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TDR estimation of electrical conductivity and saline solute concentration in a volcanic soil

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Abstract

Relative to montmorillonitic or kaolinitic soils, volcanic soils have atypical dielectric characteristics that interfere with the applicability of the Time Domain Reflectometry (TDR) technique for soil moisture (θ) determination when common, empirical calibration equations are used. This particular dielectric response affects estimation of salinity in volcanic soils. Six TDR-based methods to estimate bulk electrical conductivity (σ_a) on a range of KCl saline reference solutions were compared, with Nadler's method giving the best results ($R^2_{1:1}$=0.988). Three models (linear, non-linear and empirical) for predicting soil solution electrical conductivity (σ_w) based on σ_a and θ, were experimentally tested on 24 hand-packed soil columns varying in salinity (Br^-) from 0.2 to 4.0 dS m^{-1}, each in four θ levels (36–58%). Rhoades' linear model performed better, especially for large water contents, than the other two ($R^2_{1:1}$=0.986 vs. 0.976 and 0.983, respectively). An interpretation in terms of mobile vs. immobile volumetric fractions of water present in volcanic soils is suggested as a possible explanation for these results. The empirical model resulted over-parameterized and an alternative equation with fewer non-correlated parameters, $\sigma_a=(a\theta^2+b\theta)\sigma_w+c\theta^2$, is proposed and tested with good results in volcanic soils from the Canary Islands and New Zealand. The equation encompasses both the relative dielectric dominance of the mobile water fraction at high water content typical of volcanic soils, and of the immobile fraction at low water contents. Simultaneous measurements made with a standard four-electrode probe and TDR gave good correlation (R^2=0.964). A good linear correlation was also found between tracer concentration in the soil solution and σ_w (R^2=0.960). Nadler's and the new empirical model also tested with good results under dynamic (flow) conditions during a miscible displacement experiment in a large monolith using bromide as a tracer. The method reveals itself as a robust tool for solute transport studies under controlled salinity conditions in a volcanic soil.

Keywords: TDR calibration; TDR models; Volcanic soil; Solute transport; Electrical conductivity; Dielectrical properties; Mobile/immobile water

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1. Introduction

The Time Domain Reflectometry (TDR) technique was initially applied to soil moisture determination by relating the apparent soil bulk permittivity (ε_c) to its volumetric water content, θ (m^{-3} m^{-3}) (Topp et al., 1980). Additionally, Giese and Tiemann (1975) observed that the shape of a TDR electromagnetic wave pulse changed when a TDR probe was immersed in solutions of different electrical conductivity at 25 °C (σ_{ref}^{25}) (Fig. 1). Changes in the wave form are used to estimate the electrical conductivity of the media. When a TDR probe is inserted in the soil, the bulk electrical conductivity (σ_a) of the water–soil matrix composite can be similarly obtained. The estimation of σ_a from the TDR signal depends on θ and on the characteristics of the soil, and hence does not relate linearly the water salinity in the soil pores, i.e. the soil solution electrical conductivity (σ_w). Models have thus been developed that allow the estimation of σ_w from σ_a (Rhoades et al., 1976; Rhoades et al., 1989; Vogeler et al., 1996).

Volcanic soils display an atypical dielectric behavior that limits the applicability of TDR for measuring θ using standard equations developed for montmorillonitic or kaolinitic soils. The atypical TDR dielectric response of these soils has been attributed to their particular mineralogy (Fe oxihydroxides), low bulk density (Weitz et al., 1997; Regalado et al., 2003), and large surface area (Tomer et al., 1999). Because of the mineralogy of the soil, the permittivity of the solid phase is closer to 15 (typical of metal oxides) than to 5 (quartz), as it is the case of most mineral soils (Table A-1 in Olhoeft, 1989; see also Regalado et al., 2003). The low bulk density (high porosity) in these soils is the result of the strong natural aggregation of the allophane materials into hollow spherules. Regalado et al. (2003) found that water inside the spherules is largely responsible for deviations from Topp's equation. Finally, although negligible in most mineral soils, the large surface area of volcanic soils (as high as 500 m^2 g^{-1}), increases the contribution of rotationally hindered (bound) water to energy losses within the TDR frequency bandwidth (Or and Wraith, 1999). As a result, alternative TDR calibration curves for estimating θ have been proposed for tropical volcanic soils (Weitz et al., 1997), and temperate volcanic soils from New Zealand (Tomer et al., 1999), Japan (Miyamoto et al., 2001), and Canary Islands (Regalado et al., 2003).

The permittivity, ε_c, is a complex number such that $\varepsilon_c=\varepsilon_r+i\varepsilon_i$, where ε_r and ε_i are, respectively, the real and imaginary components of the dielectric constant ε_c (Kraszewski, 1996). While the real part of ε_c accounts for the soil water content, ε_i encompasses ionic conductivity losses. The soil solution's electrical

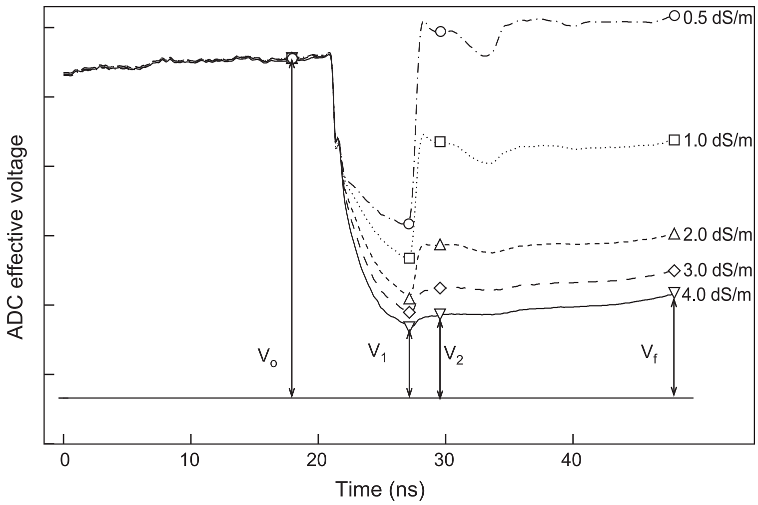

Fig. 1. Experimental results showing the salinity effect on the shape of the TDR curve. V_o denotes pulse amplitude, V_1, V_2 and V_f are characteristic voltages used to estimate the soil electrical conductivity.

conductivity and imaginary dielectric constant are interrelated via $\varepsilon_i = \sigma_w / \omega\varepsilon_o$, with ω the wave angular frequency and ε_o the permittivity of vacuum. Dielectric particularities already attributed to the real part of the permittivity of volcanic soils, are also likely to affect its imaginary part, i.e. the σ_w estimation. However, despite such differences in the dielectric properties of volcanic vs. other mineral soils their implications for soil electrical conductivity determination have received little attention (Vogeler et al., 1996).

