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Geoderma 117 (2003) 313–330

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Time domain reflectometry models as a tool to understand the dielectric response of volcanic soils

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Abstract

The transmission of an electromagnetic wave through the soil using time domain reflectometry (TDR) permits the determination of its water content, θ, given the composite dielectric constant of the soil, ε_c, via Topp's equation. This is possible since the dielectric constant of water is much larger than that of the soil's solid phase (80 vs. 5) and, therefore, changes in soil moisture content lead to variations in ε_c. However, organic soils and those of volcanic origin do not obey the "universal" relationship $\varepsilon_c - \theta$ originally obtained by Topp. Hence, several authors have proposed alternative empirical $\varepsilon_c - \theta$ relationships. Volcanic soils are particular with respect to their low bulk density, large porosity and specific surface, mainly due to the strong aggregation of particles and high concentration of Fe-oxihydroxides, and also due to the presence of allophanic clays with large surface area and water affinity. Thus, it is likely that the water retention characteristics of volcanic soils will exhibit an atypical dielectric behaviour. This work shows that physical models, which incorporate parameters such as bulk density, porosity and surface area, can interpret the anomalous dielectric behaviour of volcanic soils. Among these models, we shall distinguish those which consider three phases (water–air–soil) and those which separate the water content in two phases, i.e. free and bound water (four-phase models). Four-phase models help identify two distinct linear dielectric regimes dominated by free and bound water, respectively, for at least some soils. Soil porosity is shown to play an important role in the dielectric behaviour of volcanic soils. We also found that soil andic parameters provide an a priori diagnosis criterion to evaluate the departure of volcanic soils from Topp's curve. Additionally, we propose an alternative general $\varepsilon_c - \theta$ calibration relationship for these kinds of soils, which may be incorporated in commercial TDR devices for laboratory and field water content determination.

Keywords: TDR calibration; TDR models; Volcanic soil; Bound water; Andic parameters

1. Introduction

Time domain reflectometry (TDR) has become the most popular technique to determine soil water content. In situ, quick and nondestructive moisture determination, together with the possibility of multiplexing and automating of the TDR readings, are among the main advantages of this technique. The TDR is based on the delay produced on an electromagnetic wave that travels along a probe inserted in the soil. The dielectric constant of most mineral soils varies between 3 and 10, that of air is approximately 1 and is 81 for water (at 20 °C). Thus, small variations in the water content of an unsaturated soil lead to significant changes in the bulk air–soil–water dielec-

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doi:10.1016/S0016-7061(03)00131-9

tric constant, ε_c. The ε_c constant is determined from the transit time (t) that a voltage pulse takes to travel forward and backward along a wave-guide of length L, using the expression $\varepsilon_c=(ct/2L)^2$, where c is the velocity of light in vacuum.

Topp et al. (1980) measured this time t and fitted the calculated soil's ε_c to their gravimetrically determined water content, arriving at the following expression:

$$\theta = -5.3\times10^{-2} + 2.92\times10^{-2}\varepsilon_c - 5.5\times10^{-4}\varepsilon_c^2 + 4.3\times10^{-6}\varepsilon_c^3 \quad (1)$$

Eq. (1), although empirical, results sufficiently general (this is independent of soil texture and structure, salinity and temperature), thus, it is often referred to as a "universal" function of volumetric water content (θ) vs. soil dielectric constant. In fact, the relation $\theta - \varepsilon_c$ proposed by Topp has been one of the keys for the widespread use of TDR since it allows moisture determinations without a previous TDR calibration.

However, several exceptions of soils that do not follow Topp's equation are well known in the literature. This is, for example, the case of organic soils (Topp et al., 1980; Roth et al., 1992) and those of volcanic origin (Weitz et al., 1997; Tomer et al., 1999; Miyamoto et al., 2001). Such deviations from Topp's equation have been attributed to the low bulk density (Weitz et al., 1997), large surface area (Paterson, 1977; Tomer et al., 1999) and high organic matter content (Weitz et al., 1997) that volcanic soils exhibit. Volcanic soils also present high water holding capacity, high phosphate absorption and high aggregate stability. Such andic properties may be explained in terms of the structure of allophanic clays (hollow spherules that remain discrete at high moisture content) and of the high concentration of Fe-oxihydroxides that these soils present (Allbrook, 1984; Grandjean et al., 1984).

However, to what extent and why these factors affect the characteristic dielectric behaviour of volcanic soils has not yet been addressed, mainly because previous TDR calibrations (Weitz et al., 1997; Tomer et al., 1999; Miyamoto et al., 2001) did not carry out simultaneous determinations of specific surface, bulk density, organic matter and amorphous material content. This, for example, may explain why Miyamoto et al. (2001) found almost no influence of bulk density on water content determined by TDR in an Andisol, while Weitz et al. (1997) point towards bulk density as being responsible for the atypical TDR water content of two humid tropical soil of volcanic origin. Additionally, previous TDR calibrations of volcanic soils used repacked samples (Tomer et al., 1999; Miyamoto et al., 2001), while others point towards the need of using undisturbed soil samples, especially for andic soils, which preserve their field structure (Weitz et al., 1997), thus, making comparison of results difficult.

The strategy followed in this work to determine the origin of the atypical dielectric behaviour of volcanic soils was fitting gravimetrically determined undisturbed soil water content vs. TDR ε_c to physical models of TDR response that take into account parameters such as bulk density, porosity and specific surface previously measured in the laboratory. Among these models, there are those of three phases: water–soil–air (Roth et al., 1990), and those that distinguish between a mobile and an adsorbed water phase, also known as four-phase models (De Loor, 1964; Dobson et al., 1985). These models were then compared to Topp's "universal" equation, and conclusions were drawn about the origin of their atypical dielectric behaviour.

2. Materials and methods

2.1. Soil selection

We selected cultivated and natural volcanic soils from the Tenerife and La Palma Islands (Canary Islands, Spain) within a wide range of porosity, specific surface and amorphous material content. The soils named as Pajalillos and Las Cuevas correspond to two field plots situated in the Valle Guerra valley (Tenerife), both cultivated with bananas. The valley is enclosed by the Anaga Mountain range (altitude over 2000 m) on its NE side and is open to the Atlantic Ocean on its NW exposure. The mean annual temperature for the area is 20 °C (minimum of 15 °C in winter), and annual precipitation and crop evapotranspiration measured at the plot are around 380 and 1000 mm, respectively. These soils were transported from high-mid altitudes of northern Tenerife for banana cultivation (a normal practice in the Islands). In the case of Pajalillos, the soil can be classified as an Andisol in most of the field plot, according to the andic properties and depth requirements (Soil Survey Staff, 1999). The phosphate retention values can be lower than 85%, probably because of the high P fertilisation (Olsen P values often exceeded 100 mg kg^{-1}). Additional hydrogeological and soil characteristics of Las Cuevas may be found in Muñoz-Carpena et al. (2002).

Both Barlovento and Las Aves are natural soils (Typic Hapludands) from La Palma and Tenerife, respectively. Representative profiles of both soils were described in the Field Guide of the 1984 International Conference on volcanic soils (Department of Edafology and Geology, University of La Laguna, 1984). Some mineralogical characteristics of Las Aves are described in Gonzales-Batista et al. (1982), and further soil physic, chemical and geological characteristics may be found in Fernandez-Caldas et al. (1982).

2.2. Sampling, TDR and volumetric water content determinations

Five PVC cylinders (17 cm high and 12 cm in diameter) were used as centered, hammer-driven, undisturbed soil samplers. The lower edge of the cylinders was sharpened outwards. As the cylinders were inserted, the surrounding soil was removed to facilitate their insertion and to avoid soil compaction. The soil cores were saturated from bottom to top to overcome air entrapment, with a $CaSO_4$ and tymol solution, to minimize clay dissagregation and avoid degradation of organic matter. The lower edge of the columns was covered with a cheese cloth to minimize loss of soil material during manipulation and saturation of the cores.

The ε_c measurements were carried out with a Trase TDR equipment (Soilmoisture Equipment) with a 15-cm-long, two-rod connector® probe. The detachable guides remained permanently inserted during the calibration experiment to avoid soil erosion at the insertion, thus, ensuring a close contact between the soil and the TDR guides at all times. The soil volume measured with the TDR may be approximated to a cylinder whose longitudinal axis is placed in between the two guides and whose diameter is approximately 1.4 times the guide interspace (Topp and Davis, 1985). Taking into account the distance between guides (5 cm) and their length (15 cm), the volume sampled by the TDR is approximately one-third the total volume of the soil cores. TDR measurements taken over this volume fraction were considered to be representative of the total soil volume. Additionally, this set-up discards artifacts due to edge effects (such as soil compaction in the periphery of the cylinders).

