THERMAL PROPERTIES FOR PEATY SOIL UNDER VARIABLE SATURATION AND THEIR CORRELATION TO MASS TRANSPORT PARAMETERS IN GASEOUS AND AQUEOUS PHASES

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ABSTRACT

A thorough understanding of the various heat and mass transport processes inside peaty soils is vital for assessing and simulating the greenhouse gas emissions, especially methane from the wetlands. This doctoral work is presented in three main studies that include new laboratory measurements on the key soil heat and mass transport properties (for heat, gas, and water movement) on different peats from Japan and Sri Lanka (under moisture conditions ranging from wet to dry), the development of new descriptive and predictive parameters models including a unified model approach for heat, and gas, and water transport properties built on the classical Archie (1942) model, testing and validation of the predictive models on both dependent and independent data sets, and introducing the concept of “most likely windows” for heat and mass transport parameters in variably saturated peat soils; the latter for examples highly useful for predicting the most likely effects of peat and wetland areas (including the effects of planned changes in area use and land management) in local-, continental-, and global-scale climate simulation models.

KEYWORDS: Peaty soil, Heat and Mass Transport, Soil Physical Properties

1. INTRODUCTION

Wetlands are recognized as a significant element in the natural environment. The wetland is also known as a source of atmospheric methane, typically produced by microbiological and chemical processes under anaerobic conditions. Physical, chemical and biological processes inside the wetland are depending on the heat and mass transfer processes in the soil. Thus the knowledge of mass and heat transport characteristics is important for accurate assessments of the environmental functions of the wetland and developments, hereunder understanding and simulating the emissions of the greenhouse gases from the wetlands.

Peaty soil can be found in many types of wetlands. Peat is one of several biolites and its properties can be varying even for samples from adjacent part of a wetland (Tuncer et al., 1986). Peat contains high organic matter content, resulting in high water holding capacity (Hobbs, 1986) and high total porosity around 90%. Volume shrinkage during drying processes is also an important characteristic found in peaty soils (Oleszczuk and Brandyk, 2008).

1.1 Heat and Mass Transport in Peaty Soils

Heat transport in the soil is mainly governed by soil thermal properties such as thermal conductivity (\(\lambda\)) and the volumetric heat capacity (C). Soil thermal conductivity refers to the ability of soil to conduct heat. Thermal conductivity of a soil depends on volumetric properties of the soil components (i.e. organic matter, minerals, water and air content) and interfacial contacts between the liquid and solid phase (i.e. structural arrangement of the soil). Heat capacity is the quantity of heat required to raise the temperature of a unit volume of the substance, by one degree. This is governed by the relative proportions of soil constituents (e.g., air, water, mineral material and organic material) and the heat capacities of these constituents. Although, many studies have been conducted on thermal properties of mineral soils, there are only a limited number of studies done on thermal properties of peat soils which measured \(\lambda\) values for highly organic soils and forest litters including peaty soils (e.g., Konovalov and Roman, 1973; Sharratt, 1997; Lauren, 1997).

Gas transport in the soil is basically controlled by diffusive and advective gas transport processes. The gas diffusion coefficient, \(D_p\) (cm\(^2\) s\(^{-1}\)) governs diffusive gas transport by soil-gas concentration gradient while soil air permeability, \(k_a\) (µm\(^2\)) governs the advective gas transport induced by a soil-air pressure gradient. Many researchers have conducted studies on normal mineral soils and developed several empirical and theoretical predictive models on gas transport parameters. However, the studies reported on peaty
soils are very limited.

1.2 Objectives of this Study
To measure and characterize mass and heat transport parameters in peaty soils
To develop predictive models for transport parameters of peaty soils

2. MATERIALS AND METHODS
2.1 Study Site and Soils
Undisturbed peaty soil sample cores were collected from three different peaty soil profiles at Bibai marsh, Hokkaido in Japan for \( \lambda, D_p, k_a \) and \( k_w \) measurements. \( D_p, k_a \) and \( k_w \) data sets from previous studies on the same study site were also used in the analysis (Iiduka et al., 2008; Kawamoto et al., 2009; Dissanayaka et al., 2012).

The basic physical and chemical soil properties of the peaty soil samples are shown in Table 1. The fiber content \( H \) of the soil samples was measured by HCl washing method. The disturbed peaty soil samples were ignited in a muffle furnace at 700 \(^\circ\)C for 4 hours to determine the loss on ignition (LOI).

The carbon to nitrogen ratio (C/N ratio) and soil organic carbon (SOC) were determined using an automatic CHN analyzer (CHN corder MTL5, Yanaco, Kyoto). The pH for the extracted soil solution was weakly acidic for each sample. All soil samples were highly porous, showing total porosities at water saturation (Sat.) of more than 0.86 m\(^3\) m\(^{-3}\). The intact sample cores were initially water-saturated and subsequently drained to the desired pF \( = \log (\psi) \), (where, \( \psi \) is soil-water potential in cm H\(_2\)O) using either a hanging water column (pF = 0 - 1.9) or a pressure chamber (pF = 2 - 4.1). Air dry condition was achieved by drying the soil samples in an oven at 30\(^\circ\)C for three days and kept in a climate controlled room at 25\(^\circ\)C and a relative humidity of 60 % for three days (Dissanayaka et al., 2012). After achieving equilibrium at each pF condition, height, cross sectional area and weight of each sample were measured to determine volume shrinkage and volumetric water content (\( \theta \), m\(^3\) m\(^{-3}\)).

