Abstract
During recent years, studies have used the apparent dielectric constant ($K_a$) measured by time domain reflectometry (TDR) for determining the saturation of non-aqueous phase liquids ($\theta_{NAPL}$) in soils. The $K_a$ has been related to $\theta_{NAPL}$ using dielectric mixing models. In the unsaturated zone, the water content ($\theta_w$) had to be known (by assumptions or measured using other techniques) to utilize these models. In the present study, unlike previous research, detailed laboratory experiments were conducted to investigate the relationship between TDR measurements and $\theta_{NAPL}$. Calibration was made in homogeneous sand using three different NAPLs. It was shown that the previously used mixing model led to errors up to 0.05 m$^3$ m$^{-3}$ for saturated soils. In unsaturated soil, it was shown that measurements of only $K_a$ can not be used for estimation of $\theta_{NAPL}$ even if $\theta_w$ is known. Instead, the TDRs capability of determining both $K_a$ and bulk electrical conductivity ($\sigma_a$) was utilized to estimate $\theta_w$ and $\theta_{NAPL}$.

INTRODUCTION
The widespread use of hydrocarbons (petroleum products, kerosene, etc) is an increasing environmental threat to natural resources such as soil and water. Organic pollutants like hydrocarbons are typically not mixing with water and they are therefore called non-aqueous phase liquids (NAPLs). The presence of NAPLs in the soil system complicates the transport equations since an additional phase is introduced. Furthermore, some NAPLs are volatile and can exist both in liquid and gas phase. Thus, modeling of NAPL transport in soils is a complicated task. Still, however, there is a lack of knowledge regarding basic transport processes occurring in the soil system contaminated by NAPLs (Ewing and Berkowitz, 1998). Most of the existing knowledge about NAPL transport in soils is based on numerical experiments and experimental studies are scarce. An important reason for this is the lack of efficient observation techniques of NAPL concentration. By introducing new observation techniques allowing for more detailed spatial and temporal experimental data, this basic knowledge would improve and better predictive models could be developed.

The NAPLs are characterized by low dielectric constant and electrical conductivity compared to soil water. Thus, several geoelectrical measuring techniques have been used to measure NAPL concentration. Examples of this are ground penetrating radar, DC resistivity, and time domain reflectometry (TDR) (e.g., Redman et al., 1991). The use of TDR to measure the apparent dielectric constant $K_a$ was introduced to geophysics by Topp et al., 1980. The $K_a$ for wet soil is highly dependent on the volumetric water content ($\theta_w$). Later, Dalton et al. (1984) showed how the attenuation of the TDR signal could be related to bulk electrical conductivity ($\sigma_a$). Redman et al. (1991), Brewster et al. (1993), and Kueper et al. (1993) used $K_a$ measured by TDR to estimate $\theta_{NAPL}$ in saturated soil. They took $K_a$ readings before and after a controlled NAPL (tetrachloroethylene) spill. It was assumed that since $K_a$ of water is about 80 and for NAPL 2.3, the decrease in bulk $K_a$ could be used to determine $\theta_{NAPL}$. In
later studies, instead a dielectric mixing model was utilized for the calculation of \( \theta_{\text{NAPL}} \) in saturated soil (Redman and DeRyck, 1994). The contaminated saturated soil is a three-phase system (soil matrix-water-NAPL). The contaminated unsaturated zone is, however, a four-phase system (soil matrix-air-water-NAPL), which makes \( \theta_{\text{NAPL}} \) measurements impossible using only \( K_a \) if \( \theta_w \) is unknown. DeRyck et al. (1993) used both TDR and neutron probe and could thus estimate both \( \theta_w \) and \( \theta_{\text{NAPL}} \). They concluded that the sum of \( \theta_w \) and \( \theta_{\text{NAPL}} \) was fairly constant in the unsaturated zone for steady state conditions. Using this assumption, the decrease in \( K_a \) can be directly related to \( \theta_{\text{NAPL}} \) also in unsaturated soil (Redman and DeRyck, 1994).