The water content was determined gravimetrically. In the early stages, the soil columns, initially saturated, were left to drain freely. Then, TDR readings and weights were recorded while the columns were dried at room temperature, oven dried at 50–70 °C and finally at 105 °C until constant weight was achieved. In all instances, the soil columns were left to reach room temperature before TDR readings in order to diminish possible temperature effects on the dielectric constant of water (Pepin et al., 1995) and to allow homogenisation and stabilisation of the moisture content. Preliminary experiments where temperature was not controlled showed a greater data dispersion (results not shown), thus, pointing towards a complex temperature dependence of TDR dielectric measurements (Or and Wraith, 1999). TDR readings and weighing were carried out in intervals of 5–8% in volumetric water content. The total duration of the experiment was about 1 month.

2.3. Determination of the soil physical properties

The soil texture was determined by the method of the Bouyoucos densimeter, with hexametaphosphate as the dispersing agent (Métodos Oficiales de Análisis, 1986). In the particular case of Pajalillos, previous studies indicate that the use of exchange resins as dispersing agent (Bartoli et al., 1991), modified the proportion of the sand fraction in benefit of the clay content to almost threefold (Regalado et al., 2001). Also, the texture of Typic Hapludands from Tenerife, in similar environments as Las Aves, can change from sandy, using the conventional method, to clay when using resins (Department of Edafology and Geology, University of La Laguna).

For the specific surface (S_e) determination, the soils were first sieved to 2 mm, then placed in weighing bottles (six replicates of 1 gr.) and dried in vacuum to constant weight over diphosphorus pentaoxide. Finally, these were saturated to constant weight by adsorption in a sulfuric acid atmosphere (Newman, 1983). The data was compared with that obtained with an alternative method whereby the soil is dried before saturation with $LiNO_3$ (Newman, 1983). We chose these two methods instead of other more widely used, such as the ethylene glycol method, because it is well known that the latter overestimates the specific surface in these soils (Gonzales-Batista et al., 1982; Fernandez-Caldas et al., 1982).

The organic matter content was determined by the Walkey–Black method (Métodos Oficiales de Análisis, 1986). Bulk density and porosity were determined by standard methods (Klute, 1986). Clay mineralogy was determined by X-ray diffraction in randomly oriented specimens and oriented samples with glycerol and heat treatments (Philips PW 1720).

2.4. Physical models of TDR calibration

With the aim of determining the soil water content from TDR measurements of the soil dielectric constant, several physical models have been proposed (De Loor, 1964; Dobson et al., 1985; Roth et al., 1990) which relate the composite dielectric constant of the media, ε_c, to the dielectric constant of each individual phase. Within the soil, we may distinguish three phases: solid matrix, water and air. The TDR models developed under this assumption are known as three-phase models and take the following form (Roth et al., 1990):

$$\theta = m\varepsilon_c^\alpha - b, \quad m = \frac{1}{\varepsilon_w^\alpha - \varepsilon_a^\alpha}; \qquad b = \frac{(1-\phi)\varepsilon_s^\alpha + \phi\varepsilon_a^\alpha}{\varepsilon_w^\alpha - \varepsilon_a^\alpha} \tag{2}$$

where ϕ (cm^3/cm^3) is the soil porosity, θ is the volumetric water content. ε_w, ε_a and ε_s correspond to the dielectric constant of water, air and solid, respectively. $\varepsilon_w = 78.5$ (at 25 °C), $\varepsilon_a = 1$ and ε_s may be computed from

$$\varepsilon_s = \prod_{i=1}^{n} \varepsilon_i^{\theta_i}, \tag{3}$$

where ε_i is the dielectric permittivity of each mineral constituent and θ_i their volumetric fraction. However, X-ray diffraction is a semi-quantitative technique and, therefore, the permittivity of the solid phase cannot be computed using Eq. (3). For most soils, ε_s varies within a narrow range 3–7 (Alarthi and Lange, 1987). However, given the mineralogy of volcanic soils (Table 1), the permittivity of their solid phase is more likely close to 10 (e.g. $\varepsilon_s = 8.4$ for gibbsite, 11.7 for goethite, 7.9 for halloysite, 10.0 for illite; Table A-1 in Olhoeft, 1989; see also Dirksen and Dasberg, 1993). We have, thus, adopted values of ε_s based on fitting criteria.

Some experimental results indicate that the water molecules in contact with the surface of clay particles (adsorbed water) have lower mobility than the free water molecules. A four-phase mixing model, which distinguishes between these two states of the water phase (Dobson et al., 1985), has, thus, been proposed:

$$\theta = m\varepsilon_c^\alpha - b, \quad m = \frac{1}{\varepsilon_w^\alpha - \varepsilon_a^\alpha}; \qquad b = \frac{(1-\phi)\varepsilon_s^\alpha + \phi\varepsilon_a^\alpha + \theta_{bw}(\varepsilon_{bw}^\alpha - \varepsilon_w^\alpha)}{\varepsilon_w^\alpha - \varepsilon_a^\alpha} \tag{4}$$

Table 1
Classification and physico-chemical parameters of the soils under study

Soil	Classification	Mineralogy[a]		Texture (USDA)[b]	Porosity, ϕ (%)	Bulk density, ρ_b (g/cm^3)	Specific surface, S_e[c] (m^2/g)	O.M. (%)
		Dominant	Minor					
Pajalillos	Cultivated (Andisol)	A, H	I	L-S	66.4 ± 2.4	0.87 ± 0.08	200 ± 17	2.3 ± 0.5
Barlovento	Typic Hapludand	A, $Al(OH)_3$	K, I	L-S	69.2 ± 3.6	0.82 ± 0.02	322 ± 4	12.8 ± 0.5
Las Cuevas	Cultivated	H	I	L-C	53.2 ± 1.1	1.12 ± 0.03	68 ± 22	2.3 ± 0.8
Las Aves	Typic Hapludand	A>Im	Gi	L-S	76.7 ± 2.6	0.65 ± 0.05	296 ± 7	5.7 ± 0.4

[a] A: allophane, Im: imogolite, Gi: gibbsite, $Al(OH)_3$: poorly crystalline Gi and amorphous, I: illite, H: halloysite, K: kaolinite.

[b] L = loamy, S = sand, C = clay (hexametaphosphate dispersion).

[c] H_2SO_4 method.

where θ_{bw} refers to the volume fraction of adsorbed water, with dielectric constant ε_{bw}. θ_{bw} can be obtained from (Dirksen and Dasberg, 1993):

$$\theta_{bw} = l\delta\rho_b S_e, \tag{5}$$

where l is the number of monolayers of water molecules of thickness δ bounded to the soil particles. We chose $l = 1$, the lower bound of absorbed molecules; S_e is the soil specific surface; ρ_b is the soil bulk density obtained from $\rho_b = \rho_s\,(1-\phi)$, where ρ_s corresponds to the soil's specific density.

The α parameter in Eqs. (2) and (4) reflects the geometry of the media with respect to the applied electromagnetic field, with $-1 < \alpha < 1$ (Roth et al., 1990). It can be shown that this parameter is related to the distribution of depolarization factors inside the material (Zakri et al., 1998) and, therefore, α may be correlated with the internal structure of the medium: fine dispersion or strong stratification, round or elongated particles or menisci, etc. For a complex media such as soil, α takes values close to 0.5, but in general it is unknown and, thus, becomes a fitting parameter. This represents an important drawback to the use of such α-models if, as in our case, one tries to isolate the parameters responsible for the particular dielectric behaviour of a soil.

Alternatively, the Maxwell–De Loor model solely includes physical parameters, subjected to the following assumptions: the soil solids are considered a host medium, containing randomly distributed and oriented disk-shaped (water and air) inclusions, with no interaction between adjacent soil particles (De Loor, 1964; Dobson et al., 1985),

$$\varepsilon_c = \frac{3\varepsilon_s + 2(\theta-\theta_{bw})(\varepsilon_w-\varepsilon_s) + 2\theta_{bw}(\varepsilon_{bw}-\varepsilon_s) + 2(\phi-\theta)(\varepsilon_a-\varepsilon_s)}{3 + (\theta-\theta_{bw})(\varepsilon_s/\varepsilon_w-1) + \theta_{bw}(\varepsilon_s/\varepsilon_{bw}-1) + 2(\phi-\theta)(\varepsilon_s/\varepsilon_a-1)}. \tag{6}$$

3. Results and discussion

3.1. Soil characterisation

The classification of the soils under study and their physico-chemical characteristics are summarised in Table 1. Pajalillos has loamy-sand texture (13% clay, 21% silt, 66% sand), bulk density 0.87 ± 0.08 g/cm^3, porosity 66.4 ± 2.4% and specific surface 200 ± 17 m^2 g^{-1}.

