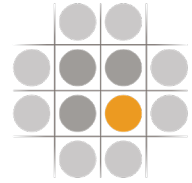


SoBRA

The Society of Brownfield Risk Assessment



SOCIETY OF BROWNFIELD RISK ASSESSMENT

Light Non-Aqueous Phase Liquid – Guidance Notes for their Assessment in Contaminated Land Scenarios in the UK

6. ADVICE TOWARDS UNDERSTANDING THE POTENTIAL FOR LNAPL TRANSMISSIVITY AND RESIDUAL SATURATION

Version 1.0

February 2026

PUBLICATION

This series of reports and tools is published by the Society of Brownfield Risk Assessment (SoBRA). It presents work undertaken by a SoBRA sub-group composed of volunteers listed in the acknowledgments below. This publication is part of a series of work packages designed to address various issues in data collection and evaluating risks associated with non-aqueous phase liquid (NAPL).

This document outlines transmissivity and discusses the concept of residual saturation with its application to LNAPL behaviour in the field. As set out in the text, it is imperative that users have read and understand the basis for the report and its limitations as described in the supporting text presented herein.

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1 INTRODUCTION

The Society of Brownfield Risk Assessment (SoBRA) is a UK-based learned society that aims to:

- improve technical knowledge in risk-based decision-making related to land contamination applications; and
- enhance the professional status and profile of risk assessment practitioners.

The society has a number of working groups (“sub-groups”) comprising volunteer SoBRA members working on particular aspects to help achieve these aims. This report presents one of several outputs of the non-aqueous phase liquid (NAPL) sub-group.

The technical aims of the sub-group are to:

- support technical excellence in the assessment, estimation and evaluation of risks associated with NAPL; and,
- encourage best practice by delivering practical advice to support decisions regarding the appropriate management of NAPL risks.

It should be noted from the outset it is not the intention of the sub-group or any of its deliverables to replicate existing NAPL guidance. Instead, the overarching aim is to address gaps in current guidance, and to provide practical advice to SoBRA members when undertaking risk assessments at sites where NAPL could be or is present.

1.1 Evolution and overall strategy of sub-group

The evaluation of contaminated land risk relies on understanding sub-surface processes. NAPL can be difficult to measure, meaning conceptual site models (CSM) may be data deficient. Following several requests from our members, SoBRA created the NAPL sub-group in 2019 with a call out to the SoBRA membership for volunteers to participate.

Once the group of volunteers was assembled, initial sub-group meetings identified and prioritised areas where existing NAPL UK risk assessment guidance was lacking or would benefit from practical advice. As a result of this screening process, a series of seven working groups was formed, each tasked with producing a document or tool to address the identified need.

The overall approach developed by the sub-group to address NAPL risk assessment is summarised in Figure 1. The seven working groups cover all stages of risk assessment,

ranging from establishing whether NAPL is likely to be present at a site or not, through to designing an appropriate remediation strategy. The position of this particular document within this strategy is highlighted.

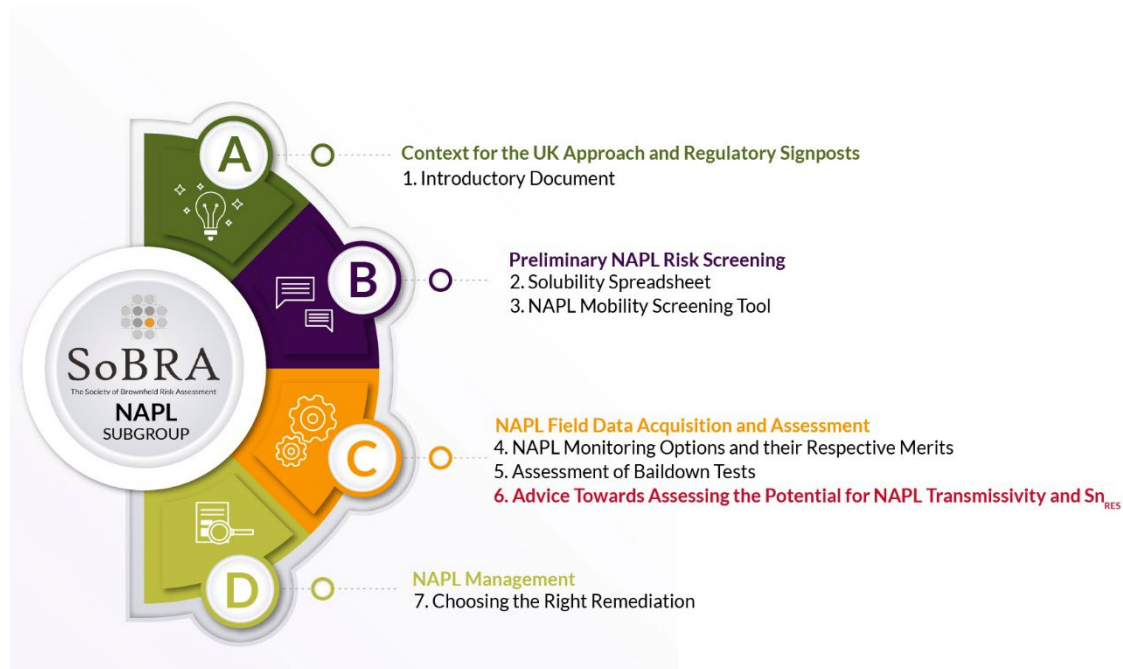


Figure 1. Publication strategy for NAPL sub-group

1.2 Background

Light non-aqueous phase liquid (LNAPL) is a common contaminant and is often recovered through pumping. In recent years, guidance publications have been produced by the Interstate Technological and Regulatory Council (ITRC) in 2009 (ITRC, 2009) and updated in 2018 (ITRC, 2018) in the United States and by Contaminated Land; Application in Real Environments (CL:AiRE) in 2014 in the United Kingdom, which was followed by Tomlinson et al. (2017). These publications provide an excellent introduction to the theoretical background of LNAPL characteristics, the broader concerns and the usefulness of metrics for recovery. There has been a concerted effort across the contaminated land industry to frame the recoverability of LNAPL in terms of transmissivity (Simon, 2012). Less frequently are remediation targets discussed in terms of LNAPL thickness, as stakeholders more commonly understand that the presence of several centimetres (cm) of LNAPL in a borehole is, by itself, not a meaningful metric. LNAPL transmissivity is an expression of the mobility of the LNAPL and is directly proportional to LNAPL recoverability, whereas LNAPL thickness is not.

1.3 Problem formulation

LNAPL transmissivity – an expression of the LNAPL mobility – has emerged as a useful metric for measuring the mobility of an LNAPL. The mobility of an LNAPL can be related to the saturation of an LNAPL, if the LNAPL and soil properties are known. When the mobility of an LNAPL is low, hydraulic recovery can cease to be an efficient remediation process, and other technologies may be required for remediation. The precise point for this is site-specific. The remaining LNAPL is *sometimes* referred to as ‘residual LNAPL saturation’, though any remediation technology change may take place before this. The LNAPL transmissivity is a property which may vary even without recovery, and the mechanisms that influence LNAPL movement at low saturation have not, to date, been discussed in the context of a document for industry guidance. The latter has led to sometimes some problematic discussions where single examples of LNAPL residual saturation from sites with differing geologies and histories of NAPL inputs are used to frame remediation objectives for other sites, and some organisations propose that small accumulation of LNAPL in wells can be removed by ‘aggressive pumping’.

