Bound Water, Phase Configuration, and Dielectric Damping Effects on TDR-Measured Apparent Permittivity

Miles Dyck,* Teruhito Miyamoto, Yukiyoshi Iwata, and Koji Kameyama

The time domain reflectometry (TDR) method measures the soil apparent permittivity ($K_a$), which is the basis for estimation of soil volumetric water content ($\theta$) via an empirical calibration equation or dielectric mixing model. The relationship between $K_a$ and $\theta$ [i.e., $K_a(\theta)$] in soils with significant volumetric fractions of bound water and with bimodal pore-size distributions displays a distinct increase in slope after $\theta$ exceeds a threshold value. The interpretation of this change in slope has been aided with application of dielectric mixing models through the inclusion of a bound water phase and/or $\theta$-dependent changes in phase configuration. However, $K_a$ measured with time-domain reflectometry (TDR) in soils with significant volumetric fractions of bound water has been previously observed to change as a function of the effective frequency of the soil-attenuated bandwidth. Therefore, the main objective of this work was to investigate the influence of bound water and phase configuration in four, high-surface-area Japanese Andisols with bimodal pore-size distributions using dielectric mixing models alone or coupled with a dielectric damping model. Soil-specific $K_a(\theta)$ relationships were measured in the laboratory using standard methods and were simulated with two frequency-independent, real-valued dielectric mixing models and a complex-valued, frequency-dependent model coupled with a dielectric damping model. The results of the simulations indicate that frequency-dependent dielectric permittivity of the bound water phase significantly influences TDR-measured $K_a(\theta)$, suggesting that soil- and probe-specific calibrations may be required for soils with significant volumetric fractions of bound water.

Abbreviations: EM, electromagnetic; FDM, frequency-dependent model; FPM, four-phase model; MRC, moisture retention curve; PCM, phase configuration model; TDR, time domain reflectometry.

Soil bulk dielectric permittivity is sensitive to volumetric water content ($\theta$) because water has a much higher permittivity ($\sim 80$) than soil minerals or air. Dielectric permittivity is a complex-valued property—$\varepsilon'$—that reflects the storage (real part of the dielectric permittivity, $\varepsilon''$) and dissipation (imaginary part of the dielectric permittivity, $\varepsilon'''$) of electrical energy within any homogeneous or composite material. The reorientation of polar molecules such as water according to the polarity of the incident electromagnetic (EM) field—relaxation—stores a significant amount of energy and accounts for the high $\varepsilon'$ of free water ($\sim 80$) (Robinson et al., 2003). The time domain reflectometry (TDR) method, as commonly applied in soil science, measures the soil apparent permittivity ($K_a$), which is assumed to be equal to the real part of the dielectric permittivity of the soil ($\varepsilon_{\text{soil}}'$) (Topp et al., 2000; Robinson et al., 2003). Dielectric mixing models predict $\varepsilon''$ (usually only $\varepsilon''$) of composite materials, such as soil, as a function of the dielectric permittivity and volumetric fractions of individual constituents.

The response of TDR-measured $K_a$ to increasing water content ($\theta$) in soils with bimodal pore-size distributions has been the subject of a significant number of studies in the soil science literature (Dirksen and Dasberg, 1993; Friedman, 1998; Jones and Or, 2003; Miyamoto et al., 2003, 2005; Blonquist et al., 2006; Robinson et al., 2009). The relationship between $K_a$ and $\theta$ in these soils, the $K_a(\theta)$ function, often displays a distinct increase in slope after $\theta$ surpasses a threshold value, often called the critical water content,
The interpretation of this change in slope has been aided by the application of dielectric mixing models. The change in slope of the $K_q(\theta)$ function at $\theta_{cr}$ can be simulated with dielectric mixing models via the addition of a bound water phase, accounting for soil structure (i.e., a bimodal pore-size distribution) through the use of single or dual composite dielectric mixing models or a combination of these two approaches. Bound water is generally considered to be the first few molecular layers of water adjacent to soil particles and is generally thought to have a lower permittivity than unbound soil water. In fine-textured soils with high surface area, two or three molecular layers of bound water translates to a significant volumetric fraction of soil water, potentially explaining the low slope of the $K_q(\theta)$ function at low water contents when most of the soil water is low-permittivity bound water. Dirksen and Dasberg (1993) implemented a four-phase dielectric mixing model with a bound water phase and were able to simulate the $K_q(\theta)$ function of 11 soils with clay contents ranging from 10 to 86% by optimizing the value of the bound water permittivity, $\varepsilon_{bw}$, and the volumetric fraction of bound water. The estimation of $\varepsilon_{bw}$ with mixing models is subject to considerable uncertainty because (i) it is probably a function of distance from soil particle surfaces for which there are only limited measurements available, and (ii) an average of the permittivity of all bound water layers must be calculated to represent $\varepsilon_{bw}$ in the mixing model (Friedman, 1998; Or and Wraith, 1999; Robinson et al., 2002). Bound water phases were also included in the mixing model investigations of Friedman (1998), Or and Wraith (1999), and Miyamoto et al. (2003, 2005).

The effects of a bimodal pore-size distribution on the $K_q(\theta)$ function was presented in the works of Miyamoto et al. (2005), Blonquist et al. (2006), and Robinson et al. (2009). In these investigations, the $K_q(\theta)$ function was simulated with more than one mixing model with different phase configurations for dry ($\theta \leq \theta_{cr}$) and wet ($\theta > \theta_{cr}$) portions of $K_q(\theta)$. The justification for different mixing models for dry and wet portions of $K_q(\theta)$ was based on the similarity between the value of $\theta_{cr}$ and the value of $\theta$ on the moisture retention curve where all intra-aggregate pores were water filled—often specified as the critical water content, $\theta_{cr}$, or the hydraulic critical water content, $\theta_{hc}$—beyond which the configuration of phases was assumed to change. Blonquist et al. (2006) and Robinson et al. (2009) simulated the dry portion of $K_q(\theta)$ using the composite sphere model of Friedman (1998) with a soil–water–air configuration and the wet portion of $K_q(\theta)$ using a dielectric layer model with wet and dry layers, represented by the composite sphere model of Friedman (1998) and a two-phase, saturated mixing model, respectively. They did not include a bound water phase. Friedman (1998) simulated $K_q(\theta)$ using a weighted average (weights based on saturation) of air–soil–water (dry portion) and soil–water–air (wet portion) configurations of his composite sphere model. In the case of Miyamoto et al. (2005), the $K_q(\theta)$ function was simulated using a weighted average of two composite, four-phase mixing models with unique configurations representing the dry and wet portions of $K_q(\theta)$. The mixing models for the dry and wet portions of $K_q(\theta)$ used by Miyamoto et al. (2005) were a four-phase version of the composite sphere model of Friedman (1998), with air–water–soil–air and water–soil–air–water configurations, respectively. The weights used to average the two mixing models were calculated with a symmetric effective media model.

In these investigations, it was assumed that $\varepsilon^*$ of the bulk soil and soil constituents were independent of the effective frequency of the reflected EM bandwidth (Schwartz et al., 2009b). Bulk soil $\varepsilon^*$, however, has been observed to be dependent on the effective frequency of the EM wave introduced into the soil. Dielectric spectra of soils measured with network analyzers, in the 100 MHz to 10 GHz frequency range, measured by Hoekstra and Delaney (1974), Mironov et al. (2004), Kelleners et al. (2005), Logsdon (2005), Chen and Or (2006), and Wagner et al. (2011) showed that measured $\varepsilon_{soil}'$ and $\varepsilon_{soil}''$ were greater at lower frequencies and decreased with increasing frequency of the incident EM waves. This behavior is most pronounced in relatively wet, fine- to medium-textured soils.

