Selecting and assessing strategies for remediating LNAPL in soils and aquifers

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Executive summary

Light non-aqueous phase liquid (LNAPL) petroleum hydrocarbons are complex mixtures of chemicals that variably partition into water and gaseous phases when released into subsurface environments. They pose a range of concerns – from issues of aesthetics and nuisance to acute risks to human health and the environment. The properties of LNAPL and its interaction with geological strata make effective removal of LNAPL contaminants difficult. Indeed, effective remediation and amelioration of concerns may not be possible in many situations. In addition, much uncertainty arises through an incomplete understanding of the potential effectiveness of LNAPL remediation strategies in different subsurface settings.

Major challenges in addressing LNAPL contamination include:

- knowing enough about likely LNAPL behaviour in subsurface environments
- building an adequate LNAPL conceptual site model
- adequately assessing all concerns posed by LNAPL at a site
- defining technology and site end points
- balancing the need for action at a site with achievable end points
- overcoming the lack of information on the field-scale effectiveness of remediation technologies in different settings
- matching the capability of remediation technologies to desired remediation end points for a site
- having adequate measures to quantify the performance of remediation technologies
- knowing when and if remediation technologies reach their practicability limits
- determining the net environmental and social benefits of LNAPL remediation.

This report seeks to provide information and a framework that would allow some of these challenges to be addressed. It provides guidance in selecting and matching the performance of remediation technologies to a range of subsurface settings, risk reduction targets and concerns. The emphasis here is on LNAPL that has infiltrated to the water table and in settings of major relevance to Australia. One of the aims is to identify the gaps in the current understanding of remediation process and performance in the various subsurface settings. Not all the information required is available or known. As such, this document provides a status report, which can be updated as research and additional experience fills the identified gaps.

We examine existing (and some past) approaches to LNAPL remediation in Australia and internationally. In the context of risk-based remediation, the process of identifying concerns (including risks) that may trigger LNAPL remediation is described. It is then shown how the identified concerns are used to formulate remediation objectives from which remediation end points may be defined. This process is set in terms of the overall goals and long-term vision for the condition and use of a site. It is these goals and long-term vision that will drive remedial efforts. The concepts of technical impracticability, clean-up to the extent practicable and clean-up to the extent necessary are described. These may be invoked in response to encountering technical and other
factors limiting the success of remediation and preventing the desired end points being reached.

A summary of the nature and behaviour of LNAPL petroleum hydrocarbons in various subsurface settings is presented. This includes a general classification of subsurface environments and outlines the important differences in LNAPL behaviour in these settings. Descriptions of the major soil and aquifer systems of interest in Australia are also provided.

In terms of remediation technology selection, emphasis is placed on the process of identifying the risks and concerns associated with the presence of the LNAPL, defining remediation objectives to ameliorate these and establishing the remediation end points that will ensure these objectives are met. As part of this selection process, there is discussion of how specific risks may be addressed, particularly where they relate to individual constituents or classes of constituents of the LNAPL. Key to this is an understanding of how LNAPL mass reduction reduces specific risks or ameliorates particular concerns.

The report provides an extensive examination of the technologies available for LNAPL remediation. The most common in situ remediation technologies are examined along with approaches for the containment of LNAPL. These technologies are grouped as those based on: free-LNAPL recovery; volatilisation and biodegradation; engineered bioremediation; chemical flushing; in situ chemical oxidation; thermal methods and containment. Key factors in the selection of remediation technologies are identified as: the physical setting; remediation objectives and end points; and impacts of the remediation. These factors are imbedded in the steps presented for selecting a remediation technology for a particular site.

Process descriptions of 20 individual remediation technologies are provided, including how they relate to the key selection factors. To aid the preliminary screening of remediation strategies, tables of generalised effectiveness are presented. Effectiveness is rated in given settings, applicability to concerns, assessment of their impacts and other implementation factors. Such rankings and assessments are multi-dimensional in nature. Those given in the report are general in nature. However, how rankings and assessments will vary dependent on specific remediation objectives is emphasised. Also, the rankings and assessments are indicative and based on what is known of the underlying principles of the remediation technologies. The large number of permutations and lack of well dokumented, published case studies on remediation effectiveness prevent greater use of field evidence in general rankings.

Stipulation and measurement of performance indicators are seen as fundamental for assessing candidate LNAPL remediation technologies. Performance indicators are also crucial in evaluating the implementation of particular remediation schemes. Ultimately, performance indicators are also used to decide when remediation should cease. A range of performance indicators applicable to the remediation technologies evaluated here are suggested for use. Also, underlying metrics (e.g. mass of LNAPL removed) are presented on which the performance indicators may be based.

Published Australian case studies were reviewed in an attempt to extract experience and guidance on LNAPL remediation performance in settings of particular significance in Australia. This review revealed a dearth of published case studies. Those readily available covered few of the possible remediation technologies and had a sparse
coverage of the possible settings. Particular gaps were encountered in reporting of chemical flushing, in situ chemical oxidation and thermal methods. Surprisingly, some of the free product recovery techniques were also poorly reported. In relation to geological settings, gaps were evident in the experience reported for dual porosity materials and fractured rocks.

Full-scale implementation of an LNAPL remediation strategy is commonly preceded by some form of pilot-scale testing of candidate technologies. Here, the process of pilot testing is discussed in terms of how maximum benefit and appropriately representative results may be achieved. The report discusses appropriate performance indicators and metrics, variability, duration and end points of testing as well as the characterisation required for up-scaling and extrapolation.
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1. Introduction

1.1 The issue

Once released into soils and aquifers, light non-aqueous phase liquid (LNAPL) petroleum hydrocarbons can present significant risks to human health and the environment. Direct exposure to LNAPL presents a risk. However, the partitioning and transport of constituent compounds of the LNAPL into air and water phases creates further exposure pathways and potential additional risk. Remediation of sites where LNAPL is present is usually directed to removing the LNAPL mass. Complete removal can be extremely challenging – from technical, logistical, financial and environmental standpoints. Further, the benefits of partial mass removal on the magnitude and timing of the reduction in risk may be limited or greatly delayed.

Technical challenges to LNAPL removal arise due to: the specific behaviour of LNAPL and its distribution in porous materials; the architecture and heterogeneity of soils and aquifers; and the difficulties in measuring the distribution of LNAPL in the subsurface and relevant aquifer characteristics. These challenges have lead to approaches such as clean up to the extent practicable (CUTEP), clean up to the extent necessary (CUTEN) and technical impracticability (TI), which acknowledge that remediation efforts need to be tempered by practical (logistical and financial) considerations and that complete removal of LNAPL is unlikely to be achieved in most circumstances. When seeking to apply such approaches it is critical to be able to understand and match the performance of different remediation techniques to a range of soil and aquifer settings. The performance in such settings needs to meet a desired target for reducing concerns over the presence of the LNAPL. Commonly during LNAPL removal, an asymptotic condition of limited mass removal occurs over an extended period. Continuing remedial efforts during this asymptotic stage may not be effective, and increasingly the sustainability of the level of resource input is questioned.

Unfortunately, while the concepts of CUTEP, CUTEN and TI are becoming better known, there remain large gaps in information related to the initial and asymptotic performance of remediation options for LNAPL. The wide spectrum of possible physical soil/aquifer settings (e.g. porous, fractured, dual porosity), the range of petroleum types (e.g. gasoline, diesel and crude) and remedial options makes field evaluation of all possible combinations impractical. In addition, generally-agreed measurement metrics are lacking that can be used to show success and allow cessation of active management and/or remediation while being protective of human health and the environment. To address these issues, there is a need to:

- collate the available information on remediation processes and performance
- develop an agreed approach to deciding on candidate remediation techniques
- have a consistent technology assessment process that can be applied to a particular site (including pilot testing)
- have consistent measures of performance, and
- have agreed levels of performance that define practicability/impracticability.
1.2 Scope of the document

This document is presented to inform the selection of remediation strategies for removing LNAPL petroleum hydrocarbons from a contaminated site in the context of the achievable end points for remediation and practicability. The focus is on LNAPL that has infiltrated and spread in the vicinity of the water table. However, LNAPL that exists wholly or partly in the vadose zone as well as that entrapped below the water table is also addressed. The target audience for this document includes project managers of contaminated sites, remediation engineers, owners of contaminated sites and regulators of contaminated sites.