1.4 Aim of document

At the end of hydraulic recovery or where sites exist that may have transient or sporadic LNAPL accumulations, there remains some confusion as to why the LNAPL can build up in monitoring wells, even if the transmissivity is very low or for certain times of year no LNAPL is present in the monitoring wells. This document sets out to:

- Provide an outline of the use of LNAPL transmissivity and how it relates to how the behaviour of an LNAPL body can change;
- Discuss the definition of ‘residual saturation’ and its usefulness as a strict term;
- Review the scientific literature and current industry guidance concerned with low-mobility LNAPL;
- Describe what causes LNAPL to move under apparent minimal gradients and why even significant accumulations of LNAPLs in monitoring wells require contextual data to understand in terms of risk;
- Describe how soil water movement and changes in the properties of an LNAPL over time may cause LNAPL movement; and,
- Reinforce the message that LNAPL well thickness, in isolation, embodies little useful meaning.

2 KEY CONCEPTS

2.1 Transmissivity

LNAPL transmissivity is a summary metric based on the soil properties, LNAPL physical properties, and the magnitude of LNAPL saturation over a given interval of aquifer (ASTM E2856-13). It is not a fixed property of the soil and changes with fluctuations in groundwater levels and will fall with LNAPL recovery. This relationship can be complex and is related to layering of soil types (Beckett & Huntley, 2015).

Broadly, for a given soil at higher saturations, LNAPL is more mobile and the transmissivity is higher. As the saturation of LNAPL is lowered through hydraulic recovery, the mobility of the LNAPL falls in a non-linear manner. Eventually, the rate at which LNAPL can move through the soil reaches a point where continued hydraulic recovery does not cause any material change in the saturation; drainage has materially ceased, and the LNAPL has reached a state analogous to field capacity. Graphs showing LNAPL hydraulic recovery which reflect this condition are referred to as being 'asymptotic'; that is, the recovery rate will continue at a low level and will practically never reach zero. The ITRC (2009) provided guidance on the transmissivity range at which this occurs ($0.01 \text{ m}^2.\text{d}^{-1}$ to $0.07 \text{ m}^2.\text{d}^{-1}$) and provided further guidance in 2018 (ITRC 2018). More accurate values will be specific to any given site and perhaps vary within sites.

While LNAPL mobility as a metric is becoming more widespread, there is still some uncertainty about LNAPL behaviour, and several recent papers attest to this (Beckett & Huntley, 2015; Gatsios et al., 2018).

Transmissivity in the context of bulk recovery

An idealised LNAPL recovery curve is shown in Figure 2, produced in the American Petroleum Institute's (API) LNAPL Distribution and Recovery Model (LDRM) using default input data (Charbeneau, 2007). The parameters are provided in Appendix 1. This shows that at the start of LNAPL recovery, the transmissivity is high but quickly falls. The recovery rate is fast at the start but declines non-linearly with time. The time to reach the upper transmissivity cut-off point of $0.07 \text{ m}^2.\text{day}^{-1}$ is around 1.3 years (69 weeks), and the lower limit of $0.01 \text{ m}^2.\text{day}^{-1}$ takes 4.1 years. During the change in transmissivity between these two points, 4.5 m^3 of LNAPL would be recovered, compared to 28.5 m^3 in the first 1.3 years. After 5 years, 33.4 m^3 of LNAPL would be recovered. To recover the total hydraulically available LNAPL (35.75 m^3) would take around 695 years. Appendix 1 provides the modelling parameter values.

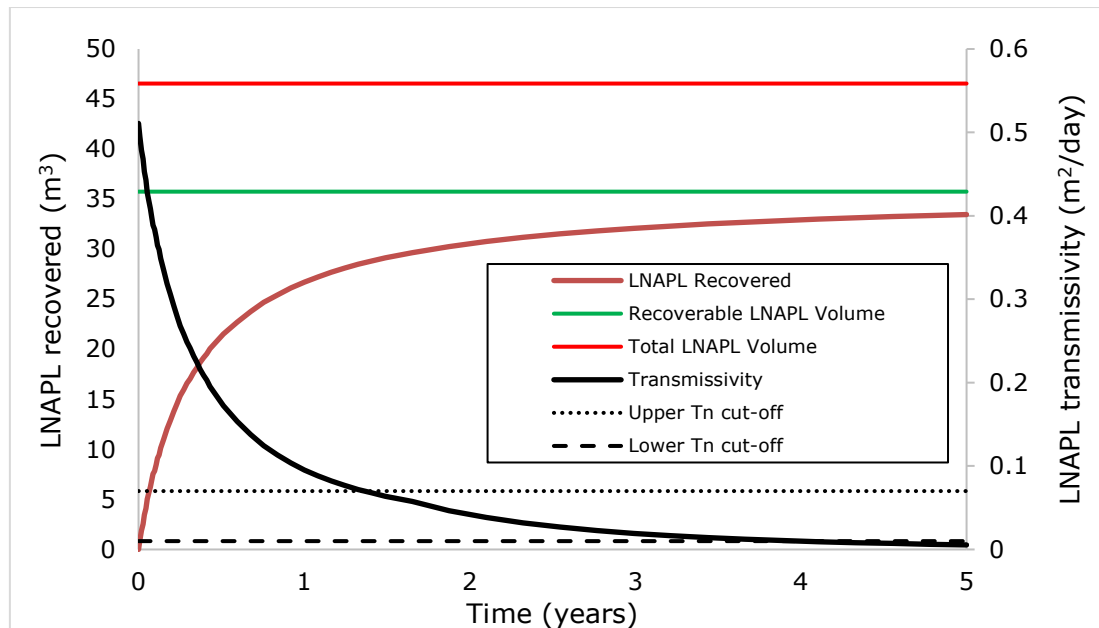


Figure 2. An idealised LNAPL recovery rate curve produced in the LDRM. The dashed horizontal lines show the ITRC recommended cut off for hydraulic recovery. Also shown are the total size of the modelled plume (red) and the hydraulically available fraction (green)

LNAPL transmissivity as a metric for starting LNAPL recovery, technology change during a treatment train approach and also for verification has been demonstrated to be a sustainable remediation approach (Maini & Holmes 2019; Holmes, 2020). This followed the definitions given in Adamski et.al., (2003) and references therein, and from concepts used in crude oil extraction, with support from the CL:AiRE LNAPL Handbook (2014) and the ITRC LNAPL guidance (2018).