Table 1. Physical and chemical properties for soil samples

<table>
<thead>
<tr>
<th>Depth</th>
<th>Layer</th>
<th>Water content</th>
<th>Particle density</th>
<th>Dry bulk density</th>
<th>Saturated hydraulic conductivity</th>
<th>Total Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm</td>
<td></td>
<td>( w_f )</td>
<td>( \rho_s ) g cm(^{-3})</td>
<td>( \rho_b ) g cm(^{-3})</td>
<td>( k_s ) cm s(^{-1})</td>
<td>Sat. A.D. A.D.</td>
</tr>
<tr>
<td>Peat 1</td>
<td>10</td>
<td>H2</td>
<td>1211</td>
<td>1.42</td>
<td>0.10 0.12</td>
<td>3.68E-03 0.93 0.91 89.3 60.6 28.0 3.1</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>H3</td>
<td>573</td>
<td>1.49</td>
<td>0.21 0.41</td>
<td>3.96E-03 0.86 0.72 36.2 33.3 19.0 5.1</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>H3</td>
<td>592</td>
<td>1.37</td>
<td>0.16 0.44</td>
<td>3.69E-03 0.89 0.68 47.5 36.5 26.0 4.8</td>
</tr>
<tr>
<td>Peat 2</td>
<td>10</td>
<td>AH</td>
<td>283</td>
<td>2.63</td>
<td>0.32 0.89</td>
<td>5.75E-03 0.88 0.66 46.5 89.7 41.7 4.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>H1</td>
<td>697</td>
<td>1.86</td>
<td>0.11 0.29</td>
<td>3.94E-04 0.94 0.85 95.2 72.9 54.5 4.6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>H2</td>
<td>922</td>
<td>1.44</td>
<td>0.13 0.30</td>
<td>2.15E-03 0.91 0.79 94.4 86.6 81.3 4.6</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>H2</td>
<td>955</td>
<td>1.80</td>
<td>0.11 0.34</td>
<td>1.72E-03 0.94 0.81 94.6 72.8 85.0 4.3</td>
</tr>
<tr>
<td>Peat 3</td>
<td>30</td>
<td>H2</td>
<td>720</td>
<td>1.54</td>
<td>0.11 0.19</td>
<td>4.61E-04 0.93 0.87 91.2 64.8 28.8 4.6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>H2</td>
<td>833</td>
<td>1.52</td>
<td>0.10 0.22</td>
<td>2.79E-03 0.94 0.86 93.3 81.2 23.8 5.0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>H3</td>
<td>953</td>
<td>1.48</td>
<td>0.08 0.19</td>
<td>1.64E-03 0.95 0.87 84.5 81.6 28.5 4.8</td>
</tr>
</tbody>
</table>

\( \text{†} \) ref is defined as near-saturation, at or around pH 1.
3. THERMAL PROPERTIES OF PEATY SOILS: NEW MODELS

3.1 Model Development

Existing Models for Thermal Conductivity

The λ model proposed by de Vries (1963) considers volumetric fractions of each phase, weighting factors which are dependent on thermal conductivities of each phase (i.e., solid, water, and air), and the geometric shape of the soil particles. The de Vries (1963) model can be written in a general form as,

$$
\lambda = \frac{\theta \lambda_{sw} + k_s \lambda_s + k_w \lambda_{app}}{\theta + k_s \sigma + k_w \varepsilon}
$$

(1a)

$$
k_s = \frac{1}{3} \sum_{i=a,b,c} \left[ 1 + \left( \frac{\lambda_s}{\lambda_{app}} - 1 \right) g_i \right]^{-1}
$$

(1b)

$$
k_w = \frac{1}{3} \sum_{i=a,b,c} \left[ 1 + \left( \frac{\lambda_{app}}{\lambda_{sw}} - 1 \right) g_i \right]^{-1}
$$

(1c)

where, $\lambda_{sw}$ is the thermal conductivity of water, $\lambda_s$ is the thermal conductivity of the solid phase (e.g., organic matter), and $\lambda_{app}$ is the apparent thermal conductivity of air-filled pore space. The $\lambda_{app}$ is made up partly of normal heat conduction ($\lambda_a$) and partly of vapor movement ($\lambda_v$). $\theta$, $\sigma$, and $\varepsilon$ are the volumetric fractions of water, solids, and air, respectively. The $k_s$ and $k_w$ variables are the weighting factors for solid and air phases determined by $\lambda$ for each phase and geometric shape of the soil particles ($g_i$), $g_a$, $g_b$, and $g_c$ represent the depolarization factor of the ellipsoid in the direction of the a-, b-, c-axis, respectively, satisfying $g_a + g_b + g_c = 1$. For highly porous materials such as peaty soils, de Vries (1963) assumed the existence of continuous air-filled pore-networks at $\varepsilon > 0.5$ and considered the soil system as volume of air with long circular cylinders of wet peat included. At $\varepsilon > 0.5$, the following equations for a predictive λ model were suggested,

$$
\lambda = \frac{\varepsilon \lambda_{app} + k_w \lambda_{sw}}{\varepsilon + k_w \lambda_{sw}}
$$

