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## Evaluation of methods for water and non-volatile LNAPL content measurement in porous media

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**Abstract:** Proper characterization of contaminants in subsurface helps to clean up effectively the contaminated sites. In this study, different methods were used to quantify non-volatile light non-aqueous phase liquid (LNAPL) and water from sample columns subjected to different water to LNAPL ratios. The objective of the study was to evaluate methods for porous media water and LNAPL contents analysis. The liquids were sampled from the sample columns using activated carbon pellets (ACP). Sample columns water content was also measured using soil moisture sensors. Dielectric mixing model (DMM) was evaluated for the estimation of LNAPL content after water and LNAPL contents of the sample columns were determined through gravimetric analysis method. The result shows that it was possible to sample both water and LNAPL using ACP proportionally but with high standard deviations. It also shows that more liquid was sampled from sample columns subjected to only one liquid compared to sample columns subjected to two liquids. On the other hand, analysis of water and LNAPL using gravimetric analysis method gave the best result although the presence of LNAPL resulted in underestimation of water content at higher LNAPL contents. Meanwhile, the presence of LNAPL modified the bulk relative permittivity ( $\epsilon_a$ ) of the sample columns and resulted in overestimation of water contents measured using soil moisture sensors at higher LNAPL content. The modification of  $\epsilon_a$  was used for the estimation of LNAPL using DMM. The evaluation of the model with known water and LNAPL contents and in estimating the LNAPL content of the other sample columns shows that the model could be used for the proper estimation of LNAPL in porous media.

**Keywords:** activated carbon pellet (ACP); dielectric mixing model (DMM); gravimetric analysis; light non-aqueous phase liquid; silica sand; soil moisture sensor

Soil water is an interest of agronomic, hydrologic and geotechnical practices among others. COOPER (2016) stated that the interactions between soil and water are the most fundamental relationships in the terrestrial environment. Disruption of these interactions may have significant long-term changes to the soil (YARON *et al.* 2012). YARON *et al.* (2008) concluded that anthropogenically-induced chemical contamination may cause irreversible changes. The change could

be structural or in properties of soil-subsurface geosystem (YARON *et al.* 2010). Soils contaminated with oil has different geotechnical properties, e.g. lower dry bulk density and lower optimum water content compared to their non-contaminated counterparts (KHAMEHCHIYAN *et al.* 2007; RAHMAN *et al.* 2010). Subsurface contamination by non-aqueous phase liquid (NAPL) is a wide range issue (SCHROTH *et al.* 1995) and a significant portion of contaminated sites contains

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NAPLs (MAYER & HASSANIZADEH 2005). NAPLs in subsurface compete for the site with water and air, and the proper characterization helps to clean up the contaminated site effectively.

Soil water content can be determined through direct methods or measured through indirect methods. Directly, it can be measured through the separation of the water from the soil matrix (TOPP & FERRÉ 2002). Thermo-gravimetric analysis method is the most commonly used direct method and used as a standard for the calibration of the other methods (COOPER 2016). However, the method itself has some limitations (BITTELLI 2011) and it could overestimate due to the evaporation loss of non-water soil constituents (TOPP & FERRÉ 2002; HILLEL 2004; COOPER 2016). There is a wide range of NAPLs that could change the value using gravimetric methods either ways as there are components that could evaporate under conventional oven temperature 105°C (TOPP *et al.* 2008) or remain as a part of solid components at oven temperature (MANSUR *et al.* 2015). GARDNER (1986) argues that the main problem in gravimetric water content determination in the porous materials is the dry state of the media itself.

In addition to their number, hydrocarbons (HCs) occur in gaseous liquid or solid states with boiling points more than 1100°C (SPEIGHT 2015). The author indicated that these differences in physical and chemical properties make difficult to develop a single analytical method for the entire range of HCs. However, though there is no standard method, there are different analytical methods with different detection ranges and separation methods. Solvent extractable HCs that are not removed during solvent evaporation at 70 to 85°C temperature and capable of being weighed can be analyzed using gravimetric analysis method (SPEIGHT 2005). The author added that the method is simple, fast and economical for the analysis of HCs with higher boiling points. There is a lot of gravimetric methods based on extracting methods and cleaning up steps. United States Environmental Protection Agency (US EPA) methods 9071B (US EPA 1998) and 1664B (US EPA 2010) are the most commonly used methods for the analysis of hexane extractable material (HEM) from solid matrix and water samples respectively (SPEIGHT 2015). The methods involve treatments of the samples with different chemicals if needed, extraction of HEM with n-hexane, separation of HEM from n-hexane, desiccating and weighing of HEM (US EPA 1998, 2010). They are suitable specifically for non-volatile and fully normal hexane extractable HCs (US EPA 1998).

