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Relationship between Initial and Residual LNAPL Saturation for Different Soil Types

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Abstract

The residual saturation of light non-aqueous phase liquids (LNAPL) plays an important role in determining LNAPL movement, recoverability and remedial endpoints. The concept of residual saturation is seemingly simple, and has largely been conceptualized by environmental professionals as a single value, solely a function of the soil and LNAPL in question. More recently, it has been increasingly recognized that not only does the concept of residual saturation need to be carefully considered within context, but it cannot be taken as a single value, depending instead on the history of fluid saturation. The issue of using a fixed single value for residual saturation and simple alternatives has also been brought to the fore by the recent development and increased use of some new tools for evaluating LNAPL distribution and recoverability. Petroleum engineering research has for some time recognized the dependence of residual LNAPL saturation on the history of fluid pressures and saturations. More recently, these concepts have been demonstrated for near-surface sandy materials in relation to a LNAPL spill. This showed a simple linear relationship between residual saturation and antecedent water saturation for a system with two fluid phases. In this paper, we further examine the dependence of residual saturation on the initial LNAPL saturation (defined as the LNAPL saturation at the drainage/imbibition reversal point preceding the establishment of the residual saturation) using laboratory measurements on a range of minimally disturbed finer textured soils. The laboratory method was designed to overcome problems of variability and also allowed the constitutive relations for the individual samples to be determined. Decane and local groundwater were used as the fluid pairs in the experiments and capillary pressure heads up to 4 m of water were used to develop a range of LNAPL saturations in the core samples. The results showed that linear relationships between residual and initial LNAPL saturations remained valid for the finer-textured soils. Further, a trend was observed for residual saturation to increase as a proportion of the initial saturation as the materials became finer in texture. Proportionality constants ranged from 0.226 to 0.564. However, we were not able to confirm this trend to the finest textured of our samples (a silty clay loam) as LNAPL saturations were not able to be reliably resolved with the experimental methodology. The developed relationships are readily amenable to inclusion in screening and scenario applications for predicting LNAPL distribution and recovery. Some simple practical examples are presented to demonstrate this. The importance of considering the fluid pressures that may exist at a typical LNAPL spill site are also discussed in relation to the magnitude of LNAPL saturations and resultant residual saturations. Further investigations suggested include an examination of the possible influence of the interfacial tension of the fluid pairs on the residual saturation relationships.

Introduction

The concept of residual LNAPL (light non-aqueous phase liquid) saturation is seemingly simple and it plays an important role in determining LNAPL movement, recoverability, and remedial endpoints. To date, environmental professionals have largely conceptualized residual saturation (immobile LNAPL fraction) as a single value that is a function solely of soil and LNAPL type (Mercer and Cohen 1990, Wilson *et al.* 1990, Brost and DeVuall 2000). However, there is an increasing recognition that the concept of residual saturation needs to be carefully defined within the context being considered - for example; the number and fluid phases present, the wetting status of the porous material; and the history of fluids in the porous media (Lenhard *et al.* 2004). Of fundamental importance are the differing mechanisms that give rise to the residual saturation in two-phase, NAPL-water, and three-phase, air-NAPL-water, water-wet porous systems. While residual saturation in two-phase systems arises through entrapment of NAPL as isolated blobs and ganglia (Wilson *et al.* 1990), non-occluded NAPL films largely account for the residual saturation in three-phase systems (Lenhard *et al.* 2004). The focus of our work in this paper is the residual saturation arising from LNAPL entrapment in two-phase systems.

The scientists involved in petroleum engineering have long recognized that residual oil saturation is, in addition to the characteristics of the fluids and the porous material, also dependant on the LNAPL spill history (Pickell *et al.* 1966) where the LNAPL saturation is determined by LNAPL fluid pressure in the field. From this, the concept arises for the residual saturation to be a function of the maximum non-wetting phase saturation experienced by the porous media (Land 1968). The issue of presuming a single fixed value for residual saturation in the environmental profession has recently become a more significant problem (Adamski *et al.* 2003) with the development and increased use of the new tools for evaluating LNAPL distribution and recoverability (Charbeneau *et al.* 1999). These tools have prompted more innovative LNAPL site assessment and characterization approaches including drastically increasing the frequency of measuring LNAPL saturations in the field. However, such tools have also required relatively simple methods for accurately describing the concepts of residual LNAPL saturation.