The soil texture of Las Aves is also loamy-sand (6.3% clay, 21.3% silt, 72.4% sand), bulk density 0.65 ± 0.05, porosity 76.7 ± 2.6% and specific surface 296 ± 7 m^2 g^{-1}. The Barlovento soil has 8.8% clay, 11.4% silt, 79.9% sand and, thus, also exhibits a USDA loamy-sand texture. Porosity is 69.2 ± 3.6% and the specific surface 322 ± 4 m^2 g^{-1} (Table 1).

In the particular case of Pajalillos, and as the result of a hydrological study in course, the specific surface of 70 additional soil samples allowed us to determine that this takes values normally distributed and, thus, the arithmetic mean is a valid statistic to define the remaining S_e determinations. We also obtained 15–25% positive differences between the $LiNO_3$ and the H_2SO_4 method.

3.2. Effect of the soil porosity, ϕ (three-phase model)

Since the three-phase model (Eq. (2)) does not take into account the specific surface but only the soil porosity, we have chosen this model to isolate the possible effect that ϕ has on the θ–ε_c relationship. In Fig. 1a and b, we can observe that the model fits well the experimental data ($\alpha = 0.322$, $R^2 = 0.988$ for Pajalillos and $\alpha = 0.173$, $R^2 = 0.982$ for Las Aves; Table 2), although for moisture content >0.5 cm^3/cm^3 there is disagreement between the predicted and measured water contents. For Pajalillos, the model overestimates the moisture content, while for Las Aves, the model predicts lower moisture contents than those observed for $\theta > 0.5$ cm^3/cm^3. We have adopted a value of $\varepsilon_s = 9$ based on fitting criteria, although good results were also obtained with $\varepsilon_s = 5$, an average value used by previous authors. This is one drawback of mixing models, since α becomes a "black-box" parameter and, thus, higher ε_s values can be accommodated by reducing the weight of α (see Fig. 5 in Todoroff and Langellier, 1998). We have though maintained the value $\varepsilon_s = 9$, taking into account the mineralogy of these soils (see above). Most of the results and conclusions obtained hereafter are, however, independent of the solid fraction permittivity values.

A decrease in the porosity values reduces the differences between the model and Topp's equation. For Pajalillos, the effect that the porosity has on θ is about 0.07 for a reduction in ϕ from 0.66 to 0.45 cm^3/cm^3,

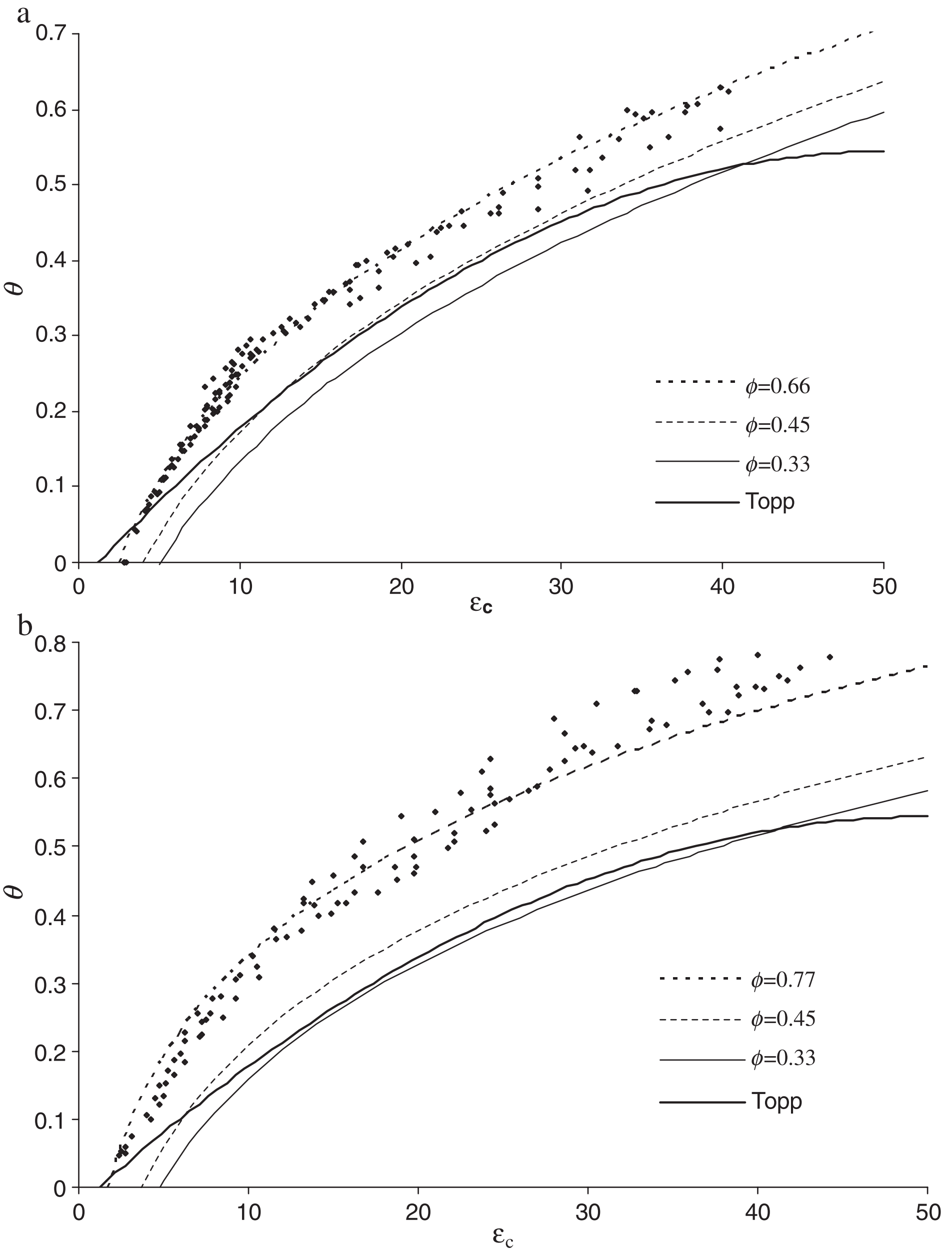

Fig. 1. Effect of the soil porosity, ϕ, on the $\theta-\varepsilon_c$ relationship. Three-phase model (Eq. (2)) with $\varepsilon_a=1$, $\varepsilon_s=9$, $\varepsilon_w=78.5$. (a) Pajalillos $\phi=0.66$ cm^3/cm^3, $\alpha=0.322$. (b) Las Aves $\phi=0.77$ cm^3/cm^3, $\alpha=0.173$.

and the difference with Topp's equation is 0.07–0.1 cm^3/cm^3 in θ. This does not represent a very significant difference in water content (see also Yu et al., 1999). However, for higher porosity values, such as Las Aves, this becomes important: of the order of 0.2 cm^3/cm^3 (Fig. 1b).

Table 2
Model parameter values and fitting results (observed vs. predicted) for Pajalillos and Las Aves

Soil	Model	α	ε_s	$R^2_{1:1}$
Pajalillos ($\phi=0.66$, $S_e=200$)	Three-phase	0.322	9	0.988
	Four-phase	0.491	9	0.980
	Maxwell–De Loor	–	2.5	0.973
Las Aves ($\phi=0.77$, $S_e=300$)	Three-phase	0.173	9	0.982
	Four-phase	0.300	9	0.985
	Maxwell–De Loor	–	7.5	0.952

3.3. Effect of the soil specific surface, S_e (four-phase model)

The four-phase model (Eq. (4)) offers the possibility of investigating the effect that the high specific surface that in general volcanic soils exhibit has on the $\theta-\varepsilon_c$ relationship. Taking into account values of $S_e=200$ m^2 g^{-1} for Pajalillos and of $S_e=300$ m^2 g^{-1} for Las Aves, the four-phase model fits well the experimental data ($\alpha=0.491$, $R^2=0.980$ for Pajalillos and $\alpha=0.300$, $R^2=0.985$ for Las Aves; Table 2). Increments (decrements) in the specific surface value bring the model predictions closer (farther) from Topp's equation (Fig. 2a and b). Notice also that an increment in S_e leads to an increase in the curvature of the fitted line in the moisture region <0.3 cm^3/cm^3.

