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Characterizing the Diffusive Transport of Stable Water Isotopes in Unsaturated Soils

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ABSTRACT
Two phase transport of the stable isotopes of water has been presented by many authors, but these studies tend to not include a detailed investigation on the volumetric water content dependencies of two phase diffusive transport. Here, a common model for two phase diffusive transport, synthesized from isotope and gas diffusion literature, is combined with tortuosity models for aqueous and vapour transport. The goal of this study is to find tortuosity models that provide the best fit to observed diffusion data collected from unsaturated double half-cell diffusion tests.

RÉSUMÉ
Le transport en deux phases des isotopes stables de l'eau a été présenté par de nombreux auteurs, mais ces études ont tendance à ne pas inclure une investigation détaillée des dépendances de la teneur volumétrique en eau du transport diffusant à deux phases. Ici, un modèle commun pour le transport diffusant à deux phases, synthétisé à partir de la littérature sur la diffusion des isotopes et des gaz, est combiné à des modèles de tortuosité pour le transport de l'eau et de la vapeur. Le but de cette étude est de trouver les modèles de tortuosité qui correspondent le mieux aux données de diffusion observée recueillies à partir d'essais de diffusion de demi-cellules doubles insaturées.

1 INTRODUCTION

Stable isotopes of water have been applied extensively to track water flow processes in unsaturated soils including infiltration, evaporation and deep percolation or recharge. For example, Allison et al. (1994), Dincer et al. (1974) and Cheng et al. (2014) used Isotope profiles to define recharge processes. Allison (1982), Allison et al. (1983), Wang and Yakir (2000) and Barnes and Allison (1988) also used Isotope profiles to estimate evaporation

The depths of peaks in the stable isotope profile associated with seasonal changes in the isotopic signature of recharge waters was employed by Adomako et al. (2010) to estimate the rate of recharge. In this method, the transport of the stable isotopes of water are idealized as piston flow. However, as these isotope peaks migrate deeper into the soil they become attenuated due to mechanical dispersion and diffusion. At great depths or long times, the large peaks seen clearly at the surface, are reduced to more diffuse, less pronounced fluctuations in isotopic composition (Bath et al., 1982). These "smoothed" out profiles can still be used to characterize historical recharge, evaporation, and transport processes (Cook et al., 1992) if the rates of diffusive/dispersion spreading can be characterized .

More detailed characterization of the diffusion process is required to extract more information from these deep isotopic profiles in unsaturated soil. Because of the free exchange of water between pore-air as vapour and liquid water, any characterization must account for transport through both vapour and aqueous phases. The objective of the study was to measure the variation of the Coefficient of Diffusion for stable isotopes of water with volumetric water content (θ_l). This measurement will then be compared to theoretical relationships for simultaneous aqueous and vapour phase diffusion in a dual phase diffusion model from the literature.

2 BACKGROUND

The most common isotopologue of water is $^1H_2{}^{16}O$, where ^1H and ^{16}O are the most abundant natural stable isotopes of hydrogen and oxygen. They make up 99.985 and 99.76 atom % of the atoms found in nature, respectively (Criss, 1999). Because the natural abundance of deuterium and oxygen 18 is extremely small (0.015% and 0.20%, Criss, 1999), the water isotopologue $^1H_2{}^{16}O$ is termed "regular" water while all other isotopologues containing ^2H and ^{18}O are referred to as stable isotopes of water.

The most fundamental method of reporting stable isotope concentrations is done by the isotope ratio R,

$$R = \frac{[\,^2H]}{[\,^1H]} \qquad [1]$$

The isotope ratio can be difficult to measure, and because it relies on the concentration of the most abundant isotope, standardization of isotope measurements is done by calculating isotope delta values (δ). The "del" values report the deviation of the measured isotope ratio, from a standard ratio, in thousandths (‰). The formula used to calculate the isotope delta value is (Fritz, 1997),

$$\delta = \left(\frac{R_{sample}}{R_{Standard}} - 1\right) 10^3 ‰\, VSMOW \qquad [2]$$

where R_{sample} is the isotope ratio of the measured sample and $R_{Standard}$ is the standard isotope ratio of Vienna

Standard Mean Ocean Water (VSMOW). The stable isotopes containing ^{2}H are denoted δD and those containing ^{18}O are denoted $\delta^{18}O$