Other, more detailed modelling efforts (Parker and Lenhard 1987, Kaluarachchi and Parker 1992) have used empirical methods based on the Land (1968) approach to incorporate the concept of residual saturation. However, very little testing has been conducted to determine the relationship between: LNAPL pressure and initial LNAPL saturation; and initial LNAPL saturation and residual LNAPL saturation for soils and conditions typical of near surface environments subject to LNAPL contamination. Steffy *et al.* (1997) measured the functional relationships between residual NAPL saturation and antecedent water saturation for two-phase, water-NAPL system for a well-sorted calcareous sand with a median grain size of 200 μm . They confirmed a simple linear relationship between residual LNAPL saturation and antecedent water saturation as conceptualized by Land (1968). For the important two-phase systems, this is equivalent to a linear relationship between residual saturation and initial LNAPL saturation. We focus on the two-phase systems because the vast majority of LNAPL spreading near the water table is in and below the capillary fringe. Our objectives here are to further assess the relationship between residual and initial LNAPL saturation for two-phase

systems, particularly for finer materials than those considered by Steffy *et al.* (1997). This paper presents the results of the initial LNAPL saturation / residual LNAPL saturation relationship for three soils: a fine-grained sand; a loamy sand; and a clay loam. We also discuss results for a more problematic silty clay loam soil. The results are also examined in relation to the maximum LNAPL pressures and saturations that may be observed in the field.

Theory

For a two-phase system, the non-wetting phase residual saturation arises as the non-wetting phase becomes entrapped as the capillary pressure head, h_c , between the fluid phases returns to zero. This was illustrated in terms of the hysteretic relationship between wetting phase saturation, S_w , and capillary pressure head by Cory (1990). Alternately, this can also be illustrated through the equivalent hysteretic relationship between non-wetting phase (i.e. LNAPL in our case) saturation, $S_n = 1 - S_w$, and h_c illustrated in Fig. 1.

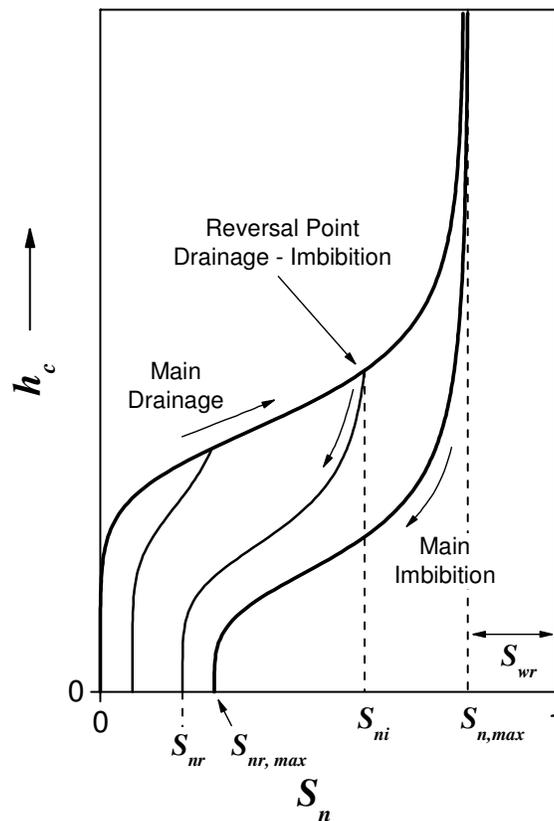


Fig. 1. Schematic showing the hysteretic relationship between NAPL saturation, S_n , and capillary pressure head, h_c , illustrating the dependence of residual NAPL saturation on the history of fluid saturation. Shown are initial NAPL saturation, S_{ni} , residual NAPL saturation, S_{nr} , maximum NAPL saturation, $S_{n,max}$ and maximum residual NAPL saturation, $S_{nr,max}$.

This shows that the non-wetting phase residual saturation, S_{nr} , is dependent on what we will call the initial non-wetting phase saturation, S_{ni} , at the point where there is a reversal from wetting phase drainage to imbibition which ultimately leads to the entrapment of the non-wetting phase. It also shows the maximum residual non-wetting phase saturation, $S_{nr,max}$, arising from that entrapped after following the main wetting phase imbibition curve. That is, after the maximum non-wetting phase saturation, $S_{n,max}$, is attained. We note that $S_{n,max} = 1 - S_{wr}$ where S_{wr} is the residual (or irreducible) wetting-phase saturation.