(2a)

$$
\lambda_{sw} = \frac{\theta \lambda_{sw} + k_s \lambda_s}{\theta + k_s \sigma}
$$

(2b)

$$
k_{sw} = \frac{1}{3} \sum_{i=a,b,c} \left[ 1 + \left( \frac{\lambda_{sw}}{\lambda_s} - 1 \right) g_i \right]^{-1}
$$

(2c)

where, $\lambda_{sw}$ and $k_w$ were the $\lambda$ and weighting factor for the solids and water mixture, respectively. de Vries (1963) also suggested using $\lambda_v$ instead of $\lambda_{app}$ for peaty soil in dry conditions ($\theta < 0.1$) and estimated the $\lambda$ for Fairbanks peat (a fibrous brown peat) using the above two-region model, showing good agreement with the experimental data.

Campbell (1985) proposed an empirical equation for estimating thermal conductivity of soil,

$$
\lambda = A + B \theta - (A - D) \exp\left[ - (C \theta)^E \right]
$$

(3)

where, $A$, $B$, $C$, $D$, and $E$ are parameters dependent on soil physical properties.

Becker et al. (1992) developed empirical correlations for predicting soil thermal conductivity as a function of the degree of water saturation and dry bulk density based on measured $\lambda$ data for soils with different soil textures. The proposed $\lambda$ model can be written as,

$$
S = k \left[ \sinh (k_2 \lambda + k_3) - \sinh (k_4) \right]
$$

(4)

where, $S$ is the degree of water saturation, $k_1$, $k_2$, $k_3$, and $k_4$ are the fitting parameters. The values of $k_1$ to $k_4$ for unfrozen peat were suggested as $k_1 = 28$, $k_2 = 6$, $k_3 = -1.9$, and $k_4 = -1.5$.

3.2 Water Retention Characteristics and Volume Shrinkage during Drying

Except for surface layers (i.e., to 10 cm depth) for both Peat 1 and Peat 2, all soils exhibited high water retention characteristics up to pF 1.8, where around 60-70% of water saturation was still maintained, indicating the formation of a well-developed organic matrix with micro-pore structure that increased with increasing degree of decomposition. After pF 1.8, most samples showed a decrease of $\Phi$ and increase of $\sigma$ with increasing pF due to volume shrinkage of the samples during the drying process.

3.3 Thermal Conductivity and Heat Capacity of Peaty Soils

Figure 1 shows the measured thermal conductivities ($\lambda$) and heat capacities ($C$) for all peaty soil samples as a function of $\theta$. Each figure also shows regression lines and the 95% confidence interval curves for the estimates by the t-test.

Both thermal properties ($\lambda$ and $C$) showed a linear increase with increasing volumetric water content. In general, for mineral soils such as sandy soils, $\lambda$ is known to rapidly increase with increasing $\theta$, especially at dry conditions since soil water improves thermal contacts between soil particles, which have a higher thermal conductivity than water (0.57 Wm$^{-3}$K$^{-1}$) (Hamamoto et al., 2010; Becker et al., 1992).
The linear increase of $\lambda$ with $\theta$ for the peaty soils suggests that water content is the most controlling factor for the $\lambda$ as supported by the fact that the thermal conductivity of organic matter is much lower ($0.25 \text{ Wm}^{-1}\text{K}^{-1}$) than that of water (de Vries, 1963). In addition, increased solids content ($\sigma$) due to the volume shrinkages after pF 1.8 did not significantly affect the linear $\lambda$ and $C$ trends with $\theta$ at dry conditions, again indicating small contributions of organic matter to thermal properties and less effects of volume shrinkage on thermal properties.

The slopes in Fig. 1a and 1b (0.51 and 3.66 respectively) are slightly lesser than the expected values which $\lambda$ ($\lambda = 0.57 (\lambda_w)$ from de Vries, 1963), and $C$ for water ($C = 4.18 (C_w)$ from de Vries, 1963) correspondingly. These deviations are possibly due to the water phase tortuosity and existence of isolated water as well as volume shrinkage with drying since water in high organic soils has highest $\lambda$ and $C$ of the three phases (i.e., organic matter, water, and air). The clear linear trends of $\lambda$ and $C$ with $\theta$ suggest the applicability of simple linear functions of volumetric water content for the prediction of thermal properties.

Fig. 1. (a) Thermal conductivities ($\lambda$) and (b) heat capacities ($C$) as a function of volumetric water content ($\theta$) for Peaty soil samples. Regression lines, Eqs. (9) and (10), and 95% confidence curves are given.