Another important property of isotopes is isotope fractionation. When an isotopologue goes through a phase transition (e.g. evaporation) the lighter isotope is preferentially transferred to the lighter phase. For example when water evaporates, the water vapour will have a lower isotope concentration than its source water. Isotope fractionation for evaporating water is defined by (Fritz, 1997),

$$\alpha_{liquid-Vapour} = \left(\frac{1000+\delta_{liquid}}{1000+\delta_{vapour}}\right) \quad [3]$$

where δ_{liquid} is the isotope content in the aqueous phase (‰ VSMOW) and δ_{vapour} is the isotope content in the vapour phase (‰ VSMOW)

The diffusive transport of water molecules in either the gas or aqueous phases can be described Fick's First Law. For example, for isotope diffusion in a saturated soil, Fick's First Law can be written as Shackelford, 1991,

$$J_d = -n\tau D_0 \frac{\partial C}{\partial z} \quad [4]$$

where J_d is the diffusive flux in the soil (kg/m^2/s), n is the soil porosity (m^3/m^3), τ is the soil tortuosity factor (-), D_0 is the free solution diffusion coefficient (m^2/s), C is the isotope concentration (kg), and z is distance (m). In many cases, such as diffusive transport, isotope delta values can be used in place of concentrations (Hendry et al., 2011a).

Equation 4 includes a term describing the cross-sectional area through diffusion is occurring (n) and a term that defines the impact of pore-size geometry on rates of diffusion (τ). The τ factor might incorporate a number of factors such as those described by Shackelford (1991);

$$\tau = \left(\frac{L}{L_e}\right)^2 \alpha\gamma \quad [5]$$

where L_e is the actually path length for transport to cover a straight line distance of L within the soil (Shackelford and Daniel, 1991), α is a mobility factor, and γ is an anion exclusion factor. Since it is often difficult to measure each of these factors separately they are most commonly lumped into an estimated value of τ.

Fick's First Law (Equation 4) can be extended to unsaturated soils using volumetric fluid contents in the place of n and a τ which is water content dependent. For example, Lim et al. (1998) described τ as a function of θ_l or the degree of saturation.

When addressing isotope diffusion in unsaturated soils, the partitioning (i.e. fractionation) of the stable isotopes of water between the vapour and aqueous phases must be incorporated into the transport equations. Transport equations for isotope advection and diffusion in two phases are presented by many authors including Shurbaji and Phillips (1995), Melayah et al. (1996), Mathieu and Bariac (1996), Braud et al. (2005), and Haverd and Cuntz (2010). The isotope transport studies have many parallels to gas diffusion literature (Aachib et al., 2004, Aubertin et al., 2000, Šimůnek and Suarez, 1993, and Mbonimpa et al., 2003). The difference between the two study types is the relative storage properties for each solute in question. While the isotopes and gas diffuse faster in the vapour/gaseous phase, isotopes have a larger storage in the aqueous phase, whereas gas studies have most of the mass stored in the gas phase.

The focus of the two areas of study is different as well. The isotope literature tends to focus on advective dominated transport near the ground surface as a result of recharge or evaporative processes. The gas transport literature tends to focus on diffusion through unsaturated soils, with less emphasis on surficial boundary conditions. The focus of two phase gas diffusion has led authors to study which τ models will best match the observed experimental data considering transport in two phases simultaneously.

3 METHODOLOGY

In this study, a theoretical framework for two phase diffusive transport of the stable isotopes of water is developed which is consistent with the existing stable isotope of water and gas transport (e.g. oxygen, carbon dioxide) literature. This theoretical description is then used to evaluate the impact that the varying models of gas phase and aqueous phase τ will have on the diffusion coefficient for the stable isotopes of water. These predictions are then compared to coefficients of diffusion for δD as measured in a double half-cell diffusion test.