Steffy *et al.* (1997) developed a linear relationship which expressed S_{nr} as a function of the antecedent water saturation, S_{wi} , at the drainage/imbibition reversal point:

$$S_{nr} = S_{nr}^{\max} - bS_{wi} \quad (1)$$

Here, Steffy *et al.* (1997) defined S_{nr}^{\max} as that with $S_{wi} = 0$ – that is, the case where water displaces a sample initially saturated with NAPL. This differs from the $S_{nr,max}$ defined above. We note that when $S_{nr} = 0$, then $S_{wi} = 1$ and thus $b = S_{nr}^{\max}$. We prefer to recast (1) in terms of S_{ni} which leads to:

$$\begin{aligned} S_{nr} &= S_{nr}^{\max} - b(1 - S_{ni}) \\ &= bS_{ni} - (S_{nr}^{\max} - b) \\ &= bS_{ni} \end{aligned} \quad (2)$$

Methods

Minimally-disturbed core samples from two locations were used as part of this study. The two locations were the BP refinery at Texas City, near Houston, Texas and a vineyard in the Swan Valley, near Perth Western Australia. The methods for collecting the cores varied. Cores from the Texas City refinery were collected during auger drilling. Core sections from depth intervals 2.44 – 3.05 m (8 – 10 feet) and 3.05 – 3.66 m (10 – 12 feet) were collected in 72-mm internal diameter steel shelby tubes (thin-walled samplers) while the section of core from 3.66 – 4.27 m (12-14 feet) was collected in a rigid plastic tube liner within a coring barrel. After collection, the tubes were trimmed and sealed for transportation. The Swan Valley samples were collected by hammering a thin-walled, 47-mm internal diameter, aluminium tube into the profile. The section from 0 to 0.3 m below ground was trimmed and sealed for use in the laboratory experiments.

To facilitate the laboratory measurements, a section of the Texas City 3.66 – 4.27 m core was extruded into 47-mm internal diameter aluminium tubing. For the laboratory measurements, 50-mm sections were cut from the cores by hand.

The determination of residual NAPL saturation was made in retention cells similar to those used by Steffy *et al.* (1997). The cells were customised to the dimensions of the samples being used. Hydrophilic and hydrophobic porous ceramic plates were held in intimate contact with the alternate ends of the core samples by sealed end caps. The samples were

wet up under a modest suction and flushed with groundwater to remove as much air as possible from the samples before being sealed in the cells. Groundwater was from the Safety Bay Sand aquifer south of Perth, Western Australia (Johnston *et al.* 1998). Hydrophobic porous plates were produced using the method described by Steffy *et al.* (1997) and saturated with decane. Reservoirs of groundwater and decane (decane dyed with oil-red-O, $\rho_n = 0.727$, was used as the NAPL in our experiments) were connected to each end of the retention cells through flexible nylon tubing with in-line tap fittings that allowed the individual weights of the cell, water and decane reservoirs to be determined. The height of the decane in the reservoir was maintained just above the top of the sample with the height of the water, 10 mm below that of the decane. A suction was applied to the water in its reservoir to create a range of capillary pressures between the water and the decane in the soil sample. The maximum capillary pressure head varied and ranged up to 4.0 m of water for the finer-textured samples.

A series of initial NAPL saturation, S_{ni} , – residual NAPL saturation, S_{nr} , pairs was determined for each sample by sequentially increasing the capillary pressure and returning the capillary pressure to zero. Equilibration times for each step in the sequence ranged up to 1 month. The volume of water displaced from the sample and the volume of NAPL imbibed were used to calculate S_{ni} and S_{nr} along with a measure of the volume of decane in the core sample at the end of the experiment. Volumes were estimated from weights of the water and decane reservoirs. To estimate evaporative losses from the reservoirs over the course of the experiments, reservoirs of each were kept as controls.

At the end of each experiment, the sample was removed from the cell and extracted with solvent to determine the total amount of decane remaining using GC-MS. Decane was added at the time of extraction as an internal standard. Following extraction, the sample was dried to determine porosity.

The sequential measurement of $S_{ni} - S_{nr}$ pairs on the one sample was designed to overcome the anticipated variability that would inevitably ensue from using a number of different minimally-disturbed samples of the same soil type. We considered it important to use the minimally-disturbed samples collected directly from the field instead of homogenising and re-packing samples in order to preserve soil structure in the finer-textured materials. These sequential measurements produce more complicated, hysteretic fluid saturation histories in the samples. However, this was expected to be a secondary influence and not dissimilar to the conditions that would be experienced in the field.