When the incident EM wave is broadband, as generated by a TDR cable tester, bulk water polarization, out-of-phase relaxation, and conductive losses preferentially filter out the highest frequencies of the bandwidth, effectively reducing the mean frequency of the reflected wave compared with the incident wave—a phenomenon called dielectric damping (Schwartz et al., 2009b). This phenomenon is most pronounced at higher water contents in fine- to medium-textured soils of relatively high surface area. Topp et al. (2000) showed that the maximum frequency of the reflected EM wave in soil samples with 20 or 55% clay content, generated by a Tektronix 1502B cable tester, ranged from 400 MHz in relatively dry samples down to 90 MHz in relatively wet samples, much lower than the incident bandwidth of approximately 1 GHz. Further, the frequency of the incident wave generated by a TDR cable tester at the probe handle is a function of the length of the probe’s cable, the cable type, and the number of cable connections (i.e., multiplexers) (Robinson et al., 2005; Schwartz et al., 2009a).

For soils where dielectric damping caused by conductive losses and out-of-phase attenuation losses are significant, the assumption that $K_{ai} = \varepsilon_{soil}'$ inherent in the basic implementation of the TDR method may not hold. At frequencies $\leq 2000$ MHz, the dielectric permittivity of free water is independent of frequency (Logsdon, 2005) because its relaxation frequency is 19 to 20 GHz, depending on temperature. The relaxation frequency of bound water, however, is significantly lower (Or and Wraith, 1999) and, as a result, the dielectric permittivity of bound water is likely to be frequency dependent, which may cause TDR-measured $K_{ai}$ in soils with significant volumetric fractions of bound water to be frequency dependent, especially at high water contents (Schwartz et al., 2009b).

Therefore, it seems that the application of dielectric mixing models in high-surface-area soils with bimodal pore-size distributions without considering dielectric damping and frequency-dependent bound water $\varepsilon^*$ may limit their utility in understanding the effects of free and bound water content, soil...
structure (bimodal pore-size distributions), and phase configuration on TDR-measured $K_{a}$. Therefore, the objective of this work was to simulate the $K_{a}(\theta)$ function of four high-surface-area Japanese Andisols using dielectric mixing models alone or coupled with a dielectric damping model to gain insight into the potential contribution of frequency-dependent $\varepsilon_{bw}$ on the measured soil $K_{a}(\theta)$ function.

**Materials and Methods**

**Soils**

The soils used in this investigation were fine- to medium-textured Japanese Andisols (Table 1). The clay minerals of Japanese Andisols are primarily allophane (Ishida et al., 2000). The soils were collected from the A horizon of an experimental field at the Institute for Rural Engineering, National Agricultural Research Organization (NARO), in Tsukuba (36°3′ N, 140°8′ E); the A and C horizons of an experimental field at the Agricultural Research Center for Hokkaido Region, NARO, in Memuro Hokkaido (42°54′ N, 143°3′ E); and the A horizon of an experimental field at the Agricultural Research Center for Kyushu Okinawa Region, NARO, in Koshi Kumamoto (32°53′ N, 130°45′ E). All the soil samples were passed through a 2-mm sieve and air dried. Basic soil properties are listed in Table 1. The specific surface of the soils was estimated according to (Dirksen and Dasberg, 1993; Miyamoto et al., 2003):

$$S = \frac{\theta_{\text{air-dry}}}{\delta \rho_{b}} \quad [1]$$

where $\theta_{\text{air-dry}}$ is the air-dry volumetric water content ($m^3 m^{-3}$), $\delta$ is the thickness of the water molecule ($3 \times 10^{-10} m$), and $\rho_{b}$ is the bulk density ($kg m^{-3}$). The Andisols investigated in this work have stable, bimodal pore-size distributions because of naturally occurring internal porosity in the volcanic ash soil particles.

**Measurement of $K_{a}(\theta)$**

The $K_{a}(\theta)$ functions of the soils were measured in laboratories in which room temperature was kept at 20°C. For measurement of $K_{a}(\theta)$ for the Tsukuba and Koshi Andisols, the ground soil was packed into acrylic cylinders of 62.8-mm diameter to a depth of 110 mm as uniformly as possible. The measurement of $K_{a}(\theta)$ was conducted using a three-rod TDR probes (3 mm in diameter, 100 mm long, and 15-mm spacing between center and outside rods). The TDR probe was inserted vertically into the soil columns. Waveform analysis was conducted using the WinTDR waveform analysis software (developed by the Environmental Soil Physics Group at Utah State University, Logan, http://www.usu.edu/soilphysics/) that enabled automated TDR control, data acquisition, and waveform analysis. The measurement of $K_{a}(\theta)$ was repeated three times for each sample. Water contents were measured by weighing the soil samples gravimetrically using an electronic balance. To prepare the samples with a higher water content, the soils were removed from the cylinders and received 15 to 30 mL of distilled water. The soils were left undisturbed for at least 24 h to allow the moisture to become evenly redistributed. The wet soils were repacked into the same cylinders with the same bulk density, and measurement of $K_{a}(\theta)$ and $\theta$ were conducted as mentioned above. These steps were repeated for 12 water contents for each soil.

For measurement of $K_{a}(\theta)$ for the Memuro (topsoil and subsoil) Andisols, the ground soil was packed into polyvinyl chloride cylinders of 83-mm diameter to a depth of 320 mm as uniformly as possible. The measurement of $K_{a}(\theta)$ was conducted using a TDR cable tester (TDR100, Campbell Scientific) connected to three-rod TDR probes (4.8 mm in diameter, 300 mm long, and 22.5-mm spacing between center and outside rods; CS605-L, Campbell Scientific). The TDR probe was inserted vertically into the soil columns. Waveform analysis was conducted using the PCTDR waveform analysis software (Campbell Scientific) that enabled automated TDR control, data acquisition, and waveform analysis. The measurement of $K_{a}(\theta)$ was repeated three times for each sample. Water contents were measured by weighing the soil samples gravimetrically using an electronic balance. To prepare the samples with a higher water content, the soils were removed from the cylinders and received 40 to 50 mL of distilled water. The soils were left undisturbed for at least 24 h to allow the moisture to become evenly redistributed. The wet soils were repacked into the same cylinders with the same bulk density, and measurement of $K_{a}(\theta)$ and $\theta$ were conducted as mentioned above. These steps were repeated for 13 water contents for the topsoil and 19 water contents for the subsoil.

**Measurement of Soil Moisture Retention Curve**

The soil moisture retention curve (SMRC) was measured independently of $K_{a}(\theta)$. Soils were packed into a cylinder (51 mm in diameter and 50 mm high) with the same soil bulk density

Table 1. Selected properties of the four Japanese Andisols investigated in this work.

<table>
<thead>
<tr>
<th>Soil location</th>
<th>Soil classification</th>
<th>Clay (&lt; 2 μm)</th>
<th>Silt (2–20 μm)</th>
<th>Sand (&gt;20 μm)</th>
<th>Organic C</th>
<th>Air-dry water content</th>
<th>Specific surface†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tsukuba (topsoil)</td>
<td>Typic Hydrudand</td>
<td>23.8</td>
<td>21.2</td>
<td>55.0</td>
<td>42.5</td>
<td>0.089</td>
<td>387</td>
</tr>
<tr>
<td>Memuro (topsoil)</td>
<td>Typic Hapludand</td>
<td>26.5</td>
<td>11.8</td>
<td>61.7</td>
<td>37.6</td>
<td>0.075</td>
<td>325</td>
</tr>
<tr>
<td>Memuro (subsoil)</td>
<td>Typic Hapludand</td>
<td>26.1</td>
<td>29.4</td>
<td>44.6</td>
<td>13.5</td>
<td>0.036</td>
<td>178</td>
</tr>
<tr>
<td>Koshi (topsoil)</td>
<td>Hydric Pachic Melanudand</td>
<td>40.5</td>
<td>34.7</td>
<td>24.8</td>
<td>67.2</td>
<td>0.080</td>
<td>290</td>
</tr>
</tbody>
</table>

† Calculated with Eq. [1].
as the soil sample for measuring the $K_a(\theta)$. Soil samples were equilibrated at pFs ranging from 0 to 3.5 using the sand column method ($\psi > -3.1$ kPa, $pF < 1.5$), and pressure plate extractor ($-320$ kPa $\psi > -3.1$ kPa, $1.5 < pF < 3.5$). Following equilibration at each potential, $\theta$ was estimated following oven drying at 105°C for 48 h. For $\psi < -320$ kPa ($pF > 3.5$), the water potential was measured with a dew point potentiometer (WP4T, Decagon Devices).