Vogeler et al. (1996) first applied the TDR technique for studying solute transport in a volcanic soil from New Zealand using Nadler et al. (1991) method and a new σ_a–σ_w relationship (Eq. (15) in Table 2). Because of its empirical origin, such a relationship could have limited predictive capability and its generality needs to be tested for other volcanic soils. Additionally, the applicability in volcanic soils of previous σ_a–σ_w mechanistic model equations (Eqs. (13) and (14) in Table 2) has not yet been examined.

The objective of this study are: (a) assess the performance of the existing equations described above for estimating σ_a, σ_w and solute concentration from TDR readings in a volcanic soil using; (b) evaluate a new alternative σ_a–σ_w relationship for volcanic soils. The equations will be experimentally tested both in small hand-packed soil columns in batch experiments, as well as in a large undisturbed monolith during a miscible displacement tracer experiment under transient solute transport conditions.

2. Materials and methods

2.1. Sampling and soil characterization

Soil samples were collected from an 800 m^2 banana field in the north of Tenerife (Canary Islands, Spain). The volcanic soil was obtained at 15 cm depth in 30 random locations around the field.

Soil organic matter (OM) was determined by Walkley and Black's method (Page et al., 1982). Soil physical properties were determined using standard methods (Klute, 1986): the hydrometer method for soil texture, gravimetry for bulk density (ρ_b), the pycnometer with ethanol method for specific density (ρ_s), and calculation from particle and bulk densities for porosity (η). For the surface area determination soil subsamples (six replicates of 1 g) where placed in weighing bottles and dried in vacuum to constant weight over di-phosphorus pentaoxyde. Finally, these were saturated to constant weight by adsorption in a sulfuric acid atmosphere (Newman, 1983).

2.2. Methods for σ_a, σ_w and solute concentration estimation from TDR signals

To obtain σ_a from the TDR wave, certain methods rely on the values of specific voltage readings defined as (Fig. 1): V_o, initial amplitude of the TDR pulse; V_1, V_2 voltages at the beginning (end of the waveguides) and end of the reflection, respectively; and V_f, voltage after a sufficiently long time. Different calculation procedures using some of these readings are presented in Table 1. Chronolog-

Table 1
Equations to calculate σ_a based on the TDR wave form

Reference	Equation	
Giese and Tiemann (1975)	$\sigma_a = \frac{\sqrt{\varepsilon_c}}{120\pi L}\left(\frac{2V_o}{V_f} - 1\right)$	(1)
Dalton et al. (1984)	$\sigma_a = \frac{\sqrt{\varepsilon_c}}{120\pi L}\left(\frac{V_1}{V_2 - V_1}\right)$	(2)
Topp et al. (1988)	$\sigma_a = \frac{\sqrt{\varepsilon_c}}{120\pi L}\ln\left(\frac{V_1(2V_o - V_1)}{V_o(V_2 - V_1)}\right)$	(3)
Yanuka et al. (1988)	$\sigma_a = \frac{\sqrt{\varepsilon_c}}{120\pi L}\ln\left(\frac{V_1 V_f - V_o(V_1 + V_f)}{V_o(V_1 - V_f)}\right)$	(4)
Zegelin et al. (1989)	$\sigma_a = \frac{\sqrt{\varepsilon_c}}{120\pi L}\frac{V_1}{V_f}\left(\frac{2V_o - V_f}{2V_o - V_1}\right)$	(5)
Nadler et al. (1991)	$\sigma_a = \frac{K_c}{Z_s} f_t$	(6)

L=TDR guide (rod) length (m); σ_a=*bulk electrical conductivity (dS m^{-1});* ε_c=bulk dielectric constant.
Effective voltage values (V_o, V_1, V_2, V_f) are defined in text and Fig. 1.

ically, Eqs. (1)–(5) in Table 1 correspond to the effort of including multi-reflection effects at the end of the TDR signal caused by discontinuities in the transmission line impedance. Eq. (6) corresponds to a different approach proposed by Nadler et al. (1991) that overcomes the aforementioned problems associated with multi-reflection and requires only two voltage readings (V_o and V_f). These authors suggested to estimate σ_a from an equation similar to that proposed by Rhoades and Van Schilfgaarde, 1976 for the four-electrodes salinity probe (4e), where K_c is the sensor's cell constant, Z_s is the soil's impedance, and f_t is a factor to account for the effect of temperature on the σ_a readings (f_t=1 at 25 °C). The impedance of the sample (soil) can be calculated as (Heimovaara et al., 1995),

$$Z_s = Z_T - Z_{cable} \tag{7}$$

where Z_{cable} (Ω) is the resistance associated with the cable, connectors and reading device, and Z_T (Ω) is the total impedance of the system defined as,

$$Z_T = Z_o(1+\rho)/(1-\rho) \tag{8}$$

Z_o is the characteristic impedance of the coaxial cable (50 Ω), and ρ (non-dimensional) is the reflection coefficient generally computed as,

$$\rho = (V_1/V_o) - 1 \tag{9}$$

When TDR probes of three or more rods are used, no balum transformer to balance the signal is required, and ρ can be estimated as (Heimovaara et al., 1995),

$$\rho = (V_f - V_o)/V_o \tag{10}$$

Once σ_a is obtained by any of the aforementioned methods, σ_w can be calculated by different approaches. For a fixed θ, Rhoades et al. (1976) proposed a linear relationship between σ_a and σ_w of the form

$$\sigma_a = \theta T \sigma_w + \sigma_s' \tag{11}$$

where T (non-dimensional), is a transmission coefficient also known as tortuosity, and σ_s' (dS m^{-1}) is the electrical conductivity of the soil's solid phase associated with ion exchange between the solid and liquid phases. For certain media (i.e. coarse sand) σ_s' can be taken as zero. In Eq. (11) the tortuosity coefficient can be expressed as a linear function of the water content, i.e.

$$T = a\theta + b \tag{12}$$

leading to a quadratic θ relationship between σ_a and σ_w (Eq. (13) in Table 2), that becomes linear for a fixed θ content. However, several authors (Nadler and Frenkel 1980; Nadler, 1982, 1997; Rhoades et al., 1989; Mallants et al., 1996) observed that for low values of σ_w the relationship is no longer linear for a given θ, since under these conditions σ_s' cannot be assumed constant. In order to include this effect, the term σ_s' can be substituted by $\delta\sigma_s$, where δ is an empirical relationship depending on θ and salinity, and σ_s is a

Table 2
Existing equations for σ_a~σ_w relationship[a]