Interfacial tensions, σ , of the fluid pairs were measured using a Du Nuoy ring tensiometer. The water was pre-equilibrated with the decane for the measurement of the decane-water interfacial tension and the water surface tension.

Particle sizes of the samples were determined using a combination of sedimentation and sieving. Mass fractions of clay ($< 2 \mu\text{m}$) and silt ($2 - 20 \mu\text{m}$) were determined by measuring the specific gravity of a suspension using the plummet balance method, similar to the hydrometer method of Gee and Bauder (1986). The sand fraction was separated by sedimentation and sieved into fine ($20 - 200 \mu\text{m}$) and coarse ($200 - 2000 \mu\text{m}$) fractions.

Results and Discussion

Soil properties

Particle size analyses of the samples are presented in Table 1. This shows a range of soil textures ranging from sand to silty clay loam. All the samples considered here are much finer in nature compared to the Safety Bay Sand studied by Steffy *et al.* (1997) which had 50% coarse sand and, although not reported, the percentage of clay and silt was less than the 7% which was measured to be less than 75 μm (the minimum size used in their sieve range).

Table 1. Particle size distributions - mass percentages of clay (< 2 μm), silt (2 – 20 μm), fine (20 – 200 μm) and coarse (200 – 2000 μm) sand, classification and porosity of soil samples.

Sample	Clay	Silt	Fine Sand	Coarse Sand	Texture classification [‡]	Soil Classification ^Δ	Porosity
Texas City							
2.44 – 3.05 m	30	35	29	6	Silty clay loam	CL	0.384
3.05 – 3.66 m	8	5	86	1	Loamy sand	SC	0.366
3.66 – 4.27 m	0	3	92	5	Sand	SP-SC	0.346
Swan Valley							
0.20 – 0.25 m	26	16	48	10	Clay loam	CL	0.348

[‡] According to Marshall (1947)

^Δ USCS estimated using grainsize, no Atterberg limits performed

Porosities of the samples were similar, ranging from 0.346 to 0.384 (Table 1) and compared to the approximate porosity of 0.50 for the Safety Bay Sand.

Fluid properties

Interfacial tensions for the fluids used in the experiments are reported in Table 2. The air-decane interfacial tension (surface tension) was similar to that reported by Steffy *et al.* (1997) as was the surface tension for groundwater equilibrated with decane. The groundwater-decane interfacial tension is higher than measured by Steffy *et al.* (1997) and is also higher than that generally observed for weathered petroleum hydrocarbons (Wilson *et al.* 1990).

Table 2. Interfacial tension of the fluid pairs used in the retention cell experiments

Fluid pair		Interfacial tension (dynes cm^{-1})
Air-groundwater	σ_{aw}	61.1
Air-decane	σ_{an}	27.5
Groundwater-decane	σ_{nw}	47.4

NAPL saturation of samples

The retention cells were, by necessity, not closed systems and because of the long duration (in excess of 300 days for some samples) of the experiments and small volume changes needing to be identified, careful accounting was required for evaporative losses and any fluid additions to the system during the tests. This accounting showed losses from the combined system of retention cell, water and decane reservoirs were greater than losses from the control reservoirs of water and decane. These extra losses were attributed to losses of water and decane from the connecting tubing, taps and the cell itself. Proportioning the extra losses was based on matching the amount of decane measured in the samples at the end of the experiment.

Figure 2 shows an example of the primary experimental data collected from the retention cells. In this case, there were good correlations between the volume of decane imbibed into the sample and the water displaced. For other samples, we found the gaskets used to seal the cells adsorbed appreciable volumes of decane. Thus, the water displaced from the cell better matched the residual decane in the sample at the end of the experiment and was generally used to estimate the volume of decane in the sample and hence S_n .