A decrease in both porosity and specific surface has a combined effect. Thus, for example, in the case of Pajalillos, the four-phase model fits Topp's equation in the moisture region $0.2<\theta<0.4$ cm^3/cm^3 for $S_e=75$, $\phi=0.45$ (Fig. 2a). This may be explained in terms of the form of b/m in Eq. (4), which determines the crossing point of the TDR curve with the x-axis (Fig. 3). Notice also that although S_e and ϕ have opposite effects on the volumetric fraction of adsorbed water (Eq. (5)), variations in S_e are two to three orders of magnitude greater than ϕ and, therefore, its influence on this term of the equation prevails. Thus, for example a decrease in S_e from 200 to 75 m^2 g^{-1} together with a decrease in soil porosity from 0.66 to 0.45 (Fig. 3) diminish 1.6 times the fraction of adsorbed water and, therefore, the term $\theta_{bw}(\varepsilon_{bw}^{\alpha}-\varepsilon_{w}^{\alpha})$ in Eq. (4). Equally, a decrease in porosity reduces the weight of the $\phi(\varepsilon_a^{\alpha}-\varepsilon_s^{\alpha})$ term in Eq. (4). Evidently, and since the solid dielectric constant, ε_s, appears in Eq. (4), this may affect the value of b. However, since ε_s varies within a narrow range, the effect that the solid dielectric constant has on ε_c is small (Yu et al., 1999). A similar reasoning is applicable in the case of Las Aves.

Therefore, we may conclude that the high specific surface that volcanic soils exhibit increases the volumetric fraction of adsorbed water, and this is at least in part responsible for their dielectric behaviour. Additionally, the high porosity values that these soils present also contributes to such an atypical dielectric behaviour, far from Topp's "universal" relationship.

3.4. Dielectric response of a low S_e and low porosity volcanic soil

If the above-proposed mechanism is correct, we should be able to find a volcanic soil with low specific surface and porosity that fits Topp's equation. The soil named as Las Cuevas has a porosity $\phi=53.2\%$ and a specific surface $S_e=68$ m^2 g^{-1}. Fig. 4 shows the $\theta-\varepsilon_c$ results for this soil. As expected, the data follows Topp's equation ($R^2_{1:1}=0.959$), thus, confirming our theoretical predictions.

3.5. Porosity vs. specific surface

So far, we have investigated the dielectric behaviour of soils with both different porosity and specific surface. Ideally, we would wish to compare soils with similar values for either of these properties. Pajalillos and Barlovento have close porosity values (66 vs. 69) and very distinct specific surface (200 vs. 322 m^2 g^{-1}). In fact, Barlovento is the soil with the highest S_e probably due to its higher content of organic matter (Table 1) and allophane, Al_o (Table 3). Fig. 4 shows the dielectric behaviour of the soils studied with respect to their water content. It can be seen that Pajalillos and Barlovento show similar responses despite the fact of their very different specific surface. This is probably a consequence of the importance of microporosity in allophanic soils in that, in most of the θ range studied, water is held more strongly in capillaries than on external surfaces (Rousseaux and Warkentin, 1976). Previous authors (Yu et al., 1999) have shown theoretical results which suggest that soil porosity has a minor effect on the $\varepsilon_c-\theta$ relationship.

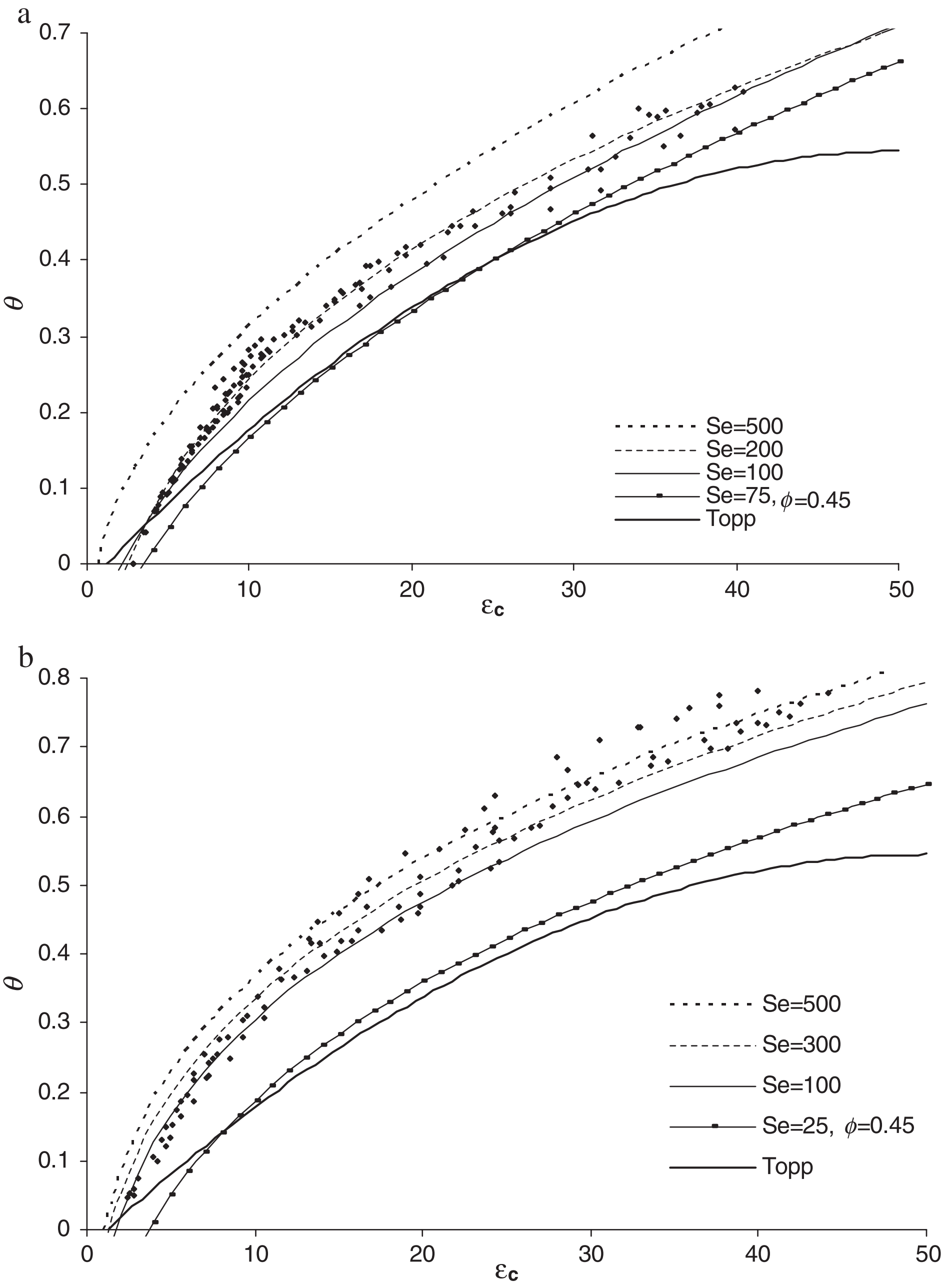

Fig. 2. Effect of the soil specific surface, S_e, on the $\theta-\varepsilon_c$ relationship. Four-phase model (Eq. (4)) with $\varepsilon_a=1$, $\varepsilon_s=9$, $\varepsilon_w=78.5$, $\varepsilon_{bw}=3.2$, $l=1$, $\delta=3\times10^{-10}$ m. (a) Pajalillos $\phi=0.66$ cm^3/cm^3, $S_e=200$ m^2/gr, $\theta_{bw}=0.054060$, $\alpha=0.491$. (b) Las Aves $\phi=0.77$ cm^3/cm^3, $S_e=300$ m^2/gr, $\theta_{bw}=0.054855$, $\alpha=0.300$.

