Combined estimation of effective electrical conductivity and permittivity for soil monitoring

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ABSTRACT

The mapping of moisture content, composition and texture of soils is attracting a growing interest, in particular with the goal of evaluating threats to soil quality, such as soil salinization. Fast non-invasive geophysical surveys are often used in this context. The aim of this work was to study constitutive models that can be used to parameterize electrical conductivity and permittivity starting from a unifying conceptual approach, and to evaluate whether the information carried by one measurement type can be used to identify soil parameters that are then used to predict the other geophysical quantity. To this end, a recently-developed constitutive model was here extended and modified to consider also the grain surface conductivity, a critical component in most natural situations. The extended model was successfully tested against laboratory measurements. In addition, the new model was compared against five other equations that use similar soil parameterizations. It was concluded that only three out of the five selected models yield similar predictions, while the remaining two predict a different geophysical response for the same soil texture. Following this analysis, a methodology was developed to estimate soil salinity starting from the simultaneous measurements of bulk electrical conductivity and permittivity and validate this methodology against laboratory experiments. The method is valid in situations where the conductivity of the pore-water remains approximately constant during the measurement period. Key features of the approach proposed to map soil salinization are (i) simplicity, (ii) absence of fitting parameters and (iii) the fact that moisture content does not need to be measured or estimated independently. The methodology was tested on a large number of soil samples and proved robust and accurate.

Keywords: hydrogeophysics, moisture content, non-invasive measurements, TDR, Archie’s law, Topp equation, dielectric constant, surface conductivity, salinization, digital soil mapping.
1. Introduction

Characterization of soil texture and monitoring of soil state are extremely important in the perspective of sustainable development, for example to preserve fertility of agricultural areas and to identify possible threats for the near surface environment, including a number of hydrological impacts. In this context, geophysical methods are used to estimate and map key soil properties, including clay and organic matter content, moisture dynamics, rooting depth, salinity and redox state [e.g. Abdel Aal et al., 2004; Atekwana, 2010; Benderitter and Schott, 1999; Binley et al., 2002; Cassiani et al., 2006, 2009; Corwin et al., 2003; Corwin and Lesch, 2005a,b; Dannowski and Yaramanci, 1999; Day-Lewis and Singha, 2008; Friedman, 2005; Hayley et al., 2009; Hubbard et al., 2001; Kästner and Cassiani, 2009; Koestel et al., 2008; Koestel et al., 2009a,b; Müller et al., 2010; Schwartz et al., 2008; Shevnin et al., 2007]. Amongst the most used geophysical tools are electrical resistivity tomography (ERT), ground penetrating radar (GPR) and time-domain reflectometry (TDR) [Rubin and Hubbard, 2005; Vereecken et al., 2006]. These geophysical techniques measure the electromagnetic properties of the soil – DC electrical conductivity for ERT, and permittivity for GPR [e.g. Huisman et al., 2003] and TDR [e.g. Robinson et al., 2003]– and rely on constitutive equations to recover variables of environmental significance from the measurements [Day-Lewis et al., 2005; Rubin and Hubbard, 2005]. Classical models used to link DC electrical conductivity to moisture content such as Archie’s law [1942] and its extensions are often modified to account for the effect of surface and grain conductivity [Clavier et al., 1984; De Lima and Sharma, 1990; Glover et al., 2000; Pride, 1994; Waxman and Smits, 1968]. The Topp et al., [1980] equation and the complex refractive index model (CRIM) [Birchack et al., 1974, Brovelli and Cassiani, 2008; Roth et al., 1990] are the relationships most frequently used to analyze the permittivity of variably-saturated porous
materials. Innovative methodologies – in particular joint inversion schemes – have been recently proposed with the aim to integrate information and measurements obtained from surveys conducted using different tools, such as measurements of electrical conductivity, permittivity, EM wave velocity and in situ soil state variables (salinity, moisture content, etc.) [e.g. Binley et al., 2001; Gallardo and Meju, 2004; Hinnell et al., 2010; Linde et al., 2006; Looms et al., 2008; Rings et al., 2010; Vereecken et al., 2006]. These approaches are receiving increasing attention because, being based on more abundant and diversified pieces of information, they potentially provide a more accurate and reliable imaging of the characteristics of the subsurface. Nearly all the data integration schemes rely on petrophysical constitutive models to link the different datasets: the constitutive model is either chosen a priori [e.g. Binley et al., 2001; Hinnell et al., 2010; Looms et al., 2008; Rings et al., 2010; Rubin and Hubbard, 2005; Vozoff and Jupp, 1975] or a ‘structural’ approach is used, that is, a common geometry is assumed and the link between the measured physical properties is derived based on the results of the joint inversion [Gallardo and Meju, 2004; Haber and Oldenburg, 1997; Linde et al., 2006]. In this second case, the petrophysical equations are used to gain insights into the physical, chemical and hydrological properties of the subsurface. The availability of reliable, physically based constitutive models is therefore of paramount importance for the success of any data integration schemes.

DC electrical conductivity and high-frequency permittivity as obtained respectively from ERT and TDR/GPR surveys, are two inter-related variables – that is, they depend, to some extent, on the same soil characteristics – and have been often combined to map texture and moisture content [Binley et al., 2001; Linde et al., 2006; Looms et al., 2008]. Owing to this similarity, the relationship between effective conductivity and permittivity has been proposed as a viable tool to map soil salinity, and few empirical equations have been proposed to construct a
‘soil salinity index’ [Hamed et al., 2003; Hilhorst, 2000; Malicki and Walczak, 1999]. Some petrophysical laws exist to model these two quantities with the same parameterization, linking the soil bulk response to its moisture content and to the geometry of the pore-space (porosity and connectivity). From a pore-scale perspective, bulk soil electrical conductivity and permittivity are different in that the electrical conductivities of the solid (skeleton) and gaseous phases are negligible, whereas permittivity is not. On the contrary, electrical conductivity is often influenced by the conductance arising from the excess of charge in the vicinity of the negatively charged solid surfaces of silica, clays and organic matter [Brovelli et al., 2005; Revil and Glover, 1997; Revil et al., 1998]. The additional contribution of the charged interface is often converted into an equivalent grain (volumetric) conductivity [Bussian, 1983; De Lima and Sharma, 1990], and therefore analogous boundary value problems can describe both bulk permittivity and electrical conductivity [Brovelli and Cassiani, 2010b; Brovelli et al., 2005; Linde et al., 2006]. Although developed using different approaches, including empirical or semi-empirical considerations [Archie, 1942; Clavier et al., 1984; Waxman and Smits, 1968], effective medium theories [Bussian, 1983; Miller, 1969; Sen et al., 1981] and volume-averaging algorithms [Linde et al., 2006; Pride, 1994], most of the petrophysical equations suited to model both DC electrical conductivity and high-frequency permittivity utilize a parameterization that is compatible with that introduced by Archie [1942]. In other words, all these models use a parameter to describe the inner topology of the pore-space (tortuosity and connectivity) that can be correlated to Archie’s cementation factor $m$, while the effect of water saturation is described by a saturation exponent $n$ that depends on the pore-size distribution and the properties (wettability/hydrophobicity) of the inner surface of the porous medium [Chen and Or, 2006; Knight and Abad, 1995; Robinson and Friedman, 2001; Suman and Knight, 1997].
Recently, Brovelli and Cassiani [2010b] proposed a novel mixing equation to compute the permittivity of geological mixtures using the same parameters introduced by Archie [1942]. The model was applied to study the electromagnetic properties of clean porous materials, that is, materials with negligible clay content and, therefore, negligible grain surface conductance. Comparison with experimental data in both saturated and variably saturated conditions demonstrated the excellent predicting capabilities of the model, even when all model parameters were independently measured.