The measured MRC data were fitted by using a bimodal retention function consisting of a linear superposition of van Genuchten (1980)-type retention models (Durner, 1994):

$$\frac{\theta - \theta_r}{\theta_s - \theta_r} = S_e \left[1 + \left(\frac{\theta - \theta_r}{\theta_s - \theta_r}\right)^{1/m}ight]^{-m}$$

where $\theta_r$ and $\theta_s$ are the residual and saturated water contents (cm$^{-3}$ cm$^{-3}$), respectively; $S_e$ is the effective saturation; $\alpha_1$ and $\alpha_2$ are weighting factors for the MRC and $K_a$; $\theta_1$ and $\theta_2$ are curve-fitting parameters; and $m_1$ and $m_2$ are related to $\theta_1$ and $\theta_2$ as $m_j = 1 - 1/\theta_j$. A summary of the soil-specific parameters is presented in Table 2.

**Estimation of Solid-Phase Permittivity**

The immersion method (Robinson and Friedman, 2003) was used to estimate the permittivity of the soil solids ($\varepsilon_{solid}$) independently of the MRC and $K_a(\theta)$. Detailed methods have been outlined in Kameyama and Miyamoto (2008). Briefly, however, two-phase samples were prepared using oven-dry soil samples saturated with fluids—air ($\varepsilon' = 1$), corn oil ($\varepsilon' = 3.2$), and acetone ($\varepsilon' = 21$) and mixtures of corn oil and acetone ($3.2 < \varepsilon' < 21$; see Table 3). Digitized TDR waveforms were collected with the WinTDR software using a Tektronix 1502B cable tester connected to a seven-rod TDR probe with six outer rods and one center rod, each 50 mm in length and 3 mm in diameter. All fluid and soil $K_a(\theta)$ measurements were made at room temperature, which was assumed to have been 7≈20°C.

**Dielectric Mixing Model**

Soil may be considered a composite of complex dielectrics, with the bulk soil and each constituent having a complex relative permittivity as a function of frequency, $\varepsilon_r(f)$ (e.g., Schwartz et al., 2009b). When subjected to an EM field, some of the energy of the incident EM waves are stored in the soil, represented by the real component of the permittivity, and some of the energy is dissipated, represented by the imaginary component of the permittivity:

$$\varepsilon_r(f) = \varepsilon_r'(f) - j\varepsilon_r''(f) + \frac{\sigma_0}{2\pi\varepsilon_0 f}$$

where $\varepsilon_r'(f)$ and $\varepsilon_r''(f)$ are, respectively, the real and imaginary components of the complex relative permittivity, $\varepsilon_r(f)$, as a function of frequency, $f = \sqrt{-1}$. $f$ is the frequency of the EM wave (Hz), $\varepsilon_0$ is the permittivity of free space (F m$^{-1}$), and $\sigma_0$ is the zero-frequency (direct current) electrical conductivity (S m$^{-1}$).

In soil, phases usually occur adjacent to one another in a non-random fashion. For example, unsaturated soil is a three-phase mixture where water is either in contact with soil solids (water–solid interface) or in contact with air (air–water interface). Even in very dry soil, thin water films coat the soil particles. Thus, for soils, composite sphere dielectric mixing models are often used to simulate the permittivity of the soil (He and Dyck, 2014; Miyamoto et al., 2003, 2005; Friedman, 1998). Thus, we chose the following four-phase, composite sphere dielectric mixing model (Sihvola, 1989; He and Dyck, 2014):

$$\varepsilon_{soil}(f) = \varepsilon_0(f) + \frac{3\varepsilon_0(f) + \varepsilon_{air}(f) - \varepsilon_{solid}(f)}}{1 - \left(\phi_1 + \phi_2 + \phi_3\right)|A|B}$$

$$-j\frac{\sigma_0}{2\pi\varepsilon_0}$$

where $A = \left[\varepsilon_1(f) - \varepsilon_0(f)\right] + 2\varepsilon_1(f) + \varepsilon_0(f) + \varepsilon_{solid}(f) - \varepsilon_0(f) + \varepsilon_{solid}(f) - \varepsilon_0(f) + \varepsilon_{solid}(f) - \varepsilon_0(f)$$

and

<table>
<thead>
<tr>
<th>Soil location</th>
<th>Parameters</th>
<th>$\alpha_1$</th>
<th>$n_1$</th>
<th>$w_1$</th>
<th>$\alpha_2$</th>
<th>$n_2$</th>
<th>$w_2$</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
<th>$\varepsilon_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tsukuba</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>- cm$^{-3}$ cm$^{-3}$</td>
<td>0.027</td>
<td>2.91</td>
<td>0.450</td>
<td>0.000028</td>
<td>1.32</td>
<td>0.550</td>
<td>0.72</td>
</tr>
<tr>
<td>Memuro (topsoil)</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-3}$ cm$^{-3}$</td>
<td>0.035</td>
<td>1.66</td>
<td>0.364</td>
<td>0.000021</td>
<td>1.39</td>
<td>0.636</td>
<td>0.67</td>
</tr>
<tr>
<td>Memuro (subsoil)</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-3}$ cm$^{-3}$</td>
<td>0.099</td>
<td>2.45</td>
<td>0.676</td>
<td>0.000020</td>
<td>1.37</td>
<td>0.323</td>
<td>0.72</td>
</tr>
<tr>
<td>Koshi</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>- cm$^{-3}$ cm$^{-3}$</td>
<td>0.020</td>
<td>1.86</td>
<td>0.448</td>
<td>0.000016</td>
<td>1.38</td>
<td>0.552</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 3. Average, measured soil apparent permittivity ($K_a$) of fluids for two-phase soil–fluid mixtures used to estimate the dielectric permittivity of the soil solids ($\varepsilon_{solid}$) and calibrate the dielectric mixing model.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Average $K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure fluids</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>1.00</td>
</tr>
<tr>
<td>Corn oil</td>
<td>3.24</td>
</tr>
<tr>
<td>Acetone</td>
<td>22.07</td>
</tr>
<tr>
<td>Corn oil/acetone mixtures</td>
<td></td>
</tr>
<tr>
<td>5:1</td>
<td>4.58</td>
</tr>
<tr>
<td>3:1</td>
<td>7.47</td>
</tr>
<tr>
<td>1:1</td>
<td>10.89</td>
</tr>
</tbody>
</table>

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The frequency-dependent model (FDM) was minimized using a Levenberg–Marquardt algorithm implemented in MathCad 15 (PTC Software).

Simulation of TDR-Measured Soil Apparent Permittivity

Frequency-Dependent Model (FDM)

In line with Schwartz et al. (2009b), the frequency-dependent soil apparent permittivity as a function of temperature and \( \theta \) — \( K_a(T, \theta) \) — was simulated according to the following steps:

1. Critical water content, bound and free water contents. The critical water content, \( \theta_{cr} \), was estimated visually from its moisture retention curve (Fig. 1). It was assumed that \( \theta_{cr} \) was equal to the water content at which all intra-aggregate pores were filled with water, determined by visual inspection of the MRCs (Fig. 1), as in Miyamoto et al. (2005) and Blonquist et al. (2006). Further, it was assumed that a significant portion of the water in the intra-aggregate pores was bound or rotationally hindered water. Thus, the water phase was divided into bound and free water phases, with bound water occupying the intra-aggregate pores and free water occupying the interaggregate pores. The volumetric proportions of bound and free water are symbolized by \( \theta_{bw} \) and \( \theta_{fw} \), respectively, with the total volumetric proportion of the water phase expressed as

\[
\theta = \frac{\phi_1 + \phi_2}{\phi_1 + \phi_2 + \phi_3} + \frac{2\varepsilon_2(T_f,f)}{\left[2\varepsilon_2(T_f,f) + \varepsilon_3(T_f,f) + \varepsilon_0(T_f,f)\right] + 2\varepsilon_0(T_f,f)}
\]

where \( \phi_1, \phi_2, \) and \( \phi_3 \) represent the volumetric fraction of the phases occupying the outer shell, inner shell and central sphere, respectively; \( \sigma_0 \) is the zero-frequency direct-current conductivity (S m\(^{-1}\)); and \( \varepsilon_0 \) is the permittivity of free space (F m\(^{-1}\)).