Additionally, soil water content can be effectively measured through fast and non-destructive indirect methods. The methods utilize different variables that could change with the change of soil water contents (BITTELLI 2011). Electromagnetic based methods which make use of the high relative permittivity,  $\epsilon_r$  (also known as dielectric constant) of water have received the most attention (KIZITO *et al.* 2008). Crude oil products and silica sand have  $\epsilon_r$  values around 2.2, while water and air have 80 and 1  $\epsilon_r$  values respectively (REDMAN 2009; FREDLUND *et al.* 2012). It is, therefore, the change of the soil water content that changes  $\epsilon_a$  of the soil decidedly. Soil moisture sensors could measure soil water content effectively based on  $\epsilon_a$  of the soil and Eq. (1) developed by TOPP *et al.* (1980) is widely used for the calculation of mineral soil water content based on  $\epsilon_a$ .

$$\theta_w = 4.3 \times 10^{-6} \epsilon_a^3 - 5.5 \times 10^{-4} \epsilon_a^2 + 2.92 \times 10^{-2} \epsilon_a - 5.3 \times 10^{-2} \quad (1)$$

where:

- $\theta_w$  – volumetric water content ( $\text{cm}^3/\text{cm}^3$ )
- $\epsilon_a$  – apparent (bulk) relative permittivity of the porous media (–)

$\epsilon_a$  of a porous media depends on its pore volumetric fluid content (FRANCISCA & MONTORO 2012) and dielectric mixing model (DMM) (Eq. (2)) can be used to estimate water and light non-aqueous phase liquid (LNAPL) contents of the porous media. DMM considers that  $\epsilon_a$  of the porous media is the sum of the results of individual phase  $\epsilon_r$  with their respective volumes (HARIDY *et al.* 2004). The decrease in the percentage of air filled pores increases the  $\epsilon_a$  of the porous media. PERSSON and BERNDTSSON (2002); HARIDY *et al.* (2004); FRANCISCA and MONTORO (2012) and COMEGNA *et al.* (2016) among others used DMM to estimate volumetric water ( $\theta_w$ ) and NAPL ( $\theta_{\text{LNAPL}}$ ) contents. For solid-water-LNAPL-air phase system, DMM can be expressed as follows:

$$\epsilon_a^\alpha = (1 - P)\epsilon_s^\alpha + \theta_w \epsilon_w^\alpha + \theta_{\text{LNAPL}} \epsilon_{\text{LNAPL}}^\alpha + (P - (\theta_w + \theta_{\text{LNAPL}}))\epsilon_{\text{air}}^\alpha \quad (2)$$

where:

- $\alpha$  – empirical parameter accounting for soil geometry with value between –1 and 1
- $P$  – porosity
- $\epsilon_s, \epsilon_w, \epsilon_{\text{LNAPL}}$  and  $\epsilon_{\text{air}}$  – relative permittivity of soil particles, water, LNAPL and air, respectively
- $\theta_w, \theta_{\text{LNAPL}}$  – volumetric water and LNAPLs contents, respectively

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Both water and LNAPL of a sample can be determined through gravimetric analysis method. Water is determined by directly removing it from the sample while LNAPL is determined first by extracting it from the sample and then by removing the solvent from the extract. Determination of both from a sample could be difficult if the oil could be lost with water at 105°C oven temperature. MATULA *et al.* (2008) and BÁŤKOVÁ *et al.* (2014) sampled both non-volatile LNAPL and water simultaneously from porous media and analyzed them using gravimetric analysis method. Due to its high porosity and high affinity for the environmental contaminants, activated carbon has been used in different treatments.

For this study sample columns subjected to different water to LNAPL ratios were prepared. Water and LNAPL contents of the sample columns were sampled using ACP and analyzed using gravimetric analysis method. Water contents of the sample columns were also measured using soil moisture sensors and their LNAPL contents were estimated from  $\epsilon_a$  of the sample columns. Finally, gravimetric water and LNAPL contents were determined from destructed samples of the sample columns. The objective of the study is to evaluate different methods for the porous media water and LNAPL contents estimation.

## MATERIAL AND METHODS

**Experimental setup.** The experiment was done in the laboratory under controlled conditions: temperature  $22 \pm 1^\circ\text{C}$  and relative humidity  $27 \pm 3\%$ . Sample columns were prepared from inert silica sand and subjected to different water to LNAPL ratios. LNAPL and water contents of the prepared sample columns were measured using different methods. The experimental setup is presented as Figure 1.

**Experimental materials.** Sample columns for the study were prepared from foundry silica sand commercially known as ST56 (Sklopísek Střeleč, a.s., Újezd pod Troskami, Czech Republic). The sand has narrow and uniform particle size distribution with 0.085 and 0.143 mm effective and median grain sizes respectively. The sand is made up of 99%  $\text{SiO}_2$  (with particle density of 2.65 g per  $\text{cm}^3$ ). It was supplied in oven dry condition. The test result from 10 samples, each 15 to 20 g, oven dried at 105°C temperature for 24 h shows that its water content was 0.04% in average by mass with 0.03 standard deviation.