The objectives of this work were:

1. to extend the model of Brovelli and Cassiani [2010b] to consider also the grain surface conductivity;
2. to verify whether the extended model can predict electrical conductivity and permittivity of soils and other geological materials where the contribution of the matrix to the bulk electrical conductivity cannot be neglected;
3. to analyze some of the other existing petrophysical laws based on the same parameterization, in order to ascertain whether the relevant calibrated parameters can be reliably used to estimate the physical properties of the soil;
4. to identify the petrophysical models that are best suited to data fusion and joint inversion schemes, including our proposed extended model;
5. to derive a relationship between bulk electrical soil properties – DC electrical conductivity and permittivity in the static limit – that can be used to map soil salinity and pore-water conductivity with fast, non-invasive soil mapping surveys.

2. Petrophysical model

2.1 Model overview
The petrophysical constitutive model of Brovelli and Cassiani [2010b] was developed by combining variational bounds for the transport properties of granular composites [Hashin and Shtrikman, 1962; Milton, 1981] and Archie’s [1942] law, a constitutive model commonly used to parameterize electrical conductivity of variably saturated porous media. The model was consistently developed for two- and three-phase materials on the basis of the same basic assumptions. In the following, only the key model equations are presented, as full details can be found in Brovelli and Cassiani [2010b]. The upper (HSU) and lower (HSL) Hashin and Shtrikman [1962] bounds e.g. for the electrical permittivity of a mixture of two phases $p_1$ and $p_2$, with volumetric fraction $(1-\varphi)$, $\varphi$ and permittivity $\varepsilon_{p_2} > \varepsilon_{p_1}$ are given by

$$\varepsilon_{\text{HSL}}(\varepsilon_{p_1}, \varepsilon_{p_2}, \varphi) = \varepsilon_{p_1} + \frac{\varphi}{(\varepsilon_{p_2} - \varepsilon_{p_1})^{-1} + \frac{1-\varphi}{3\varepsilon_{p_1}}}$$

(1)

$$\varepsilon_{\text{HSU}}(\varepsilon_{p_1}, \varepsilon_{p_2}, \varphi) = \varepsilon_{p_2} + \frac{1-\varphi}{(\varepsilon_{p_1} - \varepsilon_{p_2})^{-1} + \frac{\varphi}{3\varepsilon_{p_2}}}.$$  

(2)

The model of Brovelli and Cassiani [2010b] relies on the assumption that at the pore level the porous medium can be approximated as a mixture of two components, with bulk properties corresponding to that of the upper and lower bound, respectively. In other words, within the porous material the water phase is locally well connected (and the bulk properties are computed from the upper HS bound), while in other regions where the fluid connectivity is lower the solid phase has stronger impact (and the bulk properties are computed from the lower HS bound). Ideally, one such system should be modeled using an effective medium approximation, using the HS bounds to compute the bulk properties of the two components. The resulting expression would however be extremely difficult to manipulate. The alternative approach followed by Brovelli and Cassiani [2010b] is to assume that the two components are arranged in parallel.
rather than in a homogeneous isotropic mixture. The bulk permittivity of the assemblage, $\varepsilon_b$, is a linear combination of Equations (1) and (2):

$$\varepsilon_b = a \varepsilon_{HSU} + (1 - a) \varepsilon_{HSL}$$

(3)

with the weighting factor, $a$, derived from Archie’s [1942] law, applied to dielectric properties:

$$\varepsilon_b = \frac{\varepsilon_p}{\phi^m}.$$  

(4)

Assuming that the (displacement) current flows primarily in the pore-fluid, i.e. that $\varepsilon_s/\varepsilon_p \rightarrow 0$.

where $\varepsilon_p$ is the permittivity of the mixture that fills the pore space,

$$\varepsilon_b (\varepsilon_s, \varepsilon_p, \phi, m) = \left(\frac{3 - \phi}{2} \phi^{(m-1)}\right) \varepsilon_{HSU} (\varepsilon_s, \varepsilon_p, \phi) + \left(1 + \frac{\phi - 3}{2} \phi^{(m-1)}\right) \varepsilon_{HSL} (\varepsilon_s, \varepsilon_p, \phi),$$

(5)

where $\phi$ is porosity, $m$ is Archie’s cementation factor, $\varepsilon_s$ is the permittivity of the mineral solid matrix and $\varepsilon_p$ is the permittivity of the pore space. For 2-phase media, the permittivity of the pore-space is that of the fluid phase filling the pore space. More generally, for unsaturated materials, $\varepsilon_s$ is given by the combination of the permittivity of 2 immiscible phases (water and non-aqueous phase) with $\varepsilon_w \gg \varepsilon_{NAPL}$.

$$\varepsilon_p (\varepsilon_w, \varepsilon_{NAPL}, s_w, n) = w \varepsilon_{HSU} (\varepsilon_w, \varepsilon_{NAPL}, s_w) + (1 - w) \varepsilon_{HSL} (\varepsilon_w, \varepsilon_{NAPL}, s_w)$$

(6)

where $\varepsilon_{NAPL}$ is the permittivity of the non-aqueous phase liquid (e.g. air or oil), $s_w$ is water saturation ($0 \leq s_w \leq 1$) and $w$ is a weight function, defined as:

$$w = \frac{\varepsilon_w}{\varepsilon_{HSU} (\varepsilon_w, 0, s_w) s_w^n}$$

(7)

Owing to its derivation based upon Archie’s law, the model of Brovelli and Cassiani [2010b] is applicable to geologic materials with negligible matrix and surface electrical conductance, that is, to sediments with negligible content of clays and metal oxides.