Calibration of the Mixing Model

The paired soil–fluid \( K_a \) measurements used to estimate \( \varepsilon_{\text{solids}} \) were also used to optimize the coefficient of self-consistency, \( v \), in Eq. [4] assuming that the solids were spheres dispersed in the liquid, resulting in the following parameterization: \( \phi_1 = \phi_2 = 0 \), \( \phi_3 = 1 - \rho_l/\rho_s; \varepsilon_3(T_f,f) = \varepsilon_{\text{solids}}^2 \) and \( \varepsilon_0(T_f,f) = \) the measured \( K_a \) of the fluid [see Table 3, \( \varepsilon_3(T_f,f) = \varepsilon_{\text{solids}}^2 \)]. The mixing model (Eq. [4]) was reduced to a two-phase model by setting \( \phi_1 = \phi_2 = 0 \), and

\[
D = \varepsilon_2(T_f,f) - \varepsilon_0(T_f,f)
\]

\[
E = \varepsilon_3(T_f,f) - \varepsilon_0(T_f,f)
\]

\[
F = \varepsilon_3(T_f,f) + 2\varepsilon_2(T_f,f) + v[\varepsilon_{\text{solids}}^2(T_f,f) - \varepsilon_0(T_f,f)]
\]

where \( v \) is called the coefficient of self-consistency; \( \varepsilon_{\text{soil}}^*(T_f,f) \) is the complex permittivity of the soil as a function of temperature and frequency; \( \varepsilon_0^*(T_f,f), \varepsilon_1^*(T_f,f), \varepsilon_2^*(T_f,f), \) and \( \varepsilon_3^*(T_f,f) \) represent the complex permittivity for the phases occupying the background, outer shell, inner shell and central sphere, respectively; \( \varepsilon_{\text{solids}} \) is the zero-frequency direct-current conductivity (S m\(^{-1}\)), and \( \varepsilon_0^* \) is the permittivity of free space (F m\(^{-1}\)).

Fig. 1. Measured (symbols) and modeled (lines; Eq. [2]) moisture retention curves (MRCs) for soils from (A) Tsukuba, (B) Memuro (topsoil), (C) Memuro (subsoil), and (D) Koshi; \( \theta_{cr} \) is the critical water content at which intraaggregate pores are water-filled.
\[ \theta = \theta_{bw} + \theta_{fw} \]  
with \( \theta_{cr} \) being the upper limit of \( \theta_{bw} \), i.e., \( \theta_{bw} \leq \theta_{cr} \) and \( \theta_{fw} = \theta - \theta_{cr} \).

2. Dielectric damping. For each paired measurement of \( K_s(T, \theta) \) and \( \theta \), the effective frequency, \( f_R \), of the reflected EM pulse from the cable tester, was estimated according to the function derived by Schwartz et al. (2009b, Eq. [20]):

\[ f_R(f_S, \theta) = \frac{f_R(1, f_S, \theta)}{1 + 2L \alpha_2 [f_R(1, f_S, \theta)]^2 (t, f_S)} \]  

where

\[ f_R(1, f_S, \theta) = \frac{f_S}{1 + 2L \left( 2\pi f_S \left( \mu_0 \mu_\mu \right) / 2 \sqrt{\mu_0 \mu_0 / \epsilon_{soil} \left( t, f_S \right)} \right)} \]

and

\[ \alpha_2 [f_R(1, f_S, \theta)] = \left[ 2 \pi f_R(1, f_S, \theta) \right]^2 f_{fw} \]  

\[ \frac{2}{2} \times \left\{ \left[ \theta_{fw}^{1/2} \left[ \epsilon_{soil} \left( t, f_S \right) - \epsilon_{\infty} \right] \right] / \left( \epsilon_{soil} \left( t, f_S \right) \right) \right\} \]

where \( f_S \) is the effective frequency of the input bandwidth in the coaxial cable just before it enters the probe (Hz); \( L \) is the length of the TDR probe (m); \( \mu_0 \) is the vacuum magnetic permeability (1.257 x 10^{-6} H m^{-1}); \( p, m, a, \Lambda, \) and \( \Gamma \) are empirical parameters; \( \epsilon_{soil} \) is the real permittivity of the soil at frequency \( f_S \), estimated with Eq. [4]; \( \tau_{fw}(T) \) is the free water relaxation time (s; see Eq. [8] in Step 3); and \( \epsilon_{fw}(T) \) and \( \epsilon_{\infty} \) are the static dielectric permittivity of free water and the permittivity of free water at infinite frequency (see Eq. [10]).

The effective input bandwidth frequency, \( f_S \), is a function of the type and length of coaxial cable as well as the type and number of connectors between the cable tester and probe. Schwartz et al. (2009a) found \( f_S = 650, 450, \) and 150 MHz for probes constructed with 1.5 m of RG-8, 12 m of RG-8, and 12 m of RG-58 cable, respectively, which were routed to the cable tester through a multiplexer with 3 m of RG-8 cable. The probes in this investigation were constructed with RG-58 cable but were not connected to multiplexers, which would result in greater \( f_S \) compared with the setup of Schwartz et al. (2009a).

For the Tsukuba and Koshi soils, 10-cm TDR probes constructed with 1 m of RG-58 cable were used. For the Memuro soils, 30-cm CS610-L (Campbell Scientific) TDR probes constructed with 75 m of RG-58 cable were used. Robinson et al. (2005) found that the effective frequency of the reflected wave for well-constructed, low-loss probes in course-textured soils was 700 to 1000 MHz. The manufacturer-specified rise times for the Tektronix and Campbell cable testers are 200 and 300 ps, resulting in a maximum input frequency of 1.8 and 1.3 GHz, respectively. Considering the different rise times for the two cable testers, different cable lengths for the probes, and some laboratory measurements (data not shown), we assumed \( f_S = 1250 \) MHz for the Tektronix cable tester (Tsukuba and Koshi soils) and \( f_S = 900 \) MHz for the Campbell TDR 100 cable tester (Memuro topsoil and subsoil).