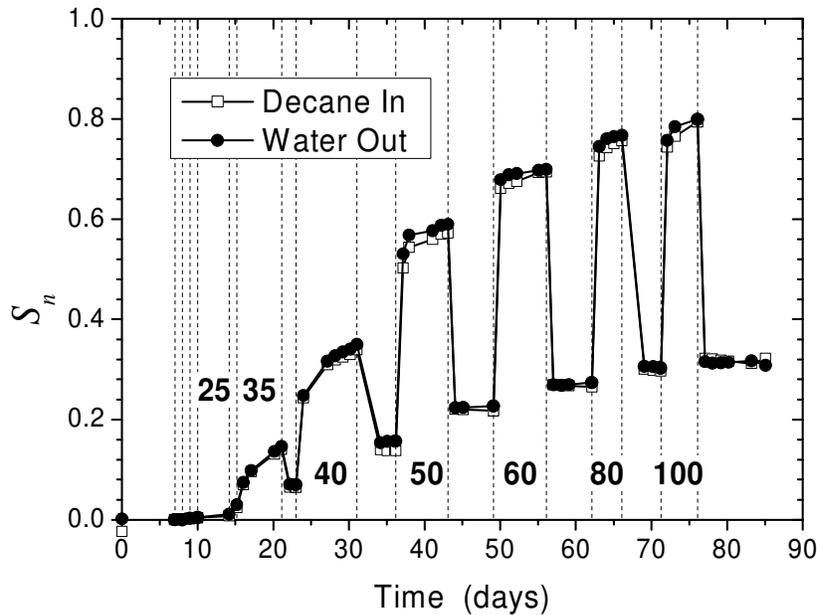


Fig. 2. Time sequence of NAPL saturation, S_n , for increasing capillary pressure head, h_c , with intervening periods of zero capillary pressure (sample – Texas City 3.66 – 4.27 m). Vertical dashed lines indicate times that h_c was changed and numbers indicate the non-zero capillary pressure head (cm water) applied.

In the case of the 2.44 – 3.05-m sample from Texas City, the losses of both decane and water along with the ingress of air into the cell prevented any reliable estimates of NAPL saturations. The measured volume of decane in the sample after 273 days of testing and maximum h_c of 4.0 m of water was only 0.42 mL, equivalent to $S_n = 0.005$. The magnitude of evaporative losses and small amounts of air entering the end of the cell made other estimates of S_n over the course of the experiment unreliable.

NAPL-water retention characteristics

While the capillary pressure and NAPL saturation did not increase monotonically over the whole course of the experiments, Fig. 2 suggests that a NAPL-water retention characteristic is able to be constructed for water drainage conditions. Implicitly we assume that the $S_n - h_c$ relationship returned to the main drainage curve after each excursion to zero capillary pressure. These resultant measured characteristics are shown in Fig. 3. As well as the samples measured in this study, the experimental data reported by Steffy *et al.* (1997) for the Safety Bay Sand sample are also included for comparison. The retention characteristics reflect the textures of the samples and also suggest they can be reasonably described by van Genuchten's (1980) model for such constitutive relationships.

A model for describing the NAPL saturation, S_n , as a function of the NAPL-water capillary pressure head, h_c , is developed from that for water:

$$S_w = S_{wr} + (1 - S_{wr}) \left[1 + (\alpha h_c)^n \right]^{\left(\frac{1}{n} - 1 \right)} \quad (3)$$

where α and n are the van Genuchten parameters. Noting that $S_n = 1 - S_w$ then we can write Eqn 3 as:

$$S_n = (1 - S_{wr}) \left\{ 1 - \left[1 + (\alpha h_c)^n \right]^{\left(\frac{1}{n} - 1 \right)} \right\} \quad (4)$$

Non-linear least square fits (Microcal 1999) to Eqn 4 for the experimental data are shown in Fig. 3 while the fitted parameters are presented in Table 3. These confirm that the experimental data can be well described by the van Genuchten model. It should be noted, however, that the derived values of S_{wr} can only be viewed as fitting parameters. Particularly for the finer-textured samples, the true irreducible water saturation is expected to be much lower, and achieved at far higher capillary pressure head.