Model	Reference	Equation		Parameters
Linear	Rhoades et al. (1976)	$\sigma_a = (a\theta^2 + b\theta)\sigma_w + \sigma_s'$	(13)	a, b, σ_s'
Non-linear	Rhoades et al. (1989)	$\sigma_a = [\theta - (c\theta + d)]\sigma_w + \dfrac{(\theta_{sol} + c\theta + d)^2}{\theta_{sol}}\sigma$	(14)	c, d, σ_s, θ_{sol}
Empirical	Vogeler et al. (1996)	$\sigma_a = (c\theta - d)\sigma_w + (a\theta - b)$	(15)	a, b, c, d

[a] θ in (m^{3}m^{-3}); σ in (dS m^{-1}).

constant for each soil type (Nadler and Frenkel, 1980). One of such non-linear relationships (Eq. (14), Table 2) is that proposed by Rhoades et al. (1989), where the δ factor includes the effect of solute distribution in the soil's mobile fraction of water. The parameter θ_{sol} (m^3 m^{-3}) in this equation represents the volumetric solid content in the soil, calculated as the ratio between the soil's bulk density (ρ_b) and specific density (ρ_s),

$$\theta_{sol} = \rho_b/\rho_s \tag{16}$$

An empirical alternative to express the relationship between σ_a and σ_w was proposed by Vogeler et al. (1996) for aggregated volcanic soils of New Zealand (Eq. (15), Table 2).

Once σ_w is estimated from the TDR curve analysis and any combination of the equations in Tables 1 and 2, it is possible to relate its value to the concentration of a saline solute (C_s) by means of a calibration function. Several authors have obtained good results with a linear C_s–σ_w relationship (Heimovaara et al., 1995; Vogeler et al., 1996, 1997; Neve et al., 2000).

2.3. Experimental assessment of available methods for estimating σ_a with TDR

Five KCl solutions were prepared with electrical conductivity (σ_{ref}^{25}) ranging between 0.5 and 4 dS m^{-1}. Experimental σ_a estimations of these solutions, based on equations in Table 1, were made by inserting a three-rod (20 cm long) TDR probe into a glass beaker filled with one of the KCl solutions, and registering the liquid temperature and resulting TDR wave with a TRASE system (Soilmoisture).

The parameters needed in Nadler et al. (1991) method, K_c and Z_{cable}, were obtained by fitting the measured σ_a values to the theoretical σ_{ref}^{25} using Eqs. (6) and (7).

For the remaining methods in Table 1, the required voltage values were obtained by analyzing the TDR waves previously recorded after reading in the reference solutions.

The R^2 with respect to the 1:1 line (line of perfect agreement), $R^2_{1:1}$, was calculated for each method as a goodness-of-fit parameter. This statistic is a measure of the variance about the 1:1 line (line of perfect agreement, $R^2_{1:1}$=1) of the predicted data compared to the variance of the observed data.

2.4. Experimental assessment of available methods for estimating σ_w

The soil was first mixed and placed in two 50-l containers over a 10-cm-thick filter of coarse sand on top of a nylon screen. The soil was slowly washed by irrigating the containers with water of 0.07 dS m^{-1} using a micro-sprinkler for 24 h until the bottom drainage solution reached a constant electrical conductivity value (~0.8 dS m^{-1}). The soil was then air dried and sieved below 2 mm particle size. The moisture content of the air-dried soil was determined gravimetrically in three subsamples and found θ_m=12%.

The experiment consisted of 24 hand-packed soil columns, resulting from the combination of four θ levels: 0.5η, 0.6η, 0.7η, 0.9η, where η is the soil porosity (Table 3); and six KBr solutions with electrical conductivity levels of 0.01, 0.57, 1.05, 2.29, 3.18, 4.36 dS m^{-1}. Each portion of soil (3.70 kg) was mixed with the KBr solutions in a volume equivalent to each θ level (0.84, 1.05, 1.26 and 1.46 l). The moisture was distributed uniformly by rotating the soil gently in a horizontal drum for several minutes. PVC cylinders (∅15.5×21 cm, volume=3.96 l) were filled with the soil mixtures. Hand-packing was done in five layers to ensure a homogeneous bulk density close to that found in the field (ρ_b=0.9).

Measurements were carried out sequentially (Fig. 2). Firstly, to obtain the σ_a with the TDR (σ_a-TDR) a three-rod (20 cm long, ∅ 0.3 cm, 2.2 cm spacing) TDR probe was inserted and the wave recorded. Secondly, a measurement of σ_a (σ_a–4e) was made with a standard 1–20 kHz four-electrode electrical conductivity and temperature probe (Rhoades and Van Schilfgaarde, 1976). Thirdly, the electrical conductiv-

Table 3
Physical–chemical properties of the soil used in the study

Property	Value
Clay content, Ac (%)	13.0±6.2
Texture (USDA)	Clay–loam
Organic Matter, OM (%)	2.30±0.05
Porosity, η	66.4±2.4
Bulk density, ρ_b (g cm^{-3})	0.87±0.08
Specific density, ρ_s (g cm^{-3})	2.70±0.09
Surface area (m^{2}g^{-1})	296±7
Al_o+0.5Fe_o (%)	5.7
ΔP(%)	87.6
Si_o (%)	1.2

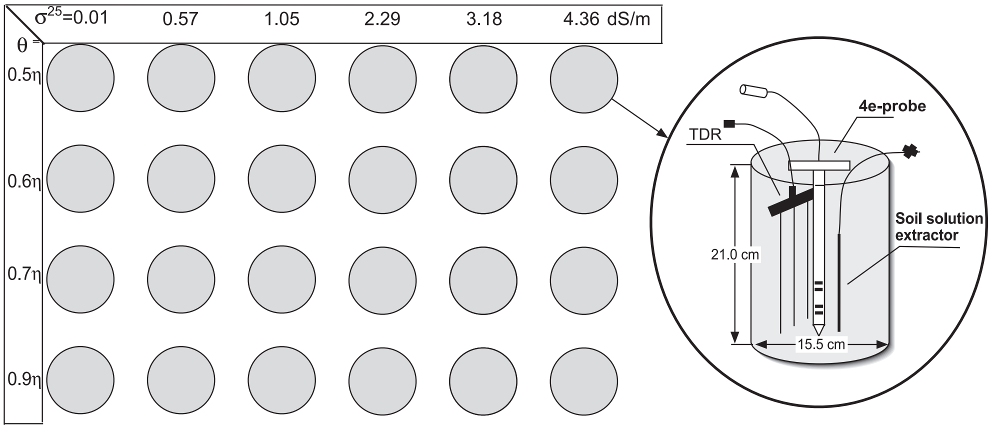

Fig. 2. Experimental set-up for calibrating soil electrical conductivity models.

ity of the soil solution (σ_w) was obtained by extracting the solution with a suction extractor (Rhizon Eijkelkamp, Holland) at 70 cbar for 2 h and then reading the value with a laboratory EC meter (Mettler, USA). This was possible since the mobile and immobile soil solution fractions are assumed to be in diffusion equilibrium under these experimental conditions (Persson, 1997). At the end of the experiment, a saturation extract (Page et al., 1982) was obtained from soil in each column. A soil subsample from each column was first air-dried, saturated with distilled water, filtered under vacuum and the electrical conductivity of the solution extract ($\sigma_{extract}$) measured with the laboratory EC-meter.