3. Complex permittivity of free water. The relaxation time of free water, \( \tau_{fw}(s) \), is frequency independent when \( f_S < 25 \) GHz (Schwartz et al., 2009b) and can be estimated as a function of temperature (°C) with

\[ \tau_{fw}(T) = \frac{1.1109 \times 10^{-10} - 3.824 \times 10^{-12} T}{2\pi} + \frac{6.938 \times 10^{-14} T^2 - 5.096 \times 10^{-16} T^3}{2\pi} \]

Using the estimated relaxation time with \( T = 20^\circ C \), the following Debye equation was used to estimate the complex dielectric permittivity of the free water, \( \epsilon_{fw}(T) \), for each attenuated frequency, \( f_R \):

\[ \epsilon_{fw}(T, \theta) = \epsilon_{\infty} + \frac{\epsilon_{fw}(T) - \epsilon_{\infty}}{1 + j \left[ 2\pi f_R(f_S, \theta) \tau_{fw}(T) \right]} \]

where \( \epsilon_{\infty} \) is the dielectric permittivity at infinite frequency (3.2), and \( \epsilon_{fw}(T) \) is the static dielectric permittivity of free water as a function of temperature (°C):

\[ \epsilon_{fw}(T) = \frac{3.70886 \times 10^4 - 82.1687 T}{4.21854 \times 10^4 + T} \]

4. Complex permittivity of bound water. The relaxation time for bound water was assumed to be a function of distance from the surface of soil particles, according to the function described by Or and Wraith (1999) and also used by Schwartz et al. (2009b):

\[ \tau_{bw}(T, x) = \frac{4\pi r^3}{kT \exp \left[ -1/(T + 273.15) \right] (b/\theta + d)} \]  

constraint: \( x = r - r_x \in [0, r] \)

where \( T \) is temperature (°C), \( x = \theta_{bw}/S \rho_b \) is the distance between the water and particle surface (m), \( S \) is the specific surface area of the soil (m^2 kg^-1), \( \rho_b \) is the bulk density (kg m^-3), \( r \) is the radius of the water molecule (\~3 x 10^-10 m), \( k \) is the Boltzmann constant (1.38064852 x 10^-23 m^2 kg s^-2 K^-1), and \( \epsilon_0 \) (Pa s), \( b \) (m), and \( d \) (K) are calibration parameters. The constraint was added to ensure that the relaxation time was constant within the first layer of bound water and because Eq. [10] is undefined at \( x = 0 \).

Or and Wraith (1999) used the viscosity of water as a function of distance from clay particles measured by McBride and Baveye (1995) along with the model of Low (1979) to derive Eq. [10] and estimate optimized values for \( \epsilon_{bw} \), \( b \), and \( d \) of 95 x 10^-7 Pa s, 1.621 x 10^-11 m, and 2047 K, respectively. However, Boyarskii et al. (2002) reported relaxation times of water as a function of the distance from clay particles measured by Klivizdie et al. (1984), and using these measurements, we found optimized values for \( \epsilon_{bw} \), \( b \), and \( d \) of 2.039 x 10^-7 Pa s, 3.616 x 10^-11 m, and 1887 K, respectively. Therefore, because there does not seem to be a consensus in the literature about the values of these parameters, we assumed they were soil specific and estimated optimized values for each of the soils in this work. The
procedures for estimating the optimized values of these parameters are presented in Step 3 of the four-phase model below. Using the optimized values of \( c_0, b, \) and \( d, \) the average complex dielectric permittivity of the bound water phase, \( \varepsilon_{bw}(T, \theta) \), at each water content and associated attenuated frequency \( f_R(f_s, \theta) \) (Eq. [6]), was estimated using the complex dielectric permittivity of the water layers, estimated using the Debye equation (see Eq. [8] above) with \( \tau_{bw} (T, x) \) estimated from Eq. [10]:

\[
\begin{align*}
\varepsilon_{bw}(T, \theta) &= \\
&= \frac{1}{x} \left( \frac{1}{\varepsilon_{\infty}} + \left[ \varepsilon_{f_s}(T) - \varepsilon_{\infty} \right] \left[ 1 + j \left[ 2 \pi f_R(f_s, \theta) \tau_{bw}(T, x) \right] \right] \right)
\end{align*}
\]

where is \( x \) is related to \( \theta \) by \( \theta = \varepsilon_{solids} \).

5. Complex permittivity of bulk soil. For each \( \theta, \varepsilon_{sol}(f_T) \) was estimated using a soil–bound water–free water–air (S-BW-FW-A) configuration (background dielectric of air and central sphere of soil solids) of Eq. [4] by setting \( \phi_1 = \varepsilon_{f_s} / \varepsilon_{solids}, \phi_2 = \varepsilon_{bw} / \varepsilon_{solids}, \phi_3 = 1 - \phi_1 / \phi_2, \phi_4 = \varepsilon_{sol}(f_T) = 1, \varepsilon_{1}^{*}(f_T) = \varepsilon_{f_s}^{*}(T, \theta), \varepsilon_{2}^{*}(f_T) = \varepsilon_{bw}^{*}(T, \theta) \) was assumed to equal zero because all \( K \) was estimated with the harmonic mean of the complex permittivity of the water layers, estimated using the Debye equation (see Eq. [8] above) with \( \tau_{bw} (T, x) \) estimated from Eq. [10]:

\[
\begin{align*}
\varepsilon_{sol}(f_T) &= \\
&= \frac{1}{x} \left( \frac{1}{\varepsilon_{\infty}} + \left[ \varepsilon_{f_s}(T) - \varepsilon_{\infty} \right] \left[ 1 + j \left[ 2 \pi f_R(f_s, \theta) \tau_{bw}(T, x) \right] \right] \right)
\end{align*}
\]

where is \( x \) is related to \( \theta \) by \( \theta = \varepsilon_{solids} \).

6. Simulated apparent permittivity. The simulated TDR-measured apparent permittivity at each water content, \( K_s(T, \theta) \), was estimated with

\[
K_s(T, \theta) = \frac{\varepsilon_{sol}^{*}(f_T, \theta)}{2 \left[ 1 + \sqrt{1 + \tan^2 \delta} \right]}
\]

where

\[
\tan \delta = \frac{\varepsilon_{sol}^{''}(f_T, \theta) + \sigma_0(T, \theta)}{2 \pi f_R(f_s, \theta) \varepsilon_0}
\]

7. Parameter optimization. Optimized values of the parameters \( p, m, \Sigma_0 \), and \( \beta \) were estimated by minimizing the mean sum of squared differences between measured and simulated \( K_s(T, \theta) \) using a Levenberg–Marquardt algorithm implemented in MathCad 15, with \( \alpha, \Lambda, \) and \( \Gamma \) set at \( 0.08, 7.442 \times 10^{-6}, 0.5904, \) and \( -0.5904 \), respectively (Schwartz et al., 2009b).

Frequency-Independent Models of \( K_s(T, \theta) \)

Four-Phase Model (FPM). Similar to the approach of Dirksen and Dasberg (1993), a frequency-independent simulation of \( K_s(T, \theta) \) was executed according to the following steps:

1. Critical water content, bound and free water contents. Selection of \( \theta_{cr} \) and partitioning of \( \theta \) into \( \theta_{bw} \) and \( \theta_{fw} \) was performed according to Step 1 of the frequency-dependent model (FDM) above.

2. Permittivity of free water. The \( \varepsilon_{fw}^{*}(T, \theta) \) was assumed to be equal to \( \varepsilon_{fw}(T, \theta) \) calculated with Eq. [9] (~80 at 20°C). The imaginary part of \( \varepsilon_{fw}^{*}(T, \theta) \) was not considered for this model.

3. Permittivity of bound water. The real component of \( \varepsilon_{bw}^{*}(T, \theta) \) was calculated with Eq. [10] and [11] assuming \( f_R = 800 \) MHz for the Tsuchi and Koshi soils measured with the Tektronix cable tester and \( f_R = 500 \) MHz for the Memuro soils measured with the Campbell TDR100 to estimate optimized values of \( c_0, b, \) and \( d. \) The assumed \( f_R \) was based on the fact that it must be less than \( f_s, \) as well as estimates of the reflected frequency of dry and unsaturated soils using the 10-cm probes (data not shown). Optimized values of \( c_0, b, \) and \( d \) were estimated by minimizing the sum of squared differences between measured and simulated \( K_s(T, \theta) \) for \( \theta \leq \theta_{cr} \) using a Levenberg–Marquardt algorithm implemented in MathCad 15. The methods for estimating \( K_s(T, \theta) \) are described in the following two steps. Because \( \varepsilon_{bw}^{*}(T, \theta) \) is a function of \( c_0, b, \) and \( d, \) and \( \varepsilon_{bw}^{*}(T, \theta) \) is used in the estimation of \( K_s(T, \theta) \) via Eq. [4], the simulated \( K_s(T, \theta) \) was also a function of \( c_0, b, \) and \( d. \)

4. Permittivity of soil. The value of \( \varepsilon_{sol}^{*}(T, f) \) was estimated using Eq. [4] with a S–BW–Fw–A configuration by setting \( \phi_1 = \varepsilon_{f_s} / \varepsilon_{solids}, \phi_2 = \varepsilon_{bw} / \varepsilon_{solids}, \phi_3 = 1 - \phi_1 / \phi_2, \phi_4 = \varepsilon_{sol}^{*}(T, \theta) = 1, \varepsilon_{1}^{*}(f_T) = \varepsilon_{bwater}^{*}(T, \theta, \tau_{bwater}(T, x)) \) was assumed to be a power function of \( \theta \) (Schwartz et al., 2009b):

\[
\sigma_0(T, \theta) = \frac{\theta}{1 - \phi_2 / \phi_1} \left[ 1 + \Delta(T - T_0) \right]
\]

where \( \Delta \) is the conductivity at saturation \( \left( \text{S m}^{-1} \right) \) at a reference temperature \( T_0, \) which is an empirical constant, and \( \Delta \) is a temperature correction factor.

