EXPRESS LETTER

The effect of NAPL on the electrical properties of unsaturated porous media

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SUMMARY

The spectral induced polarization signature of porous media contaminated with non-aqueous phase liquid (NAPL) was studied. Using an accurate measurement system, the complex electrical conductivity of unsaturated porous media contaminated with either diesel fuel or motor oil at a constant water saturation was determined. Counter intuitively, the results show that replacing air with NAPL increases the real part of the complex conductivity of unsaturated porous media. We interpret the results in terms of electrochemical polarization, and suggest that polar compounds contained in the NAPL adsorb to the mineral surface leading to release of inorganic ions to the pore water, which affects both the fluid and surface conductivity. In addition, we observed a decrease in the polarization followed by further addition of NAPL, which we relate to a lower mobility of the adsorbed polar compound. This study allows a better understanding of the electrical signature of NAPL contaminated porous media, especially in variably saturated conditions.

Key words: Electrical properties, Electromagnetic theory, Hydrogeophysics.

1 INTRODUCTION

Spectral induced polarization (SIP) is a geophysical method frequently used for various hydrological investigations such as monitoring contamination, biogeochemical processes, etc. (e.g. Sogade et al. 2006; Snieder et al. 2007). The measurement principle of SIP is to apply oscillating currents in a broad frequency range and to measure the associated potentials. As a result of energy dissipation and storage processes within the porous material, measurable phase shifts and decreases in the wave amplitude (relative to the applied wave) can be recorded. At low to medium frequencies (mHz to MHz), there are three major contributions to the SIP response of soil: membrane polarization, electrochemical polarization and interfacial polarization (Revil & Florsch 2010; Vaudelet et al. 2011). Both the membrane and electrochemical polarization are related to the polarization of the electrical double layer (EDL). According to the Gouy–Chapman–Stern model (Adamson & Gast 1997), the EDL consist of an inherent (in soils usually negative) charge at the solid’s surface compensated by an appositely charged ionic atmosphere. The ionic atmosphere is typically divided into two regions—a mono-layer of weakly adsorbed ions which is called the Stern layer, and a diffuse layer, much wider than the Stern layer, that electrically balances the excess charge from the solid surface and the Stern layer. A fundamental difference between the Stern and the diffuse layer is that in the former the ions are held by electrostatic forces and by chemical bonding, while in the diffuse layer only electrostatic forces attract the ions to the mineral surface. In the context of the EDL theory, membrane polarization refers to the accumulation and back-diffusion of charge in the diffuse layer of the EDL and in the bulk pore water, while electrochemical polarization is typically attributed to the polarization of the Stern layer (Titov et al. 2002; Revil & Florsch 2010). Application of an external electric field to the EDL leads to migration of cations in the direction of the field and to polarization of the EDL (Chelidze & Gueguen 1999; Shilov et al. 2000). In the low frequency range, Leroy et al. (2008) (see also Revil & Florsch 2010; Vaudelet et al. 2011) argue that the only contribution to the polarization of the EDL is due to polarization of the Stern layer. This is because the grain contacts prohibit charge build-up within the diffuse layer and because the required time to induce polarization at the pore scale is typically longer than the lowest frequency usually applied in SIP investigation. In addition to polarization of the EDL, application of an external electrical field to multiphase systems (such as soil) leads to charge build-up at phase interfaces differing in electric conductivity and/or permittivity in what is known as interfacial (or Maxwell-Wagner) polarization (Alvarez 1973; Sen et al. 1981; Chelidze & Gueguen 1999). This accumulation of charge leads to an increase of the bulk dielectric permittivity of the porous media (Chen & Or 2006). Although the
two mechanisms act simultaneously, the former is dominant at low frequencies (MHz to several 10’s of Hz), while the latter is more dominant at higher frequencies (in the range of KHz–MHz).