3.1 Governing Equation

The governing equation for two-phase diffusive transport is derived by combining the gas phase concentrations with the aqueous phase concentrations to create an equivalent aqueous phase concentration. The relationship between the two-phase concentrations is,

$$H = \frac{C_v}{C_l} \quad [7]$$

where C_v is the vapour phase concentration (kg/m^3), C_l is the aqueous (liquid) phase concentration (kg/m^3), and H is derived by Braud et al. (2005) as,

$$H = \alpha\frac{\rho_v}{\rho_l} \quad [8]$$

where α is the equilibrium fractionation factor (Majoube, 1971) between water and water vapour (-), ρ_v is the density of water vapour (kg/m^3), ρ_l is the density of liquid water (kg/m^3) and all factors are temperature dependent. The total isotope flux is the sum of the fluxes in each individual phase. These fluxes can then be substituted into the continuity equation, and by applying the partitioning relationship, the following governing equation (Fick's Second Law) can be written,

$$\frac{\partial C_l}{\partial t} = \frac{D^{lv}}{\Theta}\frac{\partial^2 C_l}{\partial x^2} \qquad [9]$$

where D^{lv} is the combined phase diffusion coefficient (m^2/s) and Θ is the combined storage term (m^3/m^3). D^{lv} and Θ are found in Equations 10 and 11.

$$D^{lv} = \theta_l \tau_l D_l^0 + H\theta_v \tau_v D_v^0 \qquad [10]$$

$$\Theta = \theta_l + H\theta_v$$

[11]

where θ_l and θ_v are the volumetric water and air contents (m^3/m^3), D_l^0 and D_v^0 are the free solution diffusion coefficients of isotopes in liquid and vapour (m^2/s), and τ_l and τ_v are the tortuosity factors for the aqueous and vapour phases (-). This derivation is consistent with two-phase isotope and two phase gas diffusion studies, but it is important to note that H is applied to the aqueous phase in gas diffusion studies.

The D_0 for the isotopes in water can be determined by theoretical formulae or by experimental relationships developed by various authors. To estimate D_0 in the liquid phase, the relationships presented by Easteal et al. (1984) were used. The temperature dependent relationship has the polynomial form,

$$10^9 D_l^0 = exp\left(a + b\left(\frac{1000}{T}\right) + c\left(\frac{1000}{T}\right)^2\right) \qquad [12]$$

where a, b, and c are fitting parameters (Table 1) and T is the temperature (K).

Table 1. Fitting parameters for the D_0 relationship for aqueous phase δD

Parameter	Value
a	1.62444965
b	1.72986727
c	-0.587098179

The relationship presented by Melayah et al. (1996) will be used to estimate D_0 in the vapour phase. The relationship is,

$$D_v^0 = D_v\left(\frac{D_v^0}{D_v}\right)^{n_d} \qquad [13]$$

where D_v is the free solution diffusion coefficient of water vapour in air (m2/s), $\left(\frac{D_v^0}{D_v}\right)$ is the diffusivity ratio of isotopically labeled water and regular water (Merlivat, 1978), and n_d is an exponent relating to the flow conditions (Braud et al., 2005) of the vapour (n_d = 1 for molecular diffusion). D_v is found from Kimball et al. (1976) where,

$$D_v = 0.0000229\left(1 + \frac{T}{273}\right)^{1.75} \qquad [14]$$

With the volumetric fluid contents and D_0 defined, an appropriate τ model must then be selected to determine the two-phase diffusion model for δD.

3.2 Tortuosity Models

The τ models available for aqueous solute diffusion in unsaturated soils are limited. A model used to express the aqueous phase τ - water content relationship is Padilla et al. (1999),

$$\tau_l = \tau_{sat}\left(\frac{\theta_l}{n}\right) \qquad [15]$$

where τ_{sat} is (Boudreau, 1996),

$$\tau_{sat} = (1 - 0.5\ln(n))^{-1} \qquad [16]$$

The Millington and Quirk (1961) model has been successfully applied to gas phase diffusion and adapted to aqueous phase studies with a good fit to sand diffusion data (Moldrup et al., 2003). The model is,

$$\tau_l = \frac{\theta_l^{\frac{7}{3}}}{n^2} \qquad [17]$$

A final, commonly used aqueous phase model is the Kemper and Van Schaik (1966) model. This model uses an empirical power law fit to observed data. The applicable range for the relationship is for suctions from approximately field capacity (33kPa) to wilting point (1500kPa) (Olsen and Kemper, 1968), which causes the model to breakdown at low θ_l (~0.15). This model is not appropriate for medium to coarse textured soils such as those tested in this study but is better suited to clayey soils.