2.2 Surface conductance
According to Revil and Glover [1998] the conductance associated to the excess of charge at the water-matrix interface $\Sigma_s$ is the sum of three components,

$$\Sigma_s = \int_0^\infty (\sigma(\chi) - \sigma_w)d\chi = \Sigma_s^S + \Sigma_s^D + \Sigma_s^H,$$  \hspace{1cm} (8)

where $\Sigma_s$ is the total surface conductance, $\sigma_w$ is the electrical conductivity of the bulk fluid (i.e. far from the fluid-solid interface), $\sigma(\chi)$ the local electrical conductivity at a distance $\chi$ from the surface and $\Sigma_s^S$, $\Sigma_s^D$, $\Sigma_s^H$ are the conductances associated to the Stern and diffuse layers and to proton transfer at the interface, respectively. In natural conditions, the argument in the integral in Equation 8 vanishes at a distance of - at most - a few nanometers from the solid surface, a length scale named Debye length. Microscopic approaches [e.g. Kan and Sen, 1987; Revil, 1999; Revil and Glover, 1997; 1998; Revil et al., 1998] were developed to compute the surface conductance of each component under simplified assumptions, in particular in presence of flat surfaces with uniform charge density and simple, well-defined pore water solutions. In reality, however, the identification of the parameters that characterize the surface of the skeleton is extremely difficult because the water-mineral interface is highly heterogeneous [Adamson et al., 1966; Van Riemsdijk et al., 1986]. In addition, the structure of the surface responds to changes in pore-fluid chemistry over a wide range of time scales. For this reason a macroscopic approach is often preferable, because it incorporates parameters that are more easily estimated on the basis of the composition and mineralogy of the medium (clay and organic matter content). According to one such model, the equivalent conductivity of the surface can be approximated as [Kan and Sen, 1987; Revil and Glover, 1998]:

$$\sigma_s = \frac{2}{3} \left( \frac{\phi}{1 - \phi} \right) \beta_s Q_v = \frac{2}{3} \mu_m \beta_s \text{CEC},$$  \hspace{1cm} (9)

where $\beta_s$ is the mobility of counterions in the EDL – the electrical double layer (the mobility in the EDL is lower than in the bulk fluid), $Q_v$ is the excess surface charge per unit pore volume,
\( \rho_m \) is the density of the solid phase (grains) and \( CEC \) is the cation exchange capacity of the medium (in C kg\(^{-1}\) of solid matrix). One limitation of equation (9) is that it does not explicitly incorporate the dependence of surface conductivity on the ionic strength of the bulk solution. However, Revil and Glover [1998] tested Eq. (9) against the dataset of Waxman and Smits [1968]. They found that, within a realistic range of pore fluid concentration \( C_f \) (\( C_f > 0.02 \) mol l\(^{-1}\)), the surface conductivity in soils and geological formations is approximately a constant, and therefore the dependence of \( \beta_s \) and \( Q_s \) upon ionic strength can be neglected. The numerical model developed by Brovelli and Cassiani [2010a] was used to further confirm this result. The model solves numerically the coupled equations of electrokinetic flow in cylindrical geometries, and can be used to compute the bulk conductivity and electrokinetic coupling coefficients for 3D random networks of capillaries. It was observed that for natural fresh/brackish waters, that is, in the salinity range \( 0.02 \leq C_f \leq 0.5 \) mol l\(^{-1}\), both the Debye length and \( \zeta \)-potential (the electrical potential of the Stern layer, a measure of the intensity of the EDL) decreased of about one order of magnitude. On the contrary, the bulk electrical conductivity scaled linearly with \( C_f \), confirming the relative insensitivity of surface conductance to the ionic strength of the soil solution.

### 2.3 Extension of the Brovelli and Cassiani [2010b] model.

Using Eq. (9), surface conductance \( \Sigma_s \) can be converted into an equivalent volumetric conductivity \( \sigma_s \). This approach is often referred to as the ‘equivalent grain conductivity approach’ [Bussian, 1983; De Lima and Sharma, 1990]. The surface conductance \( \Sigma_s \) and the volumetric conductivity \( \sigma_s \) are linked using a formula initially derived for charged macromolecules in aqueous solutions: \( \sigma_s = 2\Sigma_s/\langle R \rangle \) [O’Konski, 1960], where \( \langle R \rangle \) is a
characteristic length scale which for isolated smooth spherical particles corresponds to the radius of the sphere. In soils and real porous media, the grains are often non-spherical, rough and show a broad distribution of radii: in these conditions the median (or mean) grain size \cite{Brovelli et al., 2005; Linde et al., 2006} or other characteristic lengths associated to the pores \cite[e.g.][]{Johnson et al., 1986} are used to approximate $\langle R \rangle$.

Using the grain conductivity approach, the model of \textit{Brovelli and Cassiani} \cite{2010b} can be extended to represent porous media with non-negligible surface conductance. The electrical conductivity component of the model can take a form analogous to the form for electrical permittivity, thus making the model structure quasi-symmetric with respect to the two considered electrical properties:

$$\sigma_b(\sigma_s, \sigma_p, \phi, m) = \left( \frac{3-\phi}{2} \phi^{(m-1)} \right) \sigma_{HSU}(\sigma_s, \sigma_p, \phi) + \left( 1 + \frac{\phi-3}{2} \phi^{(m-1)} \right) \sigma_{HSL}(\sigma_s, \sigma_p, \phi). \quad (10)$$

The contribution of the pore-space electrical conductivity $\sigma_p$ is computed by replacing the permittivity of the water phase with the corresponding electrical conductivity in Equations (6)-(7), while setting the electrical conductivity of the non-aqueous phase to 0. Under these conditions, Equations (6)-(7) simplify to the second Archie’s \cite{1942} law:

$$\sigma_p(\sigma_w, s_w, n) = \sigma_w s_n \quad (11)$$

In addition, as the magnitude of surface conductivity becomes negligible compared to that of the bulk fluid (that is, as Dukhin number $\xi = \sigma_s/\sigma_w \to 0$) Eq. (10) reduces to the first Archie’s \cite{1942} law. Fig. 1 shows the variation of bulk electrical conductivity with increasing surface conductivity (parameterized by $\xi$) and water saturation for different soil textures (the latter being defined by porosity and Archie’s cementation exponent $m$). The plots indicate that, at full saturation, the bulk conductivity is modified by the contribution of the excess of charges at the water/mineral interface only if $\xi >$ about $5 \times 10^{-3}$. Only in relatively dry soils ($s_w < 0.3$) with
low porosity the conductivity of the surfaces has a significant effect at small Dukhin numbers. In
soils with high porosity and low cementation exponent – that is, rounded grains and poor
cementation – the bulk conductivity is even less sensitive to surface conductivity. Only in very
dry conditions ($s_w < 0.15$), with fine texture, high specific surface area and high CEC (i.e.
$\xi > 10^{-2}$, see Eq. (9)) the excess of charge at the mineral/water interface alters significantly the
bulk electrical conductivity.

Eq. (10) together with Eqs. (1), (2), (6) and (9) provides a consistent framework to compute bulk
electrical conductivity and permittivity of variably saturated soils and other porous geological
formations. Owing to its derivation based upon a weighted average of the Hashin and Shtrikman
[1962] bounds, the constitutive model will be referred in the following to as the Hashin –
Shtrikman average (HSA) model.

2.4 Other models for soil permittivity and electrical conductivity

As noted in the introduction, some constitutive equations have already been proposed in
the literature, that use the same parameterization of Archie’s laws to model the bulk electrical
conductivity of soils and shaly formations, where the contribution of the excess of charge at the
water-mineral interface cannot be neglected. These models can be used interchangeably for DC
conductivity and permittivity in the static limit. A specific objective of this work was to compare
our extended model with existing equations based on different assumptions, in order to ascertain
whether the different laws (and therefore the resulting calibrated parameters) could be used
interchangeably in soil mapping. The comparison was restricted to 2-phase mixtures, because
nearly all the equations for variably-saturated conditions reduce to $\sigma_b(s_w) = \sigma_b(s_w = 1)s_w^n$.

