soil-water retention model is a good first attempt, because the two-region behavior in the model is induced by the particle-size (or pore-size) distribution. This rectifies that the finer particles (such as clay) with larger surface area dominate the formation of the meniscus form diffusive pathway at region 1 (lower soil-water content or more negative matric potential), while coarser particles dominate the connectivity of the continuous capillary tubes at region 2 (higher water content or less negative matric potential). The insignificant contributions of silt fraction and bulk density to the \(b\) estimation were in agreement with other studies [Moldrup et al., 2007; Olesen et al., 2001; So and Nye, 1989].

The new \(\xi(\psi)\) model responds to the change of soil pore structure (revealed by \(b\) values) (Figure 3-7); therefore it has the capability to reflect the variation of \(\xi\) with liquid phase distribution, for which most empirical \(\xi(\theta)\) models can not provide. Overall, the \(b\)
value in this model plays the role of reflecting soil texture and liquid phase distribution
serve as diffusive pathway.

Figure 3-7. The sensitivity of $\xi(\psi)$ model to the soil-water retention parameter, $b$.

3.4.3 Model Modification for Application

Having acknowledged the influence of model parameters on the $\xi(\psi)$, we further
sought the possibility to simplify the model for wider application while reducing the
laboratory work.

Firstly, we tested the hypothesis of setting $\theta' = \theta_s$. The derived RMSEs are equal to
0.0020, 0.0122 and 0.0016, respectively, for the sand, sandy clay loam, and clay soils.
These RMSEs are comparable with those RMSEs derived from the best fitting (Table 3-2).
Secondly, we proposed that $\chi_1$ can be represented by a single value because it is less
influential to the model accuracy. $\chi_1$ values are tested ranging from 1.0 to 4.0. Sensitivity analysis shows that $\chi_1 = 3.0$ can still provide a reasonable overall predictive capability (Table 3-3). Therefore, we simplified the $\zeta(\psi)$ model as:

For $\xi \leq 0.01$, $\xi = 10^{-3/2} \left[1 - \left(\frac{\psi_a}{\psi}\right)^{1/2}\right]$ (3.11)

For $\xi \geq 0.01$, $\xi = \xi^* \cdot 10^{-1.8} \left[1 - \left(\frac{\psi_a}{\psi}\right)^{1/2}\right]$ (3.12)

when $\psi = 0$, $\xi = \xi^*$ (3.13)

where the $b$ value is estimated by Eq.(3.10). After simplification, the required measurements in this model to predict $\xi$ are: the tortuosity factor at saturation ($\xi^*$), matric potential at air entry ($\psi_a$), and porosity (or bulk density). Figure 3-4 showed the use of simplified model [Eq. (3.11) - (3.13)] to fit the experimental data.

Table 3-3. RMSE values of the $\chi_1$ sensitivity test (Summary).

<table>
<thead>
<tr>
<th>$\chi_1$</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.0036</td>
<td>0.0028</td>
<td>0.0022</td>
<td>0.0018</td>
<td>0.0016</td>
<td>0.0016</td>
<td>0.0016</td>
</tr>
<tr>
<td>Sandy clay loam</td>
<td>0.0121</td>
<td>0.0120</td>
<td>0.0120</td>
<td>0.0120</td>
<td>0.0121</td>
<td>0.0121</td>
<td>0.0122</td>
</tr>
<tr>
<td>Clay</td>
<td>0.0021</td>
<td>0.0018</td>
<td>0.0016</td>
<td>0.0015</td>
<td>0.0014</td>
<td>0.0013</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

In order to verify the applicability of the new $\xi(\psi)$ model [Eq. (3.11)-(3.12)], we tested it by Mehta et al.’s [1995] experimental data (Figure 3-8). Their soil physical
properties are summarized in Table 3-4, among which the $b$ value is calculated by Eq. (3.10), and the saturated soil-water content ($\theta_s$) is approximated by the total porosity based on the derived bulk density and assumed soil particle density of 2.65 g cm$^{-3}$. Because the air entry matric potential ($\psi_a$) and the tortuosity factor at saturation ($\xi^{*}$) are not attainable, we assumed $\psi_a$ to be -20 cm-H$_2$O for both soils which is the less negative matric potential applied in Mehta et al.’s [1995] study. The corresponding $\xi$ of 0.30 and 0.17 at less negative matric potential for the dune sand and the loam respectively are assumed to be the $\xi^{*}$ values. Although the actual $\xi^{*}$ and $\psi_a$ values are not available, the new $\xi(\psi)$ model [Eq. (3.10)-(3.12)] seem to provide an overall satisfactory prediction.