Gas and vapour transport in unsaturated soils has been presented with a similar theoretical framework as for solute transport in unsaturated soils. The difference between the two phases studied is the τ effects. Many more studies have been completed on gas phase τ's (Buckingham, 1904, Millington, 1959, Millington and Quirk, 1961, Marshall, 1959, Penman, 1940, Collin and Rasmuson, 1988, and Moldrup et al., 2000b) and can be applied to diffusion. Some of the best fit models to observed data, determined by Moldrup et al. (2000a) are the Penman (1940) and Millington (1959) models.

Moldrup et al. (2000a) investigated the models further and found that, if a linear reduction was added to each, the model fit observed diffusion values with a higher degree of accuracy. The linear scaling was done based on θ_v over the total soil n. The final linearly reduced form of the Penman (1940) and Millington (1959) can be found in Equations 18 and 19,

$$\tau_v = 0.66\left(\frac{\theta_v}{n}\right) \qquad [18]$$

$$\tau_v = \theta_v^{\frac{1}{3}}\left(\frac{\theta_v}{n}\right) \qquad [19]$$

In addition to the single-phase models, two-phase τ's have been applied to transport of a phase partitioning solute. Aachib et al. (2004) applies a dual phase models to oxygen gas diffusion in unsaturated cover soils. The model of Aachib et al. (2004) is a modified Millington and Shearer model (Collin and Rasmuson, 1987 and Collin and Rasmuson, 1988) and is presented in Equations 20 and 21,

$$\tau_v = \frac{{\theta_v}^{2x+1}}{n^2} \quad [20]$$

$$\tau_l = \frac{{\theta_l}^{2y+1}}{n^2} \quad [21]$$

with x and y as the solutions to Equations 22 and 23.

$${\theta_v}^{2x} + (1-\theta_v)^x = 1 \quad [22]$$

$${\theta_l}^{2y} + (1-\theta_l)^y = 1 \quad [23]$$

A second dual-phase model has been developed by Moldrup et al. (2003) where the τ for each phase is described with fitting exponents, and has a similar form to the gas phase models presented earlier. The equation for the tortuosity for each phase is,

$$\tau_v = {\theta_v}^{T-1}\left(\frac{\theta_v}{n}\right)^W \quad [24]$$

$$\tau_l = {\theta_l}^{T-1}\left(\frac{\theta_l}{n}\right)^W \quad [25]$$

where T and W are fitting parameters based on phase, soil status (repacked or undisturbed) and the particle size distribution of the soil (Moldrup et al., 2003). The T parameter for the vapour and aqueous phases were taken as 1.5 and 2, and W as 1 and 1/3 respectively. The vapour phase model has the same form as the Marshall (1959) τ model and the aqueous phase has the same form as the Buckingham (1904) model, but each contains with a water content scaling factor.

The models presented are summarized in Table 2, along with an abbreviated name used to denote each model in subsequent figures. Figures 1 and 2 show the τ models plotted against θ_l (assuming a total soil n of 0.4).

Table 2. Aqueous and vapour phase τ models to compare with observed diffusion

Model	Name	Eqn #	Phase
Padilla et al. (1999)	PD	15	Aqueous
Millington and Quirk (1961)	MQ	17	Aqueous
Aachib et al. (2004)	AC	21	Aqueous
Moldrup et al. (2003)	ML	25	Aqueous
Penman (1940)	PN	18	Vapour
Millington (1959)	MI	19	Vapour
Aachib et al. (2004)	AC	20	Vapour
Moldrup et al. (2003)	ML	24	Vapour

The aqueous phase models presented (Figure 1) all show a similar saturated τ value of about 0.7 (which is approximate for sand Penman, 1940 and Currie, 1960), with the exception of the ML model that ends at 0.4. The MQ and AC models show a similar trend and are almost indistinguishable near soil saturation. As the soils desaturate the MQ model tends to provide a lower estimate of τ. Finally, the PD model has no curvature, resulting in an estimate of τ which is higher at lower water contents when compared to the other models.

The vapour phase models (Figure 2) all have an air saturated τ between 0.63 and 0.74, which is appropriate for sand. The different models for the vapour phase have a relatively similar shape when compared to the aqueous phase. The AC and ML models show a lower τ at a higher θ_l when compared to the PN and MI models, but AC reaches a higher value at full dryness (e.g. θ_l = 0). All models but the PN model are non-linear, but when compared to the aqueous phase, the deviation of the linear model from the non-linear ones is not as large.