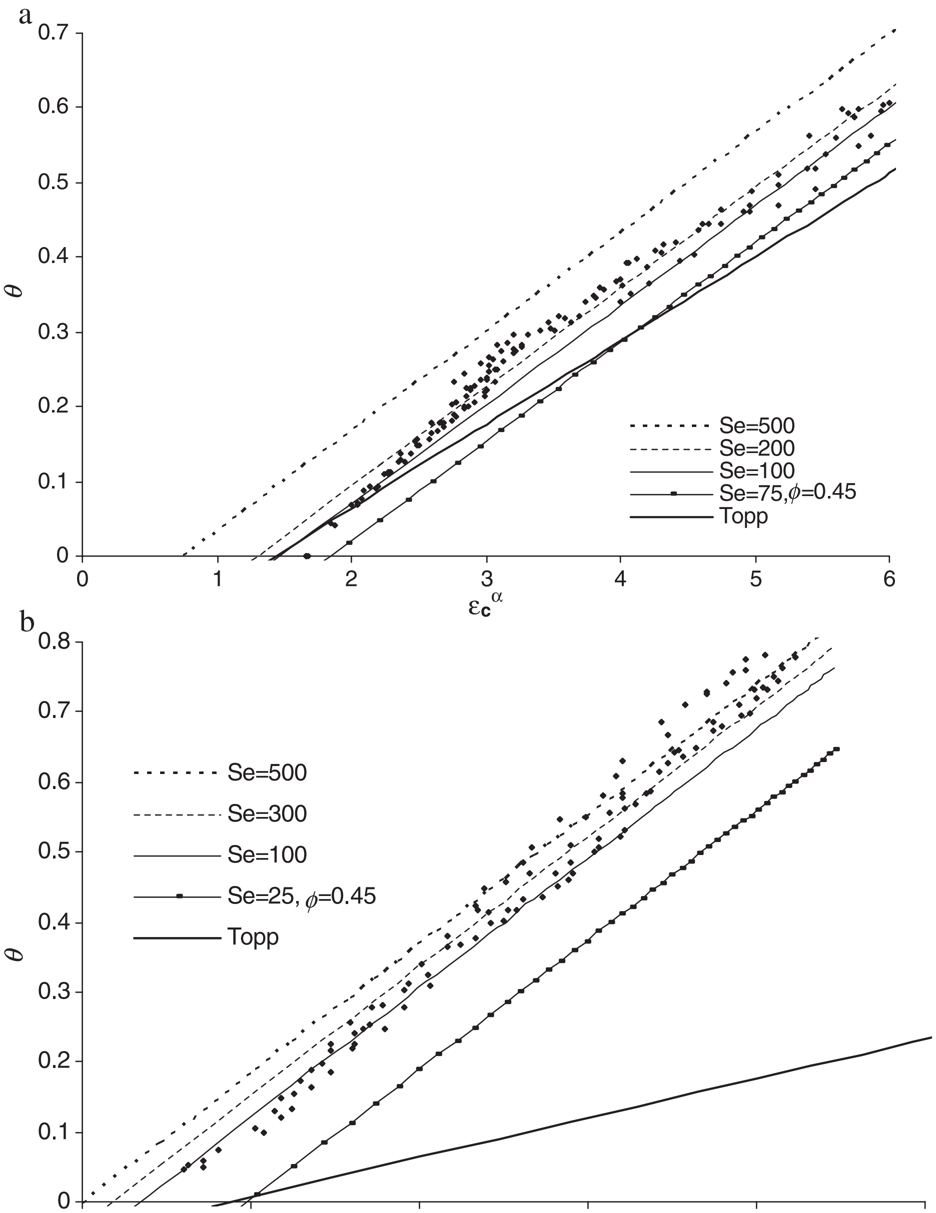

Fig. 3. Effect of the soil porosity, ϕ, and specific surface, S_e, on the $\theta-\varepsilon_c^{\alpha}$ relationship. Four-phase model (Eq. (4)) with $\varepsilon_a=1$, $\varepsilon_s=9$, $\varepsilon_w=78.5$, $\varepsilon_{bw}=3.2$, $l=1$, $\delta=3\times10^{-10}$ m. (a) Pajalillos $\phi=0.66$ cm^3/cm^3, $S_e=200$ m^2/gr, $\theta_{bw}=0.054060$, $\alpha=0.491$. (b) Las Aves $\phi=0.77$ cm^3/cm^3, $S_e=300$ m^2/gr, $\theta_{bw}=0.054855$, $\alpha=0.300$.

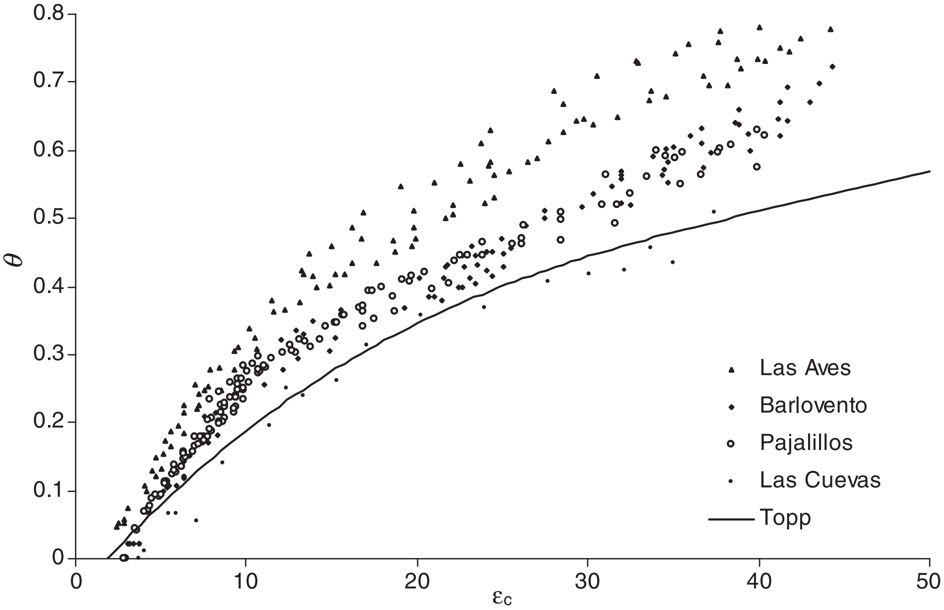

Fig. 4. A comparison of the dielectric behaviour of the different soils studied and Topp's equation. Soils follow a decreasing trend in porosity towards Topp's curve, such that higher (lower) porosity values, i.e. Las Aves ($\phi = 0.77$) vs. Las Cuevas ($\phi = 0.53$), remain further (closer) to Topp's model. For Pajalillos and Barlovento soils, with similar ϕ (0.66 vs. 0.69), such porosity tendency prevails despite their very distinct surface area (200 vs. 322 $m^2\ g^{-1}$).

The experimental results shown in Fig. 1a and b and those in Fig. 4 point in the opposite direction. Our results also agree with those of Tomer et al. (1999), who found that out of 24 volcanic soils studied, only the soil with the largest bulk density (a Dystric Eutrochrept with $\rho_b = 1.45$ g/cm^3) best fitted Topp's equation. Also, Dirksen and Dasberg (1993) found that the large difference found between TDR measured values and Topp for attapulgite were not so much due to its large specific surface ($S_e = 270$ m^2 g^{-1}) as to its very low bulk density ($\rho_b = 0.55$ g/cm^{-3}). In fact, the theoretical Maxwell–De Loor curve for a soil with $S_e = 147$ m^2 g^{-1} (such as Illite) and the bulk density of attapulgite deviated almost as much from Topp as attapulgite (Dirksen and Dasberg, 1993).

3.6. Bound vs. free water

Fig. 3 raises an additional hypothesis. Two different, almost linear, trends in the $\theta - \varepsilon_c^{\alpha}$ curve, at low and high water contents, which are more evident for Pajalillos than Las Aves (cf. Fig. 3a and b) can be observed. An abrupt change in slope was also identified for four clayey soils by Dirksen and Dasberg (1993), which the authors related to a switch from bound to free water. Hook and Livingston (1995) reported a sharp change in slope between to distinct linear regions in the $\theta - \varepsilon_c^{0.5}$ curve for two clay loam soils (see Fig. 4b and Table 3 in Hook and Livingston, 1995; see also Alarthi and Lange, 1987). A trend similar to that found by Hook and Livingston (1995) was observed by Tomer et al. (1999) for 17 samples of volcanic soils from New Zealand. Also, Knight and Abad (1995) described a linear dependence of the

Table 3
Andic parameters: percent phosphate retention (ΔP) and amounts of active aluminum (%Al_o), iron (%Fe_o) and silica (%Si_o) of the soils under study

Soil	ΔP (%)	Al_o (%)	Fe_o (%)	Si_o (%)	$Al_o + 1/2Fe_o$ (%)	Al_o/Si_o
Las Aves	96.3	6.0	3.5	2.6	7.7	2.3
Pajalillos	87.6	2.9	5.7	1.2	5.7	2.5
Barlovento	99.3	8.1	7.2	1.9	11.2	4.4
Las Cuevas	20.0	0.1	0.3	0.0	0.2	2.1

bulk dielectric constant of four quarried sandstones, with lower slope at low saturations, which was attributed to interactions between the soil matrix and near (1 nm) solid surface water (Knight and Endres, 1990).