Table 3-4. Soil physical properties of Mehta et al.’s [1995] and the estimated values of $\xi^{*}$ and $\psi_a$.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Sand %</th>
<th>Clay%</th>
<th>Bulk density</th>
<th>$b$ [Eq.(3.10)]</th>
<th>$\theta_s$</th>
<th>$\xi^{*}$</th>
<th>$\psi_a$ (cm-H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dune sand</td>
<td>93.3</td>
<td>5.7</td>
<td>1.40</td>
<td>1.9</td>
<td>0.47</td>
<td>0.30</td>
<td>20</td>
</tr>
<tr>
<td>Loam</td>
<td>60.4</td>
<td>17.4</td>
<td>0.76</td>
<td>3.0</td>
<td>0.71</td>
<td>0.17</td>
<td>20</td>
</tr>
</tbody>
</table>
Figure 3-8. Experimental data of Mehta et al.'s [1995] predicted by the new simplified $\xi$ ($\psi$) model [Eq. (3.10)-(3.12)].

3.5 Conclusion

Our measured soil-water retention data were well described by the Campbell soil-water retention model. Our three test soils all showed a two-region log ($\xi$) vs. $\theta$ linear behavior. Currently, the prediction of the solute diffusion tortuosity factors and consequently, the solute diffusion coefficients in unsaturated soils are mostly based on soil-water content and bulk density. However, our previous research (Chapter 1) indicated that such models cannot accurately predict the solute diffusion coefficients for
soils of different textures. The new $\xi(\psi)$ model, a linkage of two-region $\log(\xi)$ vs. $\theta$ linear behavior with the Campbell soil-water retention model, improves the existing tortuosity factor predictive models. It uses the Campbell soil-water retention parameter ($b$), which incorporates soil texture information (sand and clay fraction) and makes it possible to better predict the solute diffusion coefficients for different soil types. It has compatible predictive capability with previous empirical models while reduces the uncertainty in estimating the model constants. When we compare predictive capability of the new $\xi(\psi)$ model with that of the present tortuosity factor models (Chapter 1), the new $\xi(\psi)$ model generated the lowest RMSEs of the three test soils. It also incorporates the soil physical properties that influence $\xi$. The use of $\psi$ instead of $\theta$ as the variable in the model directly incorporates the soil pore structural properties, which is an advantage that the $\theta$-based empirical models do not have.

Although our model has only been examined by the repacked soils, the mathematical equation should be applicable to both aggregated soils and undisturbed soils as well. Because the two-region linear $\log(\xi)$ vs. $\theta$ relationship was also found in the aggregated soils [Hamamoto et al., 2009], and earlier studies suggested that the measured $\xi$ from repacked soils are compatible with those from undisturbed soils. The only uncertainty in applying this model to aggregated soils is the determination of $\xi'$, due to the effect that the intra-aggregate liquid phase distribution on $\xi'$ in the aggregated soil is not clear. In the mean time, there is very limit information about $\xi^*$ (tortuosity factor at 100% saturation degree) in the literature. Thus further studies should focus on $\xi^*$ and its relationship with basic soil physical properties to enhance the model applicability and to
reduce the time-consuming laboratory measurements. Studies on interfacial area, interaggregate pendular rings, and ξ conceptual models are suggested to be included in determining the ξ* and ξ’ (separation of region 1 and region 2). Furthermore, it is also desirable to exploring the potential to apply this model to account for the effect of soil-water retention hysteresis on ξ.

In addition, the new ξ(ψ) model requires only basic soil physical properties such as: porosity (or bulk density), clay and sand mass fraction. People from broad subject areas will be able to apply this model to predict solute diffusion coefficient in soils of various degrees of saturation.
3.6 References


General Conclusion

Solute diffusion in unsaturated soils refers to the transport of dissolved constituents in liquid phase from a higher to a lower concentration point. This concentration-gradient driven process in soil is described by the Fick’s equation for chemical diffusion in free water multiplied by a tortuosity factor that accounts for the flux reduction in soil. Several empirical and conceptual models were proposed to predict the solute diffusion tortuosity factor in unsaturated soils; however, they were not systematically tested and evaluated under the same conditions using soils of different textures.