When transmissivity is high, it shows that the LNAPL can be hydraulically recovered in volumes that will materially change the LNAPL saturation in the soil. When the transmissivity is low, simple hydraulic recovery is likely to be ineffectual and enhanced recovery may be needed. The risks to the wider environment will determine any remedial measures and the point at which recovery works cease.

It is important to note that as transmissivity is a function of several factors, which may change from site to site, and well to well on the same site, it does not necessarily correlate with thickness of LNAPL in wells. Should all other factors be equal however, LNAPL transmissivity will correlate with LNAPL thickness, and it can be used as a screening tool when the geology is known (SoBRA, 2023: LNAPL Mobility Screening Tool). LNAPL thickness alone and transmissivity data from several sites (Figure 3) shows that there is no relation between the

thickness of LNAPL in a well and its mobility. (NB this doesn't account for variations in geology and other factors that may affect transmissivity).

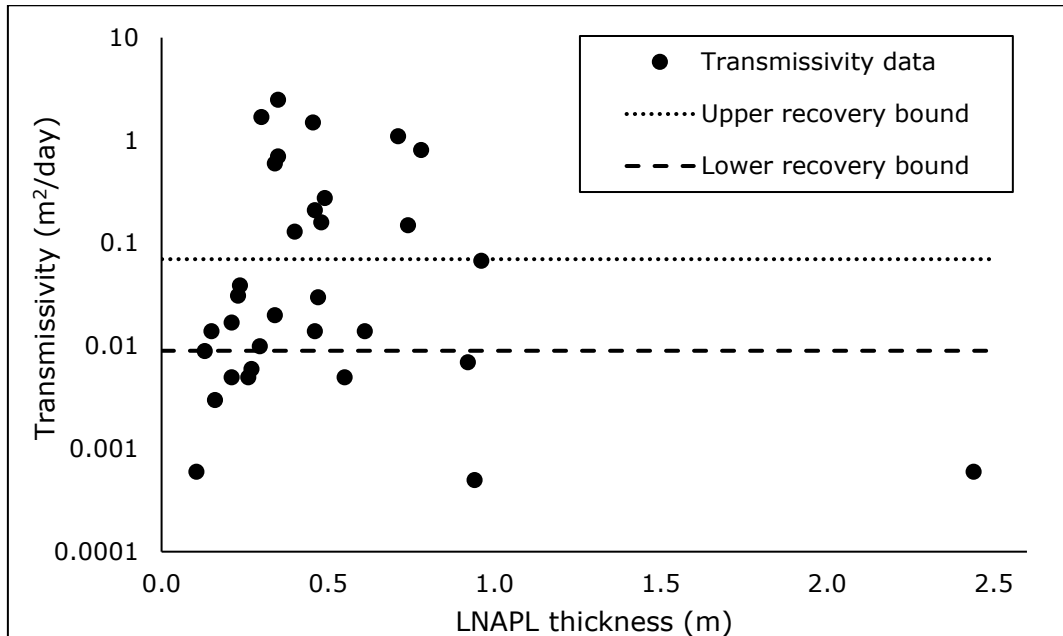


Figure 3. A range of LNAPL thicknesses and corresponding transmissivities, used with permission of Ecologia Environmental Solutions Limited. The upper and lower recovery bounds are taken from the ITRC (2009) publication.

A low transmissivity below 0.01-0.07 m²/day shows that LNAPL is not readily hydraulically recoverable, though it can accumulate in monitoring wells to an in-well LNAPL accumulation of over 2 m where the geology is low permeability, as shown in Figure 3. One of the *causes* of the low mobility for a given system is commonly a low saturation of LNAPL in the pore space, though viscous LNAPL may have an intrinsic resistance to flow which would prevent rapid recharge. Understanding the contribution of each factor is beyond the scope of this document.

An extensive thickness of LNAPL in a well, conversely, does not show that there is large volume of LNAPL within a soil surrounding a monitoring well.

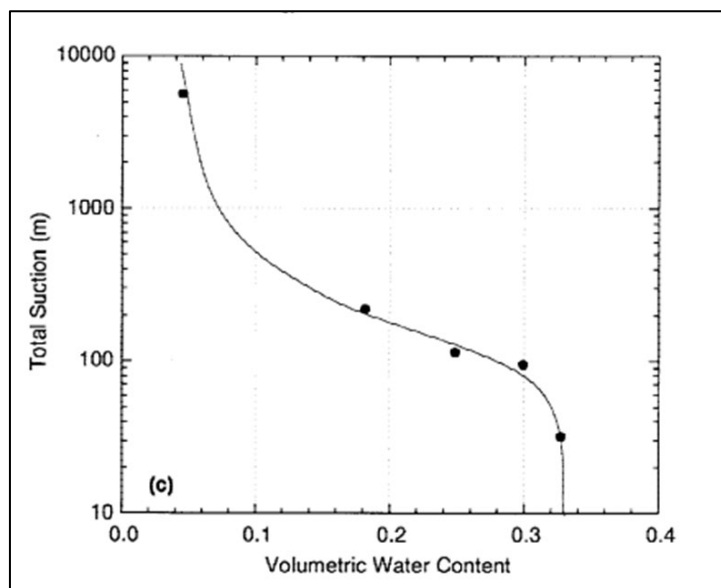
Low mobility LNAPL is sometimes referred to as 'residual LNAPL' which can lead to confusion between what is left behind during recovery and the term 'residual saturation' which is used throughout soil science.

2.2 Residual saturation in unsaturated flow

Residual saturation relates to the endpoint of *liquid* drainage from a soil. If a column of sand is saturated with water and then left to drain from the base, air is pulled in to replace the

water in large pore spaces. The water that remains does so because of matrix suction. As the wetting fluid, it coats the soil particles so that the water molecules are all in continuity. Gravity imposes an effect, so that the water at the base of the column pulls the water at the top. However generally there is not enough gravitational force to overcome the cohesive forces of adhesion and capillarity that hold the water in the smaller pores. Given sufficient height, the column of sand can generate extensive suction, yet water will remain at the top of the column. The relationship between applied suction and moisture content is not linear and depends on the soil characteristics.

A soil water characteristic curve (SWCC) or capillary pressure curve shows that a measurable quantity of water can remain even at suctions of over 5000 metres. A typical SWCC is shown in Figure 4. A curve, typically derived from the Van Genuchten (1980) or Brooks and Corey (1964) models, is fitted to data points collected through several techniques described in ASTM D6836 – 02 The Use of Hanging Columns and Pressure Plate Apparatus.



**Figure 4. A capillary pressure curve for water and air. Note the log scale for suction.
Modified from STM D6836-02**

Figure 4 shows that the suction in a soil can exceed what would be equal to an absolute vacuum, which is due to the tensile strength of water. The water cannot be moved, even as the suction tends towards infinity. The water remaining is referred to as the irreducible saturation or the residual water content. This forms the lower bound of effective saturation, or the range over which fluid can exist in a porous media, if drainage (water moving out of the soil) and imbibition (water moving into the soil) are considered. For the sake of clarity,

hysteresis has been omitted. Hysteresis refers to the different shape of the SWCC depending on whether the soil water content is falling or rising (Haines, 1930).