For the soils in this work, \( \sigma_0(T, \theta) \) was not measured so \( \Delta \) and \( \Delta/T \) were estimated by optimizing these step by step below. The value of \( \sigma_0(T, \theta) \) was assumed to equal zero because all \( K_s(T, \theta) \) was measured under isothermal conditions.

5. Simulated apparent permittivity. The simulated \( \varepsilon_{sol}(T, f) \) was estimated using Eq. [4] in the previous step was used at the simulated apparent permittivity, \( K_s(T, \theta) = \varepsilon_{sol}(T, f). \)

Phase Configuration Model (PCM). Slightly modifying the approach described by Blonquist et al. (2006) and Robinson et al. (2009), \( K_s(T, \theta) \) was simulated with a phase configuration model (PCM) according to the following steps:

1. Critical water content and bound water permittivity. The values of \( \theta_{cr} \) from the four-phase model (FPM) and FDM were used for the PCM.

2. The value of \( \varepsilon_{sol}(T, f) \) for \( \theta \leq \theta_{cr} \). The values of \( \varepsilon_{sol}(T, f) \) for \( \theta \leq \theta_{cr} \) estimated according to the FPM were for the PCM. This estimation of \( \varepsilon_{sol}(T, f) \) corresponds to \( \varepsilon_{unsat} \) in Blonquist et al. (2006) and Robinson et al. (2009).

3. The value of \( \varepsilon_{sol}(T, f) \) at saturation, \( \theta = \theta_{sat} \). Blonquist et al. (2006) and Robinson et al. (2009) used a two-phase Maxwell–Garnett model to estimate \( \varepsilon_{sol}(T, f) \) at saturation. However, we included a bound water phase at saturation, and estimated \( \varepsilon_{sol}(T, f) \) at saturation with a soil–bound water–free water (S-BW-FW) configuration of Eq. [4] by setting \( \phi_1 = 0, \phi_2 = \varepsilon_{bw} / \varepsilon_{solids}, \phi_3 = 1 - \phi_1 / \phi_2, \phi_4 = \varepsilon_{sol}(T, \theta) \) (~80; Eq. [9]), \( \varepsilon_{2}^{*}(f_T) = \varepsilon_{bw}^{*}(T, \theta) > \varepsilon_{sol}(f_T) \) and \( \varepsilon_{3}^{*}(f_T) = \varepsilon_{solids} \). This estimate of \( \varepsilon_{sol}(T, f) \) corresponds to \( \varepsilon_{sat} \) in Blonquist et al. (2006) and Robinson et al. (2009).
4. The value of $\varepsilon_{\text{soil}}(T)$ between $\theta_c$ and $\theta_a$ was estimated with the dielectric layer model (Blonquist et al., 2006):

$$\sqrt{\varepsilon_{\text{soil}}(T)} = \sqrt{\varepsilon_{\text{sat}}(\theta - \theta_{\text{cr}})} + \sqrt{\varepsilon_{\text{unsat}}(1 - \frac{\theta - \theta_{\text{cr}}}{\theta_c - \theta_{\text{cr}}})}$$

where $\varepsilon_{\text{sat}}$ is estimated in Step 3 and $\varepsilon_{\text{unsat}}$ is estimated in Step 2.

5. Simulation of apparent permittivity. The value of $K_a(T,\theta)$ was assumed to be equal to $\varepsilon_{\text{soil}}(T)$ simulated in Steps 2 through 4.

**Results and Discussion**

**Estimation of Solid-Phase Permittivity and Calibration of Dielectric Mixing Model**

Measured soil $K_a$ when saturated with the fluids listed in Table 3, plotted against measured fluid $K_a$, is presented in Fig. 2. The intersection point of the paired soil–fluid $K_a$ measurements and the 1:1 line were used as an estimate for $\varepsilon_{\text{solids}} = 4.75$. This estimate was made using linear interpolation between the paired soil–fluid $K_a$ measurements closest to the 1:1 line and is lower than the estimate for the same soils determined by Kameyama and Miyamoto (2008) because of differing interpolation methods. Kameyama and Miyamoto (2008) estimated $\varepsilon_{\text{solids}}$ with the intersection point of the 1:1 line and a power curve fitted to the two-phase permittivity measurements.

Calibration of the dielectric mixing model (Eq. [4]) consisted of optimizing the coefficient of self-consistency, $v$, using the two-phase $K_a$ measurements with $\varepsilon_{\text{solids}} = 4.75$, and the optimized values ranged between 4.2 for the subsoil from Memuro and 4.9 for the topsoil from Memuro (Fig. 2). The predictions of the calibrated mixing model for each soil is represented by the lines in Fig. 2.

The $v$ parameter in Eq. [4], as discussed by Sihvola (1989), is a way to account for the violation of the assumption of relatively large distances between dielectric inclusions (i.e., soil particles, water films) within the background dielectric of the mixture inherent in Rayleigh-type mixing models such as Maxwell–Garnett (MG) (Sihvola, 1989; Hilhorst et al., 2000). In Fig. 2, it can be seen that the well-known MG mixing model deviates from the calibrated mixing model at higher permittivities only when the background dielectric is 50 to 100% acetone. In fact, the mixing model presented in Eq. [4] reduces to the two-phase MG model when $\phi_1 = \phi_2 = 0$ and $v = 0$.

The major assumptions inherent in this two-phase calibration procedure are (i) the background dielectric fluids do not interact with the soil particles, causing a change in the permittivity of the fluid compared with its free state, and (ii) the two-phase calibration can be extended to three- or four-phase mixtures. With respect to the first assumption, acetone is weakly polar and, like free water, has a stable dielectric spectrum in the bandwidth typical of Tektronix cable testers, but Robinson (2004) observed that the permittivity of acetone may be reduced when mixed with clay minerals like montmorillonite. The clay minerals in the Andisols investigated in this work are primarily allophane (Wada, 1986; Ishida et al., 2000) with a crystal structure of short-range order and probably do interact with acetone, but the extent of this interaction has not been documented. The second assumption could not be tested with the data available for these soils. For Eq. [4], the addition of a third and fourth phase amounts to introducing additional shells around spherical inclusions representing the soil solid phase, and with more than two phases, there is more than one possible configuration of the phases. The two-phase calibration was based on changing the permittivity of the background dielectric—$\varepsilon_0$ in Eq. [4], but air is always assumed as the background dielectric for the four-phase implementation used to simulate $K_a(T,\theta)$. Further, the choice of configuration is relative straightforward for two-phase mixtures but not as straightforward for three- and four-phase mixtures.