Current knowledge of the behaviour of LNAPL petroleum hydrocarbons as well as the underlying processes and performance of a range of applicable remediation techniques is used in the development of this document. It is acknowledged that the understanding of the behaviour of LNAPL in some subsurface settings is still developing and there are significant gaps in the knowledge of the performance of various remediation techniques for a range of settings of interest. What is known is collated here, and gaps are identified.

The document also focuses on fostering an understanding of LNAPL behaviour in subsurface environments. In particular, it emphasises the significance of the expression of LNAPL observed during monitoring and site characterisation. This document is set in relation to LNAPL petroleum hydrocarbons as a source of risk and other concerns but does not address the assessment of risk per se.

A major element of this document is an assessment of the applicability and performance of LNAPL remediation techniques to different aquifer settings. Emphasis is given here to aquifers of major significance in Australia. Suggested performance metrics and indicators are defined, along with feasible end points for the remediation techniques. In addition, protocols are suggested for undertaking pilot testing of candidate remediation techniques as part of the evaluation at a specific site. Detailed engineering of different remediation techniques is not given. However, the major processes involved and how they impinge on the remediation of the LNAPL are discussed.

Typically, this document would be used to navigate through the process of:

- developing a conceptual model for LNAPL distribution and behaviour at a contaminated site
- identifying the concerns that the LNAPL poses
- formulating remediation objectives and end points for each of the identified concerns
- identifying feasible end points of different remediation strategies
- selecting appropriate remediation strategies to meet the remediation objectives set for the clean up of the site, and
- determining performance metrics and indicators against which the success of any applied remediation strategy may be measured.

Such a process will also provide a basis to explicitly identify the extent to which the clean up of the LNAPL may be necessary or practicable and at what stage the remediation of the LNAPL becomes technically impracticable.
1.3 Terminology

For clarity, we define the most important terms and concepts used in this document.

**Concerns**

Factors related to the presence of LNAPL that have the potential to require the remediation of the LNAPL contamination.

**Entrapped LNAPL**

LNAPL which exists as isolated blobs or ganglia within a single or small number of pores in a liquid-saturated medium.

**Free LNAPL**

LNAPL which exists at a fluid pressure greater than atmospheric pressure and therefore will enter a screened well or open hole.

**Immobile LNAPL**

LNAPL existing as isolated pools of liquid and/or spread as thin films that do not allow it to move under normal pressure gradients in the prevailing conditions.

**Impracticability**

Remediation end points cannot be achieved because:

- technologies are not available for the setting in which the LNAPL contamination occurs, or
- the achievement of remediation technology end points using the most appropriate technologies:
  - provides no net benefit, or
  - requires a disproportionately large effort in terms of the concerns involved.

**Intergenerational equity**

The concept of common stewardship of the environment with past and present generations and the fairness in not leaving contamination, concerns or hazards to be dealt with by the following generation.

**Migrating LNAPL**

LNAPL which is moving vertically or laterally in the subsurface.

**Mobile LNAPL**

LNAPL existing as a continuous, connected body of liquid in the porous media able to move under applied pressure gradients.

**Remediation end points**

The state of the LNAPL contamination that is necessary to achieve remediation objectives.

**Remediation objectives**

The desired level of mitigation of the concerns over the presence of LNAPL contamination.

**Remediation strategy**

The overall approach to remediation that may combine different remediation technologies and control measures.

**Remediation technology end point**

The state of the LNAPL contamination that may be achieved with skilful application of a remediation technology within the setting it is applied.
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</table>
2. Existing approaches to the specification and management of LNAPL remediation

Regulating authorities, industrial companies and groups, remediation engineers and researchers around the world have been addressing issues related to the clean up of petroleum hydrocarbon contamination for some time, most intensely since the 1980s. From this, a body of experience and guidance has developed on approaching the remediation of LNAPL petroleum hydrocarbons as well as other NAPL organic pollutants. In this chapter, a brief review is provided of the existing approaches to the management and remediation of LNAPL petroleum hydrocarbons.

2.1 Drivers

Drivers for the management and remediation of LNAPL are the risks that LNAPL poses directly or indirectly to human health and the environment as well as other factors. Factors not directly related to the risk of harm to human or ecological health include beneficial use, intergenerational equity, value or amenity of resources as well as business reputation. In recent time, there has been a general move to risk-based management of contamination and LNAPL petroleum hydrocarbons in particular (API 2003; ITRC 2009a; Lundy 1997, 2002; TCEQ 2008; US EPA 2005). Consequently, it is crucial to identify the risk and other factors associated with a site contaminated by LNAPL.

The risk and other factors (which are grouped as ‘concerns’ – ITRC 2009a; TCEQ 2008) usually include:

- accumulation of explosive vapours in subsurface and surface structures
- toxic risk to human or ecological health through direct exposure
- transfer of chemicals of concern to air, groundwater, surface water, soils and sediments
- presence of LNAPL in the subsurface or wells
- continuing movement and spread of the LNAPL, and
- nuisance and impairment of aesthetic values.

In terms of the transfer of chemicals of concern, both the primary partitioning between the non-aqueous phase (LNAPL), the aqueous phase and the air phase (where it is present) as well as subsequent mass transfer in the other phases is considered. Transport of chemicals of concern in the aqueous phase and in soil air leads to secondary contamination and exposure pathways to surface and subsurface receptors. For the aqueous phase, this is through groundwater flow and soil water movement. For the air phase it is through diffusion and advection in the soil. These secondary risks need to be assessed and are often the key drivers for remediation and control of LNAPL. This is because of the greater mobility of the contaminants of concern in these phases.

Management and remediation of LNAPL is commonly specified in terms of LNAPL being a source for contamination of groundwater, surface water, sediments, soil air and the above-ground atmosphere. This is in addition to LNAPL being a contaminant in...
itself. For instance, the presence and control of non-aqueous phase liquid sources are identified as critical to the clean up of groundwater (DEC NSW 2007; EPA SA 2009; EPA Victoria 2002; FRTR 1998). In relation to clean up of groundwater, the removal of NAPL (as a source) or other appropriate controls are stipulated. Indeed LNAPL is itself regarded as a contaminant of groundwater (DEC NSW 2007; EPA Victoria 2002) requiring it to be removed unless it can be demonstrated that:

- it does not pose an unacceptable risk to the beneficial use of the groundwater, human health or the environment (EPA SA 2009; EPA Victoria 2002), or
- further treatment or removal is not practicable (DEC NSW 2007).

In the latter case, however, the presence of NAPL in general (including LNAPL) is seen as a possible cause of the technical impracticability of the clean up and restoration of groundwater to beneficial use (EPA SA 2009; EPA Victoria 2002; FRTR 1998). This is through an acknowledgement of the difficulty of the remediation of the NAPL source.

Hydrocarbon vapours emitted from LNAPL have the potential to pose a risk in two major regards. Firstly, there may be a risk of explosion/fire where vapours may accumulate in enclosed or partially enclosed spaces. Secondly, a risk to human health may arise where toxic hydrocarbon vapours accumulate in buildings. At least the second element of risk, that of human exposure to hydrocarbon vapours in buildings, has received considerable attention. Davis et al. (2004, 2009a, 2009b) comprehensively summarise information that is assisting in the formulation of Australian guidelines for the assessment of risks from volatile contaminants as part of the National Environmental Protection (Assessment of Contaminated Sites) Measure. Guidance on assessing vapour intrusion risks arising from the presence of LNAPL petroleum hydrocarbons have also been prepared in the USA and Europe. Recent documents include ASTM (2008), Baker et al. (2009), DTSC (2009), ITRC (2007) and US EPA (2008a).