The water can be removed by other methods such as drying, but the process of drying is one of evaporation and involves a phase change of the water.

Figure 4 can also be recreated with LNAPL in place of water, or in a three phase (air-LNAPL-water) system (Kechavarzi et al., 2005; Porter et al., 2010). Figure 5 shows air-water, LNAPL-water and air-NAPL capillary pressure curves. These are different shapes: the influence of one phase on the other is different for each pair. Therefore, in an air-LNAPL system, the LNAPL saturation will be lower at a given capillary pressure than in an LNAPL-water system.

An LNAPL body may experience both situations during groundwater fluctuations, giving rise to temporal changes in LNAPL mobility when LNAPL saturation remains constant.

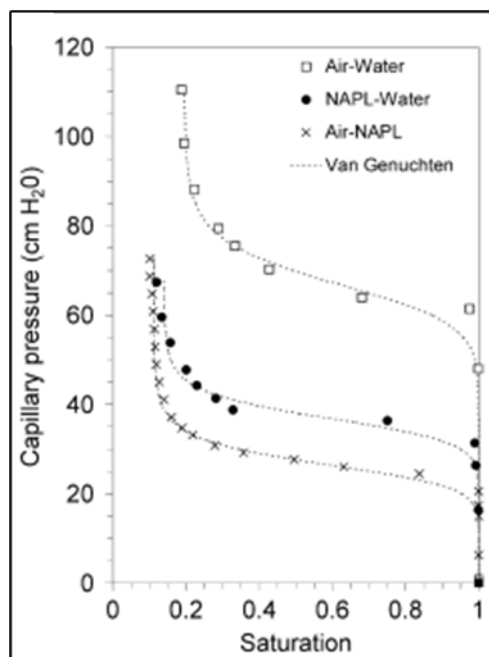


Figure 5. Capillary curves for Air-Water, LNAPL-Water and Air-LNAPL. Modified from Kechavarzi et al. (2005).

The concept of LNAPL residual saturation can then be viewed equal to the point at which LNAPL saturation cannot be reduced by suction, following the concept for water (Brooks & Corey,

Soil can hold water by capillarity. This may have minimal drainage. The same is true of NAPL: it can be held in the soil by capillary effects and drain very slowly into larger pores – monitoring wells for example. It may accumulate over time (potentially years) but is not recoverable by simple pumping in a meaningful sense.

1964). For modelling of multiphase systems, this is very useful and allows adaptation of these models to describe LNAPL during LNAPL recovery (Jeong & Charbeneau, 2014). Of note, in environmental projects insufficient NAPL is usually released to fully saturate the pore space. Hence the application of experimental data such as these examples from the literature to a specific site conceptual model should only be done with caution (Charbeneau, 2007), and they are used here for illustrative purposes.

An added complication relates to how the presence of water affects LNAPL movement. In the capillary fringe above the water table, where LNAPL will accumulate, air, LNAPL and water will be present. For the sake of simplicity, Figure 6 shows relative permeability curves for an oil-water system (air is omitted) where water is the wetting fluid. As the water saturation falls, its relative permeability decreases. Conversely, as the oil (LNAPL) saturation increases, the permeability increases. The shape of these curves is related to the soil and fluid types: a relative permeability curve where LNAPL is the wetting fluid and air is the non-wetting fluid would be of a different shape. LNAPL-impacted sites are frequently found where groundwater fluctuates and therefore the water saturation will vary, and types of relative permeability will be temporary. When the groundwater is high, the capillary fringe will be mostly LNAPL: water, when it is low, there will be greater LNAPL: air scenarios.

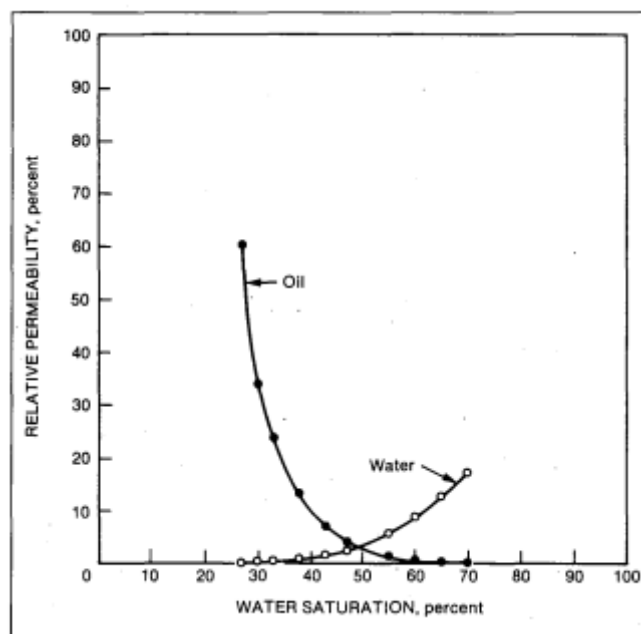


Figure 6. Relative permeability curve of oil and water. Modified from Honarpour & Mahmood (1988).

When the two predominant fluids are LNAPL and air, LNAPL becomes the wetting fluid and can become continuous, and thus drain into larger pores (i.e. monitoring wells) allowing the same

mass of LNAPL to change from immobile under high groundwater levels to apparently mobile during periods of low groundwater. This is further discussed in Section 4.1.

2.3 Field capacity

Field capacity refers to the amount of water that a soil can hold when drainage has materially stopped and is not generally precisely defined (Hillel, 2004). The concept applies also to LNAPL, where the rate of drainage (i.e. movement into a well) will slow over time with recovery as saturation is reduced (as shown in Figure 2). It is perhaps more useful to consider this the end of meaningful LNAPL recovery by hydraulic recovery, and this was discussed by Adamski et al. (2003). The remaining LNAPL in the soil would be mobile and accumulate in wells but continued recovery would not materially change the LNAPL saturation in the soil per unit time. This is shown in Figure 7, using water as an example.

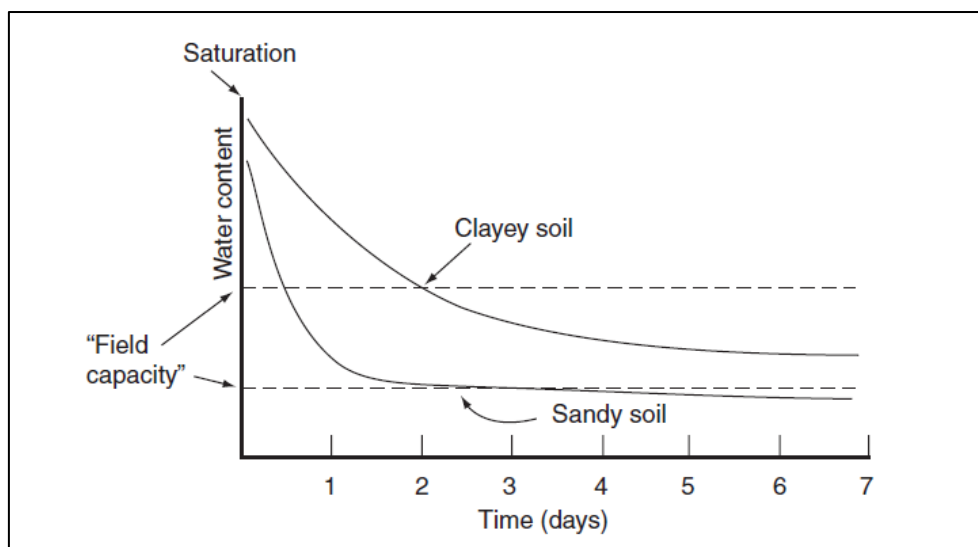


Figure 7. Example of Field capacity for two soils, using water as the fluid. Drainage (and therefore accumulation in wells) would continue beyond field capacity but accumulation would be slow. Modified from Hillel (2004).

