Measurement of NAPL saturation distribution in whole domains by the Simplified Image Analysis Method

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ABSTRACT: A Simplified Image Analysis Method devised to assess the saturation distribution of water and Non-Aqueous Phase Liquids (NAPLs) in granular soils subject to fluctuating groundwater conditions was developed and tested for ten different NAPLs of different density and viscosity values (0.73 ≤ ρ ≤ 1.20 g/cm³; 1.4 ≤ ν ≤ 1000 mPa·s). The Simplified Image Analysis Method, which is based on an extension of the Beer-Lambert Law of Transmittance that predicts the existence of a linear relationship between the saturation of water (Sw), NAPL (So), and their corresponding average optical densities (Di), was tested by photographing samples of Toyoura sand mixed with different amounts of water and NAPLs, using two digital cameras with different wavelength band-pass filters (λ = 450 nm and 640 nm), and obtaining the linear equations relating Sw, So and Di for each NAPL. Once the linear relationships were confirmed, this method was used to test the behavior of two different NAPLs subject to fluctuating groundwater tables, demonstrating that this non-intrusive and non-destructive method can be used as a reliable tool to provide water and NAPL saturation distributions in full domains, when studying the effects of porous soil contamination by NAPLs under dynamic conditions.

KEYWORDS: NAPL, simplified image analysis, saturation, optical density, column test

1 INTRODUCTION

When released in the vadose zone, Non-Aqueous Phase Liquids (NAPLs) pose significant contamination risks to the groundwater (Mercer and Cohen 1990; Capiro, Stafford et al. 2007). Remediation of these releases in an efficient and cost-effective way should be guided by field data interpreted by numerical models using the appropriate assumptions (Kechavarzi, Soga et al. 2000). To verify the accuracy of these models, laboratory tests should be run and precise saturation information should be obtained, especially under the dynamic conditions usually present in nature (Lenhard and Parker 1987; Fagerlund, Illangasekare et al. 2007; Flores, Katsumi et al. 2011). In this study, we aim to validate the Beer-Lambert Law of Transmittance, the basis of the Simplified Image Analysis Method for ten different NAPLs with different density and viscosity values, and then use this method to assess the behavior of five different NAPLs subject to fluctuating groundwater conditions, which may have a significant effect on the behavior of NAPLs, particularly with regards to their residual saturation. For this, residual saturation values at the end of drainage and imbibition stages will be compared for our different NAPLs.

2 SIMPLIFIED IMAGE ANALYSIS METHOD

The Beer-Lambert Law of Transmittance states that when a beam of monochromatic radiation I₀ strikes a block of absorbing material perpendicular to a surface, after passing through a length b of the material, its power is decreased to Iₓ as a result of absorption:

\[ D_i = \varepsilon bc = \log_{10} \frac{I_0}{I_x} \]  

(1)

where \( D_i \) is the optical density, \( \varepsilon \) a numerical constant, \( b \) the length of the path, \( c \) the number of moles per liter of absorbing solution, \( I_0 \) is the initial radiant power, and \( I_x \) the transmitted power (Sköog et al. 2007). For digital images, the average optical density \( D_i \) is defined for the reflected light intensity as:

\[ D_i = \frac{1}{N} \sum_{j=1}^{N} d_{ji} = \frac{1}{N} \sum_{j=1}^{N} \left( -\log_{10} \left( \frac{I_{ji}}{I_{ji}^0} \right) \right) \]  

(2)

where \( N \) is the number of pixels contained in the area of interest and, for a given spectral band \( f \), \( d_{ji} \) is the optical density of the individual pixels, \( I_{ji}^0 \) is the intensity of the reflected light given by the individual pixel values, and \( I_{ji} \) is the intensity of the light that would be reflected by an ideal white surface (Kechavarzi et al. 2000).