3.3 Data collection

To select which τ model(s) are the most appropriate for δD diffusion in unsaturated soils, D^{lv} must be measured over a range of θ_l. The experimental method that was used was the double half-cell diffusion tests similar to Van Rees et al. (1991), Patil et al. (1963), and Shackelford (1991). A diffusion cell is composed of two half-cells, where one side is spiked with an elevated concentration and the other is not. The two half-cells are joined and diffusion as allowed to occur.

Each half cell was constructed out of 101.6mm diameter PVC pipe, and was 200mm in length. A PVC cap was glued onto one end to seal the soil and water in the pipe. Each cell was composed of one δD tagged (~-50‰) half-cell and one untagged with tap water (~-120‰). The sand, water, and isotope (where required) were mixed in a bowl and packed into a half-cell in multiple lifts and the sides of the cell tapped to densify the sand. Once each half cell was packed two half-cells were placed together and a PVC collar glued in the middle to avoid water evaporation. Sand was left protruding out the cells by a small amount to ensure a connection between the two half-cells. Some of the limitations of this experimental method are the effects of water evaporation and particle segregation during mixing of the soil, and packing it into the half-cells.

The mass of sand for each cell was selected to yield a porosity of 0.4. Water content ranges were based on, a minimum θ_l of 8% (Wassenaar et al., 2008) when n = 0.4, and a maximum of saturation.

Ten cells were constructed and analyzed in two testing rounds. Each cell was allowed diffusion at ambient lab temperature (approximately 25°C) between two weeks to one month. The time for test termination was selected from a test cell that gave an indication of how far diffusion had progressed to that point.

Cell analysis was started by slicing the entire cell into 20 mm sections with a band saw and analyzing the θ_l, δD and $\delta^{18}O$ content, and on the second round of cells, an estimate of bulk density. The $\delta^{18}O$ profiles were used in this experiment to monitor water evaporation in the cells.

Isotope profiles were measured using the vapour equilibration method of Wassenaar et al. (2008). The delta values were normalized based on the input high and low isotope values. The data was normalized to allow the application of analytical solutions to fit the data and provide an easier method of representing isotope concentrations in two phases. A typical diffusion cell profile can be found in Figure 3.

