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MAPPING OF NON-AQUEOUS PHASE LIQUIDS USING TIME DOMAIN REFLECTOMETRY

Kartering av icke vattenlösliga vätskor med tidsdomän reflektometri

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Abstract

A two-dimensional multi-fluid flow experiment was performed in a container (45 cm x 54 cm x 20 cm) filled with fine sandy soil. A dye stained light nonaqueous phase liquid (LNAPL) was applied in four releases over a rectangular area of 5 x 20 cm at the center of the soil surface. The releases varied in the way of the application; constant rate, constant head, and variable head. 42 Time Domain Reflectometry probes (TDR) was used to detect the transport and the location of the LNAPL and water with time. In addition to the TDR measurements images about the LNPAL migration were taken using a digital camera. Significant changes in the responses of TDR were observed. Based on the information from the mapping of the LNAPLs using digital pictures and fluid mass balance calculations, it was shown that the TDR system can provide accurate information on location, distribution, and quantity of LNAPLs in the unsaturated zone in a multi-fluid system. It was possible to reach an estimation of the water content (θ_w) with an error less than 0.01 $m^3\ m^{-3}$ and the NAPL content with an error less than 0.045 $m^3\ m^{-3}$.

Key words – LNAPL, migration, detection, mapping, Time domain reflectometry

Sammanfattning

Ett tvådimensionellt transportförsök utfördes i en behållare (45 cm x 54 cm x 20 cm) fylld med fin sand. En färgad icke vattenlöslig vätska (LNAPL) spreds över en rektangulär yta, 5 x 20 cm, på försöksytan. Spridningen gjordes i fyra omgångar på olika sätt; med konstant flöde, konstant nivå och varierande nivå. Fyrtiotvå tidsdomän reflektometri (TDR) prober användes för att följa LNAPL transporten. Förutom TDR proberna följdes också transporten av LNAPL med en digital kamera som tog bilder av den transparanta framsidan på behållaren. Resultaten visar att TDR mätningarna kunde detektera transporten av LNAPL. Felet i mätningarna var 0.01 $m^3\ m^{-3}$ för vattenhaltsmätningen och 0.045 $m^3\ m^{-3}$ för LNAPL-mätningen. Resultaten visar att TDR är en lovande metod för att följa utbredningen av LNAPL i marken.

1 Introduction

Subsurface and groundwater contamination by non-aqueous phase liquids (NAPLs) is a serious environmental problem. The migration of NAPLs in the unsaturated zone is a complex process due to that they exist in several phases and due to their non mixing behaviour with water. After entering the soil surface, NAPLs migrate vertically until they pool above the groundwater table (if they are lighter than water) or below the groundwater table on layers with low permeability (if they are denser then water). They leave disconnected blobs behind in the void zone which are known as residual NAPL. If this residual part is not removed, it acts as a long term source

of groundwater pollution. Understanding the NAPL behavior in the subsurface is critical for soil cleaning and NAPLs remediation technique. Also, information about the NAPL distribution and location are required in order to design an effective remediation method.

Several laboratory experiments of LNAPL infiltration and distribution in the porous media have been carried out. Different geophysical techniques have been used for detecting the NAPL migration. Some of these involved certain types of radiation or light energy such as dual gamma radiation, X-ray absorption, X-ray attenuation, light transmission (LTM) and computerized tomography (Oostrom et al., 1997; Oostrom and Lenhard, 1998; Darnault et al., 2001). Other methods like ground penetrating radar and time domain reflectometry (TDR) rely on the changes in electrical properties of contaminated soil. Redman et al. (1991) used TDR to measure the dielectric permittivity over a period of 67 days following a controlled release of perchloroethylene (PCE). They demonstrated that PCE caused significant changes in the soil dielectric permittivity. To provide a detailed level of information about the migration and extent of NAPLs in the subsurface, geophysical techniques in conjunction with images of dye stained NAPL have also been performed (Poulsen and Kueper, 1992; Kuper et al., 1993; Brewster et al., 1995).