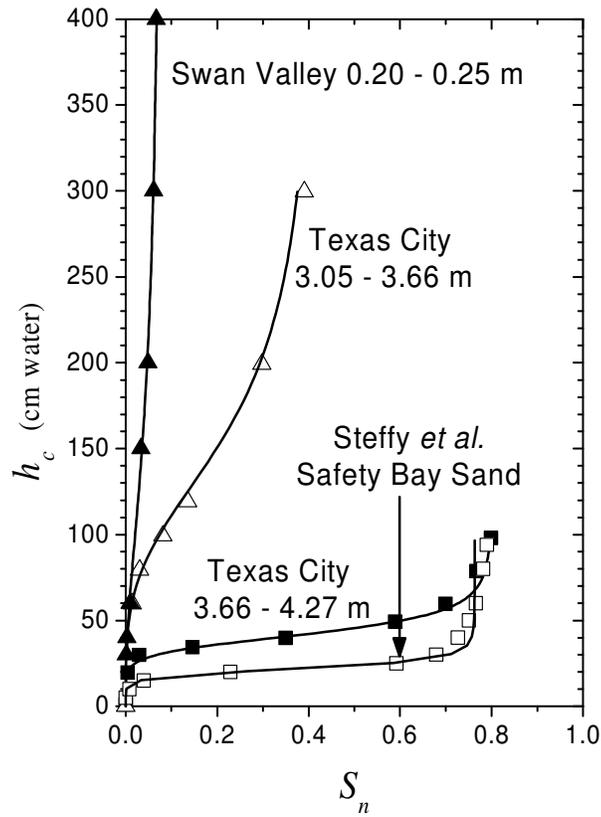


Fig. 3. NAPL saturation-capillary pressure head (S_n-h_c) constitutive relationships for decane-water in the present study and for the Safety Bay Sand reported by Steffy *et al.* (1997). Symbols show measured values and lines show fitted van Genuchten relationships.

Table 3. Fitted van Genuchten parameters for the measured decane-water saturation capillary pressure head curves

Sample	Depth Interval	α (m^{-1})	n	S_{wr}
Texas City	2.44 – 3.05 m	-	-	-
Texas City	3.05 – 3.66 m	0.72	3.74	0.58
Texas City	3.66 – 4.27 m	2.44	7.12	0.2
Swan Valley	0.20 – 0.25 m	0.82	2.32	0.92
Safety Bay Sand		4.66	8.60	0.24

Residual saturation as a function of initial saturation

The measurements of residual LNAPL saturation closely approximated linear functions of the initial LNAPL saturation for the three samples measured as part of this study. Figure 4 shows the measurements along with the fitted linear regression according to the model defined by Eqn 2. The data for the Safety Bay Sand of Steffy *et al.* (1997) are also included for comparison. Details of the linear regressions are presented in Table 4.

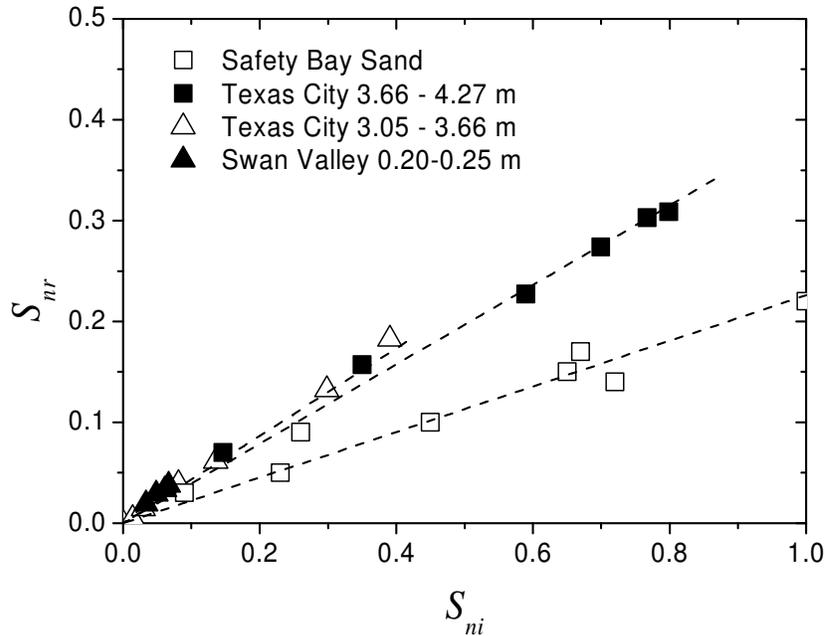


Fig. 4. Residual NAPL saturation, S_{nr} , as a function of initial NAPL saturation, S_{ni} , for the samples of the present study and for the Safety Bay Sand of Steffy *et al.* 1997. Symbols show measured values and lines show the fitted linear regression $S_{nr} = bS_{ni}$.

Table 4. Estimates of the slope, b , (absolute error in parenthesis) for the measured samples using the model $S_{nr} = bS_{ni}$ together with the regression statistics – no. is number of observations, r is the regression correlation coefficient and s.d. is the standard deviation.