The direct management and remediation of LNAPL contamination is considered by US EPA (2005), ASTM International Standard E2531-06 (ASTM International 2007), TCEQ Guidance Document RG-366/TRRP-32 (TCEQ 2008) and ITRC (2009a). These aim largely for a risk-based approach to LNAPL remediation (or more generally, concern-based) which identifies actions to ensure that risks are mitigated. However, these and other guidance documents, particularly for groundwater remediation and management, accept that there are other approaches for LNAPL remediation. The default position is that LNAPL needs to be removed (implicitly, in its entirety, or to a level where no continuing risk/concern exists) unless it can be demonstrated that no unacceptable risks exists (EPA Victoria 2002).

This is a key issue. Of particular interest is where the presence of LNAPL is deduced from observations of thicknesses in wells and how this is interpreted (see ITRC 2009a for discussion on interpreting in-well LNAPL thicknesses). Situations where LNAPL may be visible as thin thicknesses or sheens in monitoring wells, and/or only appear periodically can be contentious. Some have termed this ‘nuisance’ LNAPL (TCEQ 2008). In the absence of knowledge of the presence of LNAPL (as opposed to possible dissolved or vapour contamination), a site risk assessment may yield negligible risk, but with the knowledge of the presence of LNAPL the default position requiring removal may or may not be invoked. Costly management and remediation may flow from the consequent decisions over the need for LNAPL removal. Decisions could be:
• Take no further action where risks are shown to be negligible.
• Carry out monitoring for a set time to establish trends.
• The characterisation is not adequate so improve the conceptual site model and show the risks are still negligible.
• Review what remedial options might possibly help.
• Carry out a remediation trial to show what is feasible on the site.
• RemEDIATE at full scale, until no LNAPL is present.

Of course, the last decision with an end point of ‘no LNAPL’ is in relation to how the presence of LNAPL is defined and may not be achievable. Local circumstances and site conditions will weight decisions in one direction or the other. Balancing intergenerational equity (is it OK to leave LNAPL behind?) and wasteful resource use (e.g. energy consumption, CO₂ emissions) to achieve possibly unrealistic end points is the overall challenge.

The qualifier of practicability to the LNAPL removal is accepted (DEC NSW 2007; EPA SA 2009; EPA Victoria 2002; US EPA 1993). However, in the case that a practicable removal does not meet risk-based criteria, other source control or isolation is required (DEC-NSW 2007; EPA Victoria 2002; US EPA 1993). It should be noted that in the case where the distribution of LNAPL has not been adequately assessed, the option of risk-based approaches to remediation is not available in some jurisdictions (for example, TCEQ 2008).

It needs to be borne in mind that specific chemicals of concern in the LNAPL may be removed rather than the indiscriminate targeting of the LNAPL as a whole to mitigate particular risks. ITRC (2009a) explicitly split the concerns between those based on ‘LNAPL saturation’ and ‘LNAPL composition’ in determining guidance on LNAPL management. Targeting particular chemicals of concern may be a viable option where the chemicals of concern have favourable properties. In particular, chemicals of concern with high vapour pressure or solubility may be preferentially removed (Huntley & Beckett 2002; Johnston 2001). This is often the case, with the mono-aromatic petroleum hydrocarbons benzene, toluene, ethylbenzene and xylenes as examples.

2.2 Practicability

Practicability is a key concept in addressing LNAPL remediation. There is not a universal acceptance of the meaning of practicability and the definition may be specific to regulatory authorities. The concept of practicability was originally proposed by the US EPA as a waiver to the clean-up of groundwater with emphasis on engineering feasibility and reliability with

‘cost generally not a major factor unless compliance would be inordinately costly’ (US EPA 1993).

However, scale and complexity of the site may also contribute to impracticability even where technically feasible remediation options exist.
On the other hand, EPA Victoria (2002) stipulates that:

‘The clean up measures adopted shall be cost-effective and commensurate with the environmental issues being addressed...’

and list three elements in assessing the practicability:

- technical (physical ability to remove the contamination within a reasonable time frame)
- logistical (site access, availability of materials and infrastructure, and disposal of wastes), and
- financial (cost of the clean-up including waste treatment).

The DEC NSW (2007) explicitly adds the elements:

- the value of the groundwater resource, and
- threats the contamination poses to human or ecological health

to their list of factors against which the impracticability must be documented. In relation to source control DEC NSW (2007) note that source containment would be preferred over treatment of the source where:

‘removing or treating the source would have unavoidable severe adverse effects on other aspects of the environment’.

In effect, adverse effects on the environment are being considered as a cost of remediation and as another factor in determining practicability.

In their guidance, TCEQ (2008) require a demonstration that an LNAPL recovery system has become ineffective in reaching specific end points for LNAPL recovery. For this purpose, TCEQ distinguish between conventional and alternative technologies. Where a conventional technology is shown to be technically impracticable, an appropriate alternative technology must be tested at least at pilot scale to also show its technical impracticability. Economic analyses are required in the supporting information of the demonstration for technical impracticability, however it essentially remains based on engineering criteria.

What are generally not explicitly mentioned amongst the criteria for technical impracticability are elements of risks posed through the overt health, safety and environmental impacts of the remediation (Bracken et al. 2006; Hardisty et al. 2008). In regards to environmental effects, life cycle analyses may be included as performance measures or end points for the remediation. Risks associated with various remediation options may be used as selection criteria and also weighed against the risks posed by the LNAPL contamination.

Where technical impracticability is demonstrated or reached for the LNAPL remediation, regulatory guidance generally requires some form of control or isolation of the LNAPL source (EPA SA 2009; EPA Victoria 2002; FRTR 1998; TCEQ 2008).
2.3 End points

The detailed steps towards LNAPL remediation and management provided by US EPA (2005), ASTM International Standard E2531-06 (ASTM International 2007), TCEQ Guidance Document RG-366/TRRP-32 (TCEQ 2008) and ITRC (2009a) use a range of goals, objectives, metrics and end points that can be used for assessment of the LNAPL management. In this context, end points are sufficient conditions to ensure that objectives/goals are achieved. TCEQ (2008) for instance presents end points for a range of LNAPL response objectives for various triggers. US EPA (2005) is more generic in its description but retains the concepts of establishing end points that indicate the achievement of the goals set for the LNAPL remediation. ASTM International (2007) uses the terminology of remediation metric as a close equivalent to the end points defined by TCEQ (2008). More recently, ITRC (2009a) define end points in relation to a remediation metrics. These remediation metrics follow from setting of goals for remediation objectives.

A key comparison is required between desirable end points to meet objectives for LNAPL remediation at a site (remediation end points) and end points that are feasible through the application of LNAPL remediation techniques (remediation technology end points). As well as feasible end points, the time frame, cost and other factors will also be important in the selection of remediation techniques. However, there may be iterations or feedback between the specification of end points to reach remediation objectives and end points that are achievable with specific remediation techniques. In some cases, a staged approach to remediation may be appropriate. For example, where exposure pathways may be through groundwater and soil air, LNAPL remediation objectives may be acceptably cast such that sequential or contemporaneous remediation of groundwater and soil air can achieve overall goals for the clean up of the contamination. This might be achieved where the mass depletion of the LNAPL was sufficient to reduce the mass flux of chemicals of concern in groundwater and soil air to a level which allowed remediation of the groundwater and soil air over a more tractable time frame for clean up (EPA Victoria 2002; US EPA 1993).
3. Conceptual models of LNAPLs in soils and aquifers

An understanding of the behaviour of LNAPL petroleum hydrocarbons in soils and aquifers is required to develop an adequate LNAPL conceptual site model. This LNAPL conceptual site model provides the basis for the selection of an appropriate LNAPL remediation strategy. This chapter provides a summary of the nature of LNAPL petroleum hydrocarbons and their behaviour in different soils and aquifers. The emphasis is on the properties and behaviour that impinge on the success of remediation techniques in major soils and aquifers relevant to contaminated sites in Australia.