Despite the fact that many researcher focus on studying the response of geophysical techniques for the presence of NAPLs in the subsurface, only a small number aimed to find out a correlation between the soil dielectrical properties and the NAPL content (θ_{NAPL}). A mixing model was applied by Redman and Deryck (1994) to estimate θ_{NAPL} in a contaminated soil. Their model needed information of the water content (θ_w). Persson and Berndtsson (2002) examined the ability of TDR for measuring θ_{NAPL} in the saturated and unsaturated soil zone employing information on the soil dielectric constant (K_a) and soil electric conductivity (σ_a). They concluded that in the saturated zone knowledge on either K_a or σ_a is sufficient to estimate θ_{NAPL}. But for unsaturated conditions, even though there is information on θ_w, it is still necessary to measure both K_a and σ_a to quantify θ_{NAPL}. Haridy et al. (2004) provided a new hypothesis for estimating both θ_w and θ_{NAPL} from TDR measurements in fine sandy soil without further information on θ_w. However, studies of NAPL migration using TDR are still very rare.

The main objective of this study was to examine the ability of using TDR to detect LNAPL and water content during dynamic flow through the unsaturated zone. We used the proposed methodology by Haridy et al. (2004) to estimate both θ_w and θ_{NAPL} using TDR measurements to describe the migration behavior of LNAPL in variably saturated fine sandy soil.

2 Material and methods

2.1 Experimental set up

A two-dimensional multifluid flow experiment through variably saturated sandy soil was carried out. Soil was packed in a container; 0.54 m long, 0.55 m high and 0.20 m wide. The walls of the container were made of 0.01 m thick Plexiglas. At the bottom of the container eight drainage pipes were placed.

The bottom of the container was filled with 0.03 m of pea gravel followed by 0.02 m of coarse sand. This configuration allowed unrestricted drainage of water during the experiment. The rest of the container was packed with the target soil; a sandy soil with a grain size of 0.0005 m. The soil was packed by adding increments of 0.05 m sand to the box and tapping on the walls with a rubber hammer. The final dry bulk density was 1.61 g/cm^3.

Rape-seed oil was chosen as the LNAPL of interest because of its low solubility in water and its comparatively low vapour pressure. The oil was dyed with Sudan IV (Brewster et al. 1995), a non-volatile hydrophobic red dye, to make it easy to visually identify the oil migration. This dye was used because of its low toxicity and low sorption. Tap water containing 2 g KBr/l was used to counter the influence of the oil on the measured σ_a accurately. Pure tap water was applied at the end of the experiment to examine the ability of the TDR to distinguish between the flow of the different fluid in the same media (tap water, saline water, and LNAPL).

A computer-controlled automated TDR system with a Tektronix 1502C cable tester was employed for all measurements. A total of 42 probes were connected to the TDR through sixth SDMX50 multiplexer. The three-rod probes were 0.18 m in length and had a wire spacing of 0.04 m. Holes were made on the backside of the container to insert the probes horizontally. The probes were arranged in a rectangular net with horizontal spacing of 8 cm and vertical spacing of 5 cm. The WinTDR program (developed by the Soil Physics Group at Utah State University) was used to control the TDR and perform signal analysis to calculate the values of K_a and σ_a. Continuous measurements of K_a and σ_a using TDR were made every ten minutes for each probe during all experiments.

A schematic picture of the probes arrangement is shown in Fig. 1. Each probe was defined by two numbers: the first represented the channel and the second represented the probe number. For example probe (2.4) meant the fourth probe of the second channel. In our work the location of the probes was identified by the depth measured from the top of the soil and horizontal distance from the container center. The negative sign for

Table 1. *Constants and coefficients of equation (2), from Haridy et al. (2004).*

Water content (θ_w) $m^3\ m^{-3}$	D_1	D_2	D_3	D_4	R^2
0.00	–4.3814	5.0648	–0.9878	0.1116	0.9728
0.05	–0.0142	0.3639	0.0251	0.0470	0.9883
0.10	0.5925	–1.4027	1.2959	–0.2269	0.9608
0.15	–0.0647	0.1217	0.1092	0.0325	0.9805

the horizontal distance meant that the probe was located to the left of the container centerline.

