

## Modelling the relative permittivity of soils using soil hygroscopic water content

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### Abstract

A model describing the increase in the relative permittivity of water with distance from the soil mineral surface is presented. The model assumes an exponential increase in the value of permittivity with increasing distance from the mineral surface; arguments are presented supporting this approach. The volume of bound water (within the bandwidth of time domain reflectometry, (TDR) 0.01–1 GHz) is considered to be equivalent to the soil hygroscopic water content. The refractive index mixing equation is used as a geometric base into which the model is incorporated. The new equation is tested using measurements of permittivity collected from two drying undisturbed soil cores that contained  $\sim 10\%$  hygroscopic water. The RMSE of predicted permittivity as a function of water content was found to decrease from  $\sim 3.5$  to less than 1. The model was further tested on data previously presented in the literature and found to correspond reasonably well. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Bound water; Hygroscopic water; Soil relative permittivity; Time domain reflectometry, TDR; Dielectric constant

### 1. Introduction

The contribution of bound water to the relative permittivity of bulk soil has formed the basis of much discussion in the literature (Bockris et al., 1963; Dobson et al., 1985; Dirksen and Dasberg, 1993; Or and Wraith, 1999). Measurement of the quantity of water that has a reduced relative permittivity and is effectively bound (within the time domain reflectometry (TDR) bandwidth) is an important consideration in the modelling of the dielectric behaviour of porous materials.

Dielectric sensors such as TDR and capacitance probes are commonly used to estimate soil water content. A reliable estimate of which is often required

for monitoring purposes or as an input in many hydrological modelling applications (Gardner et al., 2001). Using a standard calibration to estimate water content such as Topp et al. (1980) for a soil that contains bound water can lead to a substantial underestimate of the absolute water content (5–10%). There is therefore a need for a simple calibration model, which incorporates the effect of bound water on the measurement of permittivity using dielectric sensors, so that improved estimates of water content might be obtained. The quantity of bound water must be easily measurable, thus we propose the use of the hygroscopic water content as an estimate of the quantity of bound water in a soil.

A range of methods have been used to study the molecular structure of water, these include; dielectric relaxation, nuclear magnetic resonance (NMR), electron spin resonance (ESR) and neutron, electron and

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X-ray diffraction (Sposito, 1984). Sposito (1984, 1989) discusses a range of adsorption mechanisms for different mineral surfaces in detail. In static fields, the first monolayer of water is believed to be held most strongly, with subsequent molecular layers becoming gradually less so with distance from the soil surface. The evidence suggests that most of the bound water is in the first 1 nm from the surface (3 monolayers), although this may increase depending on the mineralogy (Sposito, 1984).

The objective of this study is to incorporate a model describing the progressive increase of water permittivity with distance from the soil surface into a dielectric mixing formula. Our proposed method of using the hygroscopic water content is intended to provide an easily quantifiable way of linking the model to easily measured input parameters.

As early as the 1960s, Low (1961) suggested that the relative permittivity of water in soils was unlikely to behave like a single layer of ice, although its relative permittivity would be reduced at the solid–liquid interface and increase with distance from it. Thorp (1959) presented estimates of the relative permittivity of water vapour adsorbed onto silica gel, which gave values of 41 for the first monolayer and 66 for the second. Bockris et al. (1963) presented a conceptual model demonstrating how the relative permittivity of water might alter near to the mineral surface. They suggested a first layer of water with a relative permittivity of 6, a second layer with 32 and a third layer with the relative permittivity value of bulk water, 80. Sposito (1984) concluded that the evidence in the literature pointed to an average value of  $\sim 20$  for the static permittivity of bound water with three or more layers of water being affected, depending on the mineralogy.

The use of permittivity measuring devices to estimate water content has again raised the issue of bound water but now for frequencies above 0.1 GHz, which may exaggerate the quantity of bound water compared with static values. Most attempts to understand the dielectric properties of soils as a function of water content have treated bound water as a fourth dielectric component along with the air, solid and free water fractions. The relative permittivity of this component is controversial and there is little direct evidence of its value. Dirksen and Dasberg (1993) assumed a mono-molecular layer of bound water with the permittivity

of ice ( $\epsilon_r = 3.2$ ) when applying the de-Loor (1968) model to estimate soil water content. They did however, point out that both theoretical (Gur et al., 1978) and experimental (Israelachvili and Pashley, 1984) evidence pointed to a gradual increase in the relative permittivity of water with distance away from mineral surfaces. In a very detailed recent experiment, Wraith and Or (1999) and Or and Wraith (1999) presented both experimental and theoretical results describing temperature effects on the measured permittivity of soils. In their treatment of the subject, they suggested that bound water (within TDR bandwidth) was responsible for the observed changes in permittivity observed with changes of temperature. In the modelling they conducted, they used a value of 12 for the permittivity of the bound water phase and obtained good estimates of permittivity as a function of water content.