The water content for the Sandy Soil in Figure 7 falls to a near-static level after two days. If this was recovered, the recovery rate would be constant and tend towards infinity. This would form an asymptote – and show asymptotic recovery.

In a soil with an initial high LNAPL saturation, recovery would be significant in the initial stages. As the saturation falls over time, the recovery rate falls and when the soil reaches 'LNAPL field capacity' (analogous to water field capacity) the recovery rate will become asymptotic.

3 CURRENT GUIDANCE

The current guidance and scientific literature use a number of descriptions for residual saturation. These are given in Table 1, below, together with an interpretation of their meaning.

Table 2. Definitions of 'LNAPL residual saturation' from the literature and guidance

Author	Definition	Comment	Related concept
Tomlinson et al. (2017)	...residual (i.e., fraction of the pore space occupied by LNAPL that cannot be mobilized under an applied gradient	A quantitative explanation that follows the definition of residual water saturation	Irreducible saturation: not mobile
	"... when the LNAPL saturation is below residual the same well will <i>typically</i> not observe LNAPL	Of more practical use. Author's emphasis.	Minimally mobile – may appear in wells, but is in a practical sense unrecoverable
Newell et al. (1995), US EPA guidance	"not readily removed using currently available remediation technologies"	Related to the practicality of hydraulically removing LNAPL	Minimally mobile – may appear in wells, but is in a practical sense unrecoverable
Kechavarzi et al. (2005)	"...in this paper the term residual NAPL saturation used to describe the minimum NAPL saturation that occurs after NAPL drainage"	This equates to an 'NAPL field capacity'; which is different to the first definition of Tomlinson et al (2017)	Minimally mobile – may appear in wells, but is in a practical sense unrecoverable
CL:AiRE Illustrated LNAPL Handbook (2014)	"As [residual LNAPL] is held by capillary forces, residual LNAPL is <i>difficult</i> to mobilize"	Author's emphasis. 'difficult to mobilize' is not the same as 'cannot be mobilized'. It is also discussed in the handbook in the context of enhanced recovery, but it is unclear if the 'difficult to mobilize' phase means possible only with heat or surfactant injection or under a strictly hydraulic regime.	Potentially means that the LNAPL is completely immobile (i.e. irreducible saturation) and can only be mobilized by enhanced recovery techniques. LNAPL at this saturation would not appear in monitoring wells.

These are both quantitative and qualitative definitions, and are open to interpretation, especially when evaluating risk and devising risk management strategies.

ITRC (2017) guidance frames LNAPL as 'migrating', 'mobile' and 'residual'. In a practical sense, the boundary between 'mobile' and 'residual' is not constant and from a risk point of view, there is little meaningful difference between 'residual' and 'mobile' when the ability of the LNAPL to move is minimal.

LNAPL is induced to move into a well by enhancing the gradient by increasing the drawdown in a well during LNAPL recovery because LNAPL flows from high to low pressure. The drawdown is the rate limiting factor and is typically of the order of 10% of the LNAPL thickness unconfined in wells during skimming. It is possible to apply a vacuum for enhanced recovery, but this negative pressure will rapidly become discontinuous with the LNAPL as air and water are drawn in. In practice, residual saturation may be challenging to be created in the vadose zone and required extended timeframes.

In theory, it is possible to create large suctions to reduce LNAPL saturations to the point where they become residual. In practice, however, it is generally not feasible.

4 OTHER FACTORS AFFECTING LNAPL MOVEMENT DURING DRAINAGE

The vadose zone – where the soil water is not completely saturated – has been referred to as a ‘somewhat mysterious realm’ (Fetter et al., 1999). There are changes in pore water saturation through water table fluctuation and percolation from surface inputs. If LNAPL is present, this will be subject to interactions with pore water and gas as well as degradation by autochthonous microbes (Garg et al., 2017). This results in the soil being a dynamic environment and not being fixed in time with implications for the appearance of LNAPL in monitoring wells.

The following sections discuss processes taking place in the soil and how these may affect LNAPL.

4.1 Groundwater fluctuation and variability

A second factor influencing residual saturation for LNAPL is the presence of groundwater and a fluctuating water table. Groundwater fluctuations affect soil water suction. Should the groundwater level fall, the soil pore water pressure in the unsaturated zone will also decrease creating a concurrent fall in water saturation. Consequently, the LNAPL relative permeability will change as less pore space is occupied by water and LNAPL can be mobilised as water saturation falls. The presence of a second liquid can change the behaviour of the first, and vice-versa (Naeini & Hosseini, 2016).

Groundwater generally shows some degree of fluctuation and is influenced by numerous factors, including tides, variations in air pressure (Toll & Rasmussen, 2007), precipitation, or off-site pumping or other factors (Lewandowski et al., 2009).

These fluctuations and water drainage will act to cause changes to the soil-water suction. The change in soil moisture content as recorded by soil suction was documented by Smethurst et al. (2006) over several months, as shown in Figure 8. A change in the soil-water suction lowers the water saturation, which can lead to the mobilisation of LNAPL (Naeini & Hosseini, 2016).

Therefore, the mobility of LNAPL in the unsaturated zone will be influenced by the water content. As water content falls, the relative permeability of the LNAPL can increase and may lead to vertical and lateral movement of the LNAPL.