The LNAPLs migration was also photographed using a digital camera placed on a tripod and left in that position throughout the experiments. During the experiments several pictures were taken with the digital camera in order to visualize the migration. Additionally to the pictures from the front side of the box, the location of the oil front on the back side of the box was noted after every oil release.

2.2 NAPL saturation from TDR measurements

The ability of the TDR techniques to estimate both θ_{NAPL} and θ_w was first tested by Persson and Berndtsson (2002). Later, Haridy et al. (2004) introduced a new hypothesis for estimating θ_{NAPL} and θ_w via the measured σ_a and K_a. They noticed that LNAPL has no effect on the measured electric conductivity. Thus θ_w can be determined using a third- order equation of θ_w -σ_a. The fitted relationship leads to the following equation:

$$\theta_w = 33.45\sigma_a^3 - 19.37\sigma_a^2 + 4.424\sigma_a - 0.1233 \quad (1)$$

Knowing θ_w, the dielectric constant of the soil matrix when it contains water and air could be calculated using Topp's empirical equation with calibrated parameters for this soil. Then it is possible to differentiate the effect of the oil on the measured bulk dielectric constant and relate it to $\theta_{NAPL.}$ According to their methodology θ_{NAPL} can be estimated by the following equation

$$\theta_{LNAPL} = D_1^3\, K_{ao} + D_2\, K_{ao}^2 + D_3\, K_{ao} + D_4 \quad (2)$$

where K_{ao} the part of K_a which is affected by the change of θ_{NAPL}, D_1, D_2, D_3, and D_4 are constants depending on θ_w. The values of those parameters according to Haridy et al. (2004) are represented in Table 1. For more details see Haridy et al. (2004).

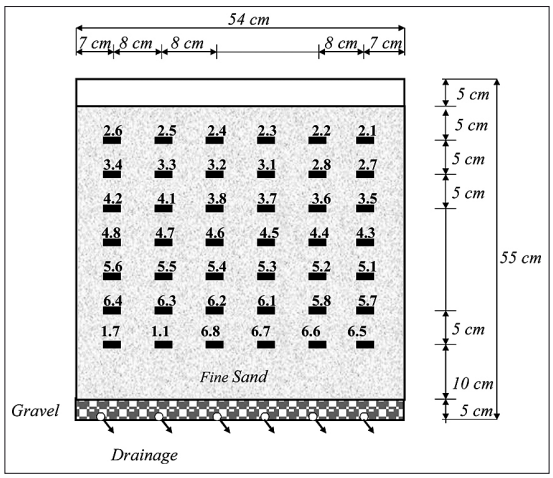

Figure 1. *Front view of the container showing the probes arrangement for the second experiment (solid rectangles represent probes).*

2.3 NAPL Experiments

The soil in the box was saturated by applying water from the bottom with constant flux. To establish uniform saturated conditions, the water level was kept 0.02 m above the soil surface for several days. Unsaturated conditions were then created by applying a suction head of –5 m at the bottom of the box using a vacuum pump during one day. Then the soil was left a two days so that the θ_w stabilized.

Once equilibrium was achieved, the oil migration experiment was started. Oil was released over an area 0.05 x 0.20 m at the centre of the surface. The oil was applied in four separate releases of varying quantities. Table 2 specifies the different oil releases. After two days (from the first release) suction of –5 m head was again applied at the bottom of the container to reduce the water content of the soil. Finally, an amount of 3.2 l tap water was added at the container surface with a constant rate of 0.133 l min^{-1} for the first 2.4 l and 0.053 l min^{-1} during the remaining time.