Medicinal grade white mineral oil commercially known as Marcol 82 (Lubstar a.s., Czech Republic) was used as LNAPL. Quality of the oil: inertness, immiscibility with water, higher boiling point and less dense compared to water were some of the considerations to select it for this experiment following MATULA *et al.* (2008) and BÁŤKOVÁ *et al.* (2014). Other liquids used in the experiment were drinking quality tap water and normal hexane (n-hexane; Penta s.r.o., Czech Republic). Hexane like Marcol 82 is an LNAPL. However, in this work the term oil and LNAPL refer to Marcol 82 only. For some of the properties of the liquids used, see Table 1.

Water and LNAPL were sampled from sample column using ACP Silcarbon SC40 (Brenntag, Ltd., Czech Republic). ACP used has the apparent density  $450 \pm 25 \text{ kg/m}^3$  with the specific surface area approximately  $1100 \text{ m}^2/\text{g}$ . SC40 is produced with average diameter 4 mm but varying length. For the whole experiment, ACP with narrow range both in diameter (around 4 mm) and length (8.5 to 10.5 mm) were used following the results from BÁŤKOVÁ *et al.* (2014) and ELSAYED *et al.* (2014). The size of the pellets was measured using a digital sliding gauge EXTOL® Premium (Všestary, Czech Republic) with an accuracy of 0.01 mm. The sampling of water and LNAPL was taken from the center of the sample column using oven-dried ACPs to a constant mass at 105°C for 24 h. ACP was placed to the sampling

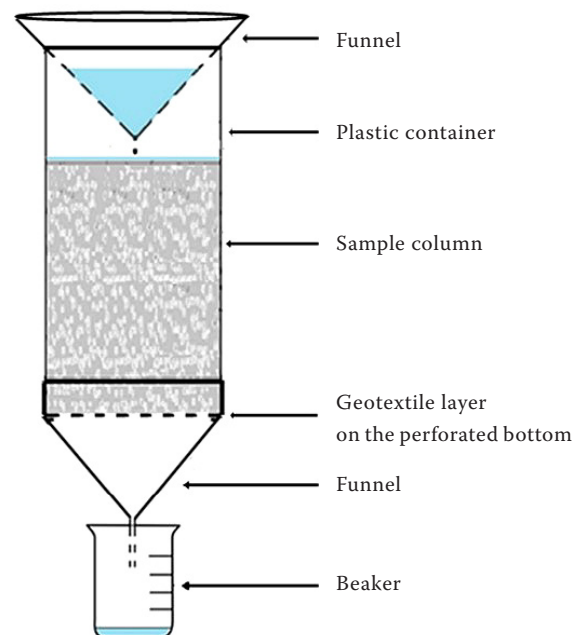


Figure 1. Schematic representation of experimental sample column setup

place using lab-built metal sampler and the detail of the sampling and analysis procedures used were based on MATULA *et al.* (2008) and BÁTĚKOVÁ *et al.* (2014). Water was removed from the sampled liquid using oven-drying process and the remaining was assumed to be the mass of LNAPL and ACP. Oven drying and handling of the ACPs during the whole experiment was taken place in temperature resistant small glass Petri Dishes. Oven-dried ACPs and the Petri Dishes were cooled down in a desiccator.

Sample column water content was measured using soil moisture sensors. Sensors used in this experiment were 5TE and ECH<sub>2</sub>O-TE with data reader ProChek (Decagon Devices Inc., Pullman, USA). The measurements were taken three times from each sample column from the top 6 cm following KIZITO *et al.* (2008); Decagon Devices (2010, 2016). The mineral soil calibration option was chosen in ProCheck reader. The reader gives volumetric water content based on  $\epsilon_a$  of the sample column (Decagon Devices 2016). Electrical conductivity (EC) readings were also taken and EC for extracted solution was calculated based on HILHORST (2000) model from bulk soil EC (Decagon Devices 2010). Sample columns' LNAPL contents were estimated from  $\epsilon_a$  after converting the volumetric water content to  $\epsilon_a$  using Eq. (1). LNAPL content was estimated using DMM (Eq. (2)) and the methodology is described in PERSSON and BERNDTSSON (2002); HARIDY *et al.* (2004); FRANCISCA and MONTORO (2012) and COMEGNA *et al.* (2016).