Few studies used the SIP method to study the influence of non-aqueous phase liquid (NAPL) on the electrical properties of porous media. Olhoeft (1985) reported that for a NAPL contaminated sample the amplitude and phase are sensitive to the presence of NAPL, and suggested a model where this response is a result of attachment of organic molecules on the clay surface and the inhibition of cation exchange processes. Borner et al. (1993) investigated the influence of different contaminants on the complex conductivity of clayey and sandy soils. Although for a clayey soil they reported a decrease in the imaginary part of the complex conductivity only for benzene, in the case of a sandy soil a decrease in the imaginary part of the complex conductivity was observed for all contaminants used (oil, hexane, benzene and dichloromethane). Similar results were also reported by Vanhala (1997) who suggested that oil replaces ions in the EDL. More recently, Cassiani et al. (2009) conducted SIP measurements on variably saturated sand contaminated with NAPL and documented an increase in the real conductivity of the contaminated sample. They attributed the increase in conductivity to NAPL segregation in the column, resulting from density differences between the NAPL and the water phase. Schmutz et al. (2010) studied the effect of NAPL at different saturation on the SIP response of sand and reported that an increase in the phase was related to NAPL saturation. In addition they also observed a decrease in the real conductivity with an increase in the NAPL saturation. It is important to note that in their work NAPL replaced water, so the porous media remained liquid saturated.

Despite the potential of the SIP method as a tool to detect NAPL contamination in the subsurface, and although the detection of NAPL in the vadose zone can significantly reduce cleanup costs and prevent groundwater pollution, the effect of NAPL on the electrical properties of unsaturated soil has received only little attention. Further, even for the saturated case the mechanisms by which NAPL affect the SIP signal are not fully resolved, especially with regard to processes at the mineral-fluid interface which greatly affect the polarization of the porous material (Knight et al. 2010). Unsaturated conditions pose the advantage of NAPL replacing air, both with very low electrical conductivity (EC). This may help isolate interfacial processes that in saturated conditions may be obscured by major changes in the fluid EC. Therefore, the aim of this study is to investigate the effect of NAPL on the electrical properties of unsaturated porous media with constant water saturation, and to relate major mechanisms governing the SIP response to the presence of NAPL.

## 2 MATERIAL AND METHODS

We measured the complex EC of a mixture of soil grains, water, NAPL and air. In all the experiments, 50 cm long PVC columns with an inner diameter of 5 cm were used. The samples were prepared by mixing air-dried sand [mean particle diameter of 160 μm (F36 quartz sand, Quarzwerke Frechen, Germany)] with 15 per cent by weight of bentonite clay (Edasil, Oscorna-Dünger GmbH, Germany). The sample was then mixed with tap water (EC ~0.42 dS m⁻¹) and then with either diesel fuel or motor oil by using a drill equipped with a mixing head. Following the mixing, the soil (containing water, NAPL and air) was packed in the column by adding small portions (~100 g) of the mixture to the column, and manually compressing it using a circular plate. For all samples, SIP measurements were taken 24 hr after packing. The porosity of each sample was calculated by using the weight of the packed column, the liquid–solid ratio (from which the bulk density of the soil is calculated) and by considering particle density of 2.65 g cm⁻³. In all measurements water saturation was constant (S_w = 0.47), and the NAPL saturation was 0 (control), 5, or 15 per cent. Three repetitions of each treatment (i.e. specific saturation of water and NAPL), with a good repeatability (Table 1) were separately prepared and measured. A similar experiment was performed with 25 per cent clay. However, the packing repeatability for that experiment was less satisfactory. Therefore, these results are used only as qualitative support for the results presented in this paper.