Many authors [e.g. Brovelli et al., 2005; Bussian, 1983; Clavier et al., 1984; De Lima and
Sharma, 1990; Glover et al., 2000; Waxman and Smits, 1968] conceptualized the bulk electrical conductivity as made of two resistances in parallel, i.e.:

$$\sigma_b = f(\phi, m)\sigma_w + g(\phi, m)\sigma_s,$$

where \( f(\cdot) \) and \( g(\cdot) \) are two appropriate geometrical scaling factors, which depend only on the soil texture. Among these models, the best known and still widely employed is perhaps the equation proposed by Waxman and Smits [1968]:

$$\sigma_b = \frac{1}{F} (\sigma_w + \sigma_s),$$

where \( F \) is the formation factor \((F = \phi^{-m})\) and the surface conductivity \( \sigma_s \) given by Eq. (9).

While Eq. (13) was developed based mainly on empirical evidences and a very simple conceptualization, a more physically sound methodology based on the volume averaging theorem was used by Pride [1994] to obtain a similar relationship, based on a two-parallel resistor parameterization:

$$\sigma_b = \frac{1}{F} [\sigma_w + (F - 1)\sigma_s].$$

This two-resistors in parallel approach is not entirely valid [for a discussion, see Brovelli et al., 2005] because it neglects the interactions of current flow between surfaces and bulk fluid. In particular, Eq. (13) is not able to predict the existence of an isoelectric point [Bolève et al., 2007] and of the non-linear behavior observed using pore solutions with low ionic strength: in these conditions the surface conductance dominates the bulk response of the medium \((\xi \to 1 \text{ or larger})\).

Accurate predictions in the whole salinity range are better achieved using petrophysical models derived using effective medium approaches [Bruggeman, 1935; Hanai, 1960]. In particular the model of Bussian [1983]:

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\[ \sigma_b = \frac{\sigma_w}{F} \left( \frac{1-\xi}{1-\sigma_b/\sigma_s} \right)^m \]  

(15)

was found to be often very accurate [Bussian, 1983; Revil and Glover, 1998]. In Eq. (15) the cementation factor \( m \) is related to Bruggeman’s [1935] depolarization factor, \( d \) as \( m = 1/(1-d) \) and therefore \( m \) can be related to the geometry and assemblage of the grains. The main limitation of Bussian’s [1983] law is that there is no exact explicit solution available. For this reason, Revil and Glover [1998] derived an approximate solution, assuming \( m = 2 \), a typical value for the cementation factor, that however show in practice a fairly large range. Revil and Glover [1998] also assumed that the electrical current in the EDL is only transported by cations, i.e. \( t^f_{(-)} = 0 \), where \( t^f \) stands for the Hittorf transport number of cations and anions (subscript + and -, respectively). As a consequence, Revil and Glover [1998] obtained:

\[ \sigma_b = \frac{\sigma_w}{F} \left[ 1 - t^f_{(+)} + F\xi + \frac{1}{2} (t^f_{(+)} - \xi) \left( 1 - \frac{\xi}{t^f_{(+)}} + \sqrt{\left( 1 - \frac{\xi}{t^f_{(+)}} \right)^2 + 4F \frac{\xi}{t^f_{(+)}}} \right) \right] \]  

(14)

3. Results

3.1 Extended model validation against experimental data

Previous comparison of the Brovelli and Cassiani [2010b] model with electrical properties of clean porous media (for example sandy soils) and in conditions where the contribution of surface conductivity is negligible \( (\xi \rightarrow 0) \) suggested that the model is well suited to model the bulk electrical response of porous systems [Brovelli and Cassiani, 2010b]. The objective of this section is to verify whether the equivalent grain conductivity approach introduced in the HSA extended model allows it to be used satisfactorily in more general conditions. In particular, the points that need to be investigated are: (i) whether the model successfully reproduces
experimental data of clayey soils, and (ii) whether the resulting textural parameters – cementsation factor and saturation exponent – and the calibrated surface conductivity have realistic values.

The comparison of the model against experimental data [from Amente et al., 2000; Binley et al., 2002; Doussan and Ruy, 2009; Friedman, 1998; Malicki and Walczak, 1999; Saarenketo, 1998] is reported in Tables 1 and 2, and in Figures 2 to 4. Table 1 compares model predictions with experimental data of soil bulk conductivity. The very high correlation coefficient ($r^2$) indicates that the fit is excellent in practically all cases, and the calibrated parameters are realistic. The datasets of Amente et al. [2000] and Malicki and Walczak [1999] were useful to further verify the assumption that surface conductivity in field conditions is almost insensitive to changes in pore-water salinity [Revil and Glover, 1998]. In these two datasets, the effective conductivity of soil samples was measured as a function of water saturation using different pore-solutions with increasing ionic strength. The HSA model was fitted simultaneously on all the resulting curves, and we found that a unique set of parameters is able to reproduce the experimental data of both sets. The surface conductivity obtained from the fitting is equal to $3.7 \times 10^{-3}$ S/m and $1.2 \times 10^{-2}$ S/m for the data of Amente et al. [2000] and Malicki and Walczak [1999], respectively. It should however be noted that the values of pore-water conductivity reported in Malicki and Walczak [1999] were not entirely realistic (for example, a conductivity equal to $0 \text{Sm}^{-1}$ was reported, see caption of their Fig. 1). For this dataset the pore-water conductivity was therefore corrected, since a de-ionized solution equilibrates very rapidly with the soil. In other words, the electrical conductivity of the soil solution should have been measured after the measurements. The two soils have moderate to high porosity, and the cementation exponent is small. According to the above discussion (Fig. 1 and paragraph 2.3) for
such materials the model fitting is sensitive to surface conductivity only if $\xi > 5 \times 10^{-3}$. For both soils this condition is satisfied, and therefore the parameter obtained from the fitting procedure is meaningful. Fig. 2 compares model predictions for the shaly sandstone data of Binley et al. [2002]. The same dataset was also used by Brovelli et al. [2005] to test a pore-scale modeling tool developed to study the electrical properties of porous media. For this specific dataset, both electrical conductivity and permittivity measurements (as a function of saturation) were available, and they were fitted simultaneously. A satisfactory model fitting was achieved, and the obtained parameters were realistic. Brovelli et al. [2005] constructed a digital representation of the same geological material and used the digital sample to independently estimate the cementation exponent, obtaining a value $m \approx 1.5$, which is compatible with, but slightly smaller than, the estimate from the HSA model fitting ($m \approx 1.7$). A possible explanation for this discrepancy may be linked to the different shape of the soil grains in the real soil and its digital representation (the random packing of Brovelli et al. [2005] consisted of spherical particles). Fig. 3 compares the HSA model with the datasets of Doussan and Ruy [2009] consisting of Fontainbleau (clean) sand, a loam, and a silty clay loam. The fitting of the model is satisfactory for the sand and the loam, and the calibrated parameters (Table 1) are consistent with previous ranges reported in the literature [see e.g. Lesmes and Friedman, 2005]. On the contrary, for the silty clay loam the HSA model reproduced well only the data in the range of water saturation $0.0 – 0.7$, whereas at higher values the measurements drift away with different slope. A possible explanation is that the soil has a dual porosity, with large pores in the intra-aggregate porosity and finer pores within the aggregates. The cementation exponent fits well the expected ranges from the literature, while the saturation exponent is higher than expected. This is consistent with the findings of Brovelli and Cassiani [2010b], who concluded that for dual
porosity materials \( n > 4 \) should be expected. The estimated surface conductivity for the samples

of *Doussan and Ruy* [2009] is negatively correlated with the mean grain diameter. \( D_{50} \) is equal to