Finally, water and LNAPL contents in the sample columns were determined using thermo-gravimetric analysis method from destructed samples, each 10 to 20 g taken from different positions, roughly from top, middle and bottom of the sample columns. The samples were oven dried at 105°C for 24 h and cooled to constant mass in a desiccator and gravimetric water content of the destructed sample was determined. Samples LNAPL content was determined by extracting LNAPL from the oven-dried samples following method 9071B of US EPA (1998)

for hexane extractable material. LNAPL was extracted from a sample three times, each time using 30 ml of hexane with 95% concentration, shaken for 10 to 20 min and left for 10 more min. The extract was flittered using filter paper (Whitman 40) and eluted through glass column. The glass column was 3 mm in diameter, 15 cm long with filter disc at the bottom outlet. It was packed with 3 to 5 g granular anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) oven dried for 12h at 140°C. Na<sub>2</sub>SO<sub>4</sub> used to remove traces of water from extracted LNAPL was from Sigma-Aldrich (Prague, the Czech Republic) with purity  $\geq 99.0\%$ . The method also recommends silica gel treatment. However, sand used for the experiment is almost free of organic matter (99% SiO<sub>2</sub>) and according to VILLALOBOS *et al.* (2008), silica gel treatment is not necessary for samples with less than 5% organic matter content. Anhydrous Na<sub>2</sub>SO<sub>4</sub> packed column with filter paper was rinsed with 10 ml of hexane at the beginning, and 10 ml of hexane was used at the end. The extracts were oven dried at 80°C for three to four h while the sand was oven dried at 105°C for 24 h and gravimetric LNAPL contents was determined. Gravimetric water and LNAPL contents were used to calculate the respective volumetric contents of the sample columns using bulk density of the sample columns (1.5 g/cm<sup>3</sup>) and densities of the liquids (Table 1).

HEM content of the sand used in the experiment and the extraction efficiency of the LNAPL were evaluated. Extraction was done from 10 to 20 g of the sand mixed with 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml of the oil, each in three replications, applied using volumetric pipette. The extraction was done also from dry sand, and oven-dried sand initially wetted with 3.0 ml of water. The extraction and treatment of the extracts from the sand samples were in the same way as that of sample columns gravimetric water and LNAPL contents determination. The mass of the sand before and after extraction, and the mass of the extracted oil were taken. The result shows that hexane could extract the oil used for the experi-

Table 1. Some properties of liquids used in the experiment

Liquid	Volume (%)	Density (g/ml) <sup>a</sup>	Boiling point (°C)	Dynamic viscosity (mPa·s)	Aqueous solubility (g/l)	Refractive index
Water	100	1	100	1.00 <sup>a</sup>	–	1.33
Marcol 82	100	0.855	> 150	29 <sup>a</sup>	immiscible	1.46–1.47
Hexane	95	0.659	69	0.30 <sup>b</sup>	9.5–13 <sup>c</sup>	1.38

<sup>a</sup>20°C; <sup>b</sup>25°C; <sup>c</sup>in distilled water at 20°C

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Table 2. Basic statistics of mass (g) of saturated sample columns with different water to LNAPL ratios

Ratio	100:0	90:10	75:25	65:35	50:50	35:65	25:75	10:90	0:100
Mean	1514.0	1511.9	1507.6	1506.6	1483.5	1465.1	1501.5	1492.1	1455.6
SD	1.28	1.79	2.06	2.03	2.99	3.62	3.98	2.70	1.50
Minimum	1512.6	1510.0	1506.0	1504.7	1480.6	1462.1	1497.0	1489.9	1454.7
Maximum	1514.8	1513.2	1509.9	1508.8	1486.5	1469.1	1504.5	1495.1	1457.3

SD – standard deviation

ment efficiently from the sand with the coefficient of determination,  $r^2 = 0.99$ . The result also shows that no value of extracts observed from the extraction of both dry and oven-dried water wetted sand samples, and hence the sand is free from HEM that could affect the result during the experiment.

**Sample column preparation.** Sample column was prepared from ST56 into plastic container with internal diameter 11.3 cm and height 8 cm, to 4 layers each 2 cm. The sand was packed with  $1.5 \text{ g/cm}^3$  dry bulk density and the porosity and a pore volume of the sample column were 43.4% and  $347 \text{ cm}^3$  respectively. To make repacking suitable, between 10 to 20% pore volume (pv) of the liquid (LNAPL or water) was applied to 300 g loose dry sand. The sand and the liquid were mixed thoroughly and repacked into the container uniformly layer by layer. The rest 90 to 80% of the liquid was applied from the top and drained down and redistributed by gravity for 24 h for the equilibrium condition. To be consistent, totally greater than one pv ( $365 \text{ cm}^3$ ) of liquid was applied to a sample column. The experiment was done on three replications of nine different LNAPL to water ratios: 100:0, 90:10, 75:25, 65:35, 50:50, 35:65, 25:75, 10:90 and 0:100 by volume. Except for the sample columns subject to either only water or LNAPL, liquid with lower amount in the ratio was used in sample packing, while the rest of it and the other liquid with higher amount in the ratio were applied from the top respectively. Basic statistics of the prepared sample columns is presented under Table 2. By neglecting the amount of lost sand during sample column preparation, which is difficult under practical condition, the total amount of liquid (water + LNAPL) could be roughly estimated from the mean value. On the other hand, from visual observation and oven dry test, the drained-out liquid by gravity from all sample columns where both water and LNAPL used were only LNAPL except from 90:10 water to LNAPL ratio, which was only water.