Soil moisture was obtained for each sample with the TDR at the time of the σ_a reading by recording the composite dielectric constant (ε_c) and applying the site specific equation developed for this volcanic soil (Regalado et al., 2003).

$$\theta = -11.2\times10^{-2} + 5\times10^{-2}\varepsilon_c - 16\times10^{-4}\varepsilon_c^2 + 2\times10^{-5}\varepsilon_c^3 \qquad (17)$$

The experimental values (σ_a–σ_w,θ) were fitted to the equations presented in Table 2.

2.5. Estimation of the experimental relationship between C_s and σ_w

Br^- concentration was analyzed in the soil solution extracted in the previous step using the Chloramine-T method in an autoanalyzer (Technicon AAII, Bran+Luebbe, Germany). The values obtained were fitted with a linear regression model to the TDR σ_w values.

2.6. Experimental assessment of σ_a–σ_w relationship to monitor the movement of a saline tracer by TDR during a miscible displacement experiment

The relationship between σ_a and σ_w was tested under transient conditions in a large undisturbed soil column (∅0.45×0.72 m) obtained at the same Tenerife site described above by means of a custom-designed hydraulic press apparatus anchored to the ground. The apparatus was used to insert a stainless steel cylinder [45 cm (∅)×85 cm×0.4 cm (wall thickness)] slowly into the soil. Once inserted into the soil, the cylinder was isolated by excavating around it, the top and bottom covered with appropriate caps, and transported to the laboratory. The experimental set-up is shown in Fig. 3 and described thoroughly in Ritter (2002). TDR readings and soil solution sampling with suction extractors were carried out at seven depths during a miscible displacement experiment. A 0.025M KBr tracer pulse with a flow rate of 1.7 mm/h was applied for 250 h and then flushed for 710 h with a standard background 0.005 M $CaSO_4$+thymol solution (Section 3.3.2.1.d in Dane and Topp, 2002). At each depth, three TDR probes (3 rods, 20 cm long) and two solution extractors were inserted and the measurements averaged to obtain effective values by layer. The K_c and Z_{cable} for each of the 21 TDR probes were obtained according to the procedure described in Section 2.3 above. During the outflow experiment,

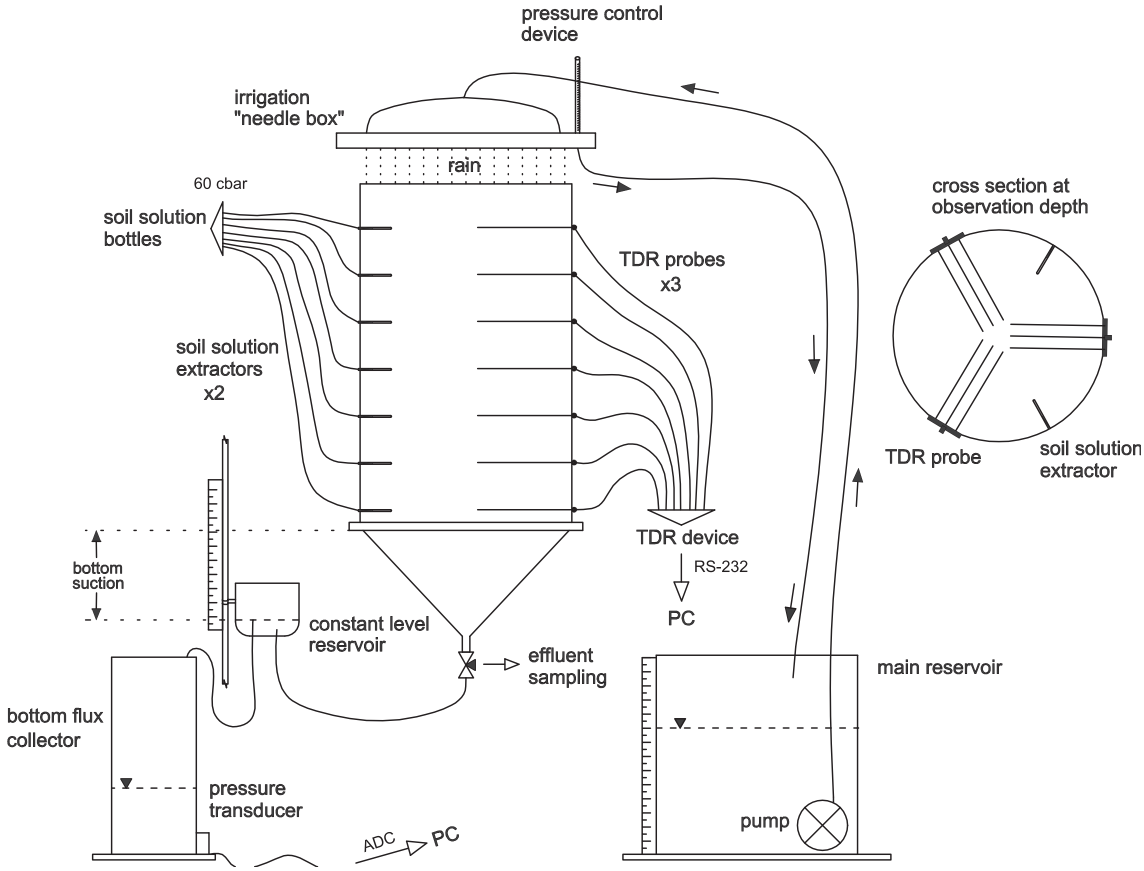

Fig. 3. Transient flow column experiment to test accuracy of the selected σ_w~σ_a model.

suction (70 cbar) was applied to the solution extractors and samples collected daily. σ_w was measured in the solution collected by these suction samplers with a laboratory EC-meter and used as the true value in the evaluation of the TDR results.