Table 2. *Information about the oil releases.*

Time	Application amount and method
1st day	Oil with constant rate (1 liter for 5 hour)
2nd day	Oil with constant head (2.5 cm for 44 min., 550 ml) Oil with variable head (5 cm to zero, 230 ml) Oil with constant rate (220 ml for 4 hours)
4th day	Water suction (–5 m) Oil with Constant rate (490 ml for 4.5 hours)
7th day	Oil with constant rate (400 ml for 4 hours)
10th day (Tap water)	Water with constant rate (133.33 ml/min. for 18 min) Water with constant rate (53.33 ml/min. For 15 min)

3 Results and discussion

3.1 Saturation and drainage

Under saturated condition, the results showed a slight variation in the calculated saturated water content (θ_s). The average θ_s varied between 0.383 and 0.425 $m^3\ m^{-3}$. This variation was probably due to variations in bulk density resulting from the effect of the soil weight at the lower layers of soil leading to compaction and difficulties to compact the soil around the probes.

After applying suction at the container bottom, equilibrium in the measured θ_w was verified by no change in the TDR response. The estimated θ_w profile using Topp's equation is shown in Fig 2. The profiles demonstrate that there was variation in θ_w not only with the depth but also slightly with the width. Below the 0.35 m depth the soil remained close to θ_s.

3.2 LNAPs Migration

After the first application of the oil at the surface, the oil infiltrated slowly downwards. At the beginning the oil front spread vertically. Then the oil also spread horizontally as it moved downwards. The horizontal spreading can be explained by capillary forces and spatial variability within the media. In particular, differences in the compaction of the soil strongly affected the migration behavior. The presence of a very thin layer (few millimetres) with low permeability inhibits downward migration of the oil and forces it to move laterally. The oil spills over such a layer and continues travelling downwards. The heterogeneity of the NAPL distribution was also clearly seen within the soil.

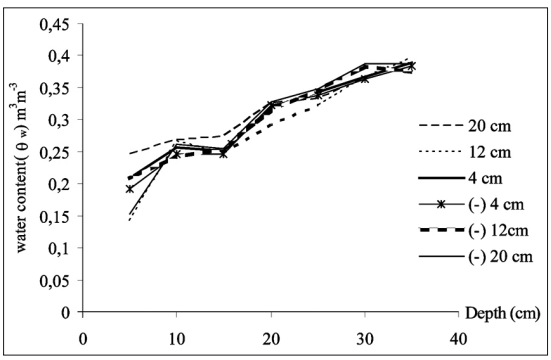

Figure 2. *The water content profile for unsaturated steady state condition at different locations just before the NAPL application.*

For all stages of the experiment, it was noticed from the observation of the back side of the tank that the dyed oil travelled slightly deeper than at the front side. This was probably due to lower bulk density around the probes which could be explained by the difficulties of compaction of the soil around the probes.

3.3 Image analysis of dye stained NAPL migration

It was easy to identify the area occupied by the dyed oil from the taken pictures. It was obvious that the NAPL distribution was heterogeneous. In order to map the location and extent of the oil, the area containing oil (defined by the outer margin) was drawn for each taken photograph. Figure 3 presents this mapping for each of the oil and water release. The mapping illustrates that after the first and the second oil release LNAPL migrated in both horizontal and vertical direction. After the third and the fourth LNAPL release the migration occurred mainly in horizontal direction. It also demonstrates that following the four oil releases the velocity of LNAPL migration decreased with increasing time. The LNAPL was found at 9, 15, and 17.5, 18 cm depths after 420 min from the first, 1020 min from the second, 10800 min after the third, and 2880 min after the fourth oil release, respectively.