In the above studies, TDR estimated \( \theta_{\text{NAPL}} \) has shown similarities to \( \theta_{\text{NAPL}} \) determined from soil cores. However, it appears that no controlled calibration experiments of the relation between \( \theta_{\text{NAPL}} \) and \( K_a \) have been conducted. Thus, there is a great need for detailed studies of how the presence of NAPLs in the soil affects \( K_a \) and \( \sigma_a \).

In the present paper I extend the above research on TDR to observe NAPLs in both saturated and unsaturated sand. The objective is to evaluate effects of different types of NAPLs on the TDR measurements and examine possibilities of using TDR for measurements of \( \theta_{\text{NAPL}} \) for both saturated and unsaturated conditions. In contrast to earlier studies of TDR and NAPLs, however, I utilize the TDR’s capability of taking both \( K_a \) and \( \sigma_a \) measurements. I provide a hypothesis to explain the observed results and close with a discussion on how the results can be practically used in monitoring schemes of NAPL migration.

**THEORY**

**Concepts of Dielectrics**

The dielectric properties of a material can be described by the dielectric constant \( K^* \). The dielectric constant consists of a real part \( K' \), and an imaginary part \( K'' \), or the electric loss. The dielectric constant can be expressed as

\[
K^* = K' + j[K'' + (\sigma_{dc}/\omega \epsilon_0)]
\]

where \( \sigma_{dc} \) is the zero-frequency conductivity, \( \omega \) is the angular frequency, \( \epsilon_0 \) is the free-space permittivity, and \( j \) is the imaginary number.

The TDR instrument sends a high frequency (20 kHz–1.5 GHz) electromagnetic step pulse through a transmission line of known length \( L \), and the pulse is reflected back at the end of the line. By measuring the apparent length of the transmission line \( L_a \) calculated from the TDR trace, the dielectric constant can be estimated as

\[
K^* = (L_a/L)^2
\]

assuming \( K'' < K' \), which is true for water at frequencies between 100 MHz and 3–4 GHz. The electrical loss in soils is normally small but it does affect the estimate of \( K^* \). Therefore, the measured dielectric constant is called the apparent dielectric constant, \( K_a \) (Topp et al., 1980).

**Dielectric Mixing Models**

Several dielectric mixing models have been developed to estimate the dielectric properties of wet soils. The models calculate the bulk dielectric constant for the soil from the dielectric properties and the volume fractions of the soil components, e.g., water, air, and soil particles. The dielectric constant is about 80 for water, 2–5 for dry soil, and 1 for air. Thus, \( K_a \) is highly dependent on \( \theta_w \). In the theoretical de Loor model (de Loor, 1964), water is considered to consist of disk-shaped foreign inclusions embedded in a homogeneous isotropic dielectric medium, the mineral phase. The de Loor model contains no calibration parameter and has been successfully applied to determine \( K_a \) of soils in several studies (Jacobsen and Schjønning, 1995). Redman and DeRyck (1994) used the law of Bruggeman, Hanai, Shen, and Sen (BHSS) (e.g., Sen et al., 1981) for calculating \( K_a \) of NAPL contaminated soil. This is a geometrical model in which the shape of the inclusion is accounted for using a depolarisation factor. Normally, spherical inclusion is assumed.

The most commonly used mixing model in TDR applications is the model presented by Birchak et al. (1974). Birchak et al. (1974) suggested a semi-empirical \( \alpha \)-model

\[
K_a^\alpha = \sum_i \theta_i K_i^\alpha
\]
where $\theta_i$ and $K_i$ are the volume fraction and the dielectric constant of component $i$, respectively, and $\alpha$ is an empirical parameter accounting for soil geometry. The value of $\alpha$ is in the range of -1 to 1. These extreme values represent a perfectly layered medium where the electric field is parallel ($\alpha=1$) or perpendicular ($\alpha=-1$) to the layering. Birchak et al. (1974) found that $\alpha=0.5$ for an isotropic medium. Thus, the $\alpha$ value summarizes the geometry of the medium in relation to the applied electric field. For a three-phase system including air, water, and soil particles, it has been shown that the average value of $\alpha$ is about 0.5 with a range from 0.46 to 0.67 (Jacobsen and Schjønning, 1995). For a four-phase system, which also includes bound water, the $\alpha$ value ranged from 0.39 to 0.81 (Jacobsen and Schjønning, 1995).