Mass measurements during the experiment were taken using digital balance Denver Instrument SI-234A

(Orville, USA) that has the precision of 0.0001 g. The values were used to compare the methods used for the determination of porous media water and LNAPL contents. Proper measurement and knowledge of water and LNAPL interaction in porous media is very useful to clean up LNAPL contaminated sites effectively. Collected data were analyzed using SPSS, Microsoft Excel 2013 and Microsoft Excel 2013 integrated with QI Macros 2015.

## RESULTS AND DISCUSSION

**Water and LNAPL sampled from sample columns using ACP.** Water and LNAPL were sampled from sample column using ACPs and the result is presented as Figure 2. The results show that ACP could sample water and LNAPL proportionally from the columns saturated with different water to LNAPL ratios with high standard deviations. Nevertheless, it could sample more liquid (LNAPL + water) when the amount of LNAPL in the applied ratio was higher, and here afterwards in this paper unless stated the first value from the ratio of applied liquids to the sample column will be the value of LNAPL. Additionally, the graph shows that ACP could sample more liquid from sample columns saturated with either LNAPL or water despite there were other sample columns with higher liquid contents (Table 2). The reason for the difference in the adsorption from the sample columns subjected to different water to LNAPL ratios could be due to the wettability preference of the sand to the liquids used, the mobility and amount of the liquid used, and/or the affinity of the ACP itself to the liquids used.

DOMENICO and SCHWARTZ (1998) among others described that pure and clean silica sand is water wettable with respect to any HCs (NAPLs). Wetting phase has stronger affinity for the solid particles and expels the other phase towards the center of the pore spaces (MAYER & HASSANIZADEH 2005). ABDALLAH *et al.* (2007) stated that large pores are LNAPL wet-

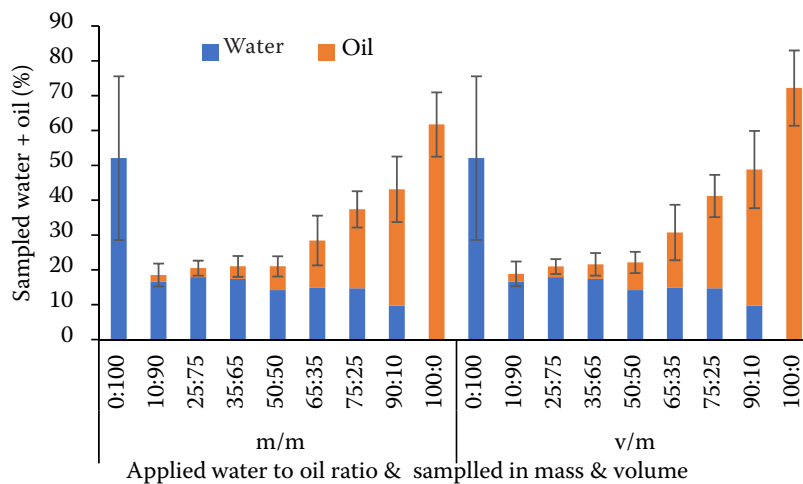


Figure 2. Amount of water and light non-aqueous phase liquid (LNAPL) (%) adsorbed to activated carbon pellets (ACP) from sample columns subjected to different water to LNAPL ratios: m/m (mass of liquid adsorbed (g) per unit mass of ACP (g)) and v/m (volume of liquid (ml) adsorbed per unit mass of ACP (g))

table while small pores are water wettable. Results from drained out liquids from all sample columns subjected to different ratios where LNAPL was a part show that all the drained-out liquid was LNAPL except from 10:90. This could show that the sand was water wettable with respect to LNAPL. Hence, the presence of non-wetting phase in the bigger pores could give mobility and adsorption opportunity for non-wetting phase over wetting phase. From the trend of the graph in general and the amount of liquid sampled from sample columns saturated with only one liquid compared to where the two liquids used, it could be concluded that ACP has stronger affinity for LNAPL with respect to water. ACP could sample more liquid from sample columns saturated with one liquid compared to where two liquids used due to the absence of capillary pressure in sample columns where only one liquid was used.

**Sample columns water content measured using soil moisture sensors.** Sample column  $\theta_w$  was measured using 5TE and ECH<sub>2</sub>O-TE soil moisture sensors from approximately the top 6 cm. The measured  $\theta_w$ , bulk sample column EC, and calculated extract solution EC and  $\epsilon_a$  are presented in Figure 3. The graph shows that both sensors responded to sample columns water content pretty good with a slight difference in measuring the water content between them, especially at lower water contents. Individual sensors measured water contents with low variance which shows both the quality of the sensors used and the uniformity of the prepared sample columns for the experiment. However,  $\pm 3\%$  for water content

values is expected using TOPP *et al.* (1980) model used for both sensors (Decagon Devices 2010). The graph also shows that EC decreases with increasing LNAPL and decreasing water content. Result from KOLAY *et al.* (2016) shows that electrical resistivity increases with increasing NAPL in kaolinite and kaolinite–sand mixtures. Meanwhile, result from DENG *et al.* (2018) among many others shows that electrical conductivity of the soil decreases with decreasing water saturation. On the other hand, both sensors responded to the bulk sample column EC in the same way and gave almost the same value. Therefore, values from 5TE which were used for the