The slopes in Fig. 1a and 1b (0.51 and 3.66 respectively) are slightly lesser than the expected values which $\lambda$ ($\lambda = 0.57 (\lambda_w)$ from de Vries, 1963), and $C$ for water ($C = 4.18 (C_w)$ from de Vries, 1963) correspondingly. These deviations are possibly due to the water phase tortuosity and existence of isolated water as well as volume shrinkage with drying since water in high organic soils has highest $\lambda$ and $C$ of the three phases (i.e., organic matter, water, and air). The clear linear trends of $\lambda$ and $C$ with $\theta$ suggest the applicability of simple linear functions of volumetric water content for the prediction of thermal properties.

Fig. 2. (a) Thermal conductivities and (b) heat capacities at dry condition, $\lambda_{dry}$ and $C_{dry}$, for Peaty soil samples as a function of volumetric solid content ($\sigma$).
\[ \lambda = 0.51\theta + 0.09 \]  
\[ C = 3.66\theta + 0.63 \]

Measured \( \lambda \) and \( C \) for sieved ground and intact samples at dry conditions (\( \lambda_{\text{dry}} \) and \( C_{\text{dry}} \)) are shown in Figs. 2a and 2b, respectively. Both \( \lambda_{\text{dry}} \) and \( C_{\text{dry}} \) linearly increased with increasing \( \sigma \). The solid lines in Figs. 2a and 2b represent conditions between the thermal properties of air (i.e., \( \sigma = 0 \)) and organic matter (i.e., \( \sigma = 1 \)) where \( \lambda \) of 0.025 and negligible \( C \) (i.e., \( C = 0 \)) values for air and \( \lambda \) of 0.25 and \( C \) of 2.5 values for organic matter were used, by referring to de Vries (1963). The two lines for \( \lambda \) and \( C \) well captured the measured \( \lambda_{\text{dry}} \) data for all samples and \( C_{\text{dry}} \) data for intact samples, respectively, showing the reliability of literature data for thermal properties representing typical natural organic matter compositions.

\[ \lambda_{\text{dry}} = 0.225\sigma + 0.025 \]  
\[ C_{\text{dry}} = 2.5\sigma \]

The simple linear functions of the volumetric solids content seem promising for evaluating the thermal properties of organic matter for soils at different compaction levels.

### 3.4 New Model Development

Based on the findings that \( \lambda \) and \( C \) increased linearly with increasing \( \theta \) and the slopes were similar to \( \lambda \) and \( C \) values of water, predictive models (in literature frequently called mixing models) based on three phase fractions (solid, water, and air phases) were developed for estimating the thermal properties of peat soils. When negligible \( \lambda \) and \( C \) values of air were assumed (since the \( \lambda \) and \( C \) values of air is comparatively lower than that of water), the mixing models for \( \lambda \) and \( C \) can be expressed as,

\[ \lambda = \lambda_{\text{dry}} + f_\lambda\theta\lambda_w \]  
\[ C = C_{\text{dry}} + f_C\theta C_w \]

where, \( f_\lambda \) and \( f_C \) are the impedance factors representing liquid phase tortuosity factors for \( \lambda \) and \( C \), respectively (Moldrup et al., 2001; Olesen et al., 2001). In this study, the ratio of the obtained slope of the \( \lambda-\theta \) relation (0.51, Fig. 1a) to \( \lambda_w \) (0.57; de Vries, 1963) and the ratio of the obtained slope of the \( C-\theta \) relation (3.66, Fig. 1b) to \( C_w \) (4.18; de Vries, 1963) were assumed to express liquid-phase tortuositites for \( \lambda \) and \( C \), respectively, giving \( f_\lambda = 0.89 \) and \( f_C = 0.88 \). When the predictive \( \lambda_{\text{dry}} \) and \( C_{\text{dry}} \) models as a function of \( \sigma \) were introduced into Eqs. 9 and 10, the proposed \( \lambda \) and \( C \) models can be written as,

\[ \lambda = (0.225\sigma + 0.025) + 0.89\lambda_w\theta \]  
\[ C = 2.5\sigma + 0.88\theta C_w \]

### 3.5 Model Performances of the Predictive Models for Thermal Properties

Figure 3a shows scatter plot comparisons of predicted and measured \( \lambda \) for the obtained linear regression, the mixing model, and existing models. Figure 3b shows scatter plot comparisons of predicted and measured \( C \) for the obtained linear regression and mixing model. In the model tests of mixing \( \lambda \) and \( C \) models and, the measured \( \sigma \) values for each measured thermal property value were considered in the calculations. The model performances against measured \( \lambda \) data are also shown in Table 2. The Becker et al. (1992) model, linear regression (Eq. (4)), and mixing model (Eq. (11)) performed well, but classical de Vries (1963) and Campbell (1985) models showed worse model performances. Although the mixing model for \( C \) (Eq. (12)) underestimated the measured \( C \) values especially at wet conditions, most of the prediction values gave less than 20% prediction error.
Table 2. Test of predictive thermal conductivity (λ) models against measured data and literature data.