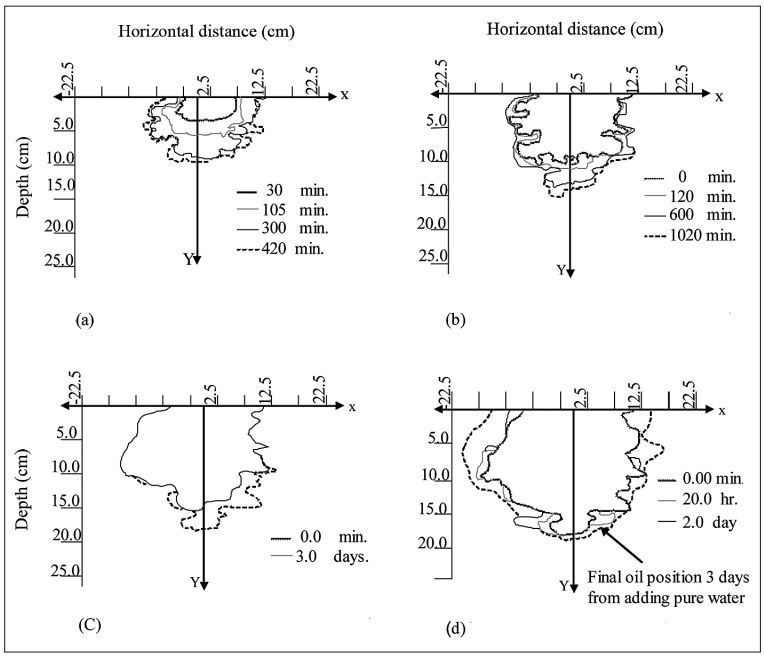

Figure 3. *Mapping of oil migration in the soil obtained from the pictures (the container front side) after the first release (a), second release (b), third release (c), and fourth release (d).*

3.4 TDR Response

TDR measurements were taken to observe the migration and distribution of the different fluids. Some of the TDR probes showed changes in the measured dielectric properties due to the presence and migration of the oil. Others showed changes only due to water movement. The TDR response for the oil presence was very different from those of saline and tap water, respectively. The TDR probes exhibited a decrease in both K_a and σ_a at some locations following the oil release indicating that LNAPL existed in the measurement volume. As an example Fig. 4 shows a comparison between the responses of three probes. Following the change in the soil electrical properties, oil was detected at different locations at discrete times. Table 3 gives the time at which the oil was detected by the TDR probes. The table shows that the zone affected by the oil was spreading in both horizontal and vertical and the second oil release resulted in mainly vertical movement until the end of the oil release. For the remaining probes either saline water or tap water movement was detected but no oil migration.

At depth 5 cm: after the first and the second oil release, increase in θ_w was detected which could be attributed to the displacement of water due to oil infiltration. This was followed by decrease due to downward movement of the saline water. No significant change was observed after the other oil releases. At the end, when tap water was added, a sudden increase in the θ_w was noticed followed by decrease caused by infiltration of water into deeper soil layers.

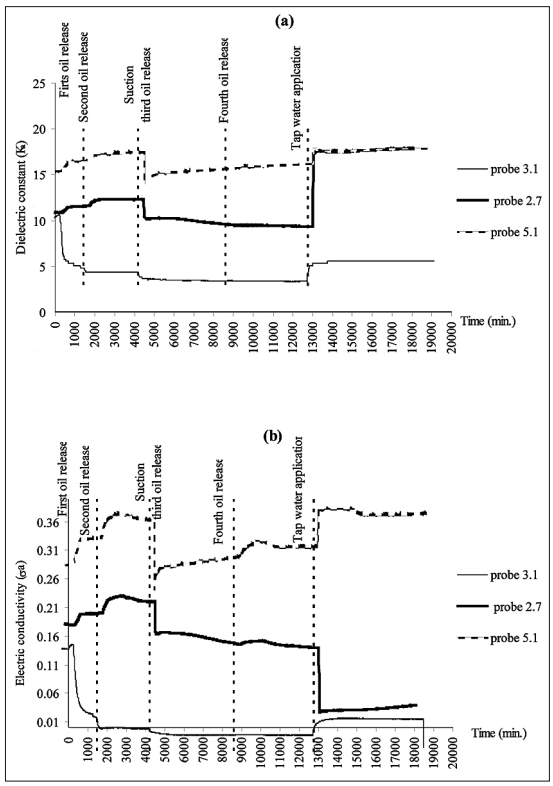

Figure 4. *Comparison between the responses in measured* K_a *and* σ_a *of three probes.*