At low moisture content ($\theta < 0.3$ cm^3/cm^3), most of the soil water is expected to be adsorbed on solid particle surfaces and, hence, the soil dielectric response would be dominated by that of bound water (ε_{bw}). For example, from Eq. (5) and assuming a monolayer of adsorbed water, the volume fraction of bound water for Pajalillos is $\theta_{bw} = 0.054$ cm^3/cm^3; this fraction is increased if two ($\theta_{bw} = 0.108$ cm^3/cm^3) or even three ($\theta_{bw} = 0.162$ cm^3/cm^3) layers of rotationally hindered water are considered, such that at least half of the water molecules would be bound to solid surfaces for $\theta < 0.3$ cm^3/cm^3. By contrast, at higher water content ($\theta > 0.3$ cm^3/cm^3), the ratio of bound to free water is small (< 20%), and the TDR response will be dominated by the free water dielectric permittivity, $\varepsilon_w \gg \varepsilon_{bw}$. These results are also consistent with the thermodielectric response of soils shown by Or and Wraith (1999).

The localisation of such an inflexion point or transition moisture value, θ_{tran}, may be determined from (Wang and Schmugge, 1980),

$$\theta_{tran} = 0.49\theta_{wp} + 0.165, \tag{7}$$

θ_{wp} is an empirical approximation of the wilting point moisture, obtained from the mass fractions of clay and sand

$$\theta_{wp} = 0.06774 - 0.00064\ \%\text{sand} + 0.00478\ \%\text{clay}, \tag{8}$$

such that the transition moisture content is a function of the soil texture (Newton, 1977; Wang and Schmugge, 1980). However, in Andisols, θ_{wp} is not related to the clay content (Warkentin and Maeda, 1980; Armas-Espinel et al., 2003), probably due to the strong aggregation that these soils exhibit and the presence of amorphous materials (Armas-Espinel, 2001). The wilting point was, thus, computed from 1.5-MPa pressure plate determinations: $\theta_{wp} = 0.29$ cm^3/cm^3 ($n = 70$) for Pajalillos. This gives $\theta_{tran} = 0.31$ cm^3/cm^3 in close agreement with the experimental results (Fig. 3a). Surprisingly, Tomer et al. (1999) also found maximum deviation from a straight line in a $\theta - \varepsilon_c^{0.5}$ calibration of 17 volcanic soil samples at $\theta = 0.30$ cm^3/cm^3. It has been proposed (Newton, 1977; Yu et al., 1999) that θ_{tran} is about one to two times the volume fraction of bound water, θ_{bw}. This would imply that for Pajalillos three layers of water with lower rotational mobility would be affecting the dielectric permittivity at low water contents ($\theta_{tran} = 0.31 \approx 2 \cdot 0.162$, see above). We arrive also at the same result by the following reasoning given by Knight and Endres (1990). The surface area to void volume ratio, S_e/V_{void}, can give an indication of the number of water monolayers, l, which uniformly cover the surface of the soil pore space at a given saturation. Thus, assuming a water monolayer thickness $\delta = 3 \times 10^{-10}$ m and a $S_e/V_{void} = 3.41 \times 10^4$ m^{-1} for Pajalillos, at the transition moisture, we have $l = 3.1$, in close agreement with the above result. Such large value for l may well be indicating that water trapped in the inner volumes of the hollow spherules of allophanes behaves as bound water (Wada, 1980).

3.7. Andic parameters and dielectric response

An important issue regarding volcanic soils is their andic character or andic soil properties, defined by the amounts of active aluminum (Al_o) and iron (Fe_o) extracted with ammonium oxalate, phosphate retention (reactivity parameter) and bulk density, and provided for the definition of andic subgroups (Soil Survey Staff, 1999). The following criteria are used to define andic soils: $Al_o + 1/2\ Fe_o > 2\%$, bulk density < 0.9 g/cm^3 and P retention >85%. Table 3 summarises such andic diagnostic parameters. It can be seen that the studied soils present a range of andic properties, that according to the above criteria we may sort in the decreasing order: Barlovento>Las Aves>Pajalillos ≫ Las Cuevas. Thus, two soil groups may be distinguished on the basis of high (Barlovento, Las Aves, Pajalillos) and low (Las Cuevas) andic characteristics. Hence, andicity provides an a priori diagnosis criterion to evaluate the dielectric response of soils with respect to Topp's curve, such that the higher the andic character the further away from Topp's dielectric behaviour. On the other hand, it is noteworthy that Barlovento is grouped with Pajalillos instead of Las Aves in Fig. 4, despite its andicity. Barlovento presents very high values of the Al/Si ratio in the oxalate extracts (Table 3) in comparison to the

Al-rich pole of allophanes (Al/Si ~ 2), which suggests that the excess Al is in the form of amorphous Al hydroxides (Parfitt, 1990). This can have a strong influence on micropore distribution (Rousseaux and Warkentin, 1976) and, hence, its $\theta-\varepsilon_c$ response.

3.8. Maxwell–De Loor model

The three- and four-phase models we have discussed above contain a fitting parameter α, and this represents an important drawback to their use as predictive models of TDR response. We shall now investigate the performance of a TDR model developed by Maxwell–De Loor, which does not have such fitting parameters. By contrast to the previous α-models, the best model fit was obtained with $\varepsilon_s = 2.5$ for Pajalillos and $\varepsilon_s = 7.5$ for Las Aves (Table 2). Such permittivity values may result rather atypical, given the mineralogy of these soils, and may be put into doubt the applicability of some of the restrictive

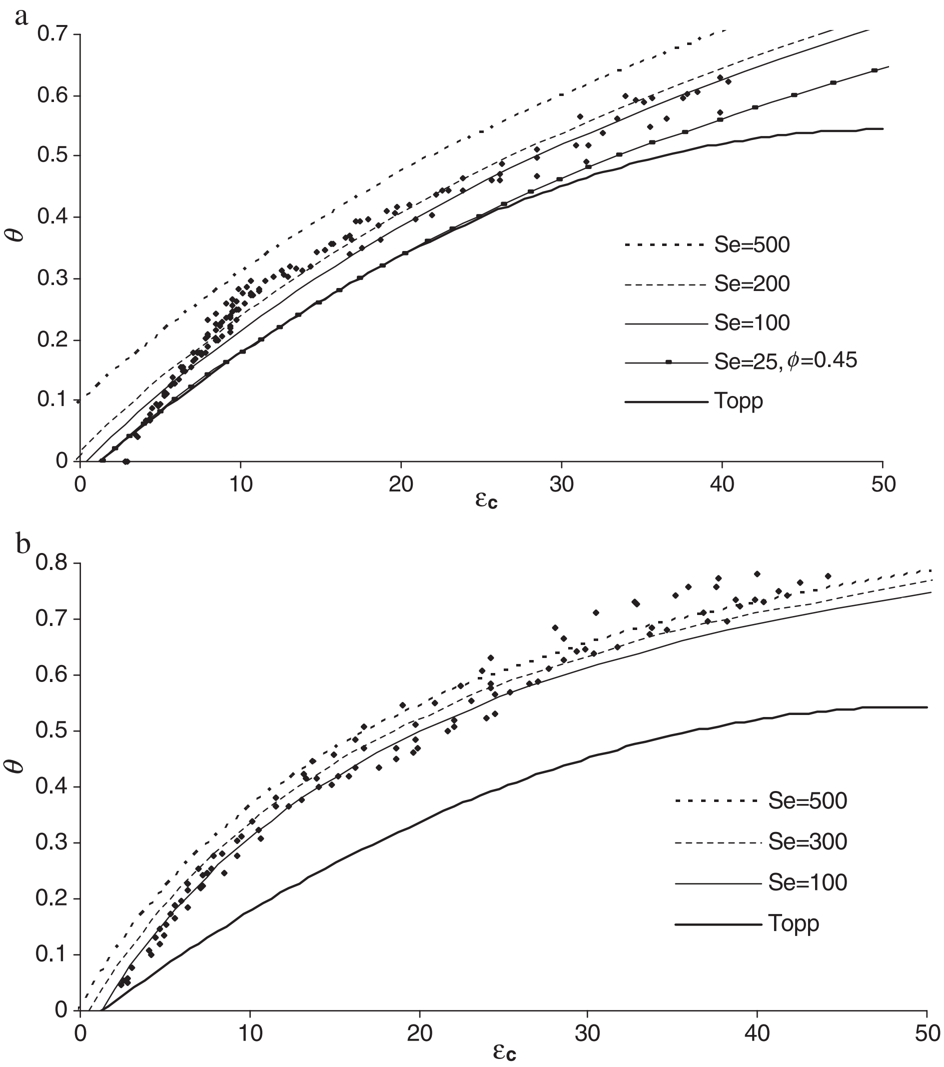

Fig. 5. Effect of the soil specific surface, S_e, on the $\theta-\varepsilon_c$ relationship. Maxwell–De Loor model (Eq. (6)) with $\varepsilon_a = 1$, $\varepsilon_w = 78.5$, $\varepsilon_{bw} = 3.2$, $l = 1$, $\delta = 3 \times 10^{-10}$ m. (a) Pajalillos $\phi = 0.66$ cm^3/cm^3, $S_e = 200$ m^2/gr, $\theta_{bw} = 0.054060$, $\varepsilon_s = 2.5$. (b) Las Aves $\phi = 0.77$ cm^3/cm^3, $S_e = 300$ m^2/gr, $\theta_{bw} = 0.054855$, $\varepsilon_s = 7.5$.