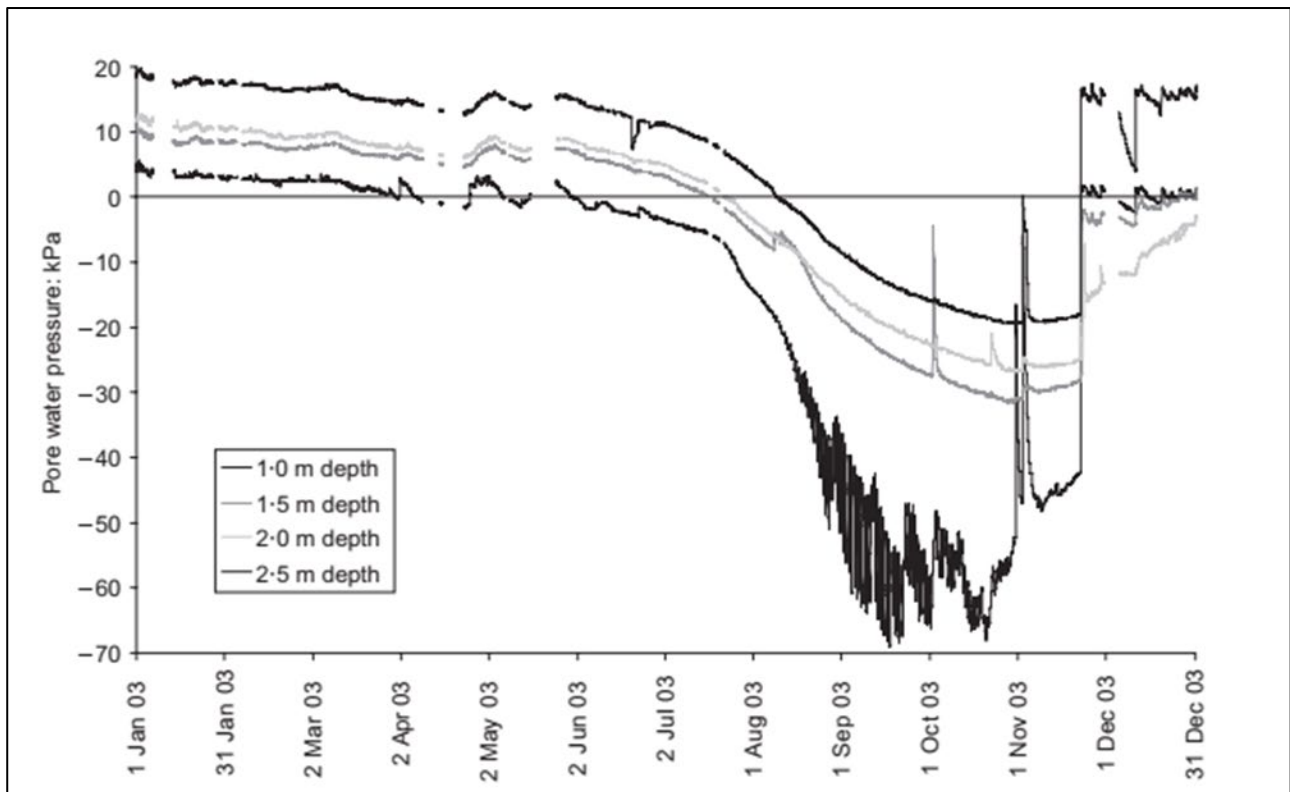


Figure 8. Changes in the soil water suction over time in a London Clay cut slope. Modified from Smethurst et al. (2006).

4.2 Soil heterogeneity

A third factor affecting residual saturation is the role of soil heterogeneity. LNAPL recovery frequently takes place in made ground which is highly heterogeneous. Other LNAPL recovery projects take place in soils that can be described as 'homogenous', but the distribution of LNAPL within them is rarely so.

On the pore-scale, soils are not homogenous. They have a range of pore sizes, pore-throat sizes, and pore connectivity. These variations will affect infiltration of a LNAPL.

Figure 9 shows a 5 x 5 cm sample of homogenous sand visualised under a light transmission technique. This figure shows there is significant heterogeneity at a scale relevant to LNAPL transport.

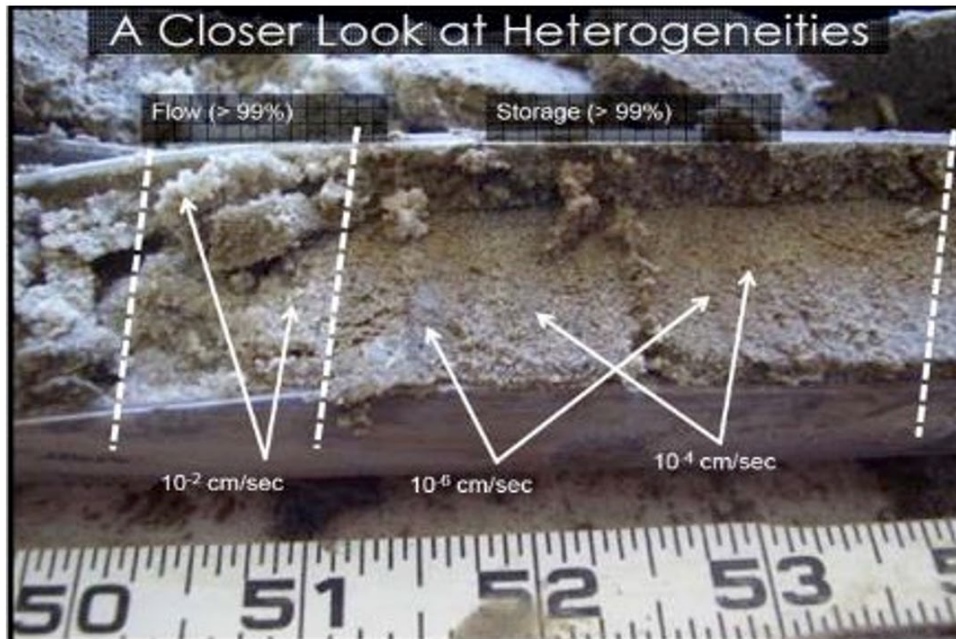


Figure 9. Local heterogeneity in an apparent homogenous sand. The units on the scale are in inches. Modified from Payne (2020).

The distribution of differing pore throat sizes leads to localised differences in the entry pressure required for a fluid to enter a given pore. This phenomenon leads to “fingering” by a fluid entering the soil, even in a supposedly homogenous media. Here, the range of pore sizes, pore throats and connectivity give rise to discrete flow channels, resulting in wide variation of fluid saturation over a small area.

Figure 10 shows the effect for water moving into a dry and homogenous sand. The figure shows the distribution of the fluid draining into the sand does not do so in a uniform manner.

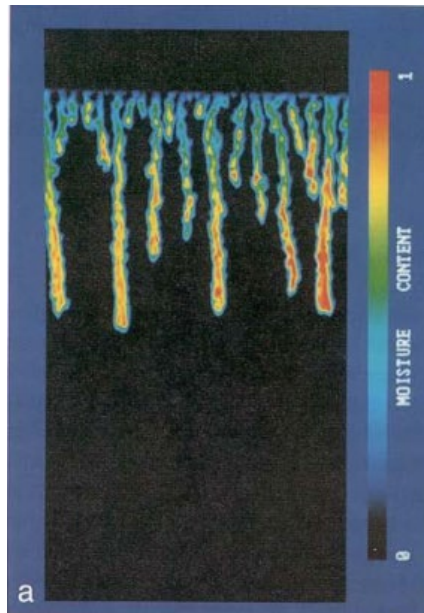


Figure 10. Viscous fingering by water in a dry homogeneous soil by. Modified from Glass et al. (1996).