In the present study, a four-phase dielectric mixing model was used to calculate $K_a$ of the soil according to

$$K_a^\alpha = \theta_s K_s^\alpha + \theta_w K_w^\alpha + \theta_{NAPL} K_{NAPL}^\alpha + \theta_{air} K_{air}^\alpha$$

where subscript $s$ stands for the mineral phase (soil particles).

### Electrical Conductivity Measurements using TDR

Attenuation of the TDR signal can be used to determine $\sigma_a$. Following the thin sample approach by Giese and Tiemann (1975), $\sigma_a$ can be described by

$$\sigma_a = K_p f_T / Z_L$$

where $Z_L$ is the impedance load of the transmission line (in $\Omega$) measured after a long time, $f_T$ is a temperature correction coefficient, $K_p$ is the cell constant of the TDR probe, a calibration constant that can be determined by immersing the probe in solutions with known conductivity.

In general, the $\sigma_a$ of the soil depends mainly on three variables, (i) the effective volumetric water content $\theta_w - \theta_0$, where $\theta_0$ is a correction factor accounting for water close to the solid particles which can be considered immobile ($\theta_0$ can be neglected in coarse textured soils like the sand used in this study), (ii) the electrical conductivity of the soil solution ($\sigma_s$), and (iii) a geometry factor, accounting for the complex geometry of the soil matrix. The $\sigma_s$ is also affected by the surface conductivity of the soil matrix $\sigma_s$. For unsaturated soils Rhoades et al. (1976) described $\sigma_s$ as

$$\sigma_s = \sigma_{soil} T(\theta_w) + \sigma_s$$

where $T(\theta_w)$ is the transmission coefficient accounting for the tortuosity of the current flow. Rhoades et al. (1976) proposed a linear relationship between $T(\theta_w)$ and $\theta_w$, i.e., $T(\theta_w) = a\theta_w + b$, where $a$ and $b$ are soil specific parameters. Other models for the $\sigma_s$-$\sigma_{soil}$-$\theta_w$ relationship have also been developed (see e.g., Persson, 1997), however, in this study only (6) was used since it accurately modeled the $\sigma_s$-$\sigma_{soil}$-$\theta_w$ relationship for the sand used.

### MATERIALS AND METHODS

#### TDR System

TDR measurements were carried out using a Tektronix 1502C cable tester with an RS232 interface connected to a laptop computer. Estimates of $K_a$ and $\sigma_a$ were calculated from the TDR trace using the WinTDR program (developed by the Soil Physics Group at Utah State University). A three-rod probe was used, 0.1 m in length, a wire diameter of 0.003 m, and a wire spacing of 0.05 m (Soilmoisture Equipment Corp., Santa Barbara, CA). The TDR probe was calibrated using the calibration utility of the WinTDR program and was found to accurately measure $K_a$ in air, ethanol, methanol, and water, and $\sigma_a$ in salt solutions containing KBr with $\sigma_a$ ranging from 0.01-4.0 dS m$^{-1}$.

#### TDR Measurements in Soil Containing Water and NAPL

The influence of NAPLs on the TDR measurements was investigated in homogeneous silica sand with a uniform particle size of 0.001 m. Properties of this sand are presented in Table 1. Three types of NAPLs were used in the experiments, sunflower seed oil, SFSO, ($K_a=3.06$), a synthetic motor oil, MO, ($K_a=2.66$), and n-paraffin, NP,
(\(K_a=2.32\)). However, most measurements were made using SFSO since it is non-volatile and non-toxic. To have a stable background \(\sigma_w\), distilled water containing 2 g KBr L\(^{-1}\) (\(\sigma_w=2.42\) dS m\(^{-1}\)) was used in all experiments. Known amounts of water, sand, and NAPL were mixed and packed into Plexiglas boxes (0.12 by 0.07 by 0.05 m) to a bulk density of 1.56 Mg m\(^{-3}\). These boxes contain the entire measurement volume of the 0.1 m TDR probe (Persson and Berndtsson, 1998b). Immediately after packing, the probe was inserted vertically into the sand.