Four electrode measurements were conducted using the ZEL-SIP04 impedance spectrometer developed especially for the measurement of soil SIP (Zimmermann et al. 2008). The system measures the complex impedance of the porous media, from which the complex conductivity and its components (i.e. the real σ' and imaginary σ'' parts of the complex conductivity) can be calculated (Sihvola 1999). Both the current and the potential electrode were made of brass. The current electrodes were 5 cm long and crossed the entire sample diameter at 5 cm from the top and bottom of the column. The potential electrodes were positioned at 20 cm from the top and bottom of the sample, and were slightly retracted from the sample within their respective holes. Electrical contact of the potential electrodes was achieved by filling the empty space between sample and electrode with the same soil material used to fill the column. To test the accuracy of the measurement system the electrical properties of tap water were measured (using the procedure described above) and the results showed very low error (<0.1 mrad) up to 1 KHz.

Supplementary to the SIP measurements, we examine the effect of NAPL and soil on the EC of the tap water. The experimental procedure can be summarized as follows: a mixture of soil (9.3 g sand and 3.1 g clay), water (19.9 g) and NAPL (3.7 g or 7.5 g of either motor oil or diesel) was filled into 50 ml vials. Next the vials were shaken manually for approximately 1 min and then rested at room temperature for 24 hr. The supernatant was extracted using a syringe equipped with a microfilter (0.45 micron, Sartorius Minisart RC25, Göttingen, Germany). The conductivity of the filtered water was then measured using a conductivity meter (WTW Cond 340i, Weilheim, Germany). Using a similar approach, the individual contribution of soil (9.3 g sand and 3.1 g clay in 19.9 g water), and of NAPL (3.7 or 7.5 g NAPL in 19.9 g water) to the water EC was also examined.

## 3 RESULTS

### 3.1 Complex conductivity

The real and imaginary part of the complex conductivity of clean, diesel contaminated and oil contaminated unsaturated soil are shown in Fig. 1. For the imaginary part of the complex conductivity we choose to focus on the low frequency spectra (up to 100 Hz) because we are mostly concerned with electrochemical polarization which

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Clean</th>
<th>5 per cent oil</th>
<th>15 per cent oil</th>
<th>5 per cent diesel</th>
<th>15 per cent diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.405</td>
<td>0.396</td>
<td>0.400</td>
<td>0.395</td>
<td>0.399</td>
</tr>
<tr>
<td>SD</td>
<td>0.005</td>
<td>0.004</td>
<td>0.002</td>
<td>0.004</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 1. Mean and standard deviation (SD) of the porosity.
SIP signature of contaminated soil

Figure 1. Real (panel a) and imaginary part (panel b) of the complex conductivity for both diesel fuel and motor oil. The error bars demonstrate the standard deviation of the triplicates. In panel c the full spectra of the imaginary part is shown.

dominates in this frequency range (Leroy et al. 2008). In addition, an example of the full spectra is given in panel (c) of Fig. 1. The error bars in Fig. 1 represent the standard deviation between the triplicates.

In all the treatments, the real part of the complex conductivity (σ’) significantly increased with NAPL addition. The maximum change in σ’ was observed for motor oil with approximately 40 per cent increase of σ’ caused by addition of 15 per cent oil (panel a in Fig. 1). A similar trend of increasing σ’ was also observed for the diesel fuel, but to a lesser extent (up to 20 per cent increase in σ’ after the addition of 15 per cent diesel, see panel a in Fig. 1). Evidently, for each type of NAPL (i.e. oil or diesel), increase in NAPL saturation resulted in a increase in σ’. The increase in σ’ due to the addition of NAPL was also observed for the case of the 25 per cent clay (not shown here), but with higher error between the triplicates.

The imaginary part of the complex conductivity (σ’’) for diesel and motor oil are also shown in panel (b) of Fig. 1. In all cases, σ’’ of the clean soil samples was higher than that of the NAPL contaminated samples. The trend in σ’’ is similar to that of σ’, but in reverse order. At the same NAPL saturation addition of oil resulted in higher reduction in σ’’ than the equivalent reduction for diesel. Also, higher NAPL saturation is associated with higher reduction in σ’’ for both types of NAPL. Again, this phenomena was also observed for the 25 per cent clay (not shown here). For both the diesel and the motor oil, the maximum difference between σ’’ of the clean and contaminated samples was observed at 100 mHz, with 44, and 88 per cent change, respectively.