3. Results and discussion

3.1. Soil characterization

The relevant soil properties for this study are summarized in Table 3. The soil presents andic characteristics defined by the amount of active aluminum (Al_o) and iron (Fe_o) extracted with ammonium oxalate (Al_o+0.5 Fe_o>2%,), phosphate retention (reactivity parameter) and low bulk density. Soils with these properties exhibit strong natural micro-aggregation that translates into large water retention capacity, porosity and saturated hydraulic conductivity. In fact, the soil can be classified as an Andisol (USDA Soil Taxonomy) (Regalado et al., 2003).

3.2. Experimental assessment of available methods for estimating σ_a with TDR

Fig. 1 presents TDR curves obtained for the five KCl reference solutions. Note that based on these results V_2 will likely be difficult to identify for salinity values >4.01 dS m^{-1}, indicating a limitation for σ_a estimation methods that depend on this value, i.e. those of Eqs. (2) and (3), at high salinity levels.

The voltage values required by the equations in Table 1 were obtained from each of the readings in the reference solutions and the σ_a was calculated for each method. Fig. 4 presents a comparison of the results

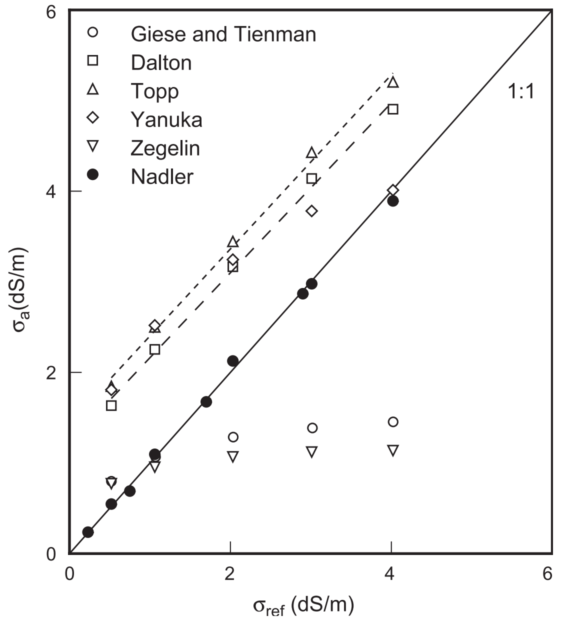

Fig. 4. Experimental comparison of TDR equations to estimate the electrical conductivity of five KCl reference solutions.

against the reference values. While results from Topp's, Dalton's, and Nadler's methods exhibit a linear relationship with the measured data, non-linearity is observed when σ_a>2 dS m^{-1} for Zegelin's, Yanuka's, Giese and Tienman's methods. Non-linear responses for these methods were also found by other authors (Zegelin et al., 1989; Mojid et al., 1997). Among the linear responses, Nadler's lies closely on the 1:1 line ($R^2_{1:1}$=0.988) confirming it as the best one

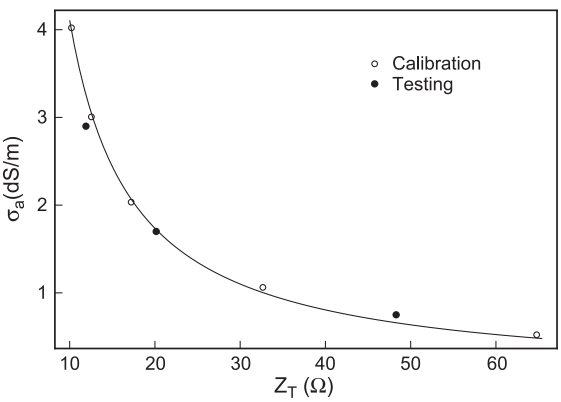

Fig. 5. Experimental fitting of Nadler's model (Eq. (6)) (K_c=30.06, Z_{cable}=2.68 Ω) to estimate the electrical conductivity of five KCl reference solutions.

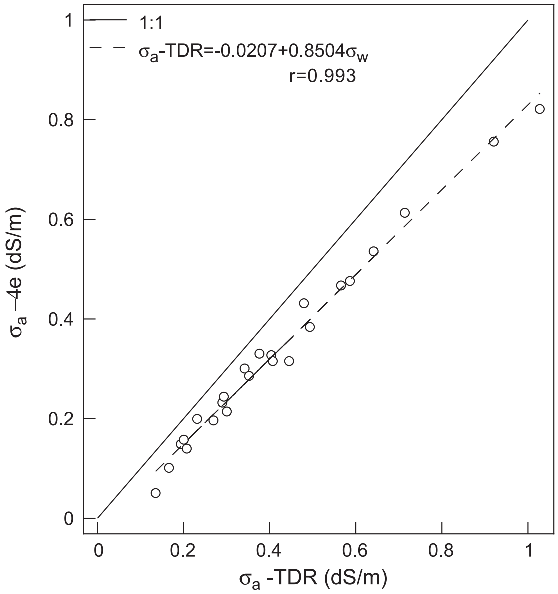

Fig. 6. Comparison of instruments to estimate soil σ_a.

for our experimental conditions. Hence, this method will be the one used hereon. The results of fitting the experimental readings with Nadler's method were independently checked against three additional testing solutions with good results (Fig. 5).

3.3. *Experimental assessment of available methods for estimating σ_w*

A comparison between σ_a measured by two instruments (standard 4e probe and TDR) is presented in Fig. 6. Although measurements with the two devices are highly correlated ($R^2_{1:1}$=0.986), TDR gave systematically somewhat lower readings (slope=0.85).

The soil solution could not be extracted from 3 of the repacked samples with the lowest moisture content (θ=35.5±1.0%). This is in agreement with the suction curves obtained for this soil and depth in a previous study (Armas Espinel et al., 2003), where at 70 cbar θ=36%. A good correlation was found between soil saturated paste extract readings ($\sigma_{extract}$, dS m^{-1}) and those of σ_w (dS m^{-1}),

$$\sigma_w = 0.0375 + 1.3425\sigma_{extract};\ r^2 = 0.88 \qquad (18)$$

Eq. (18) may be useful to compute σ_w from $\sigma_{extract}$ at low water contents (<35%), where suction extractors do not longer work, although due to its empirical nature it might not be accurate to extrapolate far from the measured range.

Results from fitting the experimental values to the equations presented in Table 2 are given in Fig. 7 and Table 4. In comparison with the other two, the linear model (Eq. (13)) yields the best results with the smallest set of parameters. Similar results were found by Neve et al. (2000) when working with KNO_3 solutions in a loamy sand soil. In addition, Fig. 7 shows how the experimental TDR values tend to the same σ_a as σ_w approaches zero, regardless of θ. Among the expressions in Table 2, only the linear model (Eq. (13)) tends to a constant value when taking the limit of the expression for $\sigma_w \rightarrow 0$.