For the calibration data series, \(\theta_{NAPL}\) varied from 0 to 0.35 m\(^3\) m\(^{-3}\) with an increment of 0.05 m\(^3\) m\(^{-3}\) and \(\theta_w\) from 0 to close to saturation \(\theta_{sat}\) resulting in totally 43 combinations. The increment in \(\theta_w\) was 0.02-0.08 m\(^3\) m\(^{-3}\). Another 25 combinations of \(\theta_w\) and \(\theta_{NAPL}\) were also prepared to get an independent data set for validation. In each mixture of soil, water, and NAPL, at least 10 measurements were taken and averaged within one hour after packing. Some samples were kept for several days to examine effects of redistribution of water within the sample. The temperature was fairly constant throughout the measurements, however, to achieve high accuracy, temperature corrections of \(\sigma_a\) were made.

To examine the effects of the distribution of NAPLs within the TDR sampling volume, two sand-water-NAPL samples in the validation data series were prepared in a different way. In these, the lower half of the Plexiglas box contained a sand and water mix, while the upper half contained a sand and SFSO mix. These samples are referred to as the layered samples. TDR measurements were taken, then the volume content was mixed like in the other samples and measurements were taken again. The \(\theta_{SFSO}\) and \(\theta_w\) used in these samples were \(\theta_{SFSO}=\theta_w=0.05\) and \(\theta_{SFSO}=\theta_w=0.10\) m\(^3\) m\(^{-3}\).

Table 1. Properties of the sand used.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter</td>
<td>0.001</td>
<td>m</td>
</tr>
<tr>
<td>Particle density</td>
<td>2.62</td>
<td>Mg m(^{-3})</td>
</tr>
<tr>
<td>Bulk density</td>
<td>1.56</td>
<td>Mg m(^{-3})</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.405</td>
<td>m(^3) m(^{-3})</td>
</tr>
<tr>
<td>Dielectric constant ((K_s))</td>
<td>4.27</td>
<td>-</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Influence of NAPLs on TDR Measurements

The presence of NAPLs in the soil clearly affected the TDR measured \(K_a\) and \(\sigma_a\). In general \(\sigma_a\) decreased as \(\theta_{NAPL}\) increased at constant \(\theta_w\). The effect of \(\theta_{NAPL}\) on \(K_a\) at constant \(\theta_w\) was not as expected from the dielectric mixing model (4). When NAPLs were present, (4) always overestimated the \(K_a\) if \(\alpha\) was kept constant.

Since most measurements were made with SFSO, these data were analyzed first. When \(\theta_{NAPL}\) was kept constant and \(\theta_w\) varied from 0 to \((\theta_{sat} - \theta_{NAPL})\) the variation in \(\sigma_a\) and \(K_a\) could be described by (4) and (6) with a modified parameter set. Thus, each set of data with constant \(\theta_{NAPL}\) was analyzed separately. The \(\theta_w\)-\(K_a\) relationship was determined using the four-phase Birchak et al. (1974) dielectric mixing model (4) with \(\alpha\) as calibration parameter. The \(K_a\) was calculated using the measured temperature to minimize temperature errors (Persson and Berndtsson, 1998a). The \(\alpha\) value decreased significantly when \(\theta_{NAPL}\) increased (Table 2).

Table 2. Parameters for (4) and (6) and their dependency on \(\theta_{NAPL}\).