## 2. Theoretical considerations

Assuming a continuum modelling approach, the permittivity of water with increasing distance from a surface might be considered to lie between the arithmetic and harmonic means. The arithmetic mean implying a water structure like capacitors connected in parallel with the mineral surface and the harmonic mean implying connection in series. Assuming a monolayer evenly spread over the mineral surface, one might intuitively expect the bound water to tend to the harmonic average when using a capacitive modelling approach (Friedman, 1998). However, we propose an alternative reasoning based on the molecular scale and consider that the permittivity of the bound water is similar to the permittivity of water near to a point charge.

Ritson and Hasted (1948) proposed that the decrease in the real part of the permittivity of an aqueous ionic solution was due to dielectric saturation in the first hydration sheath of an ion. They used two different models to demonstrate the effect of a point charge on the permittivity of water molecules surrounding it (e.g. a monovalent cation). They demonstrated that the result was reasonably independent of the model used. The result of averaging their results, fitting an empirical curve and finding the area under that curve, for distances representing the

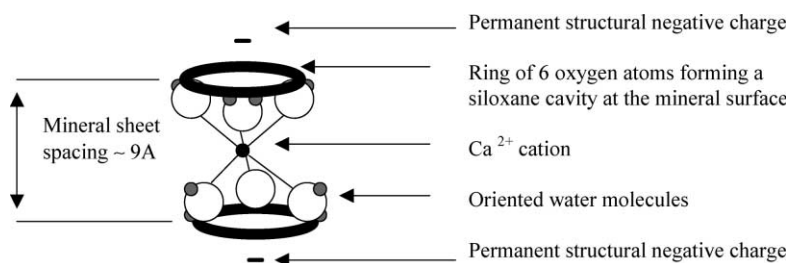


Fig. 1. Example of a possible configuration of a hydrated calcium cation co-ordinated with two siloxane cavities between clay mineral surfaces. The solid black rings represents the six surface oxygen atoms forming the cavity. The permanent negative charge is centred within the cavity.

diameter of a water molecule (2.8 Å), yielded an estimate of permittivity with respect to distance from the point charge (equivalent to a monovalent cation). The obtained values were 18, 72 and 78 for the first 3 layers of water respectively; such that, by the third layer the value of bulk water had been attained. We believe that this permittivity behaviour is in-keeping with the conceptual behaviour of water hydrating monovalent and divalent cations, for example a hydrated calcium cation counter balancing permanent structural charge at a siloxane cavity (Fig. 1). The arrangement of the water molecules around the cation is of great importance, as this will determine how

much of the charge neutralises surface charge and how much orientates the water molecules hydrating the cation. In view of the calculations performed by Ritson and Hasted (1948), their model would suggest that, if a water molecule were interposed between the charged ion and the mineral surface, little of the ion's charge would neutralise the surface charge as the water molecule would effectively shield the ion. The neutralising of surface negative charge by ions suggests that water is not directly interposed between the surface and the ion. The exact co-ordination of the water around the hydrated cation remains an interesting problem.

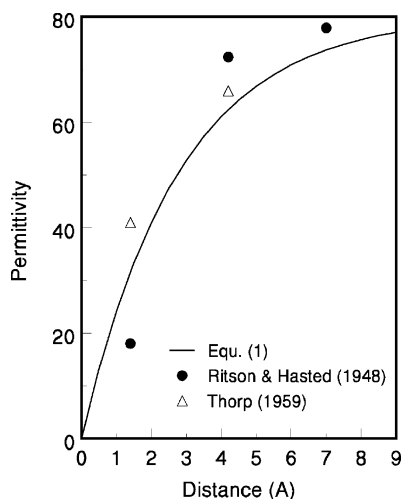


Fig. 2. The prediction by the proposed model (Eq. (1)) of water permittivity with respect to distance from a charged mineral surface. The solid circles represent permittivity estimates modelled for water molecules surrounding a point charge (Adapted from Ritson and Hasted, 1948). The triangles represent measurements of water adsorbed on silica gel taken from Thorp (1959).