The understanding of the behaviour of LNAPL has improved greatly with a number of seminal sources available for reference (Charbeneau & Chiang 1995; Charbeneau et al. 1999; Farr et al. 1990; Huntley & Becket 2002; Johnston & Adamski 2005; Lenhard & Parker 1990; Mayer & Hassanizadeh 2005; Mercer & Cohen 1990; Parker et al. 1987, 1989; Wilson et al. 1990). In overview, the conceptualisation of LNAPL release in the subsurface can be simply depicted as in Figure 1. However, complexity and heterogeneity of the subsurface abounds. This means that identification, interpretation and prediction of LNAPL behaviour continues to have significant uncertainty. Complicating factors include:

- multi-phase partitioning to soil and water below the water table
- multi-phase partitioning to soil, water and air phases above the water table
- LNAPL and water table transients, and
- changing LNAPL characteristics over time.

Of particular note is the poor understanding of LNAPL behaviour in fractured rocks and macro-porous soils (particularly fine textured materials that have dual porosity).

![Figure 1. Cartoon of an LNAPL release in a porous medium in relation to the water table and capillary fringe.](image-url)
3.1 What defines an LNAPL?

A NAPL is any immiscible liquid that maintains a stable interface with water. The presence of a stable interface means that water-NAPL fluid pairs can be characterised by a well-defined interfacial tension. An LNAPL is a NAPL that has a density less than that of water. Crude oil, refined petroleum hydrocarbon fuels and lubricating oils are therefore classified as LNAPLs because of their generally hydrophobic nature (leading to immiscibility with water) and because they have a density less than water.

3.2 Relevant properties of LNAPL petroleum hydrocarbons

LNAPL petroleum hydrocarbons are a complex mixture of many organic compounds. Typically, petroleum hydrocarbon fuels are a mixture of aliphatic (mainly alkanes and alkenes) and aromatic organic compounds derived from crude oil. The mono-aromatic compounds, benzene and alkylated benzenes (toluene, ethylbenzene and xylenes), are important natural constituents of some petroleum products because of their risk profile and mobility in the environment. At times, other additives that are significant in relation to LNAPL remediation have been used in petroleum hydrocarbon fuels. Examples of these are lead compounds, oxygenates (such as methyl tert-butyl ether (MTBE)) and ethanol. Different hydrocarbon fuel types have different molecular weight (or carbon number) ranges of compounds to suit particular uses (TPHCWG 1998). The major types of petroleum hydrocarbons are summarised in terms of the range of the carbon number of the predominant constituent compounds (Table 1).

Table 1. Predominant carbon number range for petroleum hydrocarbons.

<table>
<thead>
<tr>
<th>Petroleum hydrocarbon</th>
<th>Carbon number range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>C4-C12</td>
</tr>
<tr>
<td>Kerosene and jet fuel</td>
<td>C11-C13</td>
</tr>
<tr>
<td>Diesel and light fuel oil</td>
<td>C10-C20</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>C19-C25</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>C20-C45</td>
</tr>
</tbody>
</table>

Generally, petroleum fuels have a large proportion (55–75%) of n-alkanes (straight-carbon chain molecules), isoalkanes (branched molecules) and cycloalkanes (cyclic molecules). The distribution of these as well as aromatic and other organic compounds provides a fingerprint which characterises the particular LNAPL (Figure 2). The relative abundance and concentration of these compounds can change over time after release into the subsurface.
The prime fluid properties of LNAPL are density, viscosity and interfacial tensions (LNAPL-water and air-LNAPL interfacial tensions). Values of these properties for a range of petroleum hydrocarbon fuels are presented in Table 2.

Figure 2. Chromatograms from the gas chromatography-flame ionisation detection of petroleum hydrocarbons illustrating LNAPL fingerprinting (Source: T Bastow 2009, pers. comm.).
Table 2. Typical relative density, \( \rho_{r,n} \), viscosity, \( \mu_n \), as well as interfacial tensions, \( \sigma_{nw} \), (LNAPL-water) and, \( \sigma_{an} \), (air-LNAPL) of petroleum products along with the temperature, \( T \), of measurement.

<table>
<thead>
<tr>
<th></th>
<th>( \rho_{r,n} )</th>
<th>( \mu_n ) (cP)</th>
<th>( \sigma_{nw} ) (mN m(^{-1}))</th>
<th>( \sigma_{an} ) (mN m(^{-1}))</th>
<th>( T ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline(^{(a)})</td>
<td>0.733</td>
<td>0.48</td>
<td>22.9</td>
<td>20.5</td>
<td>22–24</td>
</tr>
<tr>
<td>Kerosene(^{(a)})</td>
<td>0.809</td>
<td>1.73</td>
<td>38.6</td>
<td>26.8</td>
<td>22–24</td>
</tr>
<tr>
<td>Jet A/A-1(^{(b)})</td>
<td>0.811</td>
<td>2</td>
<td>25.5</td>
<td>29.1</td>
<td>25</td>
</tr>
<tr>
<td>Diesel – Southern USA(^{(b)})</td>
<td>0.832</td>
<td>4</td>
<td>26.9</td>
<td>22.3</td>
<td>25</td>
</tr>
<tr>
<td>Diesel – Ottawa summer(^{(b)})</td>
<td>0.832</td>
<td>2.76</td>
<td>27.5</td>
<td>21.6</td>
<td>15</td>
</tr>
<tr>
<td>Engine oil – used(^{(b)})</td>
<td>0.886</td>
<td>175</td>
<td>31.0</td>
<td>24.4</td>
<td>15</td>
</tr>
<tr>
<td>Water – tap(^{(c)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>67.1</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Wilson et al. (1990)
\(^{(b)}\) Environmental Technology Centre, Environment Canada <http://www.etccte.ec.gc.ca/databases/OilProperties/>
\(^{(c)}\) Perth, Western Australia

Although LNAPL is immiscible with water, some of the constituent compounds of petroleum hydrocarbon fuels are sparingly soluble. LNAPL compounds that partition to adjacent water phases, such as groundwater, add a further dimension to LNAPL contamination. Aromatic compounds are the most soluble of the petroleum hydrocarbon constituents, with solubilities generally decreasing as the number of benzene rings (and molecular weight) increases (Table 3) and as they become more hydrophobic in nature. The relative hydrophobicity is indicated by the octanol-water partitioning coefficient, \( K_{ow} \) (Table 3). Alkanes have lower solubilities than the aromatic compounds. Solubilities decrease with carbon chain length and for the n-alkanes, solubilities decrease sharply from around 60 mg L\(^{-1}\) for n-propane and n-butane to less than 1 mg L\(^{-1}\) for octanol. Solubilities decrease further to the extent that the combined solubility of n-alkanes longer than n-C10 (decane) should not exceed 0.005 mg L\(^{-1}\).

Constituent compounds of LNAPL petroleum hydrocarbons also partition into an air/gas phase. The compound vapour pressure (Tables 4 and 5) is a measure of the potential for partitioning into air. The shorter alkanes have appreciable vapour pressures (represented here by the n-alkanes in Table 4). However, benzene and the other substituted single-ring aromatics (toluene, ethylbenzene and xylenes), which are often a focus of concern, also have relatively high vapour pressures. For completeness, Henry’s coefficient, \( k_{fi} \), which describes the partitioning of LNAPL constituents between the dissolved and gaseous phases, is included in Tables 4 and 5.
Table 3. Solubility and octanol-water partitioning coefficients ($K_{ow}$) of key aromatic petroleum hydrocarbon compounds at $T = 298.15 \text{ K.}$ (Source: SRC).