<table>
<thead>
<tr>
<th>(\theta_{NAPL}) [m(^3) m(^{-3})]</th>
<th>(\alpha)</th>
<th>(r^2)</th>
<th>(A)</th>
<th>(B)</th>
<th>(\sigma_a)</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.4773</td>
<td>0.9955</td>
<td>2.31</td>
<td>0.55</td>
<td>-0.013</td>
<td>0.9860</td>
</tr>
<tr>
<td>0.05</td>
<td>0.4168</td>
<td>0.9925</td>
<td>2.60</td>
<td>0.29</td>
<td>-0.001</td>
<td>0.9948</td>
</tr>
<tr>
<td>0.10</td>
<td>0.3647</td>
<td>0.9801</td>
<td>1.97</td>
<td>0.34</td>
<td>-0.004</td>
<td>0.9852</td>
</tr>
<tr>
<td>0.15</td>
<td>0.3424</td>
<td>0.9957</td>
<td>2.59</td>
<td>0.00</td>
<td>0.007</td>
<td>0.9972</td>
</tr>
<tr>
<td>0.20</td>
<td>0.3106</td>
<td>0.9753</td>
<td>2.37</td>
<td>-0.03</td>
<td>0.008</td>
<td>0.9741</td>
</tr>
<tr>
<td>0.25</td>
<td>0.2962</td>
<td>0.9783</td>
<td>0.63</td>
<td>0.16</td>
<td>0.006</td>
<td>0.9649</td>
</tr>
<tr>
<td>0.30</td>
<td>0.2598</td>
<td>0.9890</td>
<td>0.10</td>
<td>0.21</td>
<td>0.009</td>
<td>0.9969</td>
</tr>
</tbody>
</table>
In Figure 1, the \( K_a \) determined using (4) with \( \alpha \) values presented in Table 2 at \( \theta_w \) of 0.1 m\(^3\) m\(^{-3}\) is plotted against \( \theta_{NAPL} \) together with observed values. In this figure the \( K_a \) calculated using a constant \( \alpha \) value (0.4773) is also presented. The de Loor model will always give an increasing \( K_a \) when air is replaced by NAPL. Thus, this model was not further analyzed. The BHSS model was also applied to the data, but this model consistently overestimated \( K_a \) if spherical inclusion was assumed. If the depolarization factor instead is used as a fitting parameter, the BHSS model can probably be used in a similar way as the Birchak model. However, because of the simplicity of (4) and the wide use of this model in TDR applications, only (4) was evaluated in detail.

From Figure 1 it can be seen that the scatter in \( K_a \) is rather large compared to the changes in \( K_a \) induced by the presence of NAPL. This can be explained by the relatively short probe used in this study, since the sensitivity of the probe towards changes in \( K_a \) is proportional to the length of the probe. In future studies I recommend that longer probes should be used to avoid this problem.

The \( \sigma_a-\theta_w \) relationship was determined for each \( \theta_{NAPL} \) using (6). The resulting parameters are shown in Table 2. In Figure 2, measured and predicted values by (6) using the parameters in Table 2 for \( \theta_w=0.1 \) m\(^3\) m\(^{-3}\) are presented.

From the results presented above, it is obvious that both \( \sigma_a \) and \( K_a \) are needed for determining \( \theta_w \) and \( \theta_{NAPL} \) in unsaturated soils. If a relationship between \( \sigma_a \) and \( K_a \) is established, the TDR measured \( \sigma_a \) and \( K_a \) can be used for \( \theta_w \).
and $\theta_{\text{NAPL}}$ estimations in any sand-air-water-NAPL mixture. Using both (4) and (6) with the parameters for each $\theta_{\text{NAPL}}$, the relationship between $\sigma_a$ and $K_a$ can be determined. The result is presented in Figure 3. For clarity, only the $\sigma_a-K_a$ relationships for $\theta_{\text{NAPL}}=0$ and $\theta_{\text{NAPL}}=0.1$ m$^3$ m$^{-3}$ are presented together with the observed data for $\theta_{\text{NAPL}}=0.1$ m$^3$ m$^{-3}$. In the figure, the $\sigma_a-K_a$ relationship for saturated conditions is also presented. This curve was obtained by extrapolation of (4) and (6) for each $\theta_{\text{NAPL}}$ so that $\theta_{\text{w}}+\theta_{\text{NAPL}}=\theta_{\text{sat}}$, and then fitting a third-order polynomial to the data ($r^2=0.99$).