Therefore, the distribution of LNAPL which enters soil can be highly variable. Figure 11 shows a photograph of a LNAPL-containing soil core under UV light. The sample was approximately 75 mm in diameter, yet shows a range of LNAPL saturation, from around zero (darker) to more heavily saturated (lighter) areas.



Figure 11. Heterogeneity of NAPL saturation in a window sample. ©Ecologia Environmental Solutions Limited.

In practice, this means that even a homogenous soil will have a range of LNAPL saturations and therefore a range of residual saturations. The soil heterogeneity will also influence water content as described in Section 2.2.

4.3 Soil wettability

For LNAPL movement into soil, a further complicating factor is the change of wettability (Seyedabbasi et al., 2008). Wettability refers to the tendency of a fluid to spread over a solid surface. A wetting fluid will spread over a surface whereas a non-wetting fluid will tend to 'bead up'. The presence of a second fluid (either air or water) will change the wetting behaviour of the first. The characteristics of a surface also affect wetting behaviour (Hajnos et al., 2013). Increasingly LNAPL-wet conditions can lead to a reduction of the magnitude of fingering. Soils are generally water-wet initially, so fingering may be significant in the initial stages of a spill. The rate of change of wettability and reduction in fingering has however numerous uncertainties surrounding the surface properties of soils in the presence of hydrocarbons and the changes of LNAPL in the subsurface (Said, 2010; Banno, 1996).

Of special mention are asphaltenes in bunker fuels or crude oil can cause a reversing of the wettability of the LNAPL where the soil can become "LNAPL-wet" (Kim et al., 1990). Asphaltenes are large molecules which may contain both polar and non-polar parts (Mullins, 2011). In turn the LNAPL can potentially support continuous flow at much lower saturations that would otherwise be the case. The transmissivity-saturation relation (as described in Figure 2) would therefore be different to non-wetting LNAPLs. A further complication for these LNAPL is that the rate at which they can be recovered for a given saturation in a given soil is much lower than lighter LNAPLs due to their viscosity.

This effect is not only confined to NAPLs containing asphaltenes. The wettability of fresh diesel was compared to diesel recovered from a NAPL site by Drake et al. (2013). It was found that over time, the wettability of diesel changes with the soil becoming more NAPL-wet. Furthermore, it was reported the interfacial tension in the field diesel was lower than a fresh diesel (17.2 mN.m^{-1} and 28.1 mN.m^{-1} respectively) and that there were changes in the advancing and receding contact angles. The contact angle influences how a LNAPL can move into pores and is important for lower-permeability soils (and is discussed in the SoBRA 2023; LNAPL Mobility Screening Tool): typically, a LNAPL would become more viscous with time as smaller hydrocarbon components are removed by dissolution and degradation, though if the wettability is reversed its ability to flow at low saturation may increase. Note: the default input parameters shown in Appendix 1 appear to relate to a fresh diesel.

Therefore, as the NAPL properties which influence multiphase flow change over time, so may the NAPL's ability to move in the subsurface. The shapes of the curves presented previously in Figure 6 may change as the properties of the NAPL alter with time.

In a continuous fluid in a natural soil, groundwater fluctuations will cause changes in water and LNAPL suction, which may act to release LNAPL from entrapped pores. Soils may be preferentially wetted by the LNAPL, depending on both the soil type and the LNAPL components (Anderson, 1986).

4.4 Non-continuous movement

Any LNAPL that is present in the soil in isolated globules will not flow under a pressure gradient (unless within large voids such as open fractures or solution features). However, soil is subject to several processes that may cause LNAPL movement. Rainfall percolates through the soil, and so its presence will affect pore water saturations potentially changing LNAPL relative permeability. Additionally, LNAPL chemistry will change over time due to biodegradation, dissolution into water and water dissolution into LNAPL (Leharne, 2019). The capillary pressure curve of the LNAPL can also change over time due to weathering, which lowers the residual saturation, a concept described by Drake et al. (2013) as effective saturation. These effects may also induce LNAPL movement on a small scale. The soil itself does not provide a fixed pore network, that is the soil particles themselves may move albeit subtly for example during dewatering and this has been an issue in experimentation (Ren & Santamarina, 2018). The movement of soil particles means that the pore sizes may not be constant, which in turn may lead to changes in the relative permeability and thus LNAPL movement. Soil movement and therefore pore network change can be caused by surface activities such as drilling, settlement, ground improvement works and earthquakes. An example is given by Nikolaevskiy et al. (1996) who investigated seismic waves effects of crude oil production at distances of up to 200 kilometres which showed changes in the oil: water recovery ratio (the 'water cut').

5 A PRAGMATIC APPROACH

Adamski et al. (2003) presented pragmatic definitions of LNAPL residual saturation. Notably, these definitions are analogous to field capacity, that is, where drainage 'materially decreases' (Twarakavi, et al., 2009) and does not become completely immobile. In some of the first investigations aiming to define LNAPL saturation (cited in Adamski et al., 2003), Hoag and Marley (1986) ran an experiment to measure the physical volumes of LNAPL left in soil after drainage. The method allowed drainage of LNAPL from a column of sand "... for several hours leaving the soil approximating residual saturation". Importantly, this procedure would not result in a fully drained soil (residual saturation), but in a condition analogous to field capacity. The LNAPL saturation in each case was dependent on the depth of the specimen; there will be greater negative pressures acting on the LNAPL at the top of the specimen than at the bottom, even if the base is freely draining. The resulting residual LNAPL saturation was therefore variable at different points of the column, even in this relatively simple experiment.

This concept is shown in Figure 12 which shows the evolution of the capillary pressure during drainage of an organic soil during a one-step drainage in a soil column.

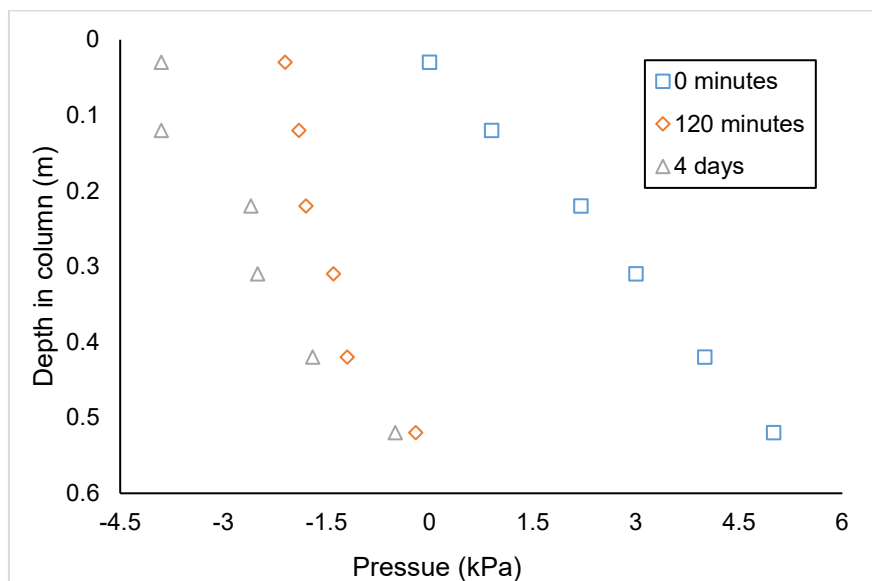


Figure 12. The evolution of the capillary pressure with depth in a one-step soil column drainage experiment. Re-drawn from Zardava (2012).