### 2.1. Model describing the relative permittivity of water with distance from the soil surface

Estimates of the size of the bound water fraction can be made from measurements of specific soil surface area with assumptions about the number of bound water layers and the value of the permittivity of these layers (Bockris et al., 1963; Or and Wraith, 1999 and the references therein). An alternative approach is to consider that the hygroscopic water represents the volume of water effectively bound and that the increase in value of the waters' relative permittivity is exponential, which will be qualified in the following argument. The advantages of using the hygroscopic water content are that it is easily measured and that it requires no assumptions made from surface area measurements. Intuitively, it appears an appropriate measurement, combining both surface area accessible to water molecules and the strength with which they are bound to the mineral surfaces. Eq. (1) describes the relative permittivity of water as a function of distance from the soil surface,

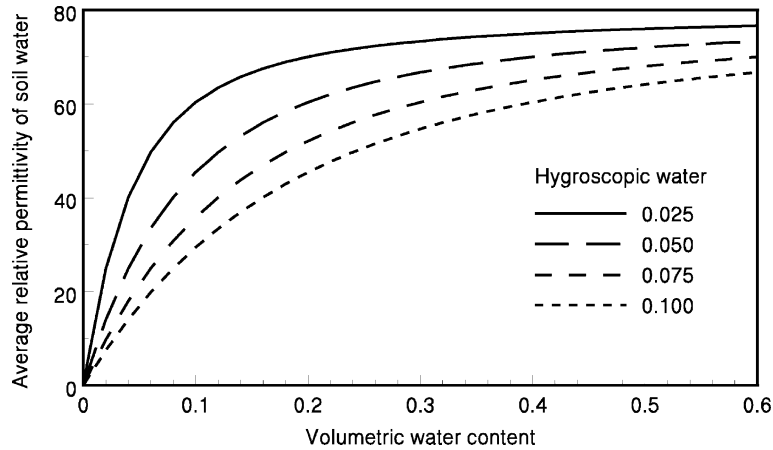


Fig. 3. Average relative permittivity of soil water as a function of the hygroscopic water content (Eq. (3)).

assuming an exponential increase in the water permittivity with distance from the mineral surface.

$$\epsilon_w = \epsilon_{fw} \left( 1 - e^{-\frac{1}{\beta}x} \right) \quad (1)$$

where,  $\epsilon_w$  is the permittivity of water with distance from the mineral surface,  $\epsilon_{fw}$  is the permittivity of free water (78.54 at 25°C),  $\beta$  is the thickness of bound water (Å) and  $x$  is the distance from the mineral surface (Å). Fig. 2 presents Eq. (1) assuming a bound water layer of thickness 2.8 Å (1 hydration sheath) and compares this with the permittivity estimates taken from Ritson and Hasted (1948), described in Section 2. The measurements of Thorp (1959) are also presented and suggest similar values to those estimated by the proposed model. The use of this form of model (Eq. (1)) appears justified based on these estimates and measurements.

Eq. (1) provides the permittivity of water as a function of distance; however, it is the mean permittivity of the water that is of interest. To obtain this, Eq. (1) is integrated with respect to  $x$ .

$$\begin{aligned} \epsilon_w(Av) &= \frac{\int \epsilon_{fw} \left( 1 - e^{-\frac{1}{\beta}x} \right) dx}{x} \\ &= \frac{\left[ \left[ x + \beta e^{-\frac{1}{\beta}x} \right] - \beta \right] \epsilon_{fw}}{x} \end{aligned} \quad (2)$$

The  $-\beta$  appearing after the integration is the

constant of integration. Eq. (2) can be rewritten for water content based on the assumption that the water content is equal to surface area multiplied by distance ( $SAx$ ) where  $SA$  is in  $m^2$

$$\epsilon_w(Av) = \frac{[(\theta + (\theta_{bw} e^{-\theta/\theta_{bw}})) - (\theta_{bw})] \epsilon_{fw}}{\theta} \quad (3)$$

where  $\epsilon_w(Av)$  is the arithmetic mean permittivity of the soil water phase,  $\epsilon_{fw}$  is the relative permittivity of free water ( $\sim 80$ ),  $\theta$  is the soil volumetric water content and  $\theta_{bw}$  is the bound volumetric water content (equivalent to the hygroscopic volumetric water content). Fig.3 illustrates how  $\epsilon_w(Av)$  changes as a function of volumetric water content for differing amounts of hygroscopic water.