It has been shown (Flores et al. 2011) that the Beer-Lambert Law of Transmittance establishes a linear relationship between optical density and the concentration of a dye:

\[ D_i = c \cdot D_0 \]  

(3)
where $D_0$ is the optical density of a solution of unit concentration, and $D_i$ the optical density of a solution of concentration $c$. Therefore, when two cameras with band-pass filters (wavelengths $\lambda = i$ and $j$) are used, and when water and NAPL are mixed with dyes whose predominant color wavelengths are also $i$ and $j$, we can obtain two different sets of linear equations that can be solved for $S_w$ and $S_o$:

$$
\begin{bmatrix}
D_{i}\text{ }mn \\
D_{j}\text{ }mn
\end{bmatrix} = \begin{bmatrix}
(D_{i}^{00} - D_{i}^{0}) \cdot S_w + (D_{i}^{10} - D_{i}^{00}) \cdot S_o + D_{i}^{00} \\
(D_{j}^{00} - D_{j}^{0}) \cdot S_w + (D_{j}^{10} - D_{j}^{00}) \cdot S_o + D_{j}^{00}
\end{bmatrix}
$$

(4)

where $m$ and $n$ are the dimensions of the matrix, $[D_i]_{mn}$ and $[D_j]_{mn}$ are the values of average optical density of each mesh element for wavelengths $i$ and $j$; $[D_i]_{00}$ and $[D_j]_{00}$ are the average optical density of each mesh element for dry sand; $[D_i]_{10}$ and $[D_j]_{10}$ for water saturated sand; and $[D_i]_{01}$ and $[D_j]_{01}$ for NAPL saturated sand. This is the base of the Simplified Image Analysis Method.

3 MATERIALS

For this study, 10 NAPLs (Table 1) were used as non-wetting fluids after being dyed red with Sudan III (1:10000). Their names were obtained from different national pollutant registry lists (Australia DSEWPC 1999; Environment Canada 2010; UK Environment Agency 2011; US EPA 2011) for their frequency as contaminants, as well as for their immiscibility (or negligible solubility) in water. Water, dyed blue with Brilliant Blue FCF (1:10000), was used as wetting fluid. Toyoura sand (Soil particle specific gravity, $G_s = 2.64$; uniformity coefficient, $C_u = 1.36$) was the porous media.

Table 1. Physical characteristics of NAPLs

<table>
<thead>
<tr>
<th>NAPL</th>
<th>Solubility in Water</th>
<th>Density $\rho$ (g/cm$^3$)</th>
<th>Viscosity $\nu$ (mPa∙s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel 2</td>
<td>Immiscible</td>
<td>0.850</td>
<td>4</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.0169 g/l</td>
<td>0.860</td>
<td>1.5</td>
</tr>
<tr>
<td>Low Viscosity Paraffin</td>
<td>Immiscible</td>
<td>0.880</td>
<td>7</td>
</tr>
<tr>
<td>Motor Oil</td>
<td>Immiscible</td>
<td>0.858</td>
<td>129</td>
</tr>
<tr>
<td>N-decane</td>
<td>0.009 ppm</td>
<td>0.730</td>
<td>1.4</td>
</tr>
<tr>
<td>N-dodecane</td>
<td>Immiscible</td>
<td>0.750</td>
<td>1.9</td>
</tr>
<tr>
<td>NEOVAC</td>
<td>Negligible</td>
<td>0.930</td>
<td>108</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.019 g/l</td>
<td>1.199</td>
<td>3.1</td>
</tr>
<tr>
<td>Paraffin Liquid</td>
<td>Immiscible</td>
<td>0.870</td>
<td>170</td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>Negligible</td>
<td>0.963</td>
<td>1000</td>
</tr>
</tbody>
</table>

4 TRANSMITTANCE TEST

For equation (3) to truly represent a linear relationship, the colorimetric characteristics of the solution of concentration $c$ (i.e., each NAPL) must not greatly change throughout the test. To verify that our selected NAPLs satisfy this condition, samples of each one were analyzed before and after being freely let evaporate at laboratory conditions.

For every NAPL (Table 1), 50 ml were dyed with Sudan III (1:10000), their transmittance curves were obtained with the Shimadzu UV-VIS Spectrometer, and were let evaporate inside 50 ml glass centrifuge tubes ($\varnothing = 29$ mm, $h = 117$ mm) for 168 h at a constant room temperature of 20˚C and humidity of 70%, after which their transmittance curves were once again calculated.