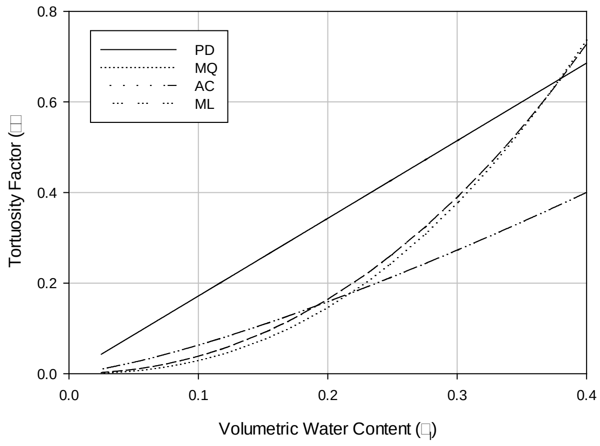

Figure 1. Tortuosity (τ) models for the aqueous phase

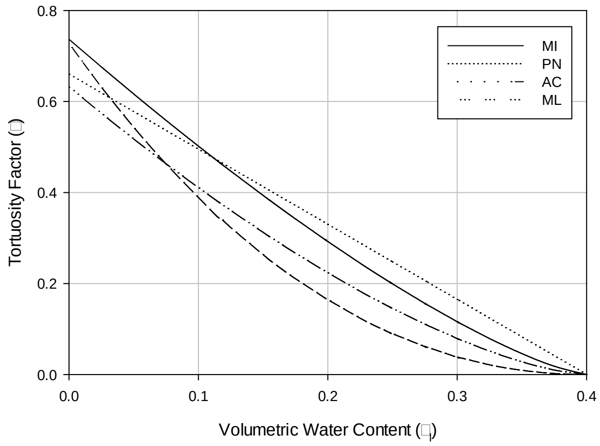

Figure 2. Tortuosity (τ) models for the vapour phase

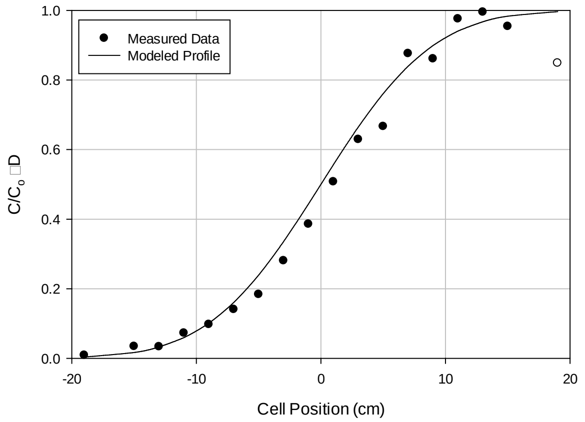

Figure 3. Typical diffusion cell profile with best fit model. From testing round 2, θ_l = 0.35. All measured data points fit with the modeled profile except for an outlying point (19cm position) which appears to be an erroneous value. Erroneous values such as this were used in the fit of the analytical solution.

When analysis was completed for test round 1, the tagged half-cell concentrations produced a poor fit to the observed cell data. After checking the water content and $\delta^{18}O$ profiles it was concluded that the difference in δD concentrations present in the tagged half-cell could not be due to water loss during testing. The difference in concentrations observed was attributed to isotope mixing with the sand that was not foreseen. To overcome the mismatched concentration limits, an appropriate spike value was selected that would give profile symmetry about the center of the cell, rather than assuming an initial normalized concentration of one on the tagged side.

D^{lv} values were determined for each cell using a least squares fit of the Ogata and Banks (1961) analytical solution. "D" in the Ogata and Banks (1961) solution was used as the free parameter for fitting. The D values collected from the experiments are numerically equal to D^{lv}/Θ, due to the form of the governing equation presented (Equation 9). Once the data was fitted to the analytical solution (Figure 3), the combined storage term was multiplied to the best fit value, to obtain D^{lv} at that water content. The data collected from the two rounds of diffusion testing is presented in Table 3.

The collected data points can be found in Figure 4. Error bars for the diffusion values collected were selected based on fitting the analytical solution to each half-cell. Comparing the error bars in Figure 4 to the profile in Figure 3, the observed data from -20cm to 0cm has a better fit to the model compared to 0cm to 20cm position. The better fit on the negative side of the cell can be seen in the asymmetrical, different length error bars (Figure 4). The observed water contents and $\delta^{18}O$ isotope profiles suggested that the water content variation within the cells was minimal, and also showed that water evaporation had not occurred.

3.4 Data and Model Comparison

Combining the four aqueous and four gas phase tortuosity models with the D^{lv} formula, 16 potential diffusion models were created. Each diffusion model was named according to the aqueous model then the gas model used. Table 4 shows the Root Mean Square Error (RMSE) between each model and all of the observed diffusion values.

Table 3. Water content and observed D^{lv} values for double half-cell diffusion tests completed

θ_l	Test Round	D^{lv} (x 1E-10 m^2/s)
0.115	1	1.577
0.156	1	1.878
0.197	1	2.007
0.238	1	3.912
0.276	1	2.492
0.117	2	3.684
0.165	2	3.476
0.249	2	3.314
0.350	2	5.330
0.301	2	3.889

The three models that produced the lowest RMSE values are compared to the measured data in Figure 4. All best fit models used the Padilla et al. (1999) τ for the aqueous phase. The τ_{sat} model used for the RMSE comparison was selected as the one that gave the lowest absolute RMSE when compared to the τ_{sat} models available in Boudreau (1996). Other models had RMSE values that were lower on average, but were not used in favor of the best fit overall.

Table 4. RMSE between 16 presented models and observed diffusion data

Model	RMSE (x 1E-10)	Model	RMSE (x 1E-10)
PD – MI	0.971	AC – MI	1.299
PD – PN	0.959	AC – PN	1.238
PD – AC	1.064	AC – AC	1.536
PD – ML	1.004	AC – ML	1.425
MQ – MI	1.469	ML – MI	1.566
MQ – PN	1.402	ML – PN	1.500
MQ – AC	1.705	ML – AC	1.783
MQ - ML	1.594	ML - ML	1.678

The two best fit models (PD – MI and PD – PN) showed a similar RMSE and a gas phase τ that has a similar shape to the aqueous phase. This observation suggested the τ relationship for the isotopes in unsaturated soils is symmetrical between the aqueous and vapour phases.