The three different NAPLs examined had similar effects on the TDR measurements. The calibrated $\alpha$ for NP was slightly larger than for SFSO for the same $\theta_{\text{NAPL}}$ but lower for MO. The relationship between $\sigma_a$ and $K_a$ for NP was not significantly different from SFSO. However, using MO the $\sigma_a$ was considerably smaller than for SFSO at low $\theta_{\text{w}}$. At higher $\theta_{\text{w}}$, the relationship between $\sigma_a$ and $K_a$ was close to the one for SFSO.

For each sample both the average and standard deviation of the TDR measurements were calculated. The average standard deviation for all samples was 0.03 and 0.003 for $K_a$ and $\sigma_a$ (in dS m$^{-1}$), respectively. When samples was left to redistribute for several days, only minor changes in $K_a$ and $\sigma_a$ were noted.

![Figure 3](image-url)

**Figure 3.** $K_a$ vs. $\sigma_a$. The solid and dotted lines represent the relationship between $K_a$ and $\sigma_a$ when $\theta_{\text{NAPL}}=0$ and $\theta_{\text{NAPL}}=0.1$ m$^3$ m$^{-3}$ respectively. The dashed line represents saturated conditions, i.e., $\theta_{\text{NAPL}}+\theta_{\text{w}}=\theta_{\text{sat}}$. The points are the measured values at $\theta_{\text{NAPL}}=0.1$ m$^3$ m$^{-3}$. Note that each measured value is the average of at least 10 measurements in the same sample.

**Explanation of the trend in $\sigma_a$ and $\theta_{\text{w}}$ with $\theta_{\text{NAPL}}$**

In this section I present a hypothesis that could explain how NAPLs affect TDR measurements. The presented data support the below hypothesis but further experiments are needed. The decreasing $\alpha$ in (4) with increasing $\theta_{\text{NAPL}}$ can be physically interpreted. The distribution of the four dielectrics (soil particles, air, water, and NAPL) is changing from totally random towards a more layered pattern where layer boundaries are crossed by electrical field lines of the electrostatic field arising between the probe rods. There is probably no change in the distribution of soil particles, and the air will still be located in the largest non-wetted pores. This means that the change in $\alpha$ is likely to be associated with the interaction between water and NAPL. Another observation is that the $\alpha$ value is independent of $\theta_{\text{w}}$ for a given $\theta_{\text{NAPL}}$. This indicates that the examined NAPLs tend to concentrate in macro inclusions as soon as the water is present in the soil and the shape and size of these inclusions seem to be independent of $\theta_{\text{w}}$. The average size of the inclusions increases with $\theta_{\text{NAPL}}$. As a consequence of the non-homogeneous NAPL distribution and the repulsion between the two liquids, water will also be increasingly non-homogeneously distributed as $\theta_{\text{NAPL}}$ increases. The decreasing $\sigma_a$ with increasing $\theta_{\text{NAPL}}$ at constant $\theta_{\text{w}}$ corroborates the NAPL-water inclusion theory. It is evident that a redistribution of the water takes place when NAPLs are present. If the NAPLs only entered the air filled pores, the major conductivity arising from ions present in the soil water would remain unchanged. Instead, however, the presence of NAPL inclusions increases the tortuosity of the electrical current flow path through the soil and in some cases disrupt flow paths existing prior to the application of NAPLs.
Estimation of NAPL Concentration in Saturated Soil

In Figure 3 it can be seen that both $K_a$ and $\sigma_a$ are unique functions of $\theta_w$ and $\theta_{NAPL}$ at saturated conditions. In Figure 4, $K_a$ at saturated conditions is plotted against $\theta_{NAPL}$. Note that in this figure, the $K_a$ is calculated from $\theta_{NAPL}$ using the $\alpha$ value corresponding to that $\theta_{NAPL}$. In the previous approach suggested by Redman and DeRyck (1994), this was not accounted for. This is done by keeping the $\alpha$-value constant and equal to the value when $\theta_{NAPL}=0$. This approach is also presented in Figure 4. The error in $\theta_{NAPL}$ using the previous approach can be up to 0.05 m$^3$ m$^{-3}$. The $\sigma_a$ measurement can also be related to $\theta_{NAPL}$. The $\sigma_a$-$\theta_{NAPL}$ relation for saturated conditions is presented in Figure 5. The decreasing $\sigma_a$ is attributed to both the decreasing $\theta_w$ and the increasing tortuosity when $\theta_{NAPL}$ increases. Thus, relating $\sigma_a$ to $\theta_{NAPL}$ in groundwater using TDR or any other geoelectrical method seems to be an efficient approach.