Different from the S-BW-FW-A configuration in this work, Miyamoto et al. (2005) used an air–bound water–soil–free water–air (A–BW–S–FW–A) configuration implemented using a dual composite sphere model: A–BW–S–A and BW–S–FW–A to simulate $K_a(T,\theta)$ when $\theta < \theta_c$ and $\theta > \theta_c$, respectively. The two composite sphere configurations were weighted as a nonlinear function of $\theta$ to estimate $K_a(T,\theta)$. Because there is connectivity between intra- and interaggregate pores, it is reasonable to assume that the bound water phase is in contact (i.e., adjacent to) the free water phase, which is represented by the S–BW–FW–A configuration assumed for this work. On the other hand, this configuration excludes contact between the free water phase and the solid phase. Using the dual composite approach of Miyamoto et al. (2005),
contact between free water and soil solids is achieved but at the expense of contact between free water and bound water.

Ideally, the predictions of dielectric mixing models should be compared with measurements on soil–fluid mixtures with a minimum of three phases with known volumetric fractions using fluids that do not interact with soil particles (i.e., known permittivity), but this would be a time-consuming and logistically challenging exercise. Without calibration, a value for the $v$ parameter would have to be assumed or an existing mixing model like the MG model would have to be assumed. As can be seen in Fig. 2, the MG model (assuming $v = 0$) does not describe the data at higher $K_a$, which would probably cause greater errors when continuing to use this model to predict $K_a(T, q)$ compared with the calibrated model.

Finally, it should be noted that an alternative set of models that are commonly used that don’t require assumptions about phase configuration assume that soil phases are discrete (He and Dyck, 2014). The four-phase de Loor model used by Dirksen and Dasberg (1993) and Schwartz et al. (2009b) assumes the phases are discrete, disk-shaped ellipsoids (de Loor, 1968).

**Bound Water Permittivity**

The moisture retention curves of the four soils with estimated $\theta_{cr}$ are presented in Fig. 1. Consistent with the approach of Blonquist et al. (2006) and Miyamoto et al. (2005), it was assumed that $\theta_{cr}$ was equal to the intra-aggregate porosity, although Blonquist et al. (2006) distinguished between a hydraulic critical water content ($\theta_{hc}$) from the MRC and $\theta_{cr}$ estimated from the $K_a(T, \theta)$ curve. We found that it was difficult to estimate $\theta_{cr}$ using only the $K_a(T, \theta)$ curve and opted to use the MRC because it clearly distinguishes between intra- and interaggregate pores; $\theta_{cr}$ was equal to 0.35, 0.41, 0.21, and 0.34 m$^3$ m$^{-3}$, which corresponded to 4.2, 5.5, 5.7, and 5.3 layers of water (estimated with

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**Fig. 3.** Summary of (A) relaxation time of estimated intra-aggregate water $\tau_{bw}(T, x)$ (s), complex dielectric permittivity of the bound water phase $\varepsilon_{bw}(T, x)$ at frequencies of (B) 800 MHz and (D) 500 MHz, and the average complex dielectric permittivity of the bound water phase $<\varepsilon_{bw}^*(T, \theta)>$ at frequencies of (C) 800 MHz and (E) 500 MHz as a function of distance from soil particles (x axis spans 0 to 6 molecular layers of water). Symbols represent measurements reported in the references cited in the legend. Lines represent estimates made with Eq. [10] and [11] using calibration parameters $c_0$, $b$, and $d$ reported in the cited literature or optimized for the Andisols in this work (see Table 4) with the exception of the Friedman (1998) model. For Boyarski et al. (2002), $c_0$, $b$, and $d$ are $2.039 \times 10^{-7}$ Pa s, $3.616 \times 10^{-7}$ m, and 1887 K, respectively. For Or and Wraith (1999), $c_0$, $b$, and $d$ are $9.5 \times 10^{-7}$ Pa s, $1.621 \times 10^{-7}$ m, and 2047 K, respectively.
the specific surface and bulk density values reported in Table 1) for the Tsukuba, Memuro (topsoil), Memuro (subsoil), and Koshi soils, respectively.

Other researchers have constrained the upper bound of $\theta_{bw}$ to the first three particle-adjacent layers of water (e.g., Schwartz et al., 2009b). Although we define $\theta_{bw}$ using $\theta_{cr}$, we do not assert that all water in the intra-aggregate pores is “bound.” Friedman (1998), Robinson et al. (2002), and Miyamoto et al. (2005) made the argument that the transition from the bound water to the free water phase was continuous and therefore the permittivity of the water phase could be estimated as a function of distance from the surface of soil particles, and we follow a similar approach. Friedman (1998) developed an isothermal, frequency-independent, harmonic mean model based on describing the permittivity of the water phase as a function of distance from soil particles with an exponential-rise-to-a-maximum function. The bound water permittivity model represented by Eq. [10] and [11] gives similar results to the harmonic mean model presented by Friedman (see Fig. 3) but is frequency- and temperature-dependent. The optimized values of $c_0$, $b$, and $d$ estimated using the procedures outlined in Step 3 of the FPM are presented in Table 4, and the plots of $\tau_{bw}(x,T)$, $\varepsilon_{bw}^*(T,\theta)$, and $<\varepsilon_{bw}^*(T,\theta)>$ as a function of distance from the soil particle surface estimated with Eq. [10] and [11] are presented in Fig. 3. As can be seen in Fig. 3, the permittivity of bound water approaches values close to free water within a distance of three to six water layers (i.e., $\theta < \theta_{cr}$) even at lower frequencies, making it unnecessary to constrain $\theta_{bw}$ to an arbitrary number of layers of water. Overall, Eq. [10] and [11] with soil-specific, optimized parameters yield predictions of $\tau_{bw}(x,T)$, $\varepsilon_{bw}^*(T,\theta)$, and $<\varepsilon_{bw}^*(T,\theta)>$ that are consistent with those of Boyarskii et al. (2002) and also with the bound water permittivity estimates of Dirksen and Dasberg (1993), Heimovaara et al. (1994), Mironov et al. (2004), and Kameyama and Miyamoto (2008), which ranged between 15 and 60.

Blonquist et al. (2006) asserted that, at the time of the publication of their study, there had been little direct evidence regarding how much the permittivity of bound water is reduced compared with free water. They rightly observed that the addition of a bound water phase into dielectric mixing models may improve mixing model estimates of $K_a(T,q)$, but this doesn’t amount to a direct measurement of $\varepsilon_{bw}^*(T,\theta)$ or $<\varepsilon_{bw}^*(T,\theta)>$. Uncertainties in the estimation of $<\varepsilon_{bw}^*(T,\theta)>$ with dielectric mixing models may be attributed to (i) uncertainty in $\varepsilon_{sols}$—these values are often assumed; (ii) an incorrect choice of mixing model in terms of particle shape (spheres vs. disks), configuration of phases (e.g., soil–water–air vs. water–soil–air or discrete vs. concentric ellipsoids); (iii) a lack of mixing model calibration or calibration is impossible; (iv) uncertainty regarding the quantity

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**Table 4. Summary of soil-specific, optimized input parameters for the frequency-dependent (FDM), four-phase (FPM), and phase configuration (PCM) models.**

<table>
<thead>
<tr>
<th>Soil location</th>
<th>$\mu$</th>
<th>$c_0$</th>
<th>$b$</th>
<th>$d$</th>
<th>$\theta_{cr}$</th>
<th>$\varepsilon_{unsat}$</th>
<th>$\varepsilon_{sat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tsukuba</td>
<td>4.52</td>
<td>1.26</td>
<td>1.67</td>
<td>2575</td>
<td>0.35</td>
<td>10.19</td>
<td>46.24</td>
</tr>
<tr>
<td>Memuro (topsoil)</td>
<td>4.90</td>
<td>0.836</td>
<td>3.99</td>
<td>2003</td>
<td>0.41</td>
<td>17.93</td>
<td>44.72</td>
</tr>
<tr>
<td>Memuro (subsoil)</td>
<td>4.20</td>
<td>1.98</td>
<td>3.81</td>
<td>1887</td>
<td>0.21</td>
<td>8.44</td>
<td>48.79</td>
</tr>
<tr>
<td>Koshi</td>
<td>4.52</td>
<td>1.23</td>
<td>1.54</td>
<td>2590</td>
<td>0.34</td>
<td>11.97</td>
<td>56.82</td>
</tr>
</tbody>
</table>

† Coefficient of self-similarity (see Eq. [4]), used in FDM, FPM, and PCM.
‡ See Eq. [10]; used to calculate $<\varepsilon_{bw}^*(T,\theta)>$ for FDM, FPM, and PCM.
§ Values of the critical water content $\theta_{cr}$ estimated from moisture retention curves (Fig. 1); used in FDM, FPM, and PCM.
¶ Used only in the PCM.
of bound water, $\theta_{bw}$; and (v) mixing models do not consider dielectric damping.