Figure 12 shows a saturated and drained column of organic soil where the soil water suction was recorded at discrete heights. The increased suction at each level is indicative of a falling water saturation.

In terms of an LNAPL remaining in the soil at either 'field capacity' residual saturation or 'immobility' residual saturation, the saturation will depend on the interactions of the soil type,

soil stratification, LNAPL type and the historic maximum LNAPL saturation, where a greater historical maximum LNAPL saturation will lead to a greater residual saturation. This is sometimes referred to as the 'f-factor' (Johnston and Adamski, 2005).

While there would be practical difficulties in measuring the exact value for the 'f-factor', a spill resulting in high LNAPL saturations would have a higher residual LNAPL saturation following hydraulic recovery than a smaller spill. Only a percentage of LNAPL is recoverable and that fraction is dependent on the soil type and maximum saturation. This has implications for the mass of LNAPL remaining following hydraulic recovery. To remove the remaining fraction, modifications of the LNAPL properties are required. These can be achieved through chemical means such as surfactant flushing (Sharma et al., 2020), or physical processes such as thermal remediation (Colombano et al., 2020).

6 DISCUSSION

There are a number of factors that can influence LNAPL mobility and lead, over time, to its accumulation in monitoring wells. Although computer models can be a powerful and cost-effective remediation design tool, it is difficult to capture all the parameter values to reflect all theoretical terms.

The combined effect of soil heterogeneity and generally limited resources available for land remediation projects limits the development of more sophisticated models, although progress is rapidly being made (Sookhak et al., 2019).

The presence of LNAPL in a monitoring well and its mobility inform one aspect of the conceptual site model (CSM). A further complication for remediation design is that hydraulically recovering LNAPL as far as practicable does not mean an end to remediation: an end to hydraulic recovery is not always a useful remediation target. Remaining LNAPL has the potential to act as a source for dissolved hydrocarbons and vapour, and this may continue for many years. Microbial action will also degrade the LNAPL at site-specific rates. Hydraulic recovery can only address saturation concerns and may not address any pathway concerns, such as transport of dissolved-phase contaminants, which are a function of LNAPL composition and the wider conceptual site model. Recovery of LNAPL will lower the total contaminant mass and decrease the time over which a site may pose a risk, and LNAPL mobility should be viewed as one aspect of characterising an LNAPL body and a part of the CSM. Hydraulic LNAPL recovery is a cost-effective process to remove LNAPL at high saturations, but when the transmissivity reaches lower levels and recovery becomes asymptotic it ceases to be a process which can lower the risk for LNAPL in an aquifer.

The processes outlined in Section 4 are unlikely to cause significant LNAPL mobilisation. However, even if the LNAPL is present at saturations where it is discontinuous, then there are still events that may cause small volumes of LNAPL to move in the soil. Therefore, LNAPL can accumulate in boreholes for reasons other than a gradient exerted through a hydraulically continuous fluid body. These mechanisms of LNAPL movement will be greater in soils that have larger pore spaces, for example in reclaimed land where LNAPL recovery commonly takes place. It would also not be practical to separate very slow continuous flow described in Section 4.4 from discontinuous flow arising from the above. The questions arising from LNAPL accumulations relate to if and how it can be recovered at rates which materially change the LNAPL saturation and how doing so would change the CSM.

7 SUMMARY

The use of transmissivity is a positive step towards incorporating the theory of LNAPL movement in soil into practice and has a demonstrated use. However, not every theoretical aspect is completely applicable to the practical aspects of remediation and contaminated land management. Any practitioner should be aware of the difficulties of bridging the gap between the textbook and the site.

It is important to be mindful that LNAPL recovery does not take place in a closed system. The deviations from idealised LNAPL behaviour discussed above may be a cause of concern. LNAPL is subject to several processes which may lead to its accumulation in a monitoring well and capturing these processes from an analytical viewpoint may not be feasible.

When described from a modelling point of view, 'residual saturation' is very simple to define: the LNAPL is held as discontinuous drops which cannot sustain a pressure gradient which in turn cannot flow. However, this definition is not very useful in practice, given that other factors such as water drainage in the vadose zone leading to an increase in relative LNAPL permeability, chemical changes in the LNAPL leading to changes in wettability and propagation of mechanical waves through the soil which may influence LNAPL behaviour in the sub-surface. Should any modelling be carried out, it is advisable that well-specific parameters are gathered. The sensitivity of parameters is discussed in SoBRA's LNAPL Mobility Screening Tool (2023).

Ultimately, when considering whether LNAPL at a given site poses a risk to the wider environmental and human health, there is little functional difference between the totally immobile and minimally mobile NAPL. This is because the difference in NAPL saturation and therefore total NAPL mass can be quite small. The NAPL should be viewed in the context of the broader risk to the wider environment. By itself, LNAPL presence in wells is a poor indicator of potential risk and should not be used as a line of evidence in isolation.

NAPL measurement is addressed in the upcoming SoBRA document '*NAPL Monitoring Options and their Merits*' (SoBRA, *in preparation*). LNAPL remediation and metrics around recovery are addressed in SoBRA's document '*Choosing an Appropriate Sustainable Remediation Approach*' (SoBRA, *in press*). The documents outline the tools and methods available to assess LNAPL and how to reduce the risks it poses. They can be combined with the approach in this document for a theoretical underpinning of LNAPL science to provide confidence to stakeholders that a scientific-based approach to managing LNAPL sites has been taken.

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APPENDIX 1

LNAPL Distribution and Recovery Model Parameter Values

Unless otherwise stated, the parameter values are the model defaults. The units follow those in the model.

Aspect	Parameter	Unit	Value
Well geometry	Ground Surface Depth	m	0
	Groundwater Table Depth	m	2
	Water Vertical Gradient	-	0
Fluid Characteristics	LNAPL Density	g.cm ³	0.8
	LNAPL Viscosity	cp	2
	Water Surface Tension	Dyne.cm	65
	LNAPL Surface Tension	Dyne.cm	25
	LNAPL/Water Interfacial Tension	Dyne.cm	15
Soil Characteristics	Relative Permeability Model	-	Burdine
	Soil Porosity	-	0.4
	Hydraulic Conductivity	m.day	1.5
	van Genuchten 'N'	-	3.5
	van Genuchten 'α'	m ⁻¹	6.5
	Water Residual Saturation	-	0.25
	NAPL Residual Saturation	-	0.1
	LNAPL f-Factor	-	-
Recovery Characteristics	Recovery Time (increased from default)	Years	5
	Radius of Skimmer Well	m	0.06
	Radius of Capture (decreased from default)	m	5