Comparison of σ_a~σ_w (Eqs. (13)–(15) shows that, since the linear model differs from the other two in the quadratic dependence in θ of the slope, this may be the key term for the soil studied. Porosity is unusually large in volcanic soils (66% in this soil, Table 3) and therefore, as is the case with the linear model (Eq. (13)), high order terms in the water content dependence of the σ_a–σ_w slope dominate at high water contents. These results can be also interpreted in terms of mobile vs. immobile water. Rousseaux and Warkentin (1976) showed the importance of microporosity in allophanic soils where, in most of the θ range, water is predominantly held in capillaries and micropores rather than on external clay surfaces. At low θ (<30%), the ratio of bound (immobile) to free (mobile) water is large (>0.2) and most of the soil water is expected to be adsorbed in capillaries. Hence, the soil dielectric response would be dominated by that of bound water. There is a transition (θ>30% in

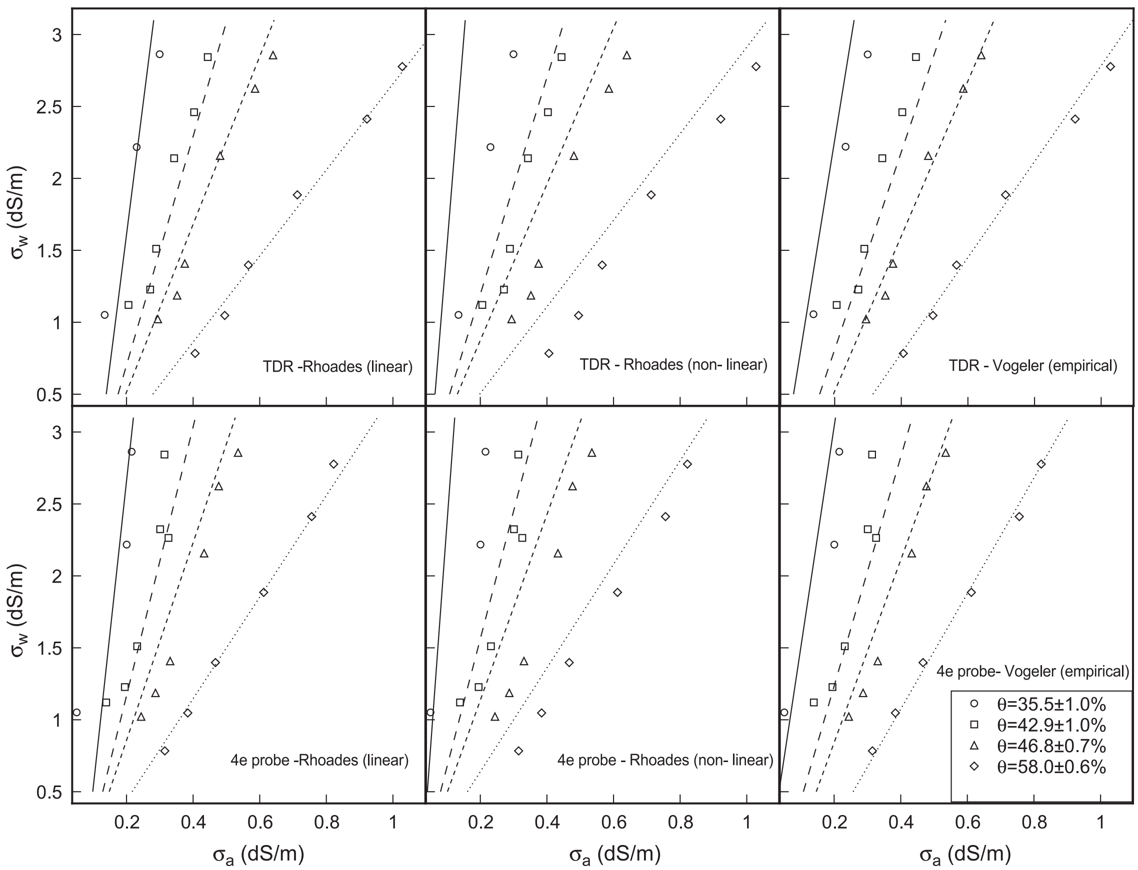

Fig. 7. Performance of models presented in Table 2 relating σ_a and σ_w.

Table 4
Fitting results corresponding to the existing and proposed models used to estimate σ_w

Model (eq.[a])	a	b	c	d	σ_s	$R^2_{1:1}$
TDR						
Linear (Eq. (13))	1.876	−0.512	–	–	0.112	0.986
Non-linear[b] (Eq. (14))	–	–	−0.323	0.435	0.094	0.976
Empirical (Eq. (15))	0.547	0.153	1.023	0.293	–	0.983
New empirical (Eq. (19))	1.423	−0.289	0.470	–	–	0.989
4e-probe						
Linear	1.583	−0.430	–	–	0.075	0.968
Non linear[a]	–	–	−0.093	0.357	0.059	0.966
Empirical	0.581	0.204	0.817	0.225	–	0.974

[a] Equation number in Table 2 or text.
[b] θ_{sol}=0.3455 m^3 m^{-3}.

this soil; see Regalado et al., 2003) where larger pore spaces between micro-aggregates are filled with mobile water, and this fraction starts to dominate the dielectric behavior of the soil in turn (Wang and Schmugge, 1980; Saarenketo, 1998; Regalado et al., 2003). This upper range of θ in these soils is typically the most relevant in agricultural and contaminant transport scenarios, and is the one explored herein. According to Rhoades et al. (1989), the slope of the linear model (Eq. (13)) accounts for the mobile water fraction, and this depends non-linearly on the water content, θ. Such a quadratic dependence on θ of Eq. (13), which is linear in the other two models (Eqs. (14) and (15)), better describes the TDR salinity response in this soil at this θ range, where the mobile water phase is dominant. Notice how the non-linear model fails to describe the σ_a–σ_w data, especially for large water contents (Fig. 7).

Regarding the empirical model (Eq. (15)), the correlation matrix between the parameters presented in Table 4 (results not shown) indicates that the parameters obtained are highly correlated (r=0.98 for c~d and a~b; r=0.93 for c~a and d~b), indicating that in our case the model could be over-parameterized. We analyzed the original data used by Vogeler et al. (1996) when presenting the empirical model and found that a high correlation ($|r|$=0.83–0.98) also existed among all the parameters in that study. A further look to our results shows that, by eliminating one parameter (fixing c=1) and fitting the model again, parameter correlation disappears (r<0.5 for all pairs) while the goodness-of-fit is maintained ($R^2_{1:1}$=0.983). The analysis of variance conducted with Ho (null hypothesis): c=1, showed these empirical models with 4 and 3 (c=1) parameters not to be significantly different (p=0.86), illustrated by the fact that the values parameters obtained in both cases are close (Table 5). Thus, a three parameter model, σ_a=$(\theta-d)\sigma_w$+$(a\theta-b)$, would be sufficient in our case if an empirical model was chosen.