## 2.2. The refractive index mixing model

The relative permittivity of soils has been measured and empirical equations fitted to the data by Topp et al. (1980); it has also been modelled using more physically based descriptions (Dirksen and Dasberg, 1993; Friedman, 1998). Soil is a composite dielectric whose measured permittivity ( $\epsilon$ ), is a function of the relative permittivity and abundance of each of the various dielectric components. A common expression represents the relative permittivity of the soil, when raised to some power,  $\alpha$ , as the sum of the individual relative permittivities raised to the same power weighted,

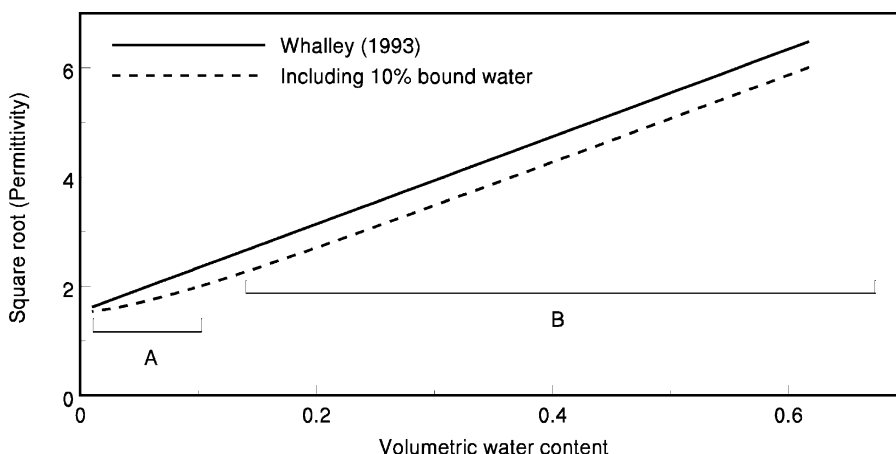


Fig. 4. Modelled curves demonstrating how the presence of bound water is likely to effect the shape of the relationship between water content and soil refractive index. (A) The presence of bound water reduces the square root of the permittivity as a function of water content. (B) As the relative permittivity of the soil water reaches that of free water so the second curve parallels the first.

according to their respective volumes

$$\epsilon^\alpha = \sum_i V_i \epsilon_i^\alpha \quad (4)$$

where,  $V_i$  is the volume fraction and  $\epsilon_i$  is the relative permittivity of the  $i$ th soil component. Models of this form have been presented by a number of authors (Looyenga, 1965; Birchak et al., 1974; Dobson et al., 1985; Roth et al., 1990; Whalley, 1993; Heimo-vaara et al., 1994). A value of 0.5 for the exponent gives the refractive index model (Birchak et al., 1974; Whalley, 1993). Although the physical basis of this model describes a layered dielectric system, it is often found to give a reasonable representation of  $\epsilon$ . Written for 3 layered phases, Whalley (1993) presented the model as:

$$\sqrt{\epsilon_{\text{soil}}} = \theta(\sqrt{\epsilon_w} - 1) + \frac{\rho_b}{\rho_s}(\sqrt{\epsilon_s} - 1) + 1 \quad (5)$$

where,  $\theta$  is the volumetric water content,  $\epsilon_w$  is the relative permittivity of water,  $\epsilon_s$  is the relative permittivity of the solid,  $\rho_s$  is the density of the solid and  $\rho_b$  is the dry bulk density of the mixture.

Insertion of the value of  $\epsilon_w(A_v)$  calculated from Eq. (3) into Eq. (5) in place of  $\epsilon_w$ , gives the relative permittivity of the soil as a function of the solid, gas, hygroscopic (bound) and free water and results in an implicit equation which can be solved for water

content

$$\theta \left[ \sqrt{\frac{[(\theta + (\theta_{bw} e^{-\theta/\theta_{bw}})) - (\theta_{bw})]\epsilon_{fw}}{\theta}} - 1 \right] + \frac{\rho_b}{\rho_s}(\sqrt{\epsilon_s} - 1) + 1 - \sqrt{\epsilon_{\text{soil}}} = 0 \quad (6)$$

The result is shown in Fig. 4 where the reduced permittivity of a soil with 10% hygroscopic water can be seen to reduce the value of the soil relative permittivity below that which would be obtained if all the water were assumed free. At higher water contents (section marked B), the curve parallels the line predicted using the relative permittivity of free water (Whalley, 1993). This is in agreement with observed data such as that of Topp et al. (1980) who showed that, in vermiculite and organic soils, the apparent permittivity of the soil was lower than in mineral soils with comparatively low surface areas.