Estimating NAPL Concentration in Unsaturated Soil

Looking at Figure 1, it is interesting to note that $K_a$ is not a unique function of $\theta_{NAPL}$ even if $\theta_w$ is known. Thus, it is not possible to measure $\theta_{NAPL}$ in unsaturated soils using the TDR determined $K_a$ only. If we instead look at Figure 3, each pair of measured $K_a$ and $\sigma_a$ are related to a pair of $\theta_w$ and $\theta_{NAPL}$. A three-dimensional second-order surface was thus fitted to the $\sigma_a$-$K_a$-$\theta_w$ relationship. Using this surface, any combination of $K_a$ and $\sigma_a$ yields a $\theta_w$. In Figure 6, the known $\theta_w$ is plotted against the $\theta_w$ calculated using this surface ($r^2=0.995$).
A similar function was calculated for the $\sigma_a-K_a-\theta_{NAPL}$ data. The fit was good, but this approach was very sensitive to small changes in $\sigma_a$. Instead an alternative two-step approach was utilized. First, I used (4) and solved it for $\theta_w$. The resulting expression was inserted into (6). The measured $K_a$ was then used in the combined equation using the different parameters for values of $\theta_{NAPL}$ in Table 2. Now, for every given $K_a$, $\sigma_a$ can be calculated for $\theta_{NAPL}$ from Table 2. Next, the measured $\sigma_a$ was used to calculate the $\theta_{NAPL}$ by interpolating between the two closest $\sigma_a$. The result is presented in Figure 7, where actual vs. calculated $\theta_{NAPL}$ are plotted. The calculated $\theta_{NAPL}$ is normally within a few m$^3$m$^{-3}$ of the actual $\theta_{NAPL}$ ($r^2=0.922$, root mean square error=0.031 m$^3$m$^{-3}$). There was a slightly decreasing trend in the residual of the $\theta_{NAPL}$ estimation when plotted against $\theta_{NAPL}$. That is, the relative error in the $\theta_{NAPL}$ estimation was larger when $\theta_{NAPL}$ was low.

Effects of the Distribution of NAPLs within the Sampling Volume

Another important issue is how NAPLs distribute in the soil within the sample area (A) perpendicular to the long axis of the probe rods. The calibration experiments conducted in mixed samples of soil, air, water, and NAPL indicated that both water and NAPL condensed in some macro inclusions depending on the NAPL concentration. A change in the distribution of dielectrics within A results in a change of the weighting function determining the weight a given dielectric is contributing to the total, or effective, $K_a$. Baker and Lascano (1989), e.g., showed that the TDR sampling volume is concentrated between the probe rods with the greatest sensitivity close to the rods. That is, although the
area occupied by various dielectrics within \( A \) is unchanged, their position has a great influence on \( K_{\alpha} \). This is the reason why \( \alpha \) decreased with increasing \( \theta_{NAPL} \) and why \( K_{\alpha} \) decreased although air was substituted by NAPL. The mixed samples represent the NAPL distribution in residual phase. These samples are macroscopically homogeneous, i.e., water and air are distributed evenly within the pore space, but the NAPL exists in larger inclusions. As long as the NAPL inclusions are distributed homogeneously within \( A \) the method presented above will give accurate \( \theta_{NAPL} \) and \( \theta_{w} \) estimations. During NAPL transport in soils the NAPL can also exist in a continuous non-wetting phase occupying a fraction of the wetted pore space. When a part of the TDR sample volume contains a continuous NAPL phase, the location of this with respect to the orientation of the TDR probe becomes important. The two layered samples represent the case when the upper half of the TDR sampling volume contains a continuous NAPL phase and the lower half a continuous water phase. In these both samples, \( \theta_{w} \) was slightly over-estimated and \( \theta_{NAPL} \) slightly underestimated when they were calculated using the methods described above. However, these errors were less than about 0.02 m\(^3\) m\(^{-3}\). The \( K_{a} \) and \( \sigma_{a} \) can be calculated theoretically, however, for a specific case. This is when the center of the TDR rods are located at the boundary between the water and NAPL phases. For this case, the \( K_{a} \) and \( \sigma_{a} \) were calculated as the geometrical average of \( K_{a} \) and \( \sigma_{a} \) of the respective phase (see Persson and Berndtsson, 1998b). When the resulting \( K_{a} \) and \( \sigma_{a} \) were used for calculating \( \theta_{w} \) and \( \theta_{NAPL} \), the \( \theta_{w} \) was slightly overestimated but the \( \theta_{NAPL} \) was significantly underestimated. These results indicate that the approach presented is best suited for \( \theta_{NAPL} \) determination when the NAPL exists mainly in residual phase. In migration experiments the method could also work if the NAPL front is passing the probe perpendicular to the long axis of the probe rods.