In this work, efforts have been made to address at least some of these uncertainties through direct estimation of $\varepsilon_{\text{solids}}$ and calibration of the dielectric mixing model through optimization of the $v$ parameter using two-phase soil–fluid mixtures, which, to our knowledge, was not performed in previous investigations (e.g., Friedman, 1998; Robinson et al., 2002, 2009; Miyamoto et al., 2005; Blonquist et al., 2006). These steps increase our confidence in the estimates of bound water permittivity for the Andisols in this work.

**Comparison of $K_a(T,\theta)$ Simulations**

The $K_a(T,\theta)$ relationship for each of the four soils and simulated $K_a(T,\theta)$ with the FDM, FPM, and PCM are presented in Fig. 4, and optimized and input parameters for the FDM, FPM, and PCM are presented in Tables 4 and 5. It is clear in Fig. 4 that the FDM model best simulated the observed $K_a(T,\theta)$ relationship for all four soils. The FDM model, however, had four additional optimized parameters. All models used the same optimized $v$ (Eq. [4]) and the same optimized parameters for Eq. [10] used to estimate $\langle \varepsilon_{bw}(T,\theta) \rangle$ with Eq. [11]. Because the parameters for Eq. [10] were optimized using $K_a(T,\theta)$ for $\theta \leq \theta_{cr}$, it is not surprising that all three models agree well with the measured $K_a(T,\theta)$ values for $\theta \leq \theta_{cr}$, but the FPM and PCM models under- or overestimated $K_a(T,\theta)$ for $\theta > \theta_{cr}$ to varying degrees for each soil. For the soils from Tsukuba and Memuro (topsoil and subsoil), the FPM model underestimated and the PCM model overestimated $K_a(T,\theta)$ for the highest six water contents. For the Koshi soil, the FPM model underestimated and the PCM model overestimated $K_a(T,\theta)$ for the highest two and four water contents, respectively.

It should be emphasized that the optimized parameters of the FDM presented in Table 5 contain a significant degree of uncertainty because there weren’t any measurements of electrical conductivity as a function of water content available to constrain the values of the $\Sigma_0$ and $\beta$ parameters, and this probably also caused uncertainty in the $p$ and $m$ parameters. For the Koshi soil, $\Sigma_0 < 0$, which is unrealistic but consistent with a scenario where salinity does not significantly affect $K_a(T,\theta)$, as discussed below. However, the ability of the FDM to simulate $K_a(T,\theta)$ for

<table>
<thead>
<tr>
<th>Soil location</th>
<th>Input $f_S$ (MHz)</th>
<th>Optimized parameters $p$ (Eq. [6])</th>
<th>$m$ (Eq. [6])</th>
<th>$\Sigma_0$†</th>
<th>$\beta$ (Eq. [12])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tsukuba</td>
<td>1250</td>
<td>42.7</td>
<td>4.2</td>
<td>0.38</td>
<td>3.9</td>
</tr>
<tr>
<td>Memuro (topsoil)</td>
<td>900</td>
<td>2.4</td>
<td>1.7</td>
<td>0.24</td>
<td>1.5</td>
</tr>
<tr>
<td>Memuro (subsoil)</td>
<td>900</td>
<td>24.6</td>
<td>5.5</td>
<td>0.52</td>
<td>0.85</td>
</tr>
<tr>
<td>Koshi</td>
<td>1250</td>
<td>31.5</td>
<td>4.8</td>
<td>-0.062</td>
<td>0.52</td>
</tr>
</tbody>
</table>

† Conductivity at saturation.

**Fig. 5.** Simulated components of the frequency-dependent model: (A) $f_R(f_S, \theta)$, Eq. [6]; (B) $\langle \varepsilon_{bw}(T,\theta) \rangle$, Eq. [11]; (C) $\varepsilon_{\text{soil}}(T, f)$, Eq. [4]; and (D) $\tan \delta$, Eq. [14], as a function of water content $\theta$ for four Japanese Andisols.
\( q > q_{cr} \) generates an important hypothesis about the frequency dependence of the bound water permittivity because of dielectric damping at high water contents in soils with a significant volumetric fraction of bound or rotationally hindered water.

A further breakdown of the components of the FDM model for all four soils is presented in Fig. 5. A key, unique feature of the FDM shown in Fig. 5B is that it predicts that \( \langle \varepsilon_{bw}^*(T,\theta) \rangle \) continues to increase even after \( q > q_{cr} \) (Schwartz et al., 2009b). Therefore, the FDM predicts that the increase in \( K_a(T,\theta) \) with \( \theta \) is due not only to an increase in \( \theta_{tw} \) but also to an increase in \( \langle \varepsilon_{bw}^*(T,\theta) \rangle \) (Eq. [11]) because dielectric damping filters out the highest frequencies of the input EM band as soil saturation increases (Fig. 5A; Eq. [6]). The only mechanism for an increase in \( \langle \varepsilon_{bw}^*(T,\theta) \rangle \) in the FPM and PCM models is an increase in \( \theta_{bw} \) and an increase in \( \varepsilon_{bw}^*(T,x) \) farther away from the soil particles.

The loss tangent, \( \tan\delta \) (Fig. 5D), is essentially the ratio of attenuation to storage of electrical energy in the soil when exposed to an EM field. Considering Eq. [13], in cases where \( \tan\delta < 1 \),
1. A mixing model calibration method was developed using measurements generated by the immersion method (Robinson and Friedman, 2003) for estimating \( \varepsilon_{\text{solids}} \). The probable benefit of mixing model calibration is reduced uncertainty of indirect estimates of bound water permittivity and reduced uncertainty in the parameters of bound water permittivity models.

2. Based on the simulation results, a hypothesis was generated regarding the cause of unique \( K_s(T,\theta) \) functions of the Andisols in this work: that the large increase in slope of \( K_s(T,\theta) \) after \( \theta \) surpasses a threshold value, \( \theta_{cr} \), is a result of increasing \( \varepsilon_{\text{bw}}*(T,\theta) \) due to reduced frequencies at higher water contents, probably caused by bulk water polarization attenuation of the incident EM wave. This suggests that TDR measurements of soil \( K_s(T,\theta) \) should be paired with estimates of effective frequency of the reflected wave such as those presented by Topp et al. (2000) or Robinson et al. (2005).

3. Based on the significant correlation between some of the soil pore-size distribution bound water dielectric model parameters, it can be hypothesized that the influence of soil structure on phase configuration may also influence attenuation of broadband EM waves that in turn affect \( \varepsilon_{\text{bw}}*(T,\theta) \).

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References


Table 6. Relationship between the intra-aggregate pore volume \( \theta_{cr} \) mixing model coefficient of self-similarity \( v \), and bound water relaxation time model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \theta_{cr} )</th>
<th>( v )</th>
<th>( \varepsilon_0 )</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_{cr} )</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( v )</td>
<td>0.95*</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_0 )</td>
<td>-0.99*</td>
<td>-0.97*</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>( m )</td>
<td>-0.84</td>
<td>-0.96*</td>
<td>0.85</td>
<td>1</td>
</tr>
</tbody>
</table>

* Significant at \( P < 0.05 \) (df = 2).
† See Eq. [1].
‡ See Eq. [4].
§ See Eq. [10].
¶ See Eq. [6].