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMSE bias</td>
<td>RMSE bias</td>
<td>RMSE bias</td>
<td>RMSE bias</td>
<td>RMSE bias</td>
</tr>
<tr>
<td>de Vries model (1963)</td>
<td>0.035 -0.011</td>
<td>0.015 0.007</td>
<td>0.065 -0.049</td>
<td>0.062 -0.034</td>
<td>0.068 -0.043</td>
</tr>
<tr>
<td>Campbell (1985)</td>
<td>0.044 0.044</td>
<td>0.080 0.076</td>
<td>0.043 -0.007</td>
<td>0.033 -0.009</td>
<td>0.085 0.004</td>
</tr>
<tr>
<td>Becker et al. (1992)</td>
<td>0.027 0.022</td>
<td>0.054 0.053</td>
<td>0.047 -0.019</td>
<td>0.036 -0.009</td>
<td>0.055 0.033</td>
</tr>
<tr>
<td>Brovka &amp; Rovdan (1999)</td>
<td>... ...</td>
<td>0.069 0.060</td>
<td>0.052 -0.028</td>
<td>... ...</td>
<td>0.061 -0.023</td>
</tr>
<tr>
<td>Linear Regression (Eq. [9])</td>
<td>0.070 0.070</td>
<td>0.109 0.107</td>
<td>0.049 0.023</td>
<td>0.057 -0.019</td>
<td>0.054 -0.027</td>
</tr>
<tr>
<td>Mixing model in this study (Eq.[15])</td>
<td>0.031 0.031</td>
<td>0.057 0.051</td>
<td>0.046 -0.017</td>
<td>0.058 -0.026</td>
<td>0.058 -0.037</td>
</tr>
</tbody>
</table>

Independent model tests using the proposed model as well as existing models were performed against the λ data for four different peaty soils from the literature (Lauren, 1997; Sharratt, 1997). Scatter plot comparisons of measured and predicted λ for each predictive model, and basic soil information of the peat soils from literature are shown in Fig. 3.

In the model tests of the proposed mixing model (Eq. 11) against four different independent data sets, constant σ values were used in the calculations based on the total porosity (Φ) for each peat soil. The model performances against the measured λ data from each literature study (RMSE and bias, are also presented in Table 2. The Becker et al. (1992) model and proposed mixing model showed the overall best model performances. However, the model performance tests against measured λ data at dry conditions showed that the new mixing model performed better as compared to the Becker et al. (1992) model, indicating that the inclusion of the predictive λdry model improved model predictions of λ at dry conditions.

As an example, RMSE for the predicted values from the mixing model after pF2 is 0.055 and it is 0.059 for the Becker et al (1992) model. Since the surface and subsurface layers of peatlands become extremely dry due to the water table depletion as a result of development activities and during extreme weather conditions. Hence, predicting thermal conductivity for dry peat is very much important to assess the environmental impact due to residential, agricultural and infrastructural development. Further, the fitted f value based on measured data also performed well against the independent data sets, suggesting the f value is well applicable for highly organic soils (i.e., peaty soils). The other two of three parameters that we are using in the model are thermal conductivity of air and thermal conductivity of organic matter from literature. Therefore, the proposed mixing model with a proposed value of the impedance factor (f = 0.89) is highly promising for predicting general λ behaviors for peat soils since it requires only information on solid- and water contents (σ and θ).

The performance of heat capacity model was not evaluated against independent data, due to lack of available literature on heat capacity for peat soils. In picturesque, further model tests will be performed on heat capacity of peat soil.

4. GAS, HEAT, AND WATER TRANSPORT PROPERTIES IN PEATY SOIL PROFILES: MEASUREMENTS AND ARCHIE’S LAW MODELS

4.1 Model Development

Under fluid-unsaturated conditions, a generalized Archie’s second law (Archie, 1942) for transport parameters with reference point can be written as;

$$\frac{P}{P_{sat}} = \left( \frac{F}{F_{sat}} \right)^{n}$$

where, P is the bulk parameter under fluid-unsaturated conditions and P_{sat} is the bulk parameter value at fluid saturation, F is the fluid content (i.e., soil air content (φ) for D_p, k_t and soil water content (θ) for soil-water retention, λ, and k_w) (m^3 m^{-3}), F_{sat} is the fluid saturation and n is the saturation exponent representing fluid-pore tortuosity–connectivity of the porous media (Table 3).