### 3. Methods

#### 3.1. Soil properties

To test the model, a soil which had a large surface area, was needed that did not shrink on drying (as this would alter the bulk density). A ferric soil from Northern Ireland, with a basaltic parent material provided

Table 1  
Soil physical and chemical properties

	Sandy soil	Ferric soil
Average dry bulk density (g cm <sup>-3</sup> )	1.61	1.05
Sand % (2000–60 µm)	93.5	38.1
Silt % (60–2 µm)	4.2	38.8
Clay % (<2 µm)	0.3	12.3
Mineralogical constituents in order of decreasing quantity	Quartz	Iron oxide Kaolinite Smectite Illite
Organic matter %	2.06	10.8
pH	6.55	5.70
EC 1:5 water extract S m <sup>-1</sup>	0.0295	0.0189

such a material. The results from this could be compared with a sandy soil with a low surface area and thus negligible bound water.

Two replicate, undisturbed cores (103 mm in diameter and 150 mm in length) of each soil were collected in plastic sleeves with a perforated base. The first was a ferric soil from the Giants Causeway, Northern Ireland (OS, 24, 944 445) the second was an agricultural sandy soil from East Anglia (TL, 698 713), with which it was compared. Their physical and chemical properties were characterised by a series of routine analyses; these included particle size, mineralogy using X-ray diffraction, organic matter via loss on ignition, pH in a 1:2.5 water extract and solution electrical conductivity in a 1:5 water extract; the properties are shown in Table 1.

The hygroscopic water content of the soil was determined by air drying a homogenised sample from each soil in the laboratory at a relative humidity between 50 and 60%. The samples were dried for a month, weighed accurately, then dried in an oven at 105°C to determine the gravimetric water loss.

### 3.2. TDR measurements on undisturbed soil cores during drying

In the laboratory, the undisturbed soil cores were saturated from the base upward with de-ionised water. After wetting, a pair of stainless steel electrodes (100 mm length and 6 mm diameter, with a centre spacing of 25 mm) was inserted into the soft soil so that measurements could be taken. The cores, with the

electrodes installed, were then allowed to dry out in the laboratory by evaporation from the open top surface and through the perforated base, ensuring as even a distribution of water within each core as possible. The laboratory temperature remained between 17 and 19°C during the drying. The relative permittivity of each core was measured with a Tektronix TDR (1502 C). In the early stages of drying, measurements were made daily then approximately two-daily. The cores were dried until no loss in mass occurred (~3 months). Each core was then examined for stones or natural voids that may have influenced the measurements; none were found. The cores were oven dried at 105°C to constant mass, so that their hygroscopic water content and dry bulk density could be determined. The hygroscopic water contents of the two cores were compared with the hygroscopic water content of an independent soil sample obtained at the same time; the measurements agree closely Core 1, 0.086, core 2, 0.087 independent sample 0.096. As a further check, a sample of soil was oven dried, cooled in a dessicator and weighed. The sample was then left in the atmosphere at a relative humidity of ~55% and the weight gain recorded with time. The hygroscopic water content after re-hydrating was the same as before drying, once equilibrium was reached.

## 4. Results and discussion

### 4.1. The use of hygroscopic water content

The proposed use of hygroscopic water content as an estimate of the bound water fraction provides an easily obtainable measurement that quantifies the amount of bound water in a soil. In our experiment, we allowed the soil samples to air-dry for a month before weighing and oven drying to obtain the hygroscopic water content (0.086). However, water absorption within a rigid soil matrix appears to be a reversible process. After oven drying, the soil samples were allowed to cool to room temperature in a dessicator. The samples were accurately weighed and then left open to the atmosphere (50–60% relative humidity) to rehydrate, the weight being measured as a function of time. The reversibility of the water adsorption can be seen in Fig. 5, after about 24 h, the soil samples

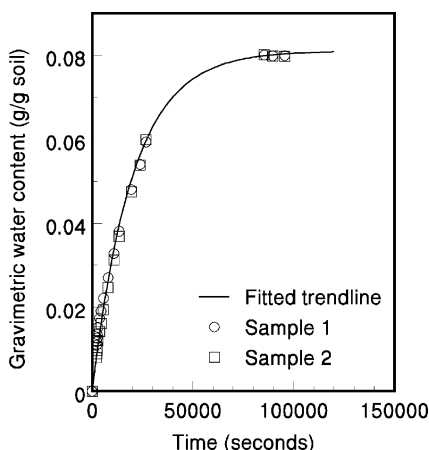


Fig. 5. The absorption of water from the atmosphere by two soil replicates as a function of time, after the soil had been oven dried. The relative humidity of the room was between 50 and 60%.

had rehydrated to their former value. This would suggest that samples removed from the field could be dried in the oven at perhaps 70°C to remove excess water and then left open to the atmosphere to equilibrate, thus greatly speeding up the measurement. As far as we are aware, this has not been tested fully, and would be a useful experimental study.