3.2 Extraction

In Fig. 2 the results from the extraction experiment are presented. For each type of NAPL the percent change of the solution EC (relatively to the tap water EC) after the extraction is shown (the error bars represent one standard deviation). Addition of 15.8 per cent and 27.3 per cent (weight of NAPL to weight of water) of motor oil to the water (without soil) results in an increase of 3.7 per cent, and 5.6 per cent in the EC, respectively. In contrast to motor oil, for diesel fuel no change in the water EC was observed. For the soil without NAPL (mixture of sand with 15 per cent clay), an increase of 8.8 per cent in the EC was observed. Interestingly, for both the oil and diesel the sum of contributions from the NAPL and soil alone cannot explain the increase in the EC of the mixture of soil and NAPL. For example a 22.3 per cent increase in the EC is associated with 27.3 per cent oil in soil, where the contribution of oil (in this concentration) and soil alone sum up to an increase of 14.4 per cent in the EC.

4 DISCUSSION AND CONCLUSIONS

Previous studies have mostly investigated saturated media in which non-conductive NAPL replaced conductive pore water (e.g. Olhoeft 1984; Borner et al. 1993; Schmutz et al. 2010). For this saturated case, replacement of a relatively conductive pore solution with the practically non-conductive NAPL results in a decrease in the EC (σ’) of the porous media (e.g. Schmutz et al. 2010). In contrast to the relatively simple case of saturated media, in unsaturated NAPL contaminated porous material where non-conductive NAPL replaces non-conductive air, the situation is more complex and requires further analysis. The increase in σ’ as a result of the addition of NAPL observed here can not be explained in terms of...
water saturation (as in saturated media), as the saturation remained constant. Alternative explanations for the increase in \( \sigma' \) as a result of the addition of NAPL should be based on the main parameters affecting the conductivity \( (\sigma') \) in unsaturated porous media.

Jougnot et al. (2010) considered the formation factor, water saturation, pore water salinity and the surface conductivity as the main parameters affecting \( \sigma' \) under unsaturated conditions. In addition, the presence of NAPL can affect the water distribution, thus possibly causing changes in the formation factor and saturation exponent. In this work, the water saturation and salinity of the added water were held constant for all the experiments. The formation factor, depending directly and indirectly (through the cementation exponent) on the porosity, is not likely to be an important factor as the porosity was kept almost constant for all experiments (Table 1). Changes in the formation factor and saturation exponent due to a different water distribution in the presence of NAPL cannot be excluded at this point, but we feel that the extraction of the pore water discussed below provides compelling evidence that exchange processes are a likely and consistent explanation for the observed strong changes in both the real part and the imaginary part of the complex conductivity.

The effect of NAPL on the EC of the pore water exhibits complex behaviour. Although both the motor oil and the diesel contain polar compounds (Schmidt et al. 2002), an increase in the water EC is only observed for the motor oil (Fig. 2). Still, for both motor oil and diesel the increase in the water EC of the mixed NAPL and soil is higher than the contribution of the NAPL and soil alone. Therefore, we conclude that addition of NAPL to the soil resulted in a release of inorganic ions to the pore water, thus increasing its EC. In addition, even for the motor oil the low frequency increase in \( \sigma' \) of the contaminated samples is much higher than expected if only the change in the water EC is considered (e.g. for the high oil concentration \( \sigma' \) increased by 40 per cent while the increase in the water EC from the oil alone was \( \sim \)6 per cent).