Graphics were prepared comparing transmittance before and after the 168 h period, for both samples that were dyed and extra samples that were kept undyed. Results show very little variation on the transmittance behavior of all NAPLs. As an example of the obtained results, Figure 1 shows the plots corresponding to two of our analyzed NAPLs: N-decane and Ethylbenzene. Similar results were obtained for all other NAPLs.

5 SATURATION VERSUS OPTICAL DENSITY TEST

Sixty soil samples were prepared with each NAPL by mixing known amounts of water, NAPL and porous media in 25 cm cylindrical sample containers ($\varnothing = 40$ mm, $h = 20$ mm). The prepared samples were positioned approximately 1.5 m in front...
of two cameras, two 500 W lights were turned on, and one picture was taken with each camera (one with a $\lambda = 450$ nm band-pass filter, and the other one with a $\lambda = 640$ nm one). To account for differences in lighting, a Kodak gray scale and a Gretamacbeth white balance card were placed next to each soil sample, and were part of each picture as well. Both cameras were set to manual mode so that aperture, shutter speed and white balance were kept constant. Room temperature was kept at 20 °C and humidity at 70%. Pictures were recorded in NEF format and then were exported to TIFF format using ViewNX 1.5.0. The TIFF images were then analyzed by an ad-hoc program written in MATLAB Release 2007a. Graphics were prepared for each NAPL, comparing water and NAPL saturation versus optical density values, for each wavelength. Figure 2 shows the plots corresponding to one of our analyzed NAPLs, N-decane, for both 450 and 640 nm. The linear fit for the first graphic (450 nm) has a coefficient of determination $R^2 = 0.89$, and for the second one (640 nm), $R^2 = 0.96$, showing that, as predicted by equation (3), the relationship between water and NAPL saturation, and optical density is linear. The regression equations and corresponding values for the coefficients of determination ($R^2$) for the ten studied NAPLs are as shown in Table 2.

6 COLUMN TESTS

Once linear relationships between water and NAPL saturation values, and optical density, were confirmed for a broad spectrum of NAPLs, we can apply the Simplified Image Analysis Method to study the behavior of different NAPLs in whole domains. Five NAPLs (Diesel 2, Ethylbenzene, Low Viscosity Paraffin, N-decane, and Paraffin Liquid) were selected for the column tests based on their diverse viscosity values ($1.4 < \nu < 170$ mPa∙s), and densities ($0.730 < \rho < 0.880$ g/cm$^3$). Similar amount of each NAPL (28 g) was injected from the top of their corresponding column and subjected to two cycles of Drainage-Imbibition in separate $3.5 \times 3.5 \times 40$ cm columns (Figure 3) filled with fully saturated Toyoura Sand. Both drainage stages lasted 72 hours ($h = -5$ cm), and both imbibition stages lasted 24 hours ($h = 40$ cm). Total duration of each test was 192 hours. Two simultaneous pictures were taken of each column every 30 minutes, and were analyzed following the Simplified Image Analysis Method described in Flores et al (2011). Saturation distributions of NAPL and water for the whole domains were plotted for all cases at $t = 0, 72, 96, 168$, and 192 hours, representing initial conditions, end of the first drainage, end of the first imbibition, end of the second drainage, and end of the second imbibition. Saturation distribution graphics of N-decane are shown in Figure 4, but similar graphics were prepared for all NAPLs.

Table 2. Regression equations for different NAPLs, for wavelengths $\lambda = 450$ nm and 640 nm