256.3 µm, 31.8 µm and 6.8 µm for sand, loam and silty clay loam, respectively. The equivalent

surface conductivity can therefore be converted to surface conductance using the relationship

\[
\Sigma_s = \sigma_s \langle R \rangle / 2 \quad \text{with} \quad \langle R \rangle = 0.5D_{50}.
\]

The corresponding surface conductances are \( 3.2 \times 10^{-9} \) S, \( 1.19 \times 10^{-7} \) S and \( 1.02 \times 10^{-7} \) S for sand, loam and silty clay loam. These values are consistent with

previous findings [see a summary in *Brovelli et al.*, 2005]. Indeed, *Bolève et al.* [2007] criticized

the values reported in *Brovelli et al.* [2005] on the basis that triple layer calculations [*Leroy and

Revil, 2004; Revil and Glover, 1997; Revil et al., 1998*] found that for all porous media \( \Sigma_s \approx

5 \times 10^{-9} \) S. A possible reason for the observed discrepancies is related to the identification of a

suitable length scale \( \langle R \rangle \), as observed by *Bolève et al.* [2007]. A difference of about two orders of

magnitude (in terms of the estimated surface conductance) suggests that it may be not

appropriate to use the average grain size, at least for sediments having also a fine-grained soil

fraction, to estimate the equivalent surface conductivity. Note that, based on the surface


concluded that the grain size distribution of the same shaly sandstone considered by *Binley et al.*

[2002] must have had expected values in the 1 µm range, while in reality the Sherwood

Sandstone has a median grain size in the 200 µm range [see e.g. Fig.4 in *Binley et al.*, 2005].

Table 2 reports the comparison of the HSA model with bulk permittivity data for clayey

soils. The data of *Malicki and Walczak* [1999] (first row) were measured on the same soil sample

used for bulk conductivity measurements, and therefore the parameters were not estimated

independently from the permittivity data, but the values reported in Table 1 were used directly in

a predictive manner. Even without fitting parameters the HSA model compares well with the
experimental results (high $r^2$ in Table 2, plot not shown), indicating that parameters calibrated on electrical conductivity can be used to estimate permittivity, and vice-versa. Fig. 4 visually compares model predictions and laboratory measurements for the experimental data of Saarenketo, [1998] (Houston black clay and Beaumont clay) and Friedman, [1998] (Sarid clay). The model performed well with Sarid and the Houston black clays, whereas for the Beaumont clay a lower correlation was found (despite the fact that the trend observed in the data was still reproduced). This is likely an effect of the scatter in the experimental data. It was not a surprise to find that experimental data for compact clays were noisy, since – owing to the changes occurring in the sample when the moisture content is varied (for example, crack opening during desiccation or swelling during imbibition) – drainage/imbibition experiments are normally more difficult.

3.2 Comparison with other petrophysical models

Following successful validation with experimental data, the HSA model was compared with the constitutive equations discussed in § 2.4 that use Archie’s parameterization of the porous medium. For the sake of simplicity, results are presented considering saturated conditions only. Indeed, variably saturated conditions were also analyzed and the conclusions were similar to those reached for two-phase systems. In all cases reported the cementation factor $m$ was set to 2.5, but again this choice has no impact on the findings. The parameters that were varied and analyzed were porosity and surface conductivity. Figure 5 compares the HSA model with the constitutive equations of Pride, [1994] and Waxman and Smits, [1968]. The predictions with Pride’s [1994] model closely reproduce those obtained with the HSA model if porosity is moderate or large ($\phi > 0.25$) and the effect of surface conductivity is limited ($\xi < 10^{-2}$).
Outside these intervals the discrepancy between the two models increases, but indeed remains only moderate (10% difference or less). Instead, the Waxman and Smits, [1968] model shows a behavior compatible with the HSA model only as $\xi \rightarrow 0$, that is, when the two models reduce to Archie’s law. It can then be concluded that parameters estimated with the Waxman and Smits, [1968] equation are not compatible with those obtained from the HSA model.

The equations developed by Bussian, [1983] and Revil et al., [1998] are compared with the HSA model in Fig. 6. Archie’s law is also shown for comparison. For this comparison the cementation exponent $m$ was set to 2.5, and the cation Hittorf transport number ($t_{\text{c}}$) to 1 [e.g. Bolève et al., 2007]. Revil and Glover [1998] equation is however only slightly sensitive to this parameter, and the comparison with the other two models is nearly unaffected by the value used. The three models have nearly the same behavior, and the discrepancies remain very limited in the entire porosity and surface conductivity ranges investigated. Quite surprisingly, although developed on a completely different basis, the HSA and Bussian [1983] models show a remarkably good agreement. It can therefore be concluded that the three models in Figure 6 can be used interchangeably.

4. Mapping soil salinity

4.1 Theory

Based on empirical observations, some previous studies [Hamed et al., 2003; Hilhorst, 2000; Malicki and Walczak, 1999] found that the relationship between bulk electrical conductivity and bulk permittivity of variably saturated soil samples show a linear behavior for saturation larger than about 20% (or bulk permittivity larger than 8). In other words, when electrical conductivity
and permittivity are measured simultaneously and cross-plotted, the resulting curve can be parameterized as

$$\varepsilon_b = A\sigma_b + B$$  \hspace{1cm} (15)

where A and B are empirical factors. This was explained by the fact that the two electrical properties are affected by the water saturation changes in a similar way:

$$\frac{d\sigma_b}{ds_w} \simeq \frac{d\varepsilon_b}{ds_w}, \forall s_w > 0.2$$  \hspace{1cm} (16)

Malicki and Walczak [1999] and Hilhorst et al. [2000] observed that the slope A is sensitive to changes in the conductivity of the pore-water, while the intercept B is affected by the soil texture. For this reason, simultaneous measurements of DC conductivity and permittivity were used to define a ‘soil salinity index’ [Malicki and Walczak, 1999]. To further develop this idea, in this work we propose a closed-form relationship that allows the direct estimation of pore water conductivity from simultaneous measurements of bulk conductivity and permittivity. To obtain the sought relationship, two equations using the same parameterization of the soil electrical response – one for electrical conductivity, the other for permittivity – were combined to give a relationship of the form of Eq. (15). In saline soils, surface conductivity is negligible compared to water conductivity ($\xi \rightarrow 0$), and bulk soil conductivity can be computed using the second Archie’s law:

$$\sigma_b = \frac{\sigma_w}{F} s_w^n$$  \hspace{1cm} (17)