Table 3. *The time of first observed LNAPL presence at specified probe locations.*

Probe name	Depth (cm)	Horizontal distance from the centre of the container (cm)	Time
2.3	5.0	4.0	10 min after the first oil release
2.4	5.0	–4.0	10 min after the first oil release
2.2	5.0	12.0	210 min after the first oil release
3.1	10.0	4.0	240 min after the first oil release
2.5	5.0	–12.0	280 min. after the first oil release
3.2	10.0	–4.0	290 min after the first oil release
3.8	15.0	–4.0	160 min after the second oil release
3.7	15.0	4.0	210 min after the second oil release
3.3	10.0	–12.0	250 min after the second oil release
2.8	10.0	12.0	300 min after the second oil release
3.6	15.0	12.0	960 min after the second oil release
4.1	15.0	–12.0	1040 min after the second oil release
4.5	20.0	4.0	230 min after third oil release
4.6	20.0	–4.0	400 min after the third oil release

*The minus sign means that the location of the probe at the left side of the centre.

At depths 10, 15 and 20 cm: increase in θ_w was noticed after the first and the second oil release due to the infiltration from the upper layer. After that only reduction in θ_w occurred due to the downward movement of water. After adding the tap water, similar effect as for the above mentioned probes was noticed. Then after nearly 2520 min a slight increase of θ_w was observed.

At depths 25 and 30 cm: after each oil release an increase in θ_w was observed. The increase of the θ_w was due to water displacement by oil in the upper soil. After 11940 min a decrease in θ_w was observed which was caused by the downward movement of water. Following the tap water application both K_a and σ_a increased for some time as a result of the vertical penetration of the saline water. Once the tap water reached this zone, a decrease in the electric conductivity combined with a raise in the θ_w was noticed.

At depth 35 cm: the same was observed, except that no tap water reached this zone of the soil.

3.5 Accuracy of TDR measurements

To obtain the θ_w and θ_{NAPL}, the procedure of Haridy et al (2004) was used. The volumetric water content was calculated using the measured σ_a. As there was no drainage, the increase in θ_w at some location attributed to the decrease at others. Using this fact and assuming that; 1) the residual water content is 0.05 m^3 m^{-3}, and 2) the probes give an average volumetric fluid content for volume of 0.05 x 0.08 x 0.20 m, the total change in the internal amount of the water was calculated. This was calculated as the Σ (average volumetric water content × the volume affecting the probe measurements) for all probes. Then the average error in the volumetric water content was determined by dividing the calculated change in the internal water amount by the real water volume. Small errors of less than 0.01 m^3 m^{-3} were obtained. The results indicate that the procedure was able to estimate θ_w with high accuracy. Then θ_{NAPL} was calculated using the K_a information. But since Haridy's procedure was applicable only for θ_w between 0.05 and 0.20 m^3 m^{-3} it was only possible to predict θ_{NAPL} for this range. Due to this limitation, it was not possible to calculate θ_{NAPL} during the entire experiment for all points.

In order to test the validity of the procedure for estimating $\theta_{NAPL,}$ a comparison between the actual total added oil volume and the total calculated oil volume, which was equal to the estimated average oil content multiplied by the effected volume recognized from the pictures, was carried out. A close match between the actual and the calculated oil volume was obtained. Then the error in the calculated oil volume was calculated as the difference between the actual and the calculated volumes divided by the actual value. The error was less than 0.045 m^3 m^{-3}. The difference between the actual and the calculated volumes could be attributed to any small error in calculating the affected soil volume from the picture lead to an error in the estimation of the oil volume.