Neither hygroscopic water content nor surface area measurements are routinely collected by soil surveys. Hygroscopic water content is easily measured as described previously; specific surface area is usually measured by the ethylene glycol monoethyl ether (EGME) method (Carter et al., 1986). A number of workers have presented data containing surface area

determined by EGME adsorption and hygroscopic water content (Banin and Amiel, 1970; Dirksen and Dasberg, 1993). Their data, collected from 42 soils, is plotted in Fig. 6 and demonstrates a high correlation as one would intuitively expect ( $r^2 = 0.936$ ) between the hygroscopic water content and the EGME measured total specific surface area. A linear regression passing through the origin yields

$$\text{Surface area (m}^2 \text{ g}^{-1}) = 35.7 \times \text{Hygroscopic water content (\%, by volume)} \quad (7)$$

with a root mean square error (RMSE) of 28.4 m<sup>2</sup> g<sup>-1</sup>. Hence, the use of this conversion should widen the applicability of the proposed method to include data sets where soil surface area may have been measured but not hygroscopic water content.

#### 4.2. Refractive index model incorporating hygroscopic water content

The results for the sand and ferric soil cores are presented in Fig. 7 with the square root of permittivity plotted to linearise the results. The measured values for the sand are in reasonable agreement with Eq. (5) (thick dashed line), using permittivity values of 80 for  $\epsilon_{fw}$  and 5 for  $\epsilon_s$ . Differences between the measured and predicted permittivity values must be considered due to either the assumed value of the solid permittivity and/or an inadequate geometrical description of the sand, which is assumed to be layers by the refractive index model.

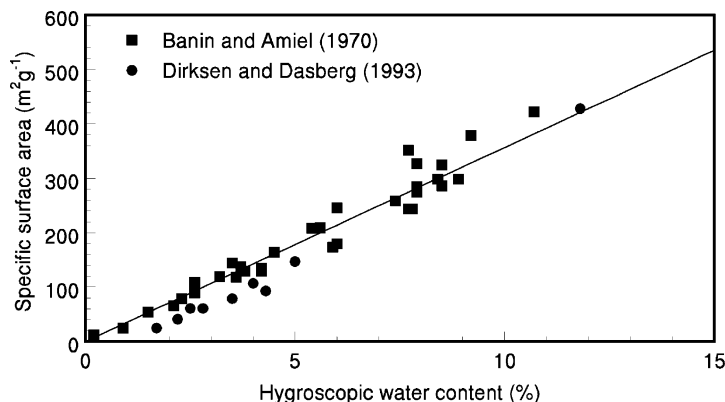


Fig. 6. Surface area as a function of hygroscopic water content. Data from Banin and Amiel (1970) and Dirksen and Dasberg, (1993).

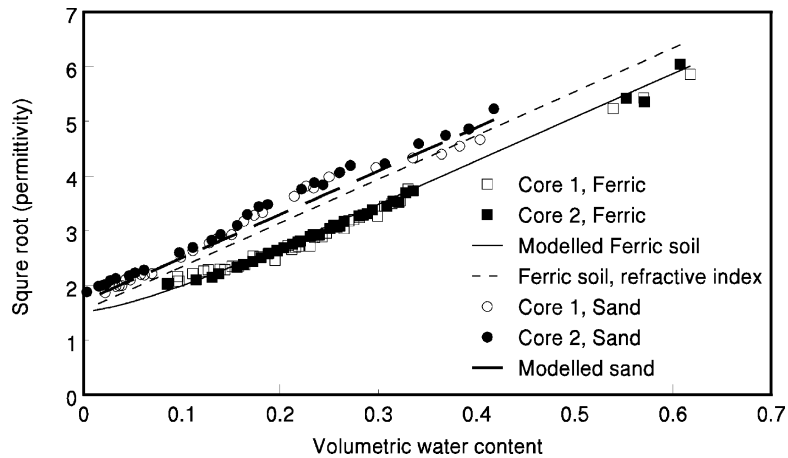


Fig. 7. The data for the sandy and ferric soils with the calibration function of Whalley (1993) fitted and the improved calibration function allowing for the effect of bound water (Eq. (6)).