A possible equation that can model soil permittivity using the same parameterization as Archie’s law is the HSA model presented in section 2. The corresponding analytical expression is however difficult to manipulate, and cannot be easily simplified to produce an analytical expression that fits the observed linear behavior. An alternative approach to model permittivity is
to use the equation proposed by Pride [1994] which was extended to variably saturated conditions by Linde et al., [2006]:

\[ \varepsilon_b = \frac{1}{F} [S_w^n \varepsilon_w + (1 - S_w^n)\varepsilon_a + (F - 1)\varepsilon_s] \]  \hspace{1cm} (18)

Eq. (18) uses the same parameterization as Archie’s law, and the influence of water saturation on bulk permittivity is similar to that described by the HSA model – that is, \(d\varepsilon_b^{PL}/ds_w \approx d\varepsilon_b^{HSA}/ds_w\), where \(\varepsilon_b^{PL}\) is the bulk conductivity obtained with the Pride [1994] and Linde et al. [2006] equation and \(\varepsilon_b^{HSA}\) is the corresponding value computed with the HSA model – for wet conditions (\(s_w > 0.3\)) and \(\frac{\varepsilon_s}{\varepsilon_w} < 10^{-1}\) (see the comparison in Brovelli and Cassiani [2010b]).

Since the derivative \(d\varepsilon_b/ds_w\) is what matters (Eq. 16), Eq. 17 and 18 can be combined – Eq. (18) is written in terms of water saturation and it is replaced in Eq. (18) – to obtain a linear relationship between conductivity and permittivity with slope:

\[ A = \frac{\varepsilon_w - \varepsilon_a}{\sigma_w} \]  \hspace{1cm} (19)

and intercept:

\[ B = \frac{\varepsilon_a}{F} + \frac{F - 1}{F} \varepsilon_s. \]  \hspace{1cm} (20)

where \(A, B\) are the parameters in Eq. 15, and \(F\) is the formation factor. The intercept \(B\) depends on the texture of the soil and permittivity of the NAPL and solid matrix, while interestingly the slope \(A\) is only affected by the properties of the mobile phases. Hilhorst [2000] studied the same relationship and on the basis of empirical observations assumed \(A = \varepsilon_w/\sigma_w\). This equation is compatible with Eq. 19 in the case \(\varepsilon_w \gg \varepsilon_a\), for example if the non wetting phase is air. For other NAPLs with larger permittivity, Eq. 19 would be more accurate.

Since water and air relative permittivity values can be assumed as constants (80 and 1, respectively), Eq. 19 can be directly used to map soil salinity (expressed in terms of electrical
conductivity of the pore water) from simultaneous measurements of bulk electrical conductivity and permittivity, with no adjustable parameter and without knowing the degree of water saturation. In practice, the bulk conductivity and permittivity of the soil (either in the laboratory or in the field) should be measured at least three times with different moisture content (that indeed can remain unknown), and a straight line must be fitted to the data. Eq. (19) is then used to convert the slope of the fitted line to pore-water electrical conductivity, assuming that such conductivity has not changed over time. In other words, model calibration in the laboratory is not necessary, and the estimation remains accurate regardless the lateral heterogeneity of the system and variations in lithology, soil texture and moisture content. The main limitation of the proposed approach is that during the measurement period the pore water electrical conductivity must remain approximately constant, that is, temperature changes and accumulation of salts in the topsoil, for example due to evaporation or plant water uptake, should be negligible.

4.2 Model verification

4.2.1 Procedure

To verify the findings above and validate the proposed methodology, we used a two-step approach. First, in order to verify the solidity of the introduced approximations – and in particular the fact that the model of Pride [1994] and Linde et al. [2006] was used – the results obtained using the linear approximation were compared with the predictions calculated using the more accurate variably saturated HSA model described above. The other aspect that needed to be addressed was the identification of the range of water saturation within which the linear approximation remains reliable. Previous experimental observations found that this limit is defined by a lower bulk relative permittivity ranging between 6 and 8 (in the following denoted
as $\varepsilon_b^{\text{min}}$ [Hilhorst et al., 2000; Persson, 2002]. Second, we compared the predictions obtained using the linear approximation with some datasets where the bulk electrical properties (conductivity and permittivity) as well as the electrical conductivity of the pore water were independently measured. Results of the first part of the validation procedure are reported in Fig. 7 (black dots). The scatter plots compare the ‘true’ water conductivity with the results of the linear approximation. This value was computed fitting with a straight line a synthetic dataset composed of a number of pairs ($\varepsilon_b, \sigma_b$) calculated using the HSA equation. The slope of the line was used to estimate water conductivity via Eq. (19), as discussed in the above paragraph. To evaluate the reliability of the linear approximation in the entire parameter space, a Monte Carlo procedure was adopted: 500 realizations were generated sampling the parameters from uniform distributions. The properties considered were porosity (in the range 0.15 to 0.50), pore-water conductivity ($10^{-3} \leq \sigma_w \leq 10 \text{ S m}^{-1}$), cementation factor ($1.3 \leq m \leq 2.5$), saturation exponent ($1.3 \leq n \leq 2.5$) and matrix permittivity ($4.0 \leq \varepsilon_z \leq 7.5$). Two cases were studied: in the first $\varepsilon_b^{\text{min}}$ was set to 7.5 (left panel of Fig. 7), in the second $\varepsilon_b^{\text{min}} = 10$ (Fig 7, right panel). In other words, only pairs ($\varepsilon_b, \sigma_b$), with $\varepsilon_b \geq \varepsilon_b^{\text{min}}$ were used in the fitting.

The correlation between true and estimated parameters is very high regardless of the $\varepsilon_b^{\text{min}}$ used, and raising the threshold from $\varepsilon_b^{\text{min}} = 7.5$ to $\varepsilon_b^{\text{min}} = 10$ resulted in a small but noticeable improvement, as indicated by the larger correlation coefficient ($r^2$ in the figure). This suggests that the devised methodology provides better estimates if soils are moderately wet (that is, if $\varepsilon_b^{\text{min}} > 10$). Therefore we concluded that $\varepsilon_b^{\text{min}} = 8$ can be considered in general an appropriate threshold. The high correlation also confirms the validity of the assumptions made, including the use of the Linde et al [2006] equation to model bulk permittivity of variably saturated soils.
4.2.2 Comparison with experimental data