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS number</th>
<th>Solubility (mg L$^{-1}$)</th>
<th>Log ($K_{ow}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>71-43-2</td>
<td>1790</td>
<td>2.13</td>
</tr>
<tr>
<td>toluene</td>
<td>108-88-3</td>
<td>526</td>
<td>2.73</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>100-41-4</td>
<td>169</td>
<td>3.15</td>
</tr>
<tr>
<td>m-xylene</td>
<td>108-38-3</td>
<td>161</td>
<td>3.2</td>
</tr>
<tr>
<td>p-xylene</td>
<td>106-42-3</td>
<td>162</td>
<td>3.15</td>
</tr>
<tr>
<td>o-xylene</td>
<td>95-47-6</td>
<td>178</td>
<td>3.12</td>
</tr>
<tr>
<td>1,2,3-trimethylbenzene</td>
<td>526-73-8</td>
<td>75.2</td>
<td>3.66</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>95-63-6</td>
<td>57</td>
<td>3.63</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>108-67-8</td>
<td>48.2</td>
<td>3.42</td>
</tr>
<tr>
<td>naphthalene</td>
<td>91-20-3</td>
<td>31</td>
<td>3.3</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>90-12-0</td>
<td>25.8</td>
<td>3.87</td>
</tr>
<tr>
<td>2-methylnaphthalene</td>
<td>91-57-6</td>
<td>24.6</td>
<td>3.86</td>
</tr>
<tr>
<td>1,2-dimethylnaphthalene</td>
<td>573-98-8</td>
<td>14.9</td>
<td>4.31</td>
</tr>
<tr>
<td>1,3-dimethylnaphthalene</td>
<td>575-41-7</td>
<td>8</td>
<td>4.42</td>
</tr>
<tr>
<td>1,6-dimethylnaphthalene</td>
<td>575-43-9</td>
<td>0.9</td>
<td>4.26</td>
</tr>
<tr>
<td>1,7-dimethylnaphthalene</td>
<td>575-37-1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,3-dimethylnaphthalene</td>
<td>581-40-8</td>
<td>1.99</td>
<td>4.4</td>
</tr>
<tr>
<td>2,6-dimethylnaphthalene</td>
<td>581-42-0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,7-dimethylnaphthalene</td>
<td>582-16-1</td>
<td>14.9</td>
<td>4.26</td>
</tr>
</tbody>
</table>
Selecting and assessing strategies for remediating LNAPL in soils and aquifers

Table 4. Properties of key aromatic compounds (Source: NIST and SRC). Vapour pressure, $P^*$, and Henry’s coefficient, $k_H$, at $T = 298.15$ K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Mol. wt (g mol$^{-1}$)</th>
<th>$T_{\text{boil}}$ (K)</th>
<th>$T_{\text{trip}}$ (K)</th>
<th>$P^*$ (bar)</th>
<th>$k_H$ (mole kg$^{-1}$ bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>C$_6$H$_6$</td>
<td>78.1</td>
<td>353</td>
<td>279</td>
<td>1.27x10$^{-1}$</td>
<td>1.8x10$^{-1}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>C$_7$H$_8$</td>
<td>92.1</td>
<td>384</td>
<td>178</td>
<td>3.79x10$^{-2}$</td>
<td>1.6x10$^{-1}$</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>C$<em>8$H$</em>{10}$</td>
<td>106.2</td>
<td>409</td>
<td>178</td>
<td>1.26x10$^{-2}$</td>
<td>1.2x10$^{-1}$</td>
</tr>
<tr>
<td>m-xylene</td>
<td>C$<em>8$H$</em>{10}$</td>
<td>106.2</td>
<td>412</td>
<td>220</td>
<td>1.11x10$^{-2}$</td>
<td>1.5x10$^{-1}$</td>
</tr>
<tr>
<td>p-xylene</td>
<td>C$<em>8$H$</em>{10}$</td>
<td>106.2</td>
<td>411</td>
<td>286</td>
<td>1.18x10$^{-2}$</td>
<td>1.6x10$^{-1}$</td>
</tr>
<tr>
<td>o-xylene</td>
<td>C$<em>8$H$</em>{10}$</td>
<td>106.2</td>
<td>417</td>
<td>248</td>
<td>8.79x10$^{-3}$</td>
<td>2.4x10$^{-1}$</td>
</tr>
<tr>
<td>1,2,3-trimethylbenzene</td>
<td>C$<em>9$H$</em>{12}$</td>
<td>120.2</td>
<td>449</td>
<td>248</td>
<td>1.98x10$^{-3}$</td>
<td>3.1x10$^{-1}$</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>C$<em>9$H$</em>{12}$</td>
<td>120.2</td>
<td>442</td>
<td>229</td>
<td>2.71x10$^{-3}$</td>
<td>1.7x10$^{-1}$</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>C$<em>9$H$</em>{12}$</td>
<td>120.2</td>
<td>438</td>
<td>228</td>
<td>3.22x10$^{-3}$</td>
<td>1.7x10$^{-1}$</td>
</tr>
<tr>
<td>naphthalene</td>
<td>C$_{10}$H$_8$</td>
<td>128.2</td>
<td>490</td>
<td>353</td>
<td>1.13x10$^{-4}$</td>
<td>2.1</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>C$<em>{11}$H$</em>{10}$</td>
<td>142.2</td>
<td>515</td>
<td>243</td>
<td>8.93x10$^{-6}$</td>
<td>2.7</td>
</tr>
<tr>
<td>2-methylnaphthalene</td>
<td>C$<em>{11}$H$</em>{10}$</td>
<td>142.2</td>
<td>514</td>
<td>308</td>
<td>7.33x10$^{-5}$</td>
<td>2.0</td>
</tr>
<tr>
<td>1,2-dimethylnaphthalene</td>
<td>C$<em>{12}$H$</em>{12}$</td>
<td>156.2</td>
<td>540</td>
<td>270</td>
<td>1.69x10$^{-5}$</td>
<td>-</td>
</tr>
<tr>
<td>1,3-dimethylnaphthalene</td>
<td>C$<em>{12}$H$</em>{12}$</td>
<td>156.2</td>
<td>538</td>
<td>-</td>
<td>3.09x10$^{-5}$</td>
<td>1.4</td>
</tr>
<tr>
<td>1,6-dimethylnaphthalene</td>
<td>C$<em>{12}$H$</em>{12}$</td>
<td>156.2</td>
<td>536</td>
<td>-</td>
<td>1.95x10$^{-5}$</td>
<td>-</td>
</tr>
<tr>
<td>1,7-dimethylnaphthalene</td>
<td>C$<em>{12}$H$</em>{12}$</td>
<td>156.2</td>
<td>536</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,3-dimethylnaphthalene</td>
<td>C$<em>{12}$H$</em>{12}$</td>
<td>156.2</td>
<td>541</td>
<td>377</td>
<td>1.47x10$^{-6}$</td>
<td>1.7</td>
</tr>
<tr>
<td>2,6-dimethylnaphthalene</td>
<td>C$<em>{12}$H$</em>{12}$</td>
<td>156.2</td>
<td>536</td>
<td>383</td>
<td>-</td>
<td>8.2x10$^{-1}$</td>
</tr>
<tr>
<td>2,7-dimethylnaphthalene</td>
<td>C$<em>{12}$H$</em>{12}$</td>
<td>156.2</td>
<td>536</td>
<td>369</td>
<td>7.57x10$^{-6}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 5. Properties of key alkanes (Source: NIST). Vapour pressure, $P^*$, and Henry’s coefficient, $k_H$, at $T = 298.15$ K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Mol. wt (g mol$^{-1}$)</th>
<th>$T_{boil}$ (K)</th>
<th>$T_{triple}$ (K)</th>
<th>$P^*$ (bar)</th>
<th>$k_H$ (mole kg$^{-1}$ bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-propane</td>
<td>C$_3$H$_8$</td>
<td>44.1</td>
<td>231</td>
<td>85</td>
<td>9.77x10$^0$</td>
<td>1.5x10$^{-3}$</td>
</tr>
<tr>
<td>n-butane</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>58.1</td>
<td>273</td>
<td>133</td>
<td>2.43x10$^0$</td>
<td>1.1x10$^{-3}$</td>
</tr>
<tr>
<td>n-pentane</td>
<td>C$<em>5$H$</em>{12}$</td>
<td>72.1</td>
<td>309</td>
<td>143</td>
<td>6.83x10$^{-1}$</td>
<td>8.0x10$^{-4}$</td>
</tr>
<tr>
<td>n-hexane</td>
<td>C$<em>6$H$</em>{14}$</td>
<td>86.2</td>
<td>342</td>
<td>178</td>
<td>2.02x10$^{-1}$</td>
<td>6.0x10$^{-4}$</td>
</tr>
<tr>
<td>n-heptane</td>
<td>C$<em>7$H$</em>{16}$</td>
<td>100.2</td>
<td>372</td>
<td>183</td>
<td>6.09x10$^{-2}$</td>
<td>4.4x10$^{-4}$</td>
</tr>
<tr>
<td>n-octane</td>
<td>C$<em>8$H$</em>{18}$</td>
<td>114.2</td>
<td>399</td>
<td>216</td>
<td>1.72x10$^{-2}$</td>
<td>3.1x10$^{-4}$</td>
</tr>
<tr>
<td>n-nonane</td>
<td>C$<em>9$H$</em>{20}$</td>
<td>128.3</td>
<td>424</td>
<td>220</td>
<td>4.59x10$^{-3}$</td>
<td>2.0x10$^{-4}$</td>
</tr>
<tr>
<td>n-decane</td>
<td>C$<em>{10}$H$</em>{22}$</td>
<td>142.3</td>
<td>447</td>
<td>243</td>
<td>1.23x10$^{-3}$</td>
<td>1.4x10$^{-4}$</td>
</tr>
<tr>
<td>n-undecane</td>
<td>C$<em>{11}$H$</em>{24}$</td>
<td>156.3</td>
<td>468</td>
<td>248</td>
<td>5.25x10$^{-4}$</td>
<td>5.6x10$^{-5}$</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>C$<em>{12}$H$</em>{26}$</td>
<td>170.3</td>
<td>489</td>
<td>264</td>
<td>1.54x10$^{-4}$</td>
<td>1.4x10$^{-4}$</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>C$<em>{13}$H$</em>{28}$</td>
<td>184.4</td>
<td>507</td>
<td>268</td>
<td>4.49x10$^{-5}$</td>
<td>4.3x10$^{-4}$</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>C$<em>{14}$H$</em>{30}$</td>
<td>198.4</td>
<td>523</td>
<td>279</td>
<td>1.26x10$^{-5}$</td>
<td>8.7x10$^{-4}$</td>
</tr>
<tr>
<td>n-pentadecane</td>
<td>C$<em>{15}$H$</em>{32}$</td>
<td>212.4</td>
<td>540</td>
<td>283</td>
<td>3.49x10$^{-6}$</td>
<td>2.1x10$^{-3}$</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>C$<em>{16}$H$</em>{34}$</td>
<td>226.4</td>
<td>554</td>
<td>291</td>
<td>9.58x10$^{-7}$</td>
<td>4.3x10$^{-3}$</td>
</tr>
<tr>
<td>n-heptadecane</td>
<td>C$<em>{17}$H$</em>{36}$</td>
<td>240.5</td>
<td>575</td>
<td>295</td>
<td>1.55x10$^{-7}$</td>
<td>1.8x10$^{-2}$</td>
</tr>
<tr>
<td>n-octadecane</td>
<td>C$<em>{18}$H$</em>{38}$</td>
<td>254.5</td>
<td>589</td>
<td>301</td>
<td>-</td>
<td>1.1x10$^{-1}$</td>
</tr>
<tr>
<td>n-nonadecane</td>
<td>C$<em>{19}$H$</em>{40}$</td>
<td>268.5</td>
<td>603</td>
<td>304</td>
<td>-</td>
<td>3.4x10$^{-1}$</td>
</tr>
<tr>
<td>n-eicosane</td>
<td>C$<em>{20}$H$</em>{42}$</td>
<td>282.5</td>
<td>616</td>
<td>310</td>
<td>-</td>
<td>3.1x10$^{0}$</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>84.2</td>
<td>354</td>
<td>280</td>
<td>1.30x10$^{-1}$</td>
<td>5.6x10$^{-3}$</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>C$<em>7$H$</em>{14}$</td>
<td>98.2</td>
<td>374</td>
<td>147</td>
<td>6.13x10$^{-2}$</td>
<td>2.5x10$^{-3}$</td>
</tr>
</tbody>
</table>