Motivated by the above results and the close fitting obtained with Rhoades' linear model we suggest an alternative empirical model for volcanic soils of the form,

$$\sigma_a = \left(a\theta^2 + b\theta\right)\sigma_w + c\theta^2 \tag{19}$$

This new equation provided the best fit of all the models studied (Table 4, Fig. 8). Eq. (19) did also fit Vogeler et al.'s (1996) original New Zealand volcanic soil data well ($R^2_{1:1}$=0.986), thus lending generality to the model (Fig. 8). In addition, since the number of parameters in Eq. (19) is lower (3 vs. 4) while avoiding parameter dependence, the new equation can represent a good alternative to Eq. (15). Note that Eq. (19) is related to Rhoades' linear (Eq. (13)) with σ'_s depending on θ^2. Eq. (19) performs better than the other models tested because it encompasses both: (i) the square dependence on θ of the slope of σ_a–σ_w that relates to the relative dominance of the mobile water fraction at high water content; and (ii) the non-linear dependence of σ_w, which better reproduces the data at low water content where the immobile water fraction controls the dielectric response in volcanic soils (Fig. 8).

Table 5
Parameter reduction in Vogeler's empirical model

Parameter	Three parameters	Four parameters
c	1.000	1.023
d	0.282	0.293
a	0.589	0.547
b	0.173	0.152

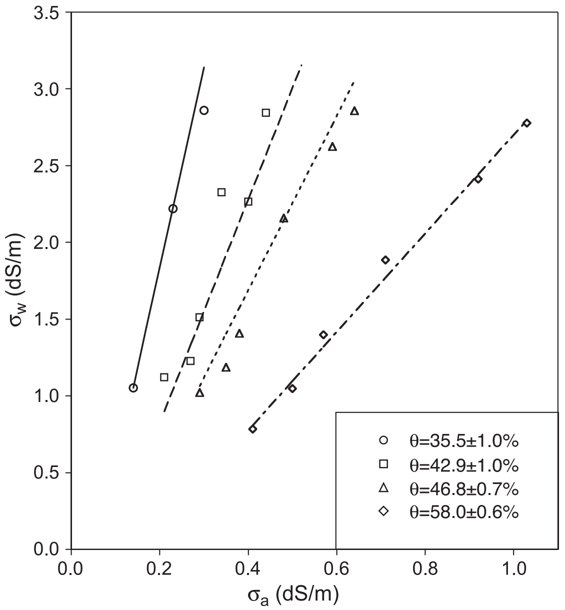

Fig. 8. Performance of proposed alternative empirical model with experimental TDR data from this study and New Zealand soils.

3.4. Experimental relationship between C_s and σ_w

A linear relationship was found between bromide tracer (mg l^{-1}) and σ_w (dS m^{-1}) (Fig. 9),

$$[Br^-] = -817.51 + 893.33\sigma_w;\ r^2 = 0.96 \qquad (20)$$

in terms of (mol l^{-1}) and (S m^{-1}), the relationship is,

$$[Br^-] = -0.0102 + 0.112\sigma_w;\ r^2 = 0.96 \qquad (21)$$

Eq. (21) results are in the range of those presented by other authors (Vogeler et al., 1996, 1997; Neve et al., 2000) for other tracers (Cl^- and NO_3^-, respectively), with slopes 0.076–0.100 and independent term −0.0007 to −0.0012.

3.5. Experimental assessment of σ_a–σ_w relationship to monitor the movement of a saline tracer by TDR during a miscible displacement experiment

Analysis of Nadler's K_c and Z_{cable} calibration values from the 21 probes showed that variability among probes was low (CV=2.9%). A comparison of breakthrough curves obtained from TDR probes in the column with those obtained from the soil solution extractors is given is given in Fig. 10.

Several authors discuss the applicability of σ_w–σ_a models derived from batch experiments under transient (solute transport) conditions. First, Blackmore (1978) postulates that the different composition of mobile and immobile water fractions when not in equilibrium, i.e. such as under transient conditions, will degrade the predictions of σ_w based on σ_a. This is further exacerbated by the fact that suction samplers, the standard method used to estimate σ_w, mainly sample mobile water (Vanclooster et al., 1995), while TDR measurements represent an average of the mobile and immobile solutions. Thus, if mobile and immobile soil solutions are not in equilibrium the solution extracted with the suction samplers will not exactly represent the actual resident concentration (Persson, 1997). Second, since the transmission coefficient T accounts for the tortuosity of the soil matrix, differences in soil structure between the small hand-packed soil columns and the large undisturbed monolith will yield local differences in T (Mallants et al., 1996).

To assess the validity of the linear Rhoades' model σ_w–σ_a (Eq. (13)) under transient conditions in

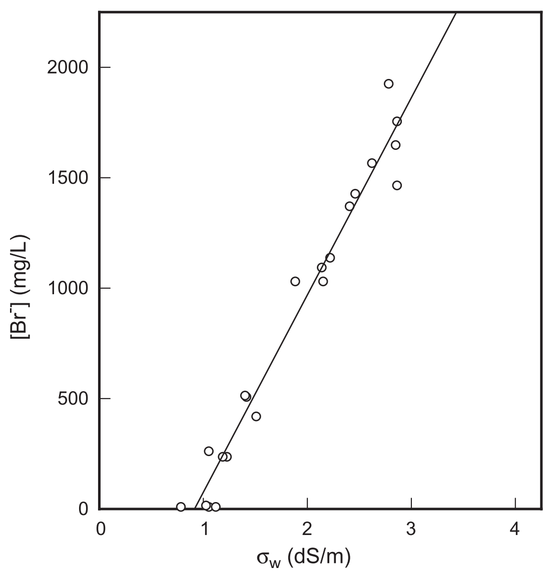

Fig. 9. Relationship between [Br^-] tracer concentration and soil solution electrical conductivity.