3.6 Comparison of photos and TDR measurements

Comparison was made between the observed location of oil from TDR measurements, the photo analysis, and the manual observation at the back side of the box.

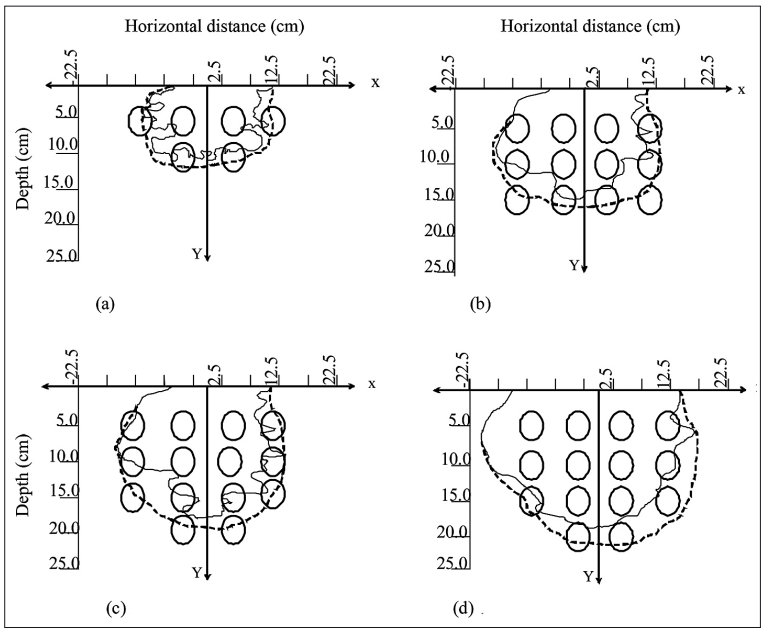

Figure 5. *Comparison between the locations of the LNAPL detected by: the digital photos (solid line), the manual observation at the container back side (dotted line) and the TDR determination (rings) after the first release (a), second release (b), third release (c), and fourth release (d).*

Figure 5 gives the final oil location after each release based on the photos (solid line) and the detected location by the TDR probes (the circles). The dotted line represents the manually observed location at the back side of the container. The results shows that predicted location after each oil release by the TDR was within the area of the oil as observed from photos and observation at the container back side, whereas better agreement for the one captured at the container back side was achieved. This is reasonable since the measured K_a and σ_a is an average in an approximately cylindrical volume, 4 cm in diameter and 18 cm in length, parallel to the probe while the photos represent only the front vertical surface of the soil. The results also confirm the fact that the LNAPL migration occurred in both vertical and horizontal direction, noticeable by comparing the arrival time of LNAPL at different probe location. It also validated the image analysis results that the LNAPL are spreading mainly vertically after the third and the fourth oil applications.

4 Discussion and conclusion

In this work, a 42 channelled TDR system was used to map the propagation of LNAPLs in a multi-fluid system (LNAPL, saline water, and tap water). Additionally to the TDR measurements digital photos were taken to visualize LNAPL migration. Our results show that the direction of the LNAPL migration and the location within the subsurface are strongly controlled by the variation in the permeability even if this variation is at a millimetre scale. LNAPL was observed to spread over soil layers with lower permeability which caused lateral movement of the NAPL. The primary reason for this variability is probably variations in bulk density caused by difficulties in compacting the soil uniformly around the probes.