Once released into the subsurface, the individual constituents of petroleum fuels may volatilise, dissolve in the water phase and be transformed by biological processes. This means that the physical properties and indeed primary nature of the LNAPL will change over time. This is generally referred to as weathering of the LNAPL and is considered natural source zone depletion (ITRC 2009b; Parsons Engineering Science Inc. 2003). Typically, the density and viscosity of the LNAPL will increase over time. The increase in viscosity may be appreciable. The preferential loss of particular constituents through volatilisation and dissolution, as well as losses and transformations through biological processes, change the chemical composition of the LNAPL. Such losses may significantly reduce the LNAPL mass.
3.3 Partitioning of constituents between phases

When a multi-component LNAPL is in contact with water and air, the concentration of LNAPL components in each of the phases can be estimated from relatively simple partitioning relationships. These take the form of a linear relationship between the concentration and/or mass fraction of the components in each of the phases. These relationships are important in predicting what contaminants the LNAPL may transfer to the air and water phases.

Partitioning between the LNAPL and air phases under equilibrium conditions may be described by Raoult’s Law which gives the concentration of the \( i \)-th compound in air, \( C_{i,a} \), as (Corapcioglu & Baehr 1987):

\[
C_{i,a} = \frac{\omega_i p_i^* \chi_i \gamma_{i,a}}{RT}
\]

[Equation 1]

where \( \omega_i \) is molecular weight, \( p_i^* \) is vapour pressure of the pure compound, \( \chi_i \) is mole fraction in the NAPL, \( \gamma_{i,a} \) is activity coefficient in the LNAPL, \( R \) is the universal gas constant and \( T \) is temperature.

Although not so important in the presence of LNAPL in direct contact with the gas phase, for completeness we also consider partitioning of volatile organics between the water and gas phases. When dissolved in water, the partial pressure of a species, \( p_i \), in equilibrium with the water phase is governed by Henry’s Law (Noggle 1985) via:

\[
p_i = k_{H,i} C_{i,w}
\]

[Equation 2]

where \( k_{H,i} \) is the Henry’s coefficient and \( C_{i,w} \) is concentration in water. From this it follows that:

\[
C_{i,a} = \frac{\omega_i k_{H,i} C_{i,w}}{RT}
\]

[Equation 3]

A form of Raoult’s Law may also be developed (Banerjee 1984; Cline et al. 1991; Mackay et al. 1991) to calculate the dissolved concentration \( C_{i,w} \) of a particular compound in equilibrium with the multi-component LNAPL via:

\[
C_{i,w} = C_{i,w}^s \frac{\chi_i \gamma_{i,a} \gamma_{i,p}}{\gamma_{i,w}}
\]

[Equation 4]

where \( C_{i,w}^s \) is solubility of the pure compound in water, \( \gamma_{i,w} \) is the activity coefficient in the water and \( \gamma_{i,a} \) is the activity coefficient of the pure compound. Under assumptions of ideal behaviour (negligible interactions and chemically similar compounds), the activity coefficients may be taken as unity to yield:

\[
C_{i,w} = C_{i,w}^s \chi_i
\]

[Equation 5]
Simplifying assumptions that neglect the effect of activity coefficients usually do not hold for chemically heterogeneous mixtures such as petroleum hydrocarbon fuels. Thus, equilibrium concentrations of petroleum hydrocarbons in groundwater in contact with LNAPL would be expected to deviate from those suggested by Equation 5. Another difficulty is determining the mole fraction of constituents in the LNAPL mixture. Direct observation of aqueous concentrations is sometimes a necessarily pragmatic approach.