We explain the release of inorganic ions to the pore water as an exchange process between the polar organic compounds and the inorganic ions adsorbed on the mineral surface (e.g. Mihelicic et al. 1993; Schmidt et al. 2002). Therefore, the observed increase in \( \sigma' \) following the addition of NAPL is, at least partially, related to an increase in the pore water conductivity (Fig. 2). This explanation was already proposed by Olhoeft (1985) and Vanhala (1997), but they did not conduct measurements of the water EC. In addition Cassiani et al. (2009) also observed an increase in \( \sigma' \) by addition of NAPL to unsaturated porous media, but their experimental setup allow heterogeneous distribution of the NAPL phase, and therefore they attributed their results to segregation between the NAPL and the water, resulting from density differences between the NAPL and the water phase (in our work the extensive mixing of the different phases and the low permeability of unsaturated soil prevent such segregation).

The surface conductivity of porous media is also affected by the composition of the Stern layer (Leroy et al. 2008). Therefore, the adsorption of organic polar compounds to the surface is also expected to contribute to the observed changes in \( \sigma' \) although, at this point the nature of such a change was not directly studied. Furthermore, as \( \sigma'' \) is sensitive to electrochemical processes (such as adsorption) at the mineral-fluid interface (e.g. Leroy et al. 2008; Knight et al. 2010), the decrease in \( \sigma'' \) followed by the addition of NAPL (Fig. 1 panel b) is also likely related to changes in the composition of the Stern layer.

A possible explanation for the decrease in \( \sigma'' \) of the NAPL contaminated treatments is that some of the organic cations that can be found in the NAPL are adsorbed to the mineral surface, and have a lower mobility in the Stern layer compared to the cations that were exchanged. One reason for the reduced mobility of the adsorbed organic cations relates to stronger binding between these cations and the mineral surface. In contrast to some inorganic cations that retain part of their hydration shell in the adsorption process, the organic cations lack this shell. Therefore, the interaction between the organic cations and the mineral surface is more intense (Margulies et al. 1988). The stronger binding of the organic cations reduces their ability to move under the influence of an external electric field which explains the observed decrease in \( \sigma'' \) of the NAPL contaminated samples. The relation between ion mobility and electrochemical polarization was recently studied by Vaudelet et al. (2011), who demonstrated both theoretically and experimentally that adsorption of ions with low mobility in the Stern layer resulted in a reduction of polarization.

It is interesting to note that the difference between \( \sigma'' \) of clean and contaminated samples decreased with increasing frequency. We interpret this frequency dependent behaviour as a superposition between the two main mechanisms affecting the SIP response of porous media namely, electrochemical and interfacial (Maxwell–Wagner) polarization where the former is dominant at low frequencies, and the latter is dominant at high frequencies (Lemeses & Frye 2001; Leroy et al. 2008).

The SIP method has high potential in detecting and monitoring NAPL contaminated porous media. The research conducted so far (e.g. Vanhala et al. 1992; Atekwana et al. 2000; Segade et al. 2006; Cassiani et al. 2009; Vaudelet et al. 2011) is still not conclusive and many questions remain open, especially with respect to unsaturated environments. In this work, we showed that addition of NAPL to unsaturated porous media (with constant water saturation) resulted in an increase of the EC (\( \sigma' \)) and a decrease in the polarization as expressed by \( \sigma'' \). We argued that the increase in \( \sigma' \) is related to the adsorption of polar compounds to the mineral surface and the associated release of ions to the pore water, affecting both the surface conductivity and the pore water conductivity. In addition, we concluded that the decrease in polarization of the NAPL contaminated media is related to stronger binding of the NAPL polar compounds to the mineral surface relative to inorganic cations. In contrast to most of the previous studies that dealt with the effect of NAPL on the electrical properties of saturated porous media, we focused on unsaturated conditions with fixed water saturation. Therefore, we were better able to relate the presence of NAPL and processes at the mineral–fluid interface (e.g. adsorption).

The results presented here for unsaturated porous media clearly show strong signals related to the presence of NAPL that were not previously reported for three-phase systems. The data are difficult to reconcile with existing theory, but the results hold great promise for the detection and quantification of NAPL contamination in the unsaturated zone. Further research is required to complete the picture, and to derive a mechanistic model that relates NAPL and electrical properties of variably saturated porous media for both low and higher frequencies.

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