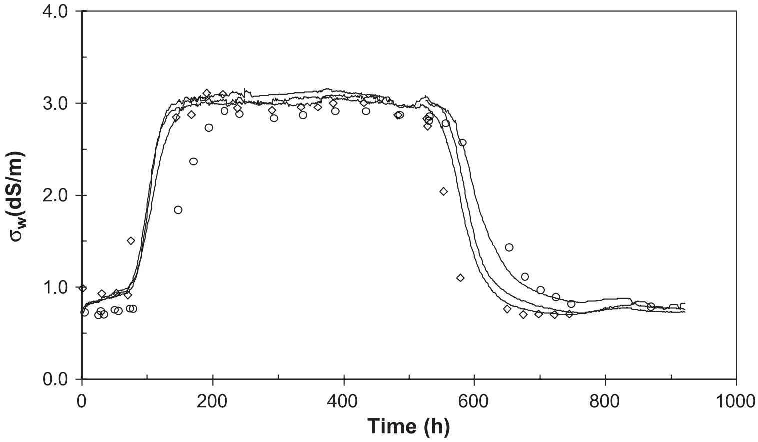

Fig. 10. Comparison of breakthrough curves obtained at the center of the soil column using TDR (lines) and solution extractors (symbols).

the large undisturbed monolith tracer experiment the following quadratic relationship with θ is derived by rearranging Eq. (13) with the coefficients in Table 4:

$$(\sigma_a - \sigma_s')/\sigma_w = a\theta^2 + b\theta(\sigma_a \to 0.112)/\sigma_w = 1.876\theta^2 - 0.512\theta \tag{22}$$

Fig. 11 compares the terms on the left and right sides of Eq. (22) calculated from the column experiment values. Thereby, with σ_w measured in the suction extractors samples taken at different depths and σ_a and θ estimated from TDR measurements, a satisfactory correlation is obtained ($R^2_{1:1}$=0.96) between both sides of Eq. (22) (Fig. 11). The correlation confirmed the model's basic assumption of the quadratic dependence on θ and the applicability of the equation also under transient conditions. As discussed before, the quadratic σ–θ relationship is an important feature of the model related to the relative dominance of the mobile water fraction at high water content, characteristic of soils with real or apparent (i.e., naturally aggregated) coarse texture. Persson (1997) also found a quadratic trend in a similar tracer experiment on a large column of homogeneous sand. On the other hand, a linear relationship between σ and θ was observed by Risler et al. (1996) in a column of clay loam soil, and by Persson and Berndtsson (1998) in a loamy sand monolith. This would indicate that the tortuosity factor was constant (Eq. (11)) (contrary to the assumption in our selected model, Eq. (12)), although it must be noted that for a limited θ range the relationship can appear linear.

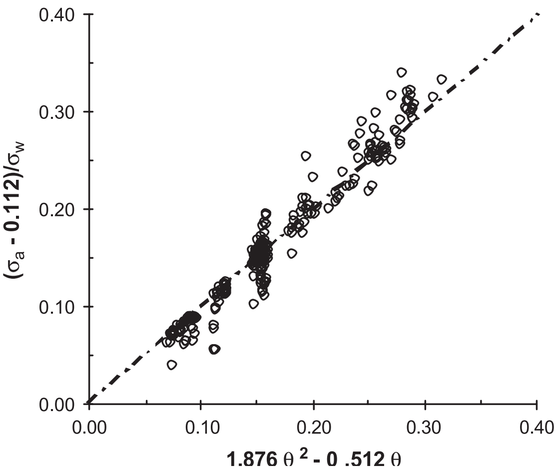

Fig. 11. Experimental results obtained with the proposed σ_w~σ_a model under transient conditions in the undisturbed monolith tracer study (Eq. (22)).

Although the results are acceptable, the scatter observed in Fig. 11 indicates that some of the effects artifacts introduced by the solution extractors and the move from hand-packed to undisturbed samples are also present here but not accounted for. However, given the advantages of the method, where two of the most important state variables in solute transport experiments can be recorded simultaneously with a single device (TDR), the results are considered satisfactory.

4. Conclusions

Volcanic soils differ from the others in their dielectric properties requiring separate relationships to measure θ by TDR. The different dielectric response could also affect the estimation of electrical conductivity by TDR under both equilibrium and transient conditions. Three experiments were carried out to assess models to estimate the soil electrical conductivity with TDR in the case of a volcanic soil. Six equations were tested for σ_a determination. Nadler et al. (1991) yielded the best results. Although it requires calibration, it performed better than the other five in our conditions and only required two parameters. Among three types of models (linear, non-linear and empirical) tested for the σ_w determination, the linear (for a fixed θ) model by Rhoades et al. (1976) gave the best results while requiring the least parameters (three), which is explained in terms of the particular ratio of mobile/immobile water phase distribution of volcanic soils. The σ_w results using the empirical model (Vogeler et al., 1996) show that this model uses too many parameters. An alternative empirical model, $\sigma_a=(a\theta^2+b\theta)\sigma_w+c\theta^2$, is proposed having less parameters while encompassing both: (i) the square dependence on θ of the slope of σ_a–σ_w reflecting the relative dominance of the mobile water fraction at high water content; and (ii) the non-linear dependence of σ_w, which better reproduces the data at low water content where the immobile water fraction controls the volcanic soils dielectrics. This new model was tested for volcanic soils from two different regions giving good results. Tracer (bromide) concentration was successfully estimated from σ_w using a linear equation (R^2=0.96).

Further testing of these results was done under the demanding transient conditions of a miscible displacement tracer experiment in a large undisturbed volcanic soil column. Good agreement was obtained between observed values (in soil solution extracted from the column) and those predicted by the equations selected. These results show that TDR, in conjunction with Nadler's and the newly proposed equations, can be used in volcanic soils as a powerful tool to obtain two of the most important state variables in flow and transport experiments: water content and solute concentration.

List of symbols

Roman

a, b, c, d	empirical constants in various equations [–]
f_t	temperature correction coefficient [–]
L	length of TDR probe [m]
K_c	TDR probe "cell" constant [m^{-1}]
V_o	zero reference voltage [V]
V_f	final reflected voltage at very long time [V]
V_1	voltage of incident step [V]
V_2	voltage after reflection from probe end [V]
Z_{cable}	impedance of TDR cable, connectors and reading device [Ω]
Z_o	characteristic impedance of TDR coaxial cable [Ω]
Z_s	impedance of the soil sample [Ω]
Z_T	total impedance of TDR system [Ω]

Greek

ε_c	bulk dielectric constant [–]
η	soil porosity [–]
ρ	reflection coefficient [–]
ρ_b	soil bulk density [kg m^{-3}]
ρ_s	soil specific density [kg m^{-3}]
σ_a	bulk electrical conductivity [S m^{-1}]
$\sigma_{extract}$	electrical conductivity of the soil saturated paste extract [S m^{-1}]
σ_{ref}^{25}	electrical conductivity of reference solution at 25 °C [S m^{-1}]
σ'_s	electrical conductivity of the soil's solid phase [S m^{-1}]
σ_w	soil solution electrical conductivity [S m^{-1}]
θ	volumetric water content [m^3 m^{-3}]
θ_m	gravimetric water content [kg^3 kg^{-3}]

Abbreviations

4e	four-electrode salinity probe
TDR	Time Domain Reflectometry

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