Each diffusion model is composed of an aqueous phase diffusion model added to a vapour phase diffusion model. If the components of D^{lv} are plotted with the observed data (Figure 5), additional information of the diffusive transport may be extracted. If the phases present in the soil become discontinuous at a point that is not near residual fluid content, transport in only one phase may occur.

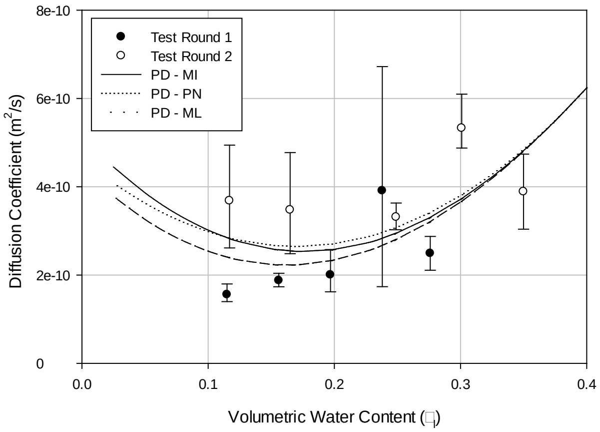

Figure 4. Observed data compared to 3 models showing lowest RMSE

The singular phase transport may be due to the packing method that was chosen for the diffusion cells. By packing the cells with mixed sand and water, a uniform water content could be achieved. However, this led to unnatural water distribution within the soil matrix. The well distributed water did not allow for natural drained channels or pathways to form, potentially giving disconnected fluid phases where they should be connected.

4 CONCLUSIONS

From the comparisons made, the Padilla et al. (1999) aqueous phase τ model in combination with either the Penman (1940) or the Millington (1959) vapour phase model (with the inclusion of the linear reduction term) provide the best fit to the shape of the observed diffusion data collected. The similar shape between the Padilla et al., 1999 and the Penman (1940) models indicates that the τ between the two phases is symmetrical and that the soils share a similar saturated τ value (water or air).

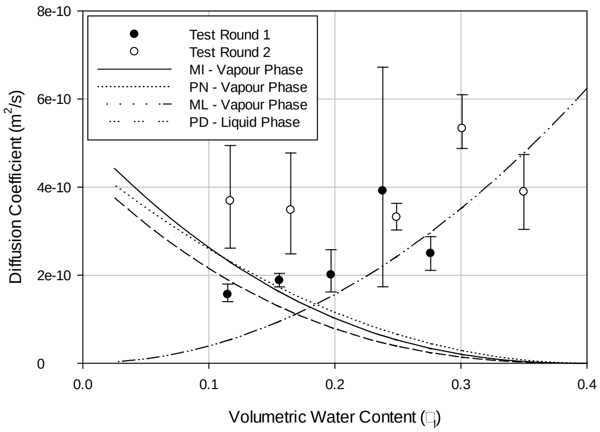

Figure 5. Observed data compared to 3 models showing lowest RMSE, where diffusion model is broken down into individual phase components

The individual phase diffusion models indicate that a modified testing procedure may be required to capture the drained pathways that would be encountered in natural systems. Creating drained diffusion cell presents its own challenges, as water content variations within the cells becomes harder to control. Additional drained cells are needed to produce observed D^{lv} values with higher confidence to compare to different diffusion models. Along with drained cells, measurements of diffusion at fluid saturations (θ_l = 0 and θ_{sat}) should be conducted to anchor the diffusion models at points where only one phase is contributing to diffusive transport.

The double half-cell method used has several limitations that should be overcome to provide more reliable diffusion data. Isotope concentrations may change during sample cutting and transport, density and water content variations may induce some advective transport. While these effects are monitored in laboratory testing, not all effects can be accounted for leaving some degree of error in the measurements.

All of the scaled models allow diffusion to occur all the way to zero saturation (either water or air), which may not be appropriate in all cases. Each of the scaled τ models can be rewritten using a normalized saturation, which causes diffusion to cease at the residual water content for aqueous movement, and at saturation for the vapour phase movement (assuming $\theta_{sat} = n$).

Based on the results of this study, analysis of deep, highly diffuse unsaturated isotope profiles may begin.

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