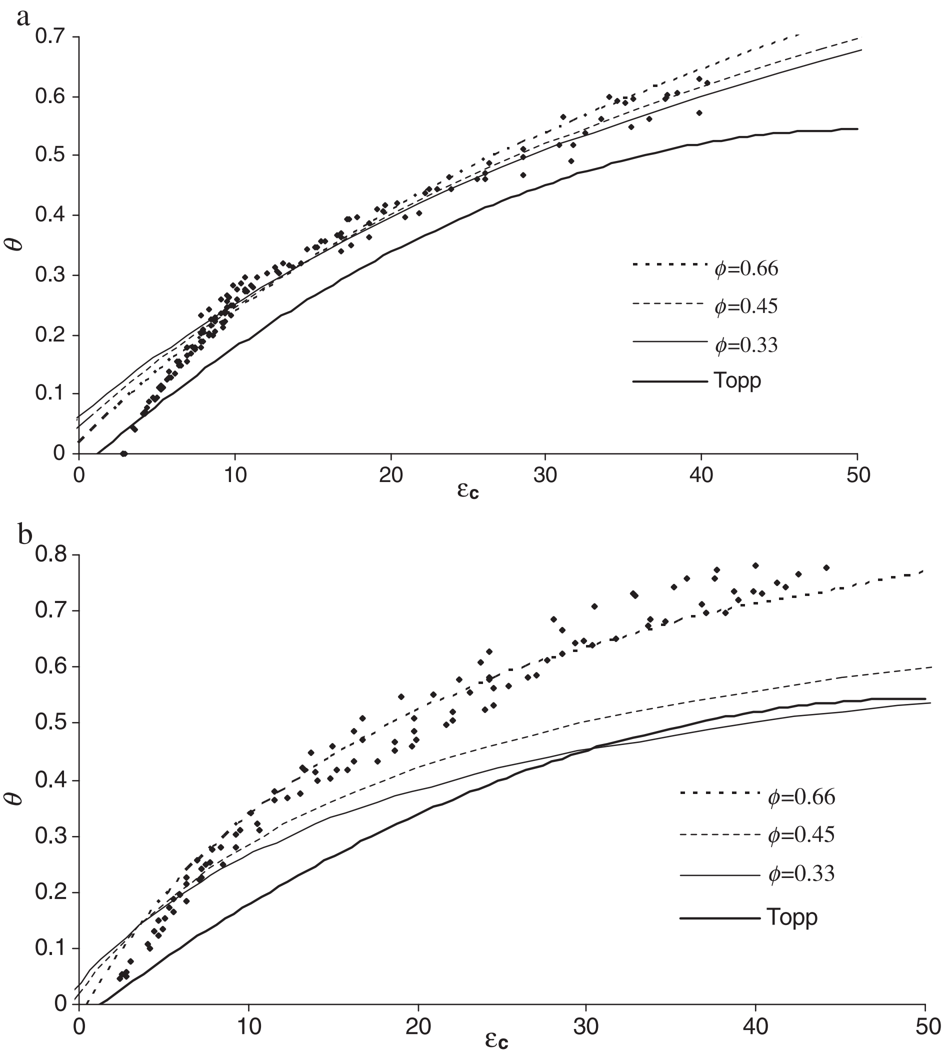

Fig. 6. Effect of the soil porosity, ϕ, on the $\theta-\varepsilon_c$ relationship. Maxwell–De Loor model (Eq. (6)) with $\varepsilon_a=1$, $\varepsilon_s=9$, $\varepsilon_w=78.5$, $\varepsilon_{bw}=3.2$, $l=1$, $\delta=3\times10^{-10}$ m. (a) Pajalillos $\phi=0.66$ cm^3/cm^3, $\varepsilon_s=2.5$. (b) Las Aves $\phi=0.77$ cm^3/cm^3, $\varepsilon_s=7.5$.

hypotheses of the Maxwell–De Loor model in volcanic soils. Dirksen and Dasberg (1993) also adjusted unusual parameter values for ε_s and ε_{bw}, in order to get reasonable fitting of six "irregular" soils to the Maxwell–De Loor model.

For Pajalillos, the model overestimates the water content, while for Las Aves, this predicts moisture content values below those observed for $\theta>0.5$ cm^3/cm^3 (Figs. 5 and 6). The Maxwell–De Loor model assumes that the water molecules are embedded in a homogeneous and isotropic solid phase. If the aqueous phase fills more than one-third of the total volume, this last hypothesis may not be satisfied, and this may explain its deviation from the experimental data near saturation (Dirksen and Dasberg, 1993).

The Maxwell–De Loor model suggests that the specific surface has an important effect on the water content. Thus, for example, in the case of Pajalillos, a variation in S_e from 100 to 500 m^2 g^{-1} yields a 0.1 cm^3/cm^3 moisture variation, while halving the porosity from 0.66 to 0.33 leads to a decrease in θ of only 0.02 cm^3/cm^3 (Fig. 5; see also Figs. 2 and 3 in

Dirksen and Dasberg, 1993). However, in our case, a decrease in specific surface on its own does not explain the behaviour, far from Topp's equation, of the measured TDR data. Thus, for example, by varying S_e from 500 to 25 m^2 g^{-1} while keeping fixed $\phi = 0.66$ cm^3/cm^3, we cannot match the Maxwell–De Loor and the Topp curves. Values of, say, $\phi = 0.45$ cm^3/cm^3, $S_e = 25$ m^2 g^{-1} are necessary to achieve this objective (Fig. 5a and b).

The algebraically complex form of the Maxwell–De Loor model (Eq. (6)) makes it difficult to analyse the effect of ϕ and S_e on the dielectric behaviour of soils. However, from Figs. 5 and 6, it follows that variations in S_e generate a family of parallel curves separated by a distance that tends to zero as $S_e \rightarrow 0$, while ϕ decides the slope of such curves at the origin. Since S_e contributes to Eq. (6) only by Eq. (5), we can explain the differences in the above figures only through the volumetric fraction of adsorbed water. The effect of the porosity is more difficult to analyse. It is, thus, evident that in order to "move" the Maxwell–De Loor model towards Topp's curve, it is necessary a decrease in both ϕ and S_e.

3.9. Empirical models

The models discussed above may be classified as physical models given their underlying motivation. However, only the Maxwell–De Loor model may be considered as such, since although both the three- and four-phase mixing models include physical parameters in their equations, this should be strictly classified as "semiempirical" because of the inclusion of a fitting parameter α. From the point of view of their applicability, the usefulness of empirical TDR calibration models is evident. This, in fact was the approach followed by Topp et al. (1980) for mineral soils with low clay content, and by Tomer et al. (1999) for volcanic soils. We now discuss the applicability of these models for the soils under study.

For Las Aves, we may fit a polynomial curve of the kind proposed by Topp or Tomer which takes the following form ($r^2 = 0.98$)

$$\theta = -4.0 \times 10^{-2} + 4.3 \times 10^{-2}\varepsilon_c - 1 \times 10^{-3}\varepsilon_c^2 + 9 \times 10^{-6}\varepsilon_c^3 \qquad (9)$$

Both curves (Topp (Eq. (1)) and Eq. (4) in Tomer et al., 1999) lie below the one fitted for Las Aves (Fig. 7b).

A simple logarithmic model is also valid for Las Aves ($r^2 = 0.97$)

$$\theta = 0.275\ln(\varepsilon_c) - 0.293, \qquad (10)$$

although this has no relation with the one proposed by Tomer for three sandy soils of volcanic origin (Eq. (5) in Tomer et al., 1999).