We further validated the methodology using experimental data [Hamed et al., 2003; Hilhorst, 2000; Malicki and Walczak, 1999; Persson, 2002b]. The tested datasets cover a large range of soil types and porous media: all estimated values are plotted in Fig. 7 (red squares, right panel) and overall the comparison is remarkably good ($r^2 > 0.8$) despite the extreme simplicity of the proposed relationship ($\varepsilon_w$ was set to 80 in all cases). Table 3 reports the comparison for three sets of data that are discussed in more detail in the following. Measurements performed on glass beads [Hilhorst, 2000] and on an organic top soil [Hamed et al., 2003] are plotted in Fig. 8 and Fig. 9, respectively. The HSA model is shown for comparison on both plots, together with the line fitted to the data to estimate the conductivity of the pore water. The estimated pore water conductivity represents very well the measured value for both materials (Table 3) and bulk permittivity increases linearly with conductivity, although for the organic top soil $\varepsilon_b^{\text{min}} = 13$ (that is, only above this value the relationship is linear). This observation suggests that if accurate results are sought, it may be appropriate to perform a preliminary laboratory study to ascertain whether the relationship is effectively linear and to define a suitable $\varepsilon_b^{\text{min}}$. Fig. 8 and 9 also show the effect of surface conductivity (in terms of Dukhin number) on the relationship. The interesting aspect is that the slope of the curve in wet conditions (defined by $\varepsilon_b > 15$) remains approximately the same regardless the intensity of surface conductivity, and the main effect is a shift of the curves towards higher conductivity values. In other words, these results indicate that pore-water conductivity can be estimated using Eq. (19) regardless the value of surface conductivity, provided that the soil is at least partly wet. A physical explanation for this observation is that at moderate to high saturation values the bulk electrical conductivity remains controlled by the conductivity of the pore fluid. This is consistent with the observations made in
Fig. 1, where it was observed that at $s_{w} > 0.5$ in natural conditions the electrical conductivity of materials with moderate to high porosity is only minimally affected by surface conductivity. It is therefore possible to conclude that in these conditions the linear approximation defined by Eq. (19) can be used to estimate water conductivity regardless the CEC of the medium.

The dataset of Malicki and Walczak, [1999] is reported in Fig. 10. The same data are also presented in §3.1 to test the applicability of the HSA model on soil electrical conductivity measurements. In §3.1 it was mentioned that the electrical conductivity of the pore fluid had to be adjusted to fit the data. This was done using the linear approximation presented in this section: each dataset was fitted with a straight line, and the conductivity computed via Eq. (19). The comparison reported in Table 3 shows that the estimated value predicted a higher electrical conductivity larger than that measured for the three solutions with lower ionic strength, while for the other two cases the match was satisfactory. This confirms the hypothesis made above that the electrical conductivity of the pore fluid changed once the ionic composition of the water equilibrated with the porous medium. The HSA model was fitted on the 5 datasets (same soil with different water conductivity) simultaneously. Quite unexpectedly the model reproduces the experimental data satisfactorily for three sets (with $r^2 \approx 0.96$ or larger, open symbols in Fig. 10), while for the remainders the model under- and over-estimate the predictions. No clear explanation for this discrepancy was found.

5. Conclusions

The analysis conducted in this work indicated that bulk electrical conductivity and permittivity can be modeled using joint constitutive models. In particular, equations based on Archie’s [1942] parameterization of the soil properties (cementation and saturation exponents, $m$ and $n$) proved suitable for this task. More specifically, in this work it was found that
• The equivalent grain conductivity approach introduced by Bussian [1983] can be used to include surface conductance in the computations of bulk soil conductivity, given that the couplings and interactions between conduction paths in the bulk fluid and at the mineral/water interface are correctly accounted for. This is true for non-linear models (such as that of Bussian [1983] and the HSA equation), but not for the ‘two-resistors in parallel’ type of models. This is consistent with previous findings of Brovelli et al. [2005] and Bolève et al. [2007], among others. One critical issue that remains open is how the equivalent grain (volumetric) conductivity can be translated into surface conductance, and vice-versa. Numerous experimental evidences suggest that the identification of the characteristic length scale \( R \) is difficult, in particular for medium- and fine-grained soil samples. This is an important aspect, and it needs to be investigated in detail in future studies. The extended HSA model was applied to several geological materials with non negligible surface conductance, and good agreement was found. The calibrated parameters were found to compare well with literature ranges.

• Among the tested models, three – the HSA model presented here, and those of Bussian, [1983] and Revil and Glover [1998] – predicted consistent results for the same soil type, saturation and ionic strength of the pore fluid. It should however be mentioned that the model of Revil and Glover [1998] is strictly applicable to electrical conductivity only (although an equivalent formulation for permittivity can be devised). These models can therefore be used in joint inversion/data fusion schemes, as they share the same parameterization and provide consistent predictions.

• The evaluation of soil salinity from simultaneous measurements of electrical conductivity and permittivity is an example of how the use of relationships based on the same parameterization
can be used to exploit the dependence of electrical properties on the same soil characteristics. The proposed methodology is simple and – at least based on the comparison with data conducted in this study – robust, in particular because no fitting parameter is needed and the procedure is not affected by heterogeneity and variation of soil properties. The main limitation is however that pore-water conductivity must remain approximately constant during the measurement period.

The key conclusion of this work was that electrical conductivity and permittivity of soils are affected in a similar way by texture, water saturation and characteristics of the mineral matrix and pore fluid. Therefore, the use of a consistent parameterization to study both properties can help in the identification of the characteristics of the soil, and reduce the uncertainty and sensitivity to measurement errors. To this end, the equations tested and validated in this study provide a suitable framework to study and estimate electrical properties of unsaturated soils.

6. Acknowledgements

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Table 1. Model testing using electrical conductivity of variably saturated soils: fitted parameters and correlation coefficients. Surface conductivity, cementation exponent $m$ and saturation exponent $n$ have been calibrated against lab data. See also Figures 2 and 3 for the fitting curves.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Conductivity (S m$^{-1}$)</th>
<th>Textural parameters</th>
<th>$r^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pore-water surface</td>
<td>$\phi$ $m$ $n$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandy loam</td>
<td>0.10</td>
<td>$3.7 \times 10^{-3}$ 0.38 1.68 1.8</td>
<td>&gt; 0.999</td>
<td>[Amente et al., 2000]</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td></td>
<td>&gt; 0.999</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td></td>
<td>&gt; 0.999</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td></td>
<td>&gt; 0.999</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td></td>
<td>&gt; 0.999</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.40</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandy loam (1)</td>
<td>$1.64 \times 10^{-1}$</td>
<td>0.982</td>
<td></td>
<td>[Malicki and Walczak, 1999]</td>
</tr>
<tr>
<td></td>
<td>$1.93 \times 10^{-1}$</td>
<td>0.926</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$5.49 \times 10^{-1}$</td>
<td>0.988</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$7.87 \times 10^{-1}$</td>
<td>0.996</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.13</td>
<td>0.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shaly sandstone</td>
<td>$6.8 \times 10^{-2}$</td>
<td>0.39 1.7 2.0</td>
<td>0.992</td>
<td>[Binley et al., 2002]</td>
</tr>
<tr>
<td>Sand</td>
<td>$6.5 \times 10^{-2}$</td>
<td>0.36 1.3 1.8</td>
<td>0.989</td>
<td>[Doussan and Ray, 2009]</td>
</tr>
<tr>
<td>Loam</td>
<td>$7.14 \times 10^{-2}$</td>
<td>0.44 1.3 1.9</td>
<td>0.994</td>
<td></td>
</tr>
<tr>
<td>Silty clay loam</td>
<td>$7.14 \times 10^{-2}$</td>
<td>0.38 1.5 11</td>
<td>0.919</td>
<td></td>
</tr>
</tbody>
</table>