In this study, the λ-λ_{dry}, D_p, k_t and k_w were considered as the bulk parameter values. λ_{dry} (W m^{-1} K^{-1}) is the thermal conductivity at air dry
Table 3. Model parameters used in this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( F ) (m³ m⁻³)</th>
<th>( F/w )</th>
<th>( F/F/w )</th>
<th>( P )</th>
<th>( P/w )</th>
<th>( P/P/w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil water Retention Parameter</td>
<td>( \theta )</td>
<td>( \theta/w )</td>
<td>( \psi )</td>
<td>( \psi/w )</td>
<td>( \psi/P )</td>
<td>( \psi/P/w )</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>( \theta - \theta_{dry} )</td>
<td>( \theta_{sat} - \theta_{dry} )</td>
<td>( (\theta_{sat} - \theta_{dry})/\lambda_{dry} )</td>
<td>( \lambda_{sat} - \lambda_{dry} )</td>
<td>( (\lambda_{sat} - \lambda_{dry})/\lambda_{dry} )</td>
<td></td>
</tr>
<tr>
<td>Gas diffusion Coefficient</td>
<td>( \epsilon )</td>
<td>( \epsilon \phi_{pF4.1} )</td>
<td>( \epsilon \phi_{pF4.1} )</td>
<td>( D_p )</td>
<td>( D_{p,pF4.1} )</td>
<td>( D_p/D_{p,pF4.1} )</td>
</tr>
<tr>
<td>Air permeability</td>
<td>( \theta )</td>
<td>( \theta/w )</td>
<td>( \psi )</td>
<td>( \psi/w )</td>
<td>( \psi/P )</td>
<td>( \psi/P/w )</td>
</tr>
<tr>
<td>Water permeability</td>
<td>( \epsilon )</td>
<td>( \epsilon \phi_{pF4.1} )</td>
<td>( \epsilon \phi_{pF4.1} )</td>
<td>( k_a )</td>
<td>( k_{a,pF4.1} )</td>
<td>( k_a/k_{a,pF4.1} )</td>
</tr>
</tbody>
</table>

Archie’s second law for water retention with reference point can be written as,
\[
\frac{\psi}{\psi_{ref}} = \left( \frac{\theta}{\theta_{ref}} \right)^n
\]
(14)
where, \( \psi \) is soil water potential. Campbell (1976) suggested this model with \( \psi_{ref} = \) air entry soil water potential and \( \theta_{ref} = \) water saturation, making \( a \) equal to the Campbell pore-size distribution index, \( b \).

When the Archie’s second law is applied to \( \lambda_{dry} \), \( k_a \) and \( k_w \), the predictive models can be written as follows.

For thermal conductivity
\[
\frac{\lambda_{sat} - \lambda_{dry}}{\lambda_{dry}} = \left( \frac{\theta_{sat} - \theta_{dry}}{\theta_{dry}} \right)^n
\]
(15)

For gas diffusivity
\[
\frac{D_p}{D_{p,pF1.8}} = \left( \frac{\epsilon}{\epsilon_{pF1.8}} \right)^n
\]
(16)
For air permeability
\[
\frac{k_a}{k_{a,sat}} = \left( \frac{\epsilon}{\epsilon_{pF4.1}} \right)^n
\]
(17)
For water permeability
\[
\frac{k_w}{k_{w,sat}} = \left( \frac{\theta}{\theta_{sat}} \right)^n
\]
(18)
Where, \( \lambda_{sat} \) and \( k_{w,sat} \) are \( \lambda \) and \( k_w \) under water saturated (wet) conditions, and \( D_{p,sat} \) and \( k_{a,sat} \) are \( D_a \) and \( k_a \) under air saturated (dry) conditions, respectively. \( \lambda_{dry} \) and \( k_{w,sat} \) are \( \lambda \) and \( k_w \) under air saturated (dry) conditions, respectively. Normalizing by each parameter value under saturated conditions respectively, and \( n \) denotes the saturation exponent.

**Modified Archie’s Law with Reference Point**

A two-region model based on Archie’s law was proposed to characterize the \( D_p \) and \( k_a \) behavior. The two-region models for \( D_p \) and \( k_a \) can be written as;
\[
\frac{D_p}{D_{p,pF1.8}} = \left( \frac{\epsilon}{\epsilon_{pF1.8}} \right)^n
\]
(19)
\[
\frac{k_a}{k_{a,pF1.8}} = \left( \frac{\epsilon}{\epsilon_{pF1.8}} \right)^n
\]
(20)
where, \( \epsilon_{pF1.8} \) is the air-filled porosity at pH 1.8, \( n_i = n_f \) for region 1 (pH ≤ 1.8; non-shrinkage region), and \( n_i = n_s \) for region 2 (pH > 1.8; shrinkage region) with reference point at pH 1.8. We selected a reference point of pH 1.8 since the volume shrinkages for most of peaty soils start after pH 1.8 (Dissanayaka et al., 2012). Hamamoto et al. (2011) used pH 2 as the reference point for bimodal mineral soils including Andisols (to separate inter- and intra-aggregate pore regions).