The ferric soil behaved distinctly differently to the sand, at water contents below 0.16, the relative permittivity increased by only a small amount as the water content increased by nearly 0.10. Above a water content of 0.16, the slope of the curve increased, so that between water contents of 0.20 and 0.30, the slope was similar to that of the sand samples that contained free water. The lower dry bulk density of the ferric soil resulted in slightly lower predictions of relative permittivity than for the sand at the same water content (Fig. 7, thin dashed line). However, the addition of a term describing the variation of the relative permittivity due to the hygroscopic water content, (Eq. (6), thin solid line), produced improved agreement. This is not only true of the overall magnitude of the relative permittivity at higher water content, but also described the curved portion of the line reasonably well at low water content. Quantification of this improvement is demonstrated by the RMSE values that improved from 3.63 and 3.51 for cores 1 and 2, respectively to 0.82 and 0.68.

#### 4.3. Model estimates using data from the literature

In an attempt to test the model further, predictions of permittivity were made based on the data presented in Dirksen and Dasberg (1993). Data for four of the soils with larger hygroscopic water contents were tested. The results are presented in Fig. 8(a)–(d) and can be compared with the empirical curve presented

by Topp et al. (1980). At lower water contents, the model gives good predictions of the data. However, at higher water contents, the model under-predicts the measured values. A number of reasons for this can be proposed and highlight areas of poor understanding in modelling the dielectric properties of soils.

The use of the refractive index as a geometric base is not an accurate physical description of soil geometry. The refractive index model (Eq. (5)), with an exponent of 0.5, can be derived for a layered system but does not account for other factors such as particle shape. Recently, Jones and Friedman (2000) demonstrated how the grain shape and geometry with respect to the applied field can have a substantial impact on the measurement of permittivity. Robinson and Friedman (2001) demonstrated that particle size distribution also affects the measured permittivity to a lesser but measurable extent. A further difficulty encountered is the value of the solid permittivity; at present, there is no method of measuring the permittivity of the solid mineral component of a granular material. The standard method presented for granular rock samples (Olhoeft, 1981) has been to use a mixing model to predict the solid permittivity of a granular sample, packed in air. This presupposes the physical correctness of the model, which as Sihvola (1999) points out is a power law approximation. As yet, according to our knowledge, there is no physically based 2-phase model that accurately describes the effective



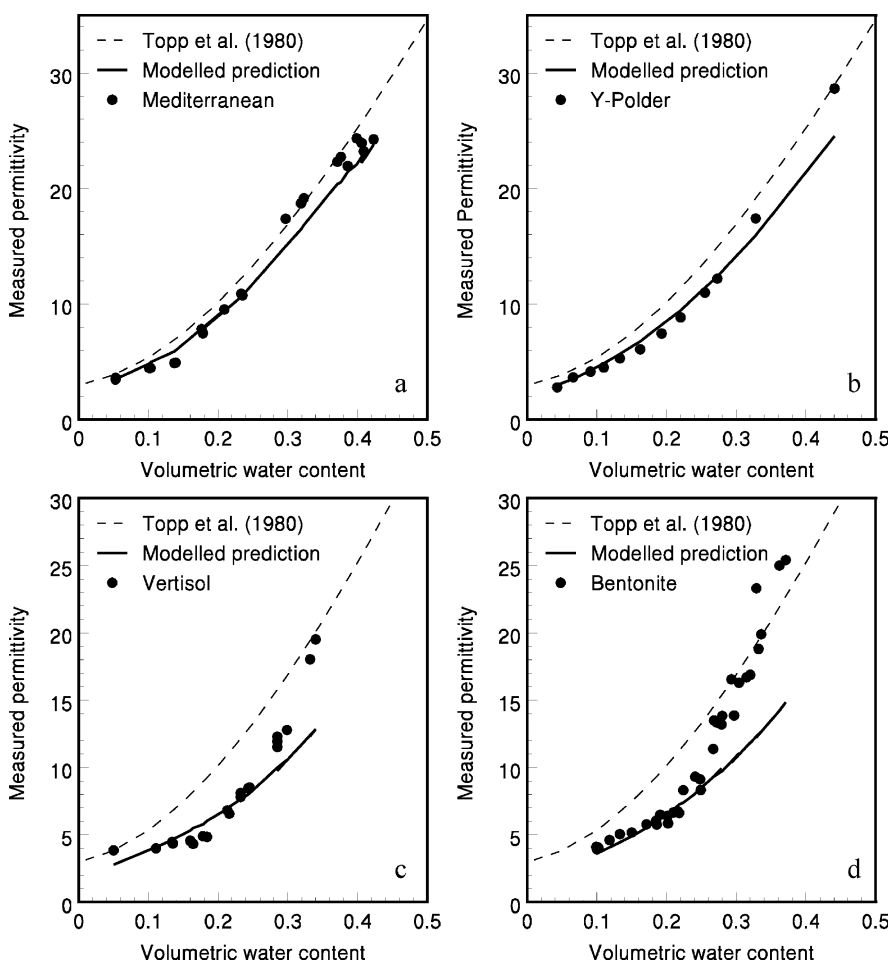


Fig. 8. Four of the data sets taken from Dirksen and Dasberg, (1993) with a range of hygroscopic water contents (a) 0.043; (b) 0.040; (c) 0.118; (d) 0.114. The predictions using the model presented in this paper are compared with the function of Topp et al. (1980) as a reference.