(1) The conductivity of the pore-water reported in the original publication for this dataset had to be slightly modified. See text for explanations.
Table 2. Application of the proposed constitutive equation to model the permittivity of variably saturated soils. Solid matrix permittivity, cementation factor $m$ and saturation exponent $n$ have been calibrated against lab data. Water permittivity was set to 80 for all samples. See also Figures 2 and 4 for the fitting curves.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>$\omega$ (MHz)</th>
<th>TDR</th>
<th>Matrix permittivity</th>
<th>$\phi$</th>
<th>$m^{(1)}$</th>
<th>$n^{(1)}$</th>
<th>$r^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy loam</td>
<td>5.5</td>
<td>0.49</td>
<td>1.4</td>
<td>2.4</td>
<td>0.998</td>
<td></td>
<td></td>
<td>[Malicki and Walczak, 1999]</td>
</tr>
<tr>
<td>Shaly sandstone</td>
<td>500</td>
<td>6.0</td>
<td>0.39</td>
<td>1.7</td>
<td>2.0</td>
<td>0.992</td>
<td></td>
<td>[Binley et al., 2002]</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.969</td>
<td></td>
</tr>
<tr>
<td>Vertisol</td>
<td>6.5</td>
<td>0.62</td>
<td>2.2</td>
<td>2.5</td>
<td>0.998</td>
<td></td>
<td></td>
<td>[Friedman, 1998]</td>
</tr>
<tr>
<td>Houston black clay</td>
<td>500</td>
<td>6.5</td>
<td>0.45</td>
<td>2.6</td>
<td>2.5</td>
<td>0.974</td>
<td></td>
<td>[Saarenketo, 1998]</td>
</tr>
<tr>
<td>Beaumont clay</td>
<td>500</td>
<td>10.5</td>
<td>0.5</td>
<td>2.5</td>
<td>2.5</td>
<td>0.919</td>
<td></td>
<td>[Saarenketo, 1998]</td>
</tr>
</tbody>
</table>
Table 3. Measured conductivity of the pore water and comparison with the estimated values using the linear approximation method presented in this paper. Additional experimental data are reported in Fig. 7 (red squares). The comparison for the dataset of Malicki and Walczak, [1999] is not fully satisfactory, as discussed in the text.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Range</th>
<th>Pore-water conductivity [$S \text{ m}^{-1}$]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass beads</td>
<td>$\varepsilon_b &gt; 10$</td>
<td>0.4</td>
<td>0.42</td>
</tr>
<tr>
<td>Top soil (organic)</td>
<td>$\varepsilon_b &gt; 13$</td>
<td>2.9x$10^{-3}$</td>
<td>2.63x$10^{-3}$</td>
</tr>
<tr>
<td>Silty loam</td>
<td>$\varepsilon_b &gt; 10$</td>
<td>3.88x$10^{-1}$</td>
<td>5.49x$10^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.25x$10^{-1}$</td>
<td>7.87x$10^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.17</td>
<td>1.13</td>
</tr>
</tbody>
</table>
Figure 1. Bulk DC electrical conductivity according to the extended constitutive model based on Brovelli and Cassiani [2010b] as a function of the Dukhin number $\xi$. The model behavior is shown for fully saturated conditions (top panels) and variably saturated conditions (bottom panels). The area shaded in gray defines the possible range of variation of the bulk properties according to the Hashin and Shtrikman [1962] bounds.
Figure 2. Comparison of the constitutive equation presented in this work with bulk electrical resistivity and permittivity data taken from pore-scale modelling results (open diamonds, Brovelli et al. [2005]) and experimental data Binley et al. [2002] for a shaly sandstone. Model parameters and correlation coefficients are reported in Table 1 (electrical conductivity) and Table 2 (permittivity).
Figure 3. Validation of the HSA equation using experimental data of three variably-saturated soils with different texture [Doussan and Ruy, 2009]: sand (negligible surface conductivity), loam and silty clay loam. Model parameters and correlation coefficients are listed in Table 1. While for the sandy and loamy soils the comparison is satisfactory in the entire range of saturation, for the clayey material the model fails to predict the increase in conductivity at saturation larger than 0.75.
Figure 4. Model validation for the permittivity of variably saturated clayey soils [Friedman, 1998; Saarenketo, 1998]. The comparison is overall satisfactory, although for one case (Beaumont clay) the model under-predicts the permittivity at low water content ( ). This might be due to changes in the geometry of the solid phase in dry conditions (for example, formation of cracks).
Figure 5. Comparison of the HSA model with the relationships of Waxman and Smits [1968] and of Pride [1994]. Archie’s [1942] law is also reported for comparison. The cementation factor was set to 2.5. The bulk conductivity was normalized using the electrical conductivity of the pore-water. The proposed model does not reproduce the behavior of the Waxman and Smits equation, and agrees well with the Pride [1994] relationship only when the surface conductance is low. The Waxman and Smits [1968] model is only slightly sensitive to changes in surface conductance, and the curves of this model for different $\xi$ are almost overlapping.
Figure 6. Comparison of the HSA model for a range of surface conductivities with the models of Bussian [1983] and Revil and Glover [1998]. The three models share the same parameterization, and reduce to Archie’s [1942] law when the electrical conductivity of the pore-fluid is much greater than the surface conductance ($\xi \to 0$).
Figure 7. Estimated pore water conductivity using the linear approximation discussed in the text. The constitutive model presented in this work was used to generate synthetic datasets of bulk electrical conductivity and permittivity for different types of soils as a function of water saturation. The estimated values compare well with the ‘true’ values, suggesting that the simplifications introduced do not affect significantly the accuracy of the model.
Figure 8. Permittivity versus electrical conductivity relationship for glass beads. Data from Hilhorst, [2000]. The dashed line shows the linear regression of the experimental data. Using Eq. (19) water electrical conductivity was estimated, and the result (0.42 Sm$^{-1}$) compares well with the measured value (0.4 S m$^{-1}$).
Figure 9. Permittivity versus electrical conductivity relationship for an organic top soil. Data from Hamed et al. [2003]. The measured electrical conductivity of the pore water was \(2.9 \times 10^{-2}\) S m\(^{-1}\). The value estimated from Eq. 19 using data in the range with linear behavior (\(\xi = 1 \times 10^{-4}\)) was very similar, \(2.63 \times 10^{-2}\) S m\(^{-1}\). This dataset was measured varying the moisture content in the range.
Figure 10. Electrical conductivity vs. permittivity for a clayey soil (experimental data from Malicki and Walczak, [1999]). The 5 datasets are relevant to the same soil sample at increasing conductivity of the pore water. The dashed line is the HSA constitutive model presented in this work. The same parameters (texture, solid phase permittivity and surface conductivity) were used to fit all datasets. Pore-water conductivity was estimated using the linear approximation approach, because it was not possible to match some datasets using the measured values. The model parameters are reported in Table 1 and predicted vs. measured water conductivities are reported and compared in Table 3.