**Reference Point Models for Gas Diffusivity at pH 1.8**

Call (1957) modified the Penman (1940) model, which is the most widely used one parameter model for \( D_p/D_a \) of porous media, by including a threshold inactive air-filled porosity \( \epsilon_{th} \). The Penman-Call linear \( D_p/D_a \) model proposed by Moldrup et al. (2005) at pH 1.8 is,
\[
\frac{D_p}{D_{a,pF1.8}} = P(\epsilon_{pF1.8} - \epsilon_{th})
\]
(21)
where, \( P \) is a constant and Penman (1940) suggested \( P = 0.66 \). Millington (1959) proposed a general power-law type \( D_p \) model, based on the classical one parameter soil air diffusivity model, developed by Buckingham (1904). According to the model, \( D_p/D_a \) at pH 1.8 can be written as,
\[
\frac{D_{p,pF1.8}}{D_{a}} = (\epsilon_{pF1.8})^{4/3}
\]
(22)
The most widely used model for predicting \( D_p \) is the Millington and Quirk (1961) model,
\[
\frac{D_{p,pF1.8}}{D_0} = (\frac{\varepsilon_{pF1.8}}{\phi})^{0.3} \tag{23}
\]

Kawamoto et al (2006) proposed and equation to predict \(k_a\) at a given pF value,

\[
k_{a,pF1.8} = G \frac{D_{p,pF1.8}}{D_0} \tag{24}
\]

where, \(G\) is a constant depending on the soil type.

4.3 Soil-water Retention Characteristics of Peat

Figure 4 shows Campbell \(b\) value as a function of volume shrinkage (VS). According to the figure, there is a clear relationship between Campbell \(b\) parameter and volume shrinkage of peaty soils. Campbell \(b\) is increasing with increasing volume shrinkage except for the 20cm layer of peat 1. Schwarzel et al (2002) also observed a clear relationship between volume shrinkage and water retention characteristics of peaty soils.

4.4 Measured Soil Transport Parameters of Peaty Soil under Variably Saturated Conditions

Figure 5 shows measured gas diffusivities \((D_p/D_0)\) and air permeabilities \((k_a)\) as functions of soil air content \((\varepsilon)\) and, thermal conductivities \((\lambda)\) and water permeabilities \((k_w)\) as functions of volumetric water content \((\theta)\) for two different peaty soil samples, and Toyoura and Narita sand samples respectively. All four transport properties showed increase with increasing fluid content (i.e., soil water content or soil air content, m\(^3\) m\(^{-3}\)).
Higher $D_p/D_0$ values for Toyoura and Narita sands were observed as compared to those for peaty soil samples especially at dry region, indicating enhanced gas diffusion and advection occurred through the continuous large-pore networks for sands. And $k_a$ values observed for sandy soil samples were lower compared to the values for peaty soil samples. Air permeability of a soil material is an indicator of the possibility for convective air exchange in the soil and it is basically depends on the existence of larger pores. Convective air exchange is prominent in peaty layers due to its high macroporosity (Lauren et al., 2000). Pore organization ($PO = k_a/\varepsilon$) values calculated across variable moisture conditions for the all peat soil samples studied are generally above 200 suggesting a highly structured behavior of the soil.

Thermal conductivity ($\lambda$) of the mineral soils is rapidly increasing with increasing $\theta$ especially at dry conditions due to improved thermal contacts between soil particles by soil water (Becker et al., 1992; Hamamoto et al., 2010). A linear increase of $\lambda$ with increasing $\theta$ was observed in all three peat soils. This suggests that water content and liquid-phase tortuosity are the most controlling factors for the $\lambda$, as supported by the fact that the thermal conductivity of organic matter (0.25 Wm$^{-1}$K$^{-1}$) is much lower than that of water (0.57 Wm$^{-1}$K$^{-1}$) (de Vries, 1963; Brovka & Rovdan, 1999).

According to the figure 5d, water permeability ($k_w$) of peaty soil samples varied over a wide range with changing volumetric water content. Peaty soils are mainly consist of larger (macro pores) and smaller (micro pores) channel systems.

![Fig. 6. Normalized parameter values, $P/P_{sat}$, for (a) gas diffusivity ($D_p$); (b) air permeability ($k_a$); (c) thermal conductivity ($\lambda$); and (d) water permeability ($k_w$) as a function of normalized fluid content, $F/F_{sat}$, for peat soils, and Narita and Toyoura sand](image)

Fig. 6. Normalized parameter values, $P/P_{sat}$, for (a) gas diffusivity ($D_p$); (b) air permeability ($k_a$); (c) thermal conductivity ($\lambda$); and (d) water permeability ($k_w$) as a function of normalized fluid content, $F/F_{sat}$, for peat soils, and Narita and Toyoura sand
At a given saturation level, water flow is mainly occurred through larger macro pores. When the saturation level is decreasing, water tends to drain first from the macro pores and therefore water permeability of a porous medium falls rapidly with decreasing water content.

This kind of behavior is presented in the study of saturated and unsaturated permeabilities of North German peats by Loxham and Burghardt (1986). The big jump observed in \( k_w \) values between saturation (encircled data in figure 6d) and near-saturation together with higher PO values (>200) suggesting that peat samples studied are consisted of highly structured soil material.


Figure 6 shows the normalized parameter values, \( P/P_{sat} \) for gas diffusion coefficient \( (D_p) \), air permeability \( (k_a) \), thermal conductivity \( (\lambda) \), and water permeability \( (k_w) \) as functions of normalized fluid content, \( F/F_{sat} \) for peaty soils, and Narita and Toyoura sand. Figure 6a and 6b show normalized parameter values for \( D_p \) and \( k_a \) as functions of normalized soil air content for two peaty soils, and Narita and Toyoura sand.