**SUMMARY**

The use of TDR to simultaneously measure \( \theta_{NAPL} \) and \( \theta_{w} \) in both saturated and unsaturated soil was examined. Earlier studies have only used the TDR measured \( K_{a} \) when calculating \( \theta_{NAPL} \). Unlike these studies, the TDR’s capability of taking both \( K_{a} \) and \( \sigma_{a} \) measurements was utilized in the present paper. In a previous approach (Redman and DeRyck, 1994), a dielectric mixing model was used for estimating \( \theta_{NAPL} \). The previous approach suggested a constant \( \alpha \) value in the model by Birchak *et al*. (1974). Contrary to this, our results show that the \( \alpha \) value is depending on \( \theta_{NAPL} \). It was shown that for the sand studied, the previous approach leads to errors up to 0.05 m\(^3\) m\(^{-3}\). In the saturated zone, both \( K_{a} \) and \( \sigma_{a} \) can be related to \( \theta_{NAPL} \). In the unsaturated zone, the TDR measured \( K_{a} \) can not be used for calculations of \( \theta_{NAPL} \) even if \( \theta_{w} \) is known. However, by using observed \( \sigma_{a} \) and \( K_{a} \) as described in this study, both \( \theta_{w} \) and \( \theta_{NAPL} \) can be estimated. The fit between measured and calculated data was good with \( r^{2} \) values of 0.987 and 0.922 for \( \theta_{w} \) and \( \theta_{NAPL} \) respectively. However, since the approach requires detailed calibration data for the \( K_{a}, \theta_{w} \) and \( \sigma_{a}, \theta_{w} \) relationships for a wide range in \( \theta_{NAPL} \), and a constant background \( \sigma_{w} \), it might currently be restricted to controlled laboratory experiments in homogeneous materials. Another problem inherent in the method presented is that \( \theta_{NAPL} \) is strongly dependent on \( \sigma_{w} \). Whereas a redistribution of a certain amount of NAPL and water within the sampling volume has some effect on \( K_{a} \), the effect on \( \sigma_{a} \) can be much larger. For example, a concentration of NAPL around one of the rods will make it increasingly difficult for the current to pass through the soil. In conclusion, a NAPL distribution significantly different from the one experienced during the calibration will to some extent influence \( \theta_{w} \), but the influence on \( \theta_{NAPL} \) is expected to be far greater. Further studies are needed to examine the relationship between \( \theta_{NAPL} \) and TDR measurements in different soil types using different NAPLs. The developed approach for measuring \( \theta_{w} \) and \( \theta_{NAPL} \) in unsaturated soil could be used in laboratory experiments of NAPL transport.

**Acknowledgements**

This study was funded by the Swedish Research Council for Engineering Sciences and the Swedish Natural Science Research Council. Equipment was purchased through grants from the Crafoord and Lundberg Foundations.

**REFERENCES**