We conducted a set of diffusion experiments using three soils: a sand, a sandy clay loam and a clay, to access the strength and weakness of these models in terms of predictive capabilities, conditions of applicability, and requirements of input parameters. Our experimental data show that the test sand soil is best described by a quadratic function of volumetric soil-water content. The addition of bulk density and particle-size distribution to this model to estimate empirical constants has limited contribution to improve the model predictive capability for the test sand soil. The test sandy clay loam and clay soils are best described by a power function of soil-water content and porosity (or refers to the widely known Millington and Quirk model). Inclusion of bulk density and soil-water retention parameter to this model to estimate empirical constants improves the predictive capability for the test sandy clay loam and clay soils.

The conceptual approach model provided physical interpretation of the solute diffusion behavior in soils but has limited capability in application. It illustrated that the
diffusive pathway at lower soil-water contents is comprised by the series arranged soil-water pores and films; while at higher soil-water contents it is in a more comprehensive arrangement.

Overall, we conclude that there is no perfect model that can depict the behavior of solute diffusion tortuosity factor in soil at ranging soil-water contents across soil textures. Tortuosity factor as a function of soil-water content was observed to have a two-region behavior.

Many studies have proved that solute diffusion in soil is under the influence of both soil-water content and matric potential. Soil-water content indicates the amount of available diffusive pathway and matric potential reveals the arrangement of the available diffusive pathway. However, there was little information available about the impact of soil-water content/matric potential hysteresis on solute diffusion. We conducted experiments to obtain tortuosity factors at given soil-water contents reached by both wetting and drying processes. Firstly, the three test soils all showed the unequal soil-water content at a given matric potential when a soil is subjected to drying or wetting process (soil-water retention hysteresis). Secondly, we found that this soil-water retention hysteresis has substantial impact on solute diffusion tortuosity factor (solute diffusion hysteresis).

Overall, the measured tortuosity factors of drying are greater than those of wetting at a given soil-water content in certain soil-water content range. When fitted the solute diffusion coefficients of drying and wetting limbs by aforementioned predictive models,
the drying limb is better described by a power function of soil-water content with empirical constants estimated by particle-size distribution and bulk density; while the wetting limb is better described by a conceptual model which assumes that the solute diffusive pathway is comprised by serial arrangement of pore water and film water. Hysteresis in tortuosity factor is not a random phenomenon. We further found that the tortuosity factor of wetting at a given soil-water content can be predicted by the tortuosity factor of drying at the same soil-water content multiplied by that volumetric soil-water content.

Researches about microscopic investigation of liquid phase distribution in soil provide explanations to our experimental observations. It shows that the diffusive pathway at lower soil-water content is formed in meniscus form. As soil-water content increases, these meniscuses merge and form capillary tubes. The soil water intrudes through wetting process sequentially from relatively small pores to larger pores; while drains through drying process does not follow the same sequence. Therefore, due to the fact that the same amount of soil-water can form different diffusive pathways, hysteresis in solute diffusion is expected. Moreover, these two forms of soil liquid phase distribution patterns can also explain the observed two-region tortuosity factor to soil-water content relationship.

Since we noticed that the soil liquid phase distribution plays a role in solute diffusion tortuosity factor, we proposed a new model that incorporates more details about soil-water distribution in the model. Instead of soil-water content, the new model uses matric
potential as the variable, which directly includes the soil particle-size distribution and soil-water distribution status, to enhance the model predictive capability.

The new model is developed by linking the found significant two-region linear relationship of the soil-water content versus logarithm tortuosity with the Campbell soil-water retention model. The matric potential based new model has compatible predictive capability with aforementioned empirical models while reduces the uncertainty of empirical constants estimation. Moreover, the new model can be applied to soils of different textures and different degrees of aggregation. Our future research will explore the potential to apply this model to account for the impact of soil-water retention hysteresis on solute diffusion tortuosity factor.