Sample	Depth Interval	b	no.	r	s.d.
Texas City	2.44 – 3.05 m	-	-	-	-
Texas City	3.05 – 3.66 m	0.433 (0.006)	7	0.999	0.00318
Texas City	3.66 – 4.27 m	0.394 (0.007)	6	0.998	0.01087
Swan Valley	0.20 – 0.25 m	0.564 (0.010)	4	0.992	0.00111
Safety Bay Sand		0.226 (0.010)	8	0.973	0.01683

In all three samples of the present study, the slope, b , of the linear relationship between initial and residual saturation is greater than that of the Safety Bay Sand. And there appears an overall trend for b to increase as the texture becomes finer. It is unclear to what extent this trend may extend to even finer materials, particularly those where LNAPL may be restricted to macropore systems. Unfortunately we do not have results from the Texas City silty clay loam (2.44 – 3.05 m) which may elucidate this further. However, we noted during our experiments that the methods used here may need to be modified for macroporous clay soils. It was apparent that the forced intimate contact between the porous ceramic plate tended to smear the soil surface and it seems that entry to any macroporous system may be very difficult to preserve.

Practical applications to field studies

Relatively high capillary pressure heads were applied, particularly to the finer-textured soil samples, to develop the LNAPL saturations in this study and used to examine the behaviour of residual saturations. Capillary pressures likely to be developed in the field for typical spill scenarios are likely to be rather more modest, and residual saturations much less than some of those reported here. Consider for instance, the equilibrium vertical distributions of fluid saturations and pressures where LNAPL is observed in a monitoring well. The capillary pressure head is zero at the elevation of the LNAPL-water interface (z_{nw}) and increases with elevation according to the difference in fluid densities (Charbeneau *et al.* 1999). At the air-LNAPL interface (z_{an}), the capillary pressure head, h_c , will be given by:

$$\begin{aligned} h_c(z_{an}) &= \left(1 - \frac{\rho_n}{\rho_w}\right)(z_{an} - z_{nw}) \\ &= (1 - \rho_r) b_n \end{aligned} \quad (5)$$

Where ρ_r is the relative density (specific gravity) of the LNAPL and b_n is thickness of LNAPL in the well:

$$b_n = z_{an} - z_{nw} \quad (6)$$

Thus, for decane with $\rho_r = 0.727$, an LNAPL thickness of 1.83 m would be required to attain a capillary pressure head of 50 cm water and a 3.66-m thickness would be required to attain a capillary pressure head of 100 cm water, at the air-LNAPL interface. Inspection of Fig. 3 shows that for $h_c = 50$ cm, insignificant decane is expected in both the Texas City 3.05 – 3.66 m and Swan Valley 0.30 – 0.25 m samples. Even for a 3.66-m thickness of decane in a monitoring well, very low decane saturations are expected for the same two samples.

Predictions of LNAPL saturations for petroleum hydrocarbons other than the decane used in our study here, needs to account for the difference in interfacial tensions. In particular, the $S_n - h_c$ relationship needs to be scaled for the differences in the NAPL-water interfacial tensions. This is achieved through the scaling of the van Genuchten α according to:

$$\alpha' = \frac{\sigma_{dw}}{\sigma_{nw}} \alpha \quad (7)$$

where σ_{dw} is the decane-water interfacial tension and σ_{nw} is the NAPL-water interfacial tension of the petroleum hydrocarbon-groundwater fluid pair of interest. This scaling, together with the linear relationship between S_{nr} and S_{ni} , allow for easy prediction of residual saturation for the vertical equilibrium LNAPL distributions used in the recovery models of Charbeneau *et al.* (1999) for instance. Implicitly, we also assume that the S_{nr} and S_{ni} relationship does not change with interfacial tension. Although not rigorously tested, the data of Steffy *et al.* (1997) suggest this is a reasonable assumption. Examples of these predictions are given in Fig. 5 for a weathered gasoline for which we have assumed $\sigma_{nw} = 20$ dynes cm^{-1} and $\rho_r = 0.75$. Here we show the predicted initial vertical distribution of LNAPL saturation for the range of soils considered here and for a LNAPL thickness in a monitoring well corresponding to 2 m. The predicted residual saturations assume displacement of the LNAPL by a rising water table such that h_c goes to zero at the elevation of the initial air-LNAPL interface.