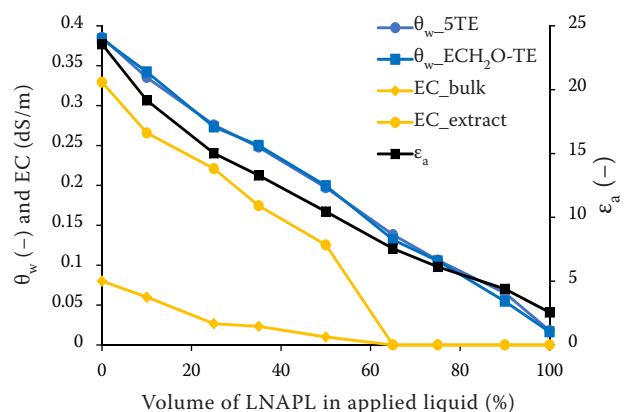


Figure 3. Graph of volumetric water content ( $\theta_w$ ), bulk electrical conductivity (EC<sub>bulk</sub>) and extract solution EC (EC<sub>extract</sub>) and bulk relative permittivity ( $\epsilon_a$ ) of sample columns subjected to different light non-aqueous phase liquid (LNAPL) to water ratios measured by soil moisture sensors

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construction of bulk EC graph were used to calculate EC for the extract solution. Calculation for the extract solution EC was based on the recommended values by Decagon Devices (2016). The calculated maximum value of extract solution EC (0.36 dS/m) is in the recommended range for the extract solution EC value by Decagon Devices (2016) to use the sensors for water content measurement (< 10 dS/m).

**Water and LNAPL content determined using gravimetric analysis method.** Water and LNAPL contents of the sample columns were determined from destructed samples taken from sample columns using gravimetric analysis method. The average values calculated from the three positions and the average values for the top and middle positions (Tomi) for different applied ratios are presented in Figure 4. The graph shows that the  $\theta_w$  and  $\theta_{LNAPL}$  from the three positions (for the sample columns) and Tomi are the same for sample columns subjected to either LNAPL or water. It also shows that  $\theta_w$  are the same for sample columns subjected to either higher or lower LNAPL to water ratios. However, for the intermediate applied LNAPL to water ratios, there were some differences in  $\theta_w$  for the sample column and Tomi though the values were in the ranges of standard deviations of the sample columns  $\theta_w$ . The result also shows that even though there were small differences in  $\theta_{LNAPL}$  values for the sample columns and Tomi,  $\theta_{LNAPL}$  value for the Tomi is with in standard deviations of  $\theta_{LNAPL}$  for the sample column.

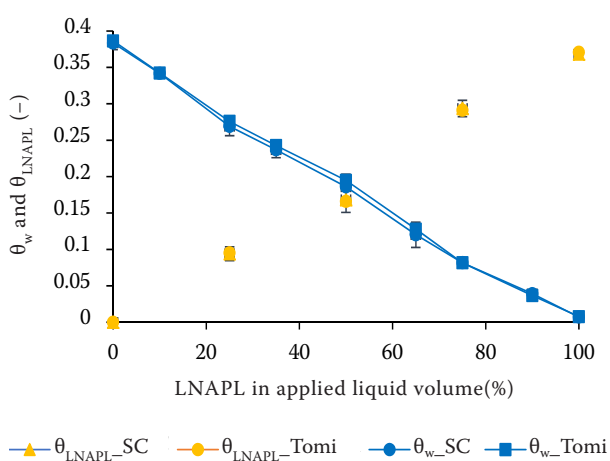


Figure 4. Graph of average volumetric water and LNAPL content ( $\theta_w$  and  $\theta_{LNAPL}$ ) for sample columns (SC) and top and middle positions (Tomi) determined through gravimetric analysis method against light non-aqueous phase liquid (LNAPL) values in applied liquid volume (%)