3.4 Transformation of LNAPL in the subsurface

3.4.1 Biodegradation and electron acceptors

In addition to LNAPL-water and LNAPL-air partitioning of constituent compounds, abiotic and biotic processes lead to a change in the composition and a loss of mass from the LNAPL. The effects of biological processes can be quite profound. Petroleum-hydrocarbon degrading microorganisms are pervasive in subsurface environments. Such microbial communities readily develop in the presence of LNAPL. For their growth and function, microbial communities require a supply of electron acceptors that support the chemical reactions that yield the energy and carbon used by the microbes. Generally, the most favourable of these is molecular oxygen (O2) that leads to aerobic degradation of the organic compounds through an oxidation reaction such as that for decane:

\[
C_{10}H_{22} + 15.5O_2 \rightarrow 10CO_2 + 11H_2O \quad [\text{Equation 6}]
\]

However, oxygen supply is usually limited by gaseous diffusion through the vadose zone from the soil surface (Davis et al. 2009a) as well as the low concentrations and fluxes dissolved in infiltrating water and groundwater.

Other electron acceptors such as nitrate, iron and sulphate that may be present in the subsurface are also used by microbial communities to degrade petroleum hydrocarbons in the absence of oxygen (i.e. under anaerobic conditions). Generally, the electron acceptors will be reduced sequentially (in the above order) according to the favourability of the energy available from the reactions (Wiedemeier et al. 1999). This gives rise to varying hydrogeochemical (redox) conditions within the subsurface. Once these electron acceptors are depleted, hydrocarbon degradation may continue through methanogenesis. This is a two-stage process of fermentation and respiration. Fermentation of the petroleum hydrocarbons produces intermediate organic chemicals that are then converted to methane and carbon dioxide. Carbon dioxide present in the aquifer (produced by the fermentation or other oxidation/reduction reactions) is combined with molecular hydrogen produced through the fermentation to produce more methane. Due to the carbon loading induced by the presence of LNAPL, the electron acceptor demand is such that methanogenic conditions commonly arise (Johnston et al. 2008a; King 2009; Salminen et al. 2006).

The common appearance of high methane levels in the vadose zone above LNAPL contamination can be a significant risk at some contaminated sites. Methane may also degas from contaminated groundwater.
Other restrictions on biodegradation rates of petroleum hydrocarbons arise through the limited access to nutrients (nitrogen and phosphorus) and trace elements. Many subsurface environments are deficient in nutrients and these become limiting when electron acceptors are more freely available. In addition, water content and temperature will impinge on the rates of biodegradation.

3.4.2 LNAPL compositional changes and mass loss

Many of the petroleum hydrocarbon compounds may be completely mineralised to CO$_2$ or CH$_4$, or converted to microbial biomass thus leading to mass loss from the LNAPL. However, microbial processes also convert hydrocarbons to other related hydrocarbon or derivative non-hydrocarbon organic compounds that increase in concentration within the LNAPL. This changes the physical and chemical nature of the LNAPL. For example, polar compounds can increase within an LNAPL mass through aerobic transformations and these may have an appreciably higher solubility than the parent compounds in the LNAPL (Lang et al. 2009).

Biodegradation of refined fuels results in the depletion of compound classes in a specific order, as has been well established for crude oils in petroleum reservoirs (Peters & Moldowan 1993). The relative abundance of these compound classes can then be used as a general guide or qualitative assessment as to the extent of biodegradation experienced by the LNAPL in the subsurface. The levels of biodegradation suggested in Table 6 (Fisher et al. 1998) could be assessed in relation to the starting composition of the LNAPL.
Table 6. Levels of biodegradation for petroleum hydrocarbons (adapted from Fisher et al. 1998).

<table>
<thead>
<tr>
<th>Level</th>
<th>Compound class</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatic</td>
</tr>
<tr>
<td>1</td>
<td>Light-end n-alkanes depleted</td>
</tr>
<tr>
<td>2</td>
<td>General depletion of n-alkanes</td>
</tr>
<tr>
<td>3</td>
<td>&gt;90% n-alkanes removed</td>
</tr>
<tr>
<td></td>
<td>Alkylcyclohexanes removed</td>
</tr>
<tr>
<td>3–4</td>
<td>n-alkanes absent</td>
</tr>
<tr>
<td></td>
<td>Acyclic isoprenoids affected</td>
</tr>
<tr>
<td></td>
<td>Alkylcyclohexanes absent</td>
</tr>
<tr>
<td>5</td>
<td>Acyclic isoprenoids absent</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>5–6</td>
<td>Bicyclic alkanes affected</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Bicyclic alkanes severely depleted</td>
</tr>
<tr>
<td></td>
<td>Steranes affected</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As well as the qualitative assessment suggested in Table 6, quantitative measurement of the extent of biodegradation and mass loss is also possible by tracking the relative abundance of specific compounds. The isoprenoids pristane and phytane are key compounds used for this purpose. Both are more resistant to biodegradation than the n-alkanes. In addition, phytane is appreciably more resistant to degradation than pristane. These factors have led to the use of the ratio of the petroleum hydrocarbons n-C17 and pristane (which elute around the same time in chromatographic analyses) to estimate the age of diesel fuel releases in the subsurface (Christensen & Larsen 1993; Hurst & Schmidt 2005). The n-C17:pristane ratio is useful up to the stage where n-C17 is completely depleted. Johnston et al. (2007a) have also used the relative abundance of phytane to estimate the extent of mass loss from a spilled diesel fuel and as a measure of relative age in the absence of n-C17.

Given sufficient time, biodegradation and other weathering processes may inflict an appreciable reduction in the mass of LNAPL that was originally released into the subsurface. However, selective biodegradation may indeed mean that the remaining LNAPL becomes increasing recalcitrant to biodegradation over time. Even under favourable engineered biodegradation, specific hazardous chemicals may persist
Selecting and assessing strategies for remediating LNAPL in soils and aquifers

Lukatelich 1999). In addition, over time the transformation processes may remove the dominant compounds and produce a myriad of other organic chemicals at such low concentration that they are hard to identify and quantify. In this case, the LNAPL can appear as an unresolved complex mixture (UCM) that even advanced analytical techniques find difficult to characterise and quantify.

3.5 Soils and aquifers

Understanding the distribution and movement of LNAPL requires knowledge of the soil and aquifer materials into which LNAPL is introduced. Here the properties of the porous geological materials that commonly constitute the soils and aquifers in which LNAPL resides and remediation may be attempted are discussed. While focusing on the natural subsurface environment, it needs to be kept in mind that many man-made structures and services are introduced into the subsurface which may impinge significantly on understanding LNAPL behaviour. For example, leakage from buried pressurised pipes can result in enhanced lateral migration and distribution of LNAPL in the subsurface as it follows the in-filled trenches in which the pipes reside.

3.5.1 Nature of porous geological materials

The main properties of porous geological materials relevant to the movement and distribution of LNAPL are the nature of the solids and the interstitial pore spaces. These are described in detail in many hydrogeological, soil, soil physics and geomorphological texts (Bear 1972; Domenico & Schwartz 1998; Hillel 1998; McKenzie et al. 2004).

The solids are generally a range of minerals with varying contents of natural organic matter depending on the origin of the geological materials. Infrequently the solids may even be predominantly organic in nature. The physical and chemical interactions of the solid surfaces with interstitial fluids are important but it is usually the size, morphology and interconnections of the pore space which are crucial in controlling the distribution of LNAPL and other fluids in geological materials.

It is convenient to consider two different types of porous geological materials:

- those which are basically granular in nature (unconsolidated sediments and sedimentary rocks), and
- those which are massive (igneous and metamorphic rocks).

The granular materials consist of a matrix of individual grains or particles which may be cemented together to varying degrees. Typical materials would be unconsolidated sands, silts and clays as well as consolidated sandstone, siltstones and the like. Their key characteristic in respect to fluid flow is the presence of a pervasive interconnected network of pores that constitute the interstitial pore space. The packing of grains produces a series of larger pore bodies interconnected by narrower pore throats. The characteristic size of the pores is largely determined by the size distribution of the individual grains while the overall porosity depends on grain size, packing and amount of secondary cementation. The pervasive nature of the pore space in these materials has allowed the development of a relatively robust (and simple) macroscopic continuum description of fluid flow based on the concept of a representative elementary volume (Bear 1972) of the soil or aquifer. Fluid pressure, fluid saturation and fluid
permeability are defined as continuous functions in the macroscopic porous domain without direct reference to the microscopic structure of the pore space.