![Graphs showing the normalized parameter values](image)

Fig. 7. Scatter-plot comparison of predicted and measured (a) gas diffusivity \( (D_p/D_0) \), (b) air permeability \( (k_a) \), (c) thermal conductivity \( (\lambda) \) and (d) water permeability \( (k_w) \) for Peat 1, and Peat 3 samples. Calculated RMSE using \( D_p/D_0 \), \( \lambda \), \( k_a \) data and log-transformed \( k_w \) data are also given.
The saturation exponent \((n)\) for \(D_p\) is ranging from 0.5 to 3 where as \(n\) for \(k_w\) is vary between 1 and 4 suggesting that classical Archie’s law model is not sufficient to describe \(D_p\) and \(k_w\) data well (Hamamoto et al., 2011). The best-fit \(n\) value of sands for \(D_p\) was higher than that for the peaty soils. This is because sandy soil is characterized with more macro-pore networks compared to the peaty soil resulting higher water blockage effect for \(D_p\). Also some of the peaty soil layers resulted \(n\) value for \(D_p\), lesser than 1 which seems unrealistic in nature. This might be due to the existence of isolated air pockets inside the porous media. When the draining continues, these air pockets can be connected and cause bi-pass flow resulting a smaller \(n\) values than expected.

Figure 6c suggests that measured \(\lambda\) can be well described with the Archie’s saturation exponent \((n)\) of around one (resulted in a linear relationship between volumetric water content and thermal conductivity) as also suggested by Dissanayaka et al. (2012).

The normalized \(k_w\) showed rapid increase at near water saturation, giving quite high \(n\) values (ranging from 10 to 100) than sands. This finding suggests the continuity of water-phase pore-network for high porous peat soils with high surface area is dramatically disconnected due to water drainage from water saturation. The lower \(n\) value for \(k_w\) in sands indicate water movement through water film around soil particles is active even under dry conditions.

4.6 Model Tests

Figure 7 shows scatter-plot comparisons of predicted and measured \(D_p/D_b, k_w, \lambda\) and \(k_a\) for Peat 1 and Peat 3 samples. New predictive models for \(D_p/D_b\), developed based on modified Millington (1959) type and Penman-Call type at pF 1.8 are compared with widely used existing models for predicting \(D_p/D_b\) in mineral soils; Millington and Quirk (1961) model and Buckingham-Burdine-Campbell (BBC) model (Moldrup et al., 1999).

According to the figure 7a and calculated RMSE values, performance of new models are far better than existing models. Performance of new \(k_w\) models based on Kawamoto et al. (2006), are compared with Moldrup et al (1998) model and Kawamoto, Moldrup, Campbell based model (Kawamoto et al., 2006). RMSE calculated based on log transformed data also shows that new \(k_w\) models are performing better than other existing models. However, the two new models for \(D_p/D_b\) and \(k_a\) are showing somewhat similar performance in predicting the parameters.

In figure 7d, Campbell (1974) model \((n = 2b + 3)\) and, Alexander and Skaggs (1986) model \((n = b + 3)\) are compared with a modified Campbell (1974) type model \((n = 4b+3)\). Assuming the water permeability \(n\) expressed by \(n = A\ b + 3\), a markedly higher value (double) of \(A\) is needed compared to the Campbell (1974) model \((A = 2)\) in order to (on the average) best describe the higher matrix pore network tortuosity for unsaturated water transport in peat soil. This is in agreement with the higher pore network tortuosities suggested by the lower \(D_p/D_b\) values for peat soils as compared to mineral soils (sands and sand size fractions). Moreover, the big jump in \(k_w\) between saturation and near-saturation for most peat layers (in perfect agreement with the data for the 9 German peat soil profiles in "Peat and Water") at the same time suggests a pronounced macro-pore network and this in agreement with very high pore organization values \((PO = k_w/\varepsilon)\) of > 200 across moisture conditions. All together this shows peaty soil as a multi-region media with both pronounced macro-pore behavior close to fluid saturation, a highly tortuous matrix pore network that can much reduce mass transport at intermediate moisture conditions, and exhibiting pore network changes at pF > 1.8, i.e. where shrinkage phenomena changes the functional pore networks and thus mass transport behavior; this likely being most pronounced for gas transport.

5. CONCLUSIONS

Thermal conductivity \((\lambda)\) and heat capacity \((C)\) of peaty soil samples were measured and predictive \(\lambda\) and \(C\) models were developed. Developed models performed well in model tests using literature data. New mixing models were underestimated the thermal properties for tropical peaty soils possibly due to mineral content.

Heat and mass transport properties; \(D_p, k_a, l\) and \(k_w\) for peaty soils were measured and characterized by Archie’s law and compared with the transport parameters Narita and Toyoura sands. Thermal conductivity and water permeability was well characterized with classical Archie’s law and behaviors were markedly different from sands.

The Archie’s law model could not describe \(D_p\) and \(k_a\) data well and a reference point based two region models were proposed. Proposed models well captured the measured \(D_p\) and \(k_a\) data which can be useful in predicting climate gas transport and emissions from peaty soils.

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