permittivity of a porous media. The closest one comes is the Maxwell-Garnett (1904) model, which applies to dilute quantities of dielectric inclusions in a dielectric background (Sihvola, 1999). There is clearly a need for a 2-phase model describing a densely packed porous media from which, perhaps, a 3-phase model may be developed. An important development must be to measure the permittivity of the solid component. This is a fundamental parameter for 3-phase mixing of dielectric materials. A value of 4.7 has been measured for quartz crystals (Carmichael, 1982) and as soils are often composed of quartz and some minerals with slightly higher permittivity values, a value of 5 does not seem an

unreasonable approximation. However, until a measurement method is developed, the value of the solid phase will remain essentially a fitting parameter and prevent the rigorous testing of dielectric mixing models.

Fig. 8(c) and (d) both show strong divergence between the model estimates and the measured values of permittivity above water contents of 0.25. The observed increase of permittivity is similar for both data sets. We speculate that this might be the contribution of the imaginary part of the relative permittivity caused by increasing bulk soil electrical conductivity. This points to another area of weakness in our understanding, which is the impact of bulk soil

electrical conductivity on the measurement of soil permittivity. Though no electrical conductivity measurements were presented for the vertisol or bentonite samples (Fig. 8(c) and (d)), it is likely that the bulk soil electrical conductivity was increasing with rising water content and was not negligible (i.e. not less than  $1 \text{ dS m}^{-1}$ ). An increase in the imaginary component leads to increased TDR travel times and so higher permittivity values according to

$$\epsilon_r = \epsilon' \left[ \frac{1 + \sqrt{1 + \tan^2\left(\frac{\epsilon''}{\epsilon'}\right)^2}}{2} \right] \quad (8)$$

where  $\epsilon_r$  is the measured relative permittivity,  $\epsilon'$  is the real part of the permittivity due to energy storage and  $\epsilon''$  is the imaginary component due to losses (White et al., 1994). This may account for the sudden rise of the permittivity with the vertisol and bentonite data for water contents above 0.2. This suggests that it is important to have a measure or estimate of the bulk soil electrical conductivity to determine its impact on the measurement of soil permittivity.

The model presented in this work improves the predicted value of soil permittivity as a function of water content and conversely should provide improved estimates of water content. The purpose of the semi-physical model presented is to obtain improved estimates of soil volumetric water content. However, as is discussed, the refractive index model is a very limited physical description of an unsaturated porous material. Its use in this work is pragmatic as a growing body of literature suggests it fits reasonably well with measurements of soil permittivity (Whalley, 1993; Heimovaara et al., 1994; Robinson et al., 1999; Or and Wraith, 1999). If we are to gain more physical understanding of porous materials, there is a need to develop more physically rigorous modelling approaches such as those presented by Sen et al. (1981) and Friedman (1998) and Jones and Friedman (2001). Twenty years after Topp et al. (1980) presented their results for soils and other porous media, there is still no physically based model that accurately describes the measured permittivity of even the unsaturated glass bead data. Clearly, this must be the challenge of future endeavours.

## 5. Conclusions

The use of hygroscopic water content (water contained in the soil when air dry) to estimate the quantity of bound water (within the TDR bandwidth) in a soil is proposed. A model is presented which incorporates the quantity of hygroscopic water in the soil to predict the effect that this 'effectively' bound water will have on the measured relative permittivity of the soil water. Incorporation of this model into the refractive index mixing equation provides soil relative permittivity as a function of solid, water, hygroscopic water and air. The equation can be rearranged into an implicit equation that can be solved for water content. Inclusion of the water phase permittivity model into the refractive index equation improved estimates of soil relative permittivity considerably. The RMSE of predicted permittivity as a function of water content was found to decrease from  $\sim 3.5$  to less than 1. Tested against other data for soils, with substantial quantities of hygroscopic water, the model gave good estimates of the measured permittivity at low water contents. At high water contents, the data and model predictions diverged, rising bulk soil electrical conductivity is suggested as a possible reason for this.

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