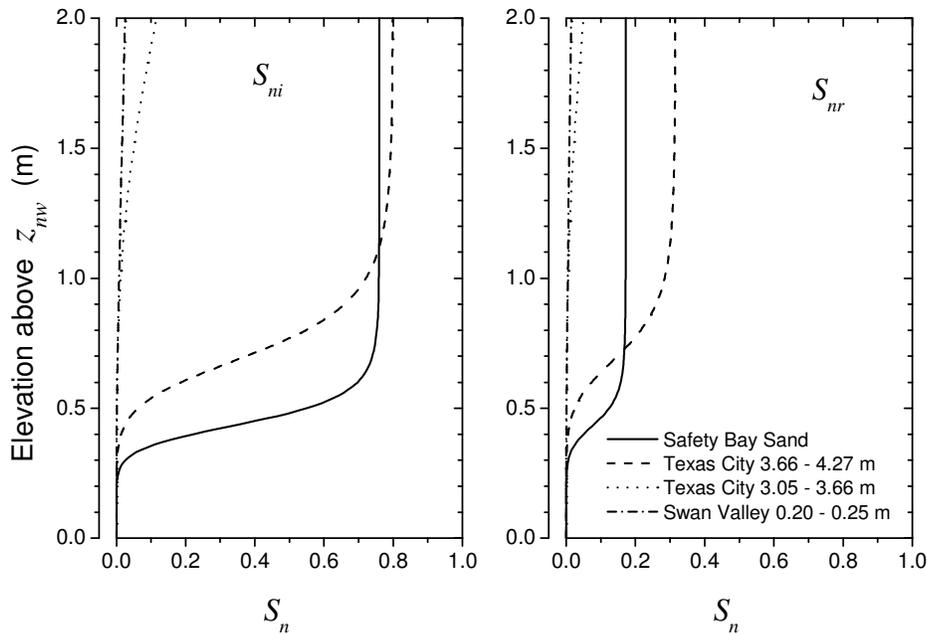


Fig. 5. Calculated vertical distributions of gasoline LNAPL saturations, S_{ni} , for hydrostatic conditions corresponding to 2 m of gasoline thickness in a monitoring well along with predicted residual saturations, S_{nr} , following displacement of the gasoline by a rising water table. Elevation given as the distance above the initial LNAPL-water interface, z_{nw} , in a monitoring well.

Conclusions

The laboratory methods used in this study were successfully applied to a range of fine-textured soil to determine the relationship between initial and residual NAPL saturation in minimally-disturbed samples. These measurements confirmed that the linear relationship identified between S_{nr} and S_{ni} for two-phase fluid systems in the sand studied by Steffy *et al.* (1997) may be extended to a range of finer-textured materials. Further, a trend for increasing slope of the linear relationship as the texture of the material becomes finer was also identified. However, the extent to which this remains true for very clayey materials remains uncertain as we were not able to determine the $S_{nr} - S_{ni}$ relationship for the most clayey of the samples in the current testing. It remains to be seen what practical importance this relationship may be for such materials given that only exceedingly low NAPL saturations may be expected to develop in these materials for normal spill scenarios. Other experimental approaches that specifically target any macropore systems in heavy clay soils would seem to be required.

Care is required in applying the maximum residual saturations seen in this study as they resulted from LNAPL saturations developed under capillary pressure heads much higher than may typically be expected under field conditions. Our results also confirm that low LNAPL saturations, and consequently low residual saturation of LNAPL would be expected in fine-textured materials under typical spill conditions.

Overall, when combined with the observed $S_n - h_c$ constitutive relationships for the soils, the linear dependence between S_{nr} and S_{ni} allows straight-forward calculation of residual LNAPL saturations, suitable for a number of applications. Prime amongst these would be the screening and scenario-based models such as those of Charbeneau *et al.* (1999). However, the observations made here could also guide the refinement of the more detailed models which incorporate hysteretic constitutive relationships that ultimately determine the calculation of residual saturation (e.g. Oostrom *et al.* 2005).

These present studies have only developed $S_{nr} - S_{ni}$ relationships for the one fluid pair (decane and groundwater). Although, Steffy *et al.*'s (1997) data do not suggest a difference for weathered diesel and decane in the Safety Bay Sand, further investigations of fluid pairs with a range of interfacial tensions in finer-textured materials may be warranted.

Acknowledgements

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