$\theta_w$  measured through indirect method using soil moisture sensors: 5TE and ECH<sub>2</sub>O-TE and determined through gravimetric analysis method are presented under Figure 5 for comparison. Because soil moisture sensors measured roughly from the top 6 cm of the 8 cm long sample columns,  $\theta_w$  of Tomi was used from gravimetric analysis method.  $\theta_w$  from Tomi before (TomiB) and after (TomiA) removing LNAPL from dry sand particle are presented under Figure 5. The graphs show that  $\theta_w$  values from both direct and indirect methods are the same for the lower LNAPL volume in applied ratios. However, for the higher LNAPL to water ratios,  $\theta_w$  from gravimetric analysis method is lower than  $\theta_w$  from measured through soil moisture sensors even after removing LNAPL from the dry sand particle. In contrary to the result, higher  $\theta_w$  could be expected from gravimetric analysis if volatile LNAPLs were used in the study. However, the oil used was nonvolatile and the loss to oven-dry temperature was tested and it was almost negligible. GARDNER (1986); TOPP and FERRÉ (2002); HILLEL (2004) and MANSUR *et al.* (2015) among others, mentioned that thermo-gravimetric analysis method water content measurement could be affected both by the oven dry loss of non-water soil constituents (substances) and by the retaining of some water in heavy clay sample or the presence of non-volatile organic liquids in the sample of interest. Figure 5 shows that LNAPL used in the study did not affect porous media water content measurement from both direct and indirect

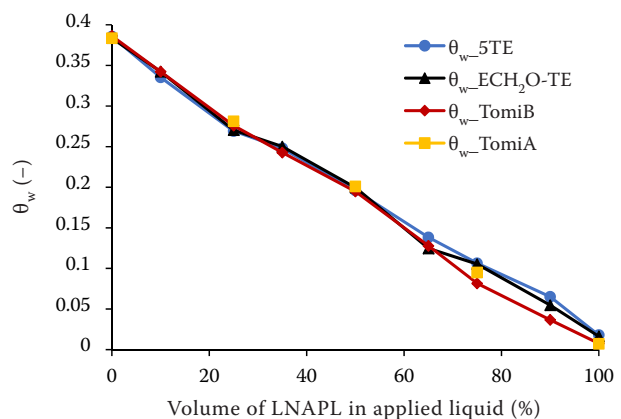


Figure 5. Graph of volumetric water content ( $\theta_w$ ) from soil moisture sensors (5TE and ECH<sub>2</sub>O-TE) and gravimetric analysis method from sample column subjected to different light non-aqueous phase liquid (LNAPL) to water ratio by volume (%): TomiB & TomiA (average values of  $\theta_w$  determined through gravimetric analysis method before and after removing LNAPL from dry sand particle)

Table 3. Estimated values of  $\alpha$  and  $\theta_{LNAPL}$  from measured values of  $\epsilon_a$ ,  $\theta_w$  and  $\theta_{LNAPL}$  using dielectric mixing model (DMM)

$\epsilon_a$ (-)	EC (dS/m)	$\theta_w^a$	$\theta_w^b$	$\theta_{LNAPL}^c$	$\alpha$ (-)	$\theta_{LNAPL}^d$ (cm <sup>3</sup> /cm <sup>3</sup> )
23.57	0.07	0.39	0.38	0.00	0.67	0.00
19.17	0.05	0.34	-	-	0.64	0.04
15.02	0.02	0.28	0.28	0.09	0.62	0.09
13.29	0.02	0.25	-	-	0.62	0.13
10.45	0.01	0.20	0.20	0.17	0.62	0.17
7.55	0.00	0.14	-	-	0.63	0.22
6.12	0.00	0.11	0.09	0.29	0.63	0.29
4.39	0.00	0.07	-	-	0.62	0.34
2.55	0.00	0.02	0.01	0.37	0.50	0.37

$\epsilon_a$  – bulk relative permittivity; EC – electrical conductivity;  $\alpha$  – an empirical parameter accounting for soil geometry; <sup>a</sup> $\theta_w$  from soil moisture sensor; <sup>b</sup> $\theta_w$  from gravimetric analysis method; <sup>c</sup> $\theta_{LNAPL}$  estimated using DMM; <sup>d</sup> $\theta_{LNAPL}$  from gravimetric analysis method

methods roughly below 50 : 50 applied LNAPL to water ratios. However, the presence of LNAPL affected both methods at higher ratios. The presence of non-volatile LNAPL increased the oven-dry mass of the solid part of the sample and resulted in under estimation of  $\theta_w$  using gravimetric analysis method. On the other hand, LNAPL modified  $\epsilon_a$  of the sample columns which resulted in higher  $\theta_w$  from soil moisture sensors.

**LNAPL volume estimation from  $\epsilon_a$ .** Figure 5 shows that the presence of non-volatile LNAPL content

affected  $\theta_w$  measured using soil moisture sensors through the modification of  $\epsilon_a$  of the porous media. Modified  $\epsilon_a$  can be used to estimate  $\theta_{LNAPL}$  using DMM (Eq. 2).  $\theta_w$  measured using soil moisture sensors (Figure 3), and  $\theta_w$  and  $\theta_{LNAPL}$  determined through gravimetric analysis method (Figure 4) were used to estimate  $\alpha$  of the model first and the applicability of DMM (Eq. (2)) for the estimation of porous media LNAPL content was assessed. PERSSON and BERNDTSSON (2002) and HARIDY *et al.* (2004) among others estimated  $\theta_{LNAPL}$  from  $\epsilon_r$  and electrical conductivity (EC) values measured from the samples. However, the EC values from the sensors used were zero for applied LNAPL to water ratios greater than 65:35. Most contaminants exist in subsurface in lower amounts. However,  $\theta_w$  from the direct and indirect methods were significantly different at higher  $\theta_{LNAPL}$  (Figure 5).