<table>
<thead>
<tr>
<th>NAPL</th>
<th>$D_{0\text{cm}}$</th>
<th>$R^2$</th>
<th>$D_{4\text{cm}}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel 2</td>
<td>0.0180 $S_w + 0.0035 S_o + 0.2457$</td>
<td>0.83</td>
<td>0.0030 $S_w + 0.0025 S_o + 0.1283$</td>
<td>0.95</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.0175 $S_w + 0.0007 S_o + 0.0680$</td>
<td>0.81</td>
<td>0.0033 $S_w + 0.0037 S_o + 0.1220$</td>
<td>0.90</td>
</tr>
<tr>
<td>Low Viscosity Paraffin</td>
<td>0.0160 $S_w + 0.0008 S_o + 0.0710$</td>
<td>0.89</td>
<td>0.0029 $S_w + 0.0036 S_o + 0.1300$</td>
<td>0.93</td>
</tr>
<tr>
<td>Motor Oil</td>
<td>0.0150 $S_w + 0.0006 S_o + 0.0750$</td>
<td>0.91</td>
<td>0.0028 $S_w + 0.0033 S_o + 0.1300$</td>
<td>0.92</td>
</tr>
<tr>
<td>N-decane</td>
<td>0.0150 $S_w + 0.0008 S_o + 0.0700$</td>
<td>0.89</td>
<td>0.0033 $S_w + 0.0040 S_o + 0.1200$</td>
<td>0.96</td>
</tr>
<tr>
<td>N-dodecane</td>
<td>0.0160 $S_w + 0.0007 S_o + 0.0700$</td>
<td>0.88</td>
<td>0.0030 $S_w + 0.0035 S_o + 0.1300$</td>
<td>0.95</td>
</tr>
<tr>
<td>NEOVAC</td>
<td>0.0140 $S_w + 0.0008 S_o + 0.0700$</td>
<td>0.85</td>
<td>0.0025 $S_w + 0.0036 S_o + 0.1300$</td>
<td>0.95</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.0130 $S_w + 0.0007 S_o + 0.0730$</td>
<td>0.85</td>
<td>0.0026 $S_w + 0.0036 S_o + 0.1300$</td>
<td>0.94</td>
</tr>
<tr>
<td>Paraffin Liquid</td>
<td>0.0140 $S_w + 0.0007 S_o + 0.0087$</td>
<td>0.88</td>
<td>0.0026 $S_w + 0.0040 S_o + 0.1360$</td>
<td>0.96</td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>0.0120 $S_w + 0.0009 S_o + 0.0690$</td>
<td>0.93</td>
<td>0.0023 $S_w + 0.0040 S_o + 0.1200$</td>
<td>0.97</td>
</tr>
</tbody>
</table>
From Figure 4 we can observe the whole domain distribution of N-decane at the end of each stage, and it is clear how a light NAPL can actually get trapped below the water table after subsequent drainage and imbibition processes. We can also observe and quantify how less N-decane penetrated the column after the second drainage process, when compared to the first drainage process, mostly due to loss of NAPL trough the top spillway during imbibition. When comparing the depth and infiltration initial speed of the five studied NAPLs, no relationship was found with either density or viscosity values. More studies are necessary to compare these migration parameters with other physical properties of NAPLs. Finally, we can also observe how regions within the column that had higher NAPL saturation values at the end of the drainage processes, had also high saturation values by the end of the imbibition. This behavior was found on all five NAPLs, as shown in Figure 5 (left).

Figure 5 (left) shows, for each one of the five different studied NAPLs, the relationship between their residual saturation values at the end of the drainage stage, when compared to their residual saturation values at the end of the imbibition stage. As can be seen, the relationship between both values is linear for each NAPL, and the general ratio of imbibition over drainage is less than 1.0 for all NAPLs, which confirms that some contaminant is removed by water during the imbibition stages. It can also be noticed how the residual saturation ratio (imbibition/drainage) is different for each NAPL, and follows the progression (from larger to smaller) N-decane > Ethylbenzene > Diesel 2 > Low Viscosity Paraffin > Paraffin Liquid, which is their exact inverse order when comparing their viscosity values. In fact, if we plot viscosity versus residual saturation ratio, we will find a logarithmic relationship between them (Figure 5, right), which could help us predict the residual saturation of any NAPL after imbibition processes, if the residual saturation after the drainage process is known. Additional NAPLs need to be tested to improve the accuracy of this relationship.

8 REFERENCES


Figure 5. Comparison of residual saturation at the end of drainage and imbibition stages for 5 different NAPLs (left) and relationship between their viscosity and residual saturation ratio (right).