For Pajalillos, both a polynomial and a logarithmic fitting are acceptable ($r^2 = 0.99$ and 0.98, respectively).

$$\theta = -11.2 \times 10^{-2} + 5 \times 10^{-2}\varepsilon_c - 16 \times 10^{-4}\varepsilon_c^2 + 2 \times 10^{-5}\varepsilon_c^3 \qquad (11)$$

$$\theta = 0.232\ln(\varepsilon_c) - 0.275 \qquad (12)$$

The logarithmic calibration curve proposed by Tomer (Eq. (4) in Tomer et al., 1999) fits the data for $\theta > 0.3$ cm^3/cm^3 (Fig. 7a).

3.10. Semiempirical logarithmic models

Notice that a logarithmic model implies a proportionality law of the form

$$e^{\theta} \propto \varepsilon_c^{k} \qquad (13)$$

where k is the value of the slope in Eqs. (10) and (12). Furthermore, raising the previous expression to the power α/k, we arrive to

$$e^{\frac{\alpha\theta}{k}} \propto \varepsilon_c^{\alpha} \qquad (14)$$

For $\alpha = 0.5$, the second term in Eq. (14) becomes the refractive index of a medium (Birchak et al., 1974) and, thus, Eq. (13) gains some physical meaning. This may be also applicable for general α given the results of Zakri et al. (1998).

Eq. (14) implies a linear calibration, crossing the origin, in the space ε_c^{α}–$e^{\alpha\theta/k}$. Given the logarithmic

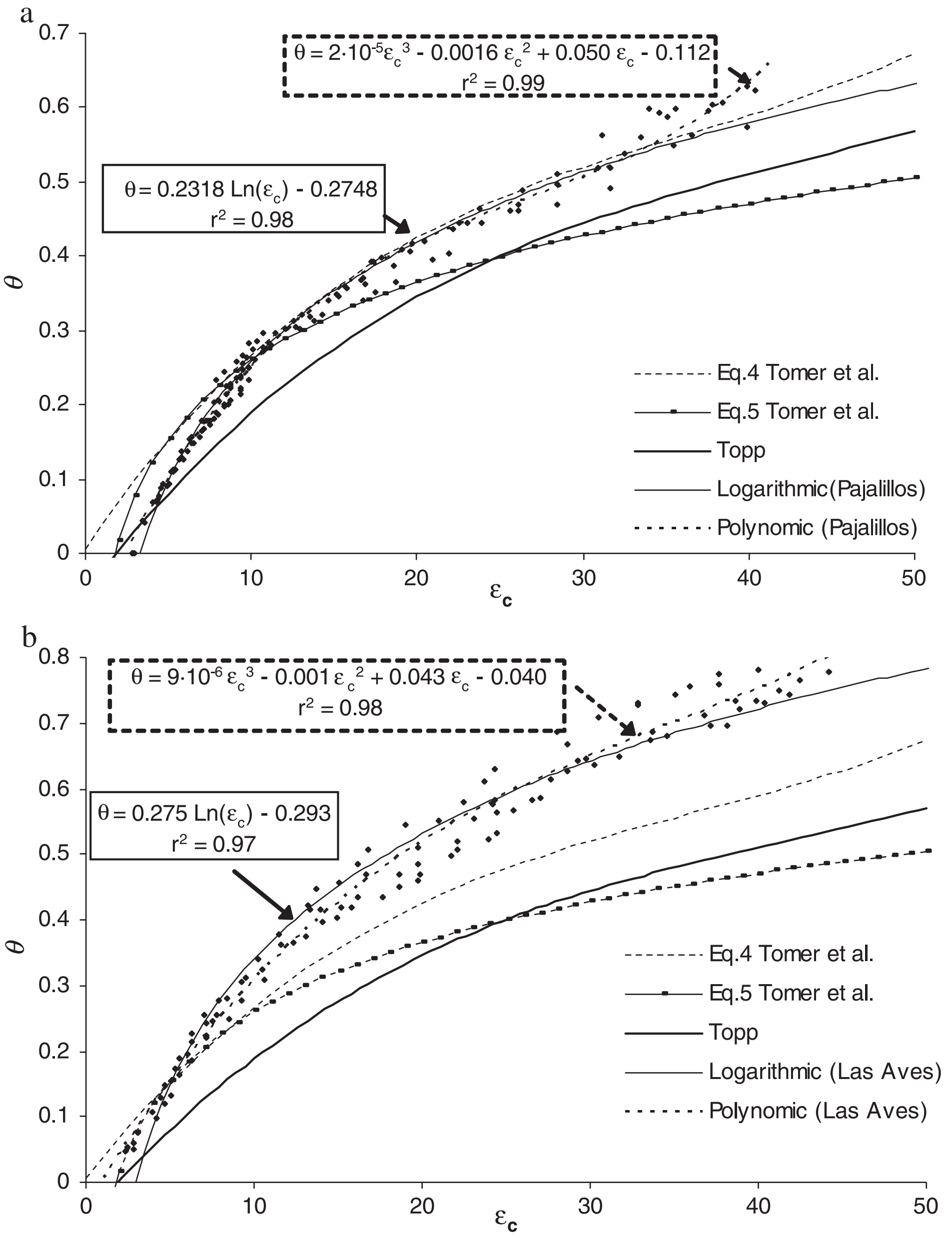

Fig. 7. Empirical (polynomic and logarithmic) models of TDR calibration and comparison with Tomer et al. (1999) and Topp's models. (a) Pajalillos, (b) Las Aves.

models proposed in this work and in Tomer et al. (1999), a working hypothesis is that mineral soils are linear in ε_c^{α}–θ while those of volcanic origin are nonlinear in their dependence of α-powers of the dielectric permittivity with water content. Coarse texture mineral soils would represent a particular case, being linear in $\varepsilon_c^{0.5}$–θ (Hook and Livingston, 1995; Malicki et al., 1996). This hypothesis would also agree with the nonlinear trend observed by Tomer et al. (1999) in a $\varepsilon_c^{0.5}$–θ calibration of 24 volcanic soils.

The suggested form of this nonlinearity is $e^{\alpha\theta/k}$. However, the physical origin and generality of this assertion requires further investigation.

4. Conclusions

The atypical dielectric response of volcanic soils, far from Topp's ''universal'' equation, may be explained in terms of physical models of TDR calibration. From a practical point of view, the empirical models have the advantage of being simple and accurate, and also avoid the sometimes cumbersome experimental determination of parameters. Among these, logarithmic calibration curves become linear after an exponential transformation, and may provide some physical interpretation to empirically derived TDR models. Empirical models, however, do not permit to investigate the influence of different parameters such us bulk density, mineralogy or surface area on the TDR readings and, therefore, their predictive capacity is very limited. Hence, the need to explore the applicability of mixing models with an experimental basis. Three- and four-phase alpha models allow comparisons within the same soil, although the presence of a fitting parameter, α, may limit their usefulness. Still, previous results indicate that such α parameter may be able to incorporate some details of the soil structure. By contrast, the Maxwell–De Loor model considers only physical parameters, although its predictions do not seem to fit the experimental data, particularly for high water contents —where the model hypotheses may not be fulfilled. Such models point towards a complex relationship between porosity and specific surface as the responsible factor for a higher fraction of water being adsorbed on the soil particles and, therefore, for a particular ε_c–θ relationship in soils with volcanic origin. Despite some previous theoretical results, we show that porosity may be the responsible factor for the dielectric behaviour of volcanic soils far from Topp's equation. In some sense this is to say that deviations from Topp in volcanic soils are more due to water filling (micro) pores than to bound water associated with large surface areas. Additionally, rotationally hindered water trapped within allophane spherules may play an important role in the dielectric response of volcanic soils for low water content up to a transitional moisture point. Such transition moisture content may be correlated with the wilting point, but not with the soil texture as it is generally the case of nonandic soils. These results are in consonance with the importance of microporosity in allophanic soils in that water is held more strongly in capillaries than on clay surfaces. This last result can be also interpreted in terms of andic parameters and, thus, these may serve as an a priori diagnosis criterion to evaluate the dielectric response of soils with respect to Topp's curve.

Acknowledgements

C.M. Regalado would like to thank M. Morawietz (University of Friburge) for his collaboration in the experiments with the soil from Pajalillos; S. Armas-Espinel and the Department of Edafology and Geology (University of La Laguna) for the determination of the andic parameters that appear in Table 3; Dr. D. Or for his helpful comments on the thermodielectric response of soils and for calling my attention to the Knight and Abad (1995) reference; and Drs. W.R. Whalley, J.P. Laurent, F. Bartoli and S.R. Mylavarapu for their very helpful comments that have greatly improved the quality of this paper. This work has been supported by the Spanish INIA-National R&D Programme (Project SC99-024-C2-1), the European Union COST Action 622, the Florida Agricultural Experiment Station, and approved for publication as Journal Series no. R-08609.

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