The procedure proposed by Haridy et al. (2004) was used to estimate the fluid volumetric content. The results presented here support the idea that the procedure is appropriate as a stand alone method for estimating θ_{NAPL} and θ_w. A comparison between the real total fluids volume and the calculated based on the predicted values of θ_w and θ_{NAPL} was performed. The results illustrate that the procedure gives outstanding accuracy of the estimation for θ_w and θ_{NAPL} with errors less than 0.01 $m^3\ m^{-3}$ for θ_w and 0.045 $m^3\ m^{-3}$ for θ_{NAPL}.

In general, it is concluded that multi-channelled TDR method resulted in detailed data about the migration and of the LNAPL in multi-fluid system both in time and space. Overall, the results showed a very close match between the propagation and location of the oil detecting from oil mapping from both digital photos and TDR response. Generally, we believe that such a detailed multi-channelled TDR system can be a good tool for providing qualitative and quantitive information to describe the migration and distribution of LNAPL in the subsurface. However, further analysis of the procedure for different soil and NAPL types are required.

References

Brewster, M.L., Annan, A.P., Greenhouse, J.P., Kueper, B.H., Olhoeft, G.R., Redman, J.D., Sander, K.A. (1995) Observed migration of a controlled DNAPL release by geophysical methods. Ground Water, 33(6): 977–987.

Darnault, C.J.G., DiCarlo, D.A., Bauters, T.W.J., Jacobson, A.R., Throop, J.A., Montemagno, C.D., Parlange, J.Y., Stennhuis, T.S. (2001) Measurement of fluid contents by light transmission in transient three- phase oil- water- air systems in sand. Water Resources Research, 37(7): 1859–1868.

Haridy, S.A., Persson, M., Berndtsson, R. (2004) Estimation of LNAPL content in fine sand using time- domain reflectometry. Journal of Hydrology; 49: 987–1000.

Keech, D.A. (1988) Hydrocarbon thickness on groundwater by dielectric well logging, Proceedings of: Petroleum Hydrocarbon and organic chemicals in ground water: prevention, detection and restoration. The association of ground water scientists and Engineerings, 275–289.

Kuper, B.H., Redman, D., Starr, R. C., Reitsam, S., Mah, M. (1993) A field experimental to study the behavior of Tetrachloroethylene below the water table: Spatial distribution of residual and pooled DNAPL. Ground Water, 31(5), 756–766.

Oostrom, M., Hofstee, C., Lenhard, R.J., Walker, R.C., Dane, J.H., White, M.D. (1997) Physical modelling of muttifluid behavior in porous media. Proc. Of Amer. Geophysics. Union 17 TH hydrol. days, 241–254.

Oostrom, M., Lenhard, R.J. (1998) Comparison of relative permeability-saturation-pressure parametric models for infiltration and redistribution of a light nonaqueous – phase liquid in sandy porous media. Advanced in Water Resources, 21(2): 145-157.

Persson, M., Berndtsson, R. (2002). Measuring nonaqueous phase liquid saturation in soil using time domain Reflectometry. Water Resources Research, 38(5), 22-1: 22-8.

Poulsen, M., Kueper, B.H. (1992) A field experiment to study the behavior of tetrchloroethylene in unsaturated porous media, Environ. Sci. Technol. 26, 889–895.

Redman, J.D., Kueper, B.H., Annan, A.P. (1991) Dielectric stratigraphy of a DNAPL spill and implication for detection with ground penetration radar. Aquifer restoration, ground water monitoring and geophysical methods 5th National outdoor action conf. pp. 1017–1030.

Redman, J.D., DeRyck, S.M. (1994) Monitoring Non-aqueous phase liquids in the subsurface with multilevel time domain reflectometry probes. proceedings of the Symposium on Time Domain Reflectometry in Environmental, infrastructure, and Mining Applications, Evanston, Illinois, Sept 7–9, U.S. Bureau of Mines, Special Publication SP 19-94, NTIS PB95-105555789, 207–215.

Topp G.C., Davis, J.L., Annan, A.P. (1980) Electromagnetic determination of soil water content: measurements in coaxial transmission lines. Water Resources Research, 16(3): 574–582.