The model was evaluated and based on the  $\epsilon_r$  of the materials used (from literature, see the introduction part). From measured values of  $\theta_w$  and  $\theta_{LNAPL}$ ,  $\alpha$  was fitted and optimized using Excel Solver Program (2016). The value of  $\alpha$  was different for different phase system used. The value was 0.67 for three-phase system (sand, water and air) and 0.50 for sand-LNAPL-air three-phase system (Table 3). For four-phase system (sand, water, LNAPL and air) the value was between 0.62 and 0.64 (Table 3). The values are in the ranges of 0.46 to 0.67 for three-phase system and 0.39 to 0.81 for four-phase system mentioned by PERSSON and BERNDTSSON (2002). The model was tested for  $\theta_{LNAPL}$  content using the  $\alpha$  values and  $\theta_{LNAPL}$  content for the other sample

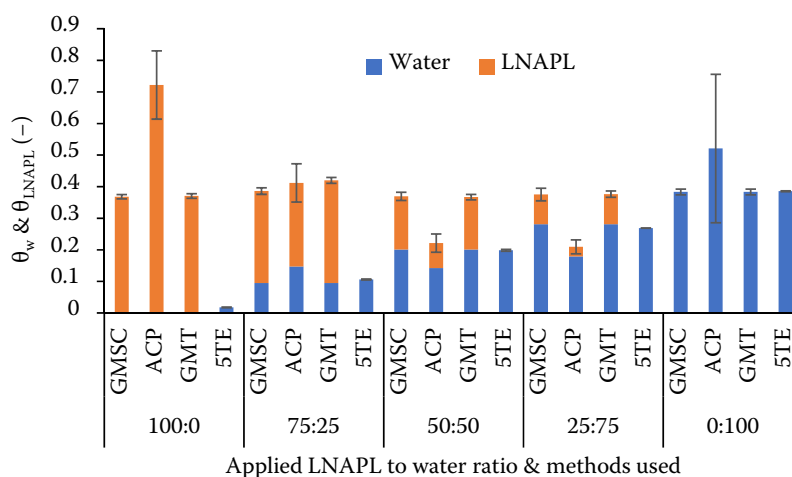


Figure 6. Amount of water and light non-aqueous phase liquid (LNAPL) obtained using different methods from sample columns subjected to different LNAPL to water ratios: GMSC & GMT (average  $\theta_w$  for the sample columns and top 6 cm respectively using gravimetric analysis method), 5TE (average  $\theta_w$  measured using soil moisture sensor) and ACP (volume of the liquid sampled per mass of activated carbon pellet)



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columns were appropriately estimated (Table 3). Similarly, COMEGNA *et al.* (2016) could estimate  $\theta_{\text{LNAPL}}$  with acceptable accuracy using DMM.

In this study, as the LNAPL used was non-volatile, it could be possible to sample and analyze both water and LNAPL using ACP. ACP used could sample both liquid proportionally, but it could sample with higher standard deviations compared to the other methods used (Figure 6). It sampled more liquid from sample columns saturated with only one liquid. The amount of sampled liquid (water + LNAPL) increases with increasing LNAPL to water ratio from sample columns saturated with both liquids (Figure 6). The non-volatility of the LNAPL also enabled the analysis of the water and LNAPL through gravimetric analysis method. However, it affected  $\theta_w$  measured using both direct and indirect methods.  $\theta_w$  determined through gravimetric method was corrected after removing LNAPL from the oven-dried sand. The presence of the LNAPL modified the  $\epsilon_a$  of the sample columns. The modified  $\epsilon_a$  was used to estimate  $\theta_{\text{LNAPL}}$  content of the sample column. Figure 6 shows that  $\theta_w$  measured using soil moisture sensors and gravimetric analysis method were the same compared to the amount of water sampled using ACP.

## CONCLUSIONS

Different methods are used to measure porous media water or LNAPL contents. Methods used in this study responded differently for the determination of porous media water and non-volatile LNAPL contents. Generally, gravimetric analysis method used was the best method to estimate sample columns water and LNAPL contents. However, since LNAPL used was non-volatile at oven temperature (105°C), water content from gravimetric analysis method was underestimated. But soil moisture sensors gave better estimation for water content for the whole ranges. It could be possible to estimate LNAPL content of the porous media from  $\epsilon_a$  using DMM. On the other hand, even though it could be possible to sample both water and LNAPL from porous media using ACP, the pellets sampled the liquids with higher standard deviations. To use ACP for the quantification purpose, more attention has to be given for the production of homogeneous pellets.

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