In comparison, the interstitial pore space of igneous and metamorphic rocks (for convenience referred to as hard rocks) exist as fractures and faults within the body of the rock. In some instances, porosity may exist as the product of isolated or connected fluid and gas inclusions in the rock (for example vesiculated basalt, Song et al. 2001). Fractured rock systems are difficult to characterise, the fractures may be relatively sparse, the fractures may typically occupy a very small fraction of the total volume, they may have poor connectivity and fluid flow may be dominated by a small number of individual fractures. Their physical attributes make it very difficult to use the equivalent porous-media approach that describes fluid flow in granular materials. Indeed, the underlying concepts of averaging over representative elementary volumes generally fail. In many cases, it is necessary to discretise to the level of individual fractures to provide reliable predictions of fluid movement. Hydrochemical weathering processes also mean further porosity develops where rock minerals are altered and some are dissolved. This may preferentially occur on the faces of fractures. The natural progression of the weathering process is to produce a regolith with a pore structure that is akin to that of granular materials.

Another class of porous geological materials, those with dual porosity, arise through secondary pedogenic and other processes. Elements such as fractures, dissolution features, and voids (from biological and even anthropogenic activity) may be superimposed on the primary porosity of granular materials. Because of the possible large size of these secondary porosity features, they may be the dominant control on fluid flow even where they constitute a small fraction of the total porosity. Particular situations that may commonly be encountered are:

- fractured clays
- fractured sandstones and other sedimentary rocks, fractured and karstic limestones, and
- near surface soils with root holes, animal burrows and dessication cracks.

Predicting fluid movement through such dual-porosity materials faces similar challenges to that of fractured rock. However, in the case of dual-porosity materials there are further complex interactions between the two pore domains – the macropore system and the micropores in the porous matrix.

In respect to understanding the behaviour of LNAPL in the subsurface it is convenient to refer to some general classification of porous geological materials. Such a classification is presented in Table 7. In order to place these general classifications in context with situations that may be encountered, typical Australian aquifer settings are discussed in Appendix A.
Table 7. General classification of porous geological materials.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconsolidated sandy materials</td>
<td>Granular sedimentary materials with grain sizes predominantly greater than 0.02 mm (sand-sized grains) with little or no cementation. Texture classes of sand, sandy loam and loam.</td>
</tr>
<tr>
<td>Finer textured unconsolidated materials</td>
<td>Granular sedimentary materials with an appreciable proportion of grain sizes less than 0.02 mm (silt- and clay-sized grains) with little or no cementation. Soil texture classes of clay loam, light clay and medium to heavy clay.</td>
</tr>
<tr>
<td>Dual porosity materials (consolidated and unconsolidated)</td>
<td>Unconsolidated and consolidated porous materials with a marked bimodal distribution of interconnected pore sizes, generally with a microporous primary porosity and secondary macroporosity arising from fractures, cracks, dissolution voids (karst), root holes and animal burrows.</td>
</tr>
<tr>
<td>Fractured hard rocks</td>
<td>Igneous and metamorphic rocks where the interconnected porosity is primarily due to fracturing and faulting.</td>
</tr>
</tbody>
</table>

3.6 LNAPL behaviour in porous materials

3.6.1 Pore-scale fluid distribution

In understanding the distribution and movement of LNAPL petroleum hydrocarbons in the subsurface, it is important to have an appreciation of the pore-scale distribution of gas, LNAPL and water phases and their interaction with the solid surfaces. This wetting state of the solids and the wetting hierarchy of the fluids are determined by the relative affinity of the fluids for the solid surfaces. Mineral soil grains usually have the greatest affinity for water when it is present and thus the solid mineral surfaces are covered with a continuous film of water. In this state the porous media can be classified as water wet. Where only water and LNAPL are present, the LNAPL would be the non-wetting fluid. In a three fluid phase system, LNAPL exists as the intermediate wetting fluid and gas is the non-wetting fluid. Water-wet porous materials is the most frequently encountered situation for instances of LNAPL contamination, particularly below surface soil horizons.

The order of wetting has important implications on the behaviour of the different fluids. Of particular importance is that water will occupy the smallest pores while non-wetting and intermediate wetting fluids will occupy the larger pores. This is crucial to the macroscopic content and transport properties of the fluids, and ultimately how it may be remediated.

Conditions can arise where natural organic matter or organic compounds wholly or partially cover the solid surface of the porous media making it oleophillic to some degree. In this state the porous media may have mixed wettability or even be hydrophobic. This changes the ordering of the water and LNAPL in the pores relative to the mineral surface and gas phase (which remains as the non-wetting fluid). The
wetting state of the porous media is generally characterised by the contact angle of the liquids.

### 3.6.2 Mobile and immobile LNAPL

Within a porous material, LNAPL may be classified as existing in one of two states:

- mobile LNAPL, or
- immobile LNAPL.

A mobile LNAPL exists as a continuous, connected body of liquid in the porous media able to move under applied pressure gradients. Immobile LNAPL is that which exists as isolated pools of liquid and/or spread as thin films that do not allow it to move under normal pressure gradients in the prevailing conditions. Changing conditions such as varying water tables can cause LNAPL to move between states of being mobile and immobile.

Following White et al. (2004), the immobile LNAPL may be subdivided into:

- residual LNAPL, or
- entrapped LNAPL.

A residual LNAPL is defined here as that LNAPL in a three-fluid phase system (i.e. above the capillary fringe) where the LNAPL is spread so thinly within the pore network, or isolated within the pores, such that it can no longer move under an applied pressure gradient (Figure 3). A fraction of the residual LNAPL may still be continuous within the porous materials.

Entrained LNAPL is that which exists as isolated blobs or ganglia within a single or small number of pores (Figure 3). The isolation of discrete blobs or ganglia arises through snap-off of the LNAPL at pore throats and fluid by-passing (Wilson et al. 1990). Macroscopic entrapment may also take place where LNAPL becomes isolated within a volume of the porous material that has a contrasting pore size (see Wilson et al. 1990).

![Figure 3](image-url)

**Figure 3.** Cartoon of the residual and entrapped LNAPL in a porous material. In the unsaturated zone (a) the LNAPL is isolated or spread as a thin, effectively immobile film. In the saturated zone, LNAPL is entrapped as blobs (b) or ganglia (c).
In the general literature, the terminology describing the state of LNAPL in a porous media is both varied and contradictory. For instance, the definition for mobile LNAPL adopted here agrees with that of White et al. (2004) and TCEQ (2008). On the other hand, the definition used here is that defined as free LNAPL by ASTM International (2007). ITRC (2009a) provide a further qualification to the definition of mobile LNAPL as that which ‘will accumulate in wells’. This is not strictly consistent with their concept of LNAPL being mobile when it is at ‘greater than residual saturation’.

The use of the term mobile in this report allows the further classification into:

- stationary LNAPL
- migrating LNAPL, and
- free LNAPL.

Stationary LNAPL is that which is above residual or entrapped saturations but is not moving because of restrictions on its movement. These restrictions may include hydraulic and physical barriers or the lack of a driving pressure gradient.

The definition of migrating LNAPL is that adopted by TCEQ (2008) which describes it as that LNAPL which is moving vertically or laterally in the subsurface. This is referred to as mobile LNAPL in ASTM International (2007).

Here we use the term free LNAPL to describe that LNAPL which will enter a screened well or open hole. By definition, this is the LNAPL which exists at a fluid pressure greater than atmospheric pressure (i.e. air pressure). This LNAPL is free in the sense that it is free of capillary forces. It should be noted that the classification is not mutually exclusive and indeed the free LNAPL may constitute a portion of the migrating and even stationary LNAPL.

There is a tendency in the NAPL literature to use the term residual to describe all the LNAPL that is immobile under the prevailing conditions. Here we make a distinction based on the processes leading to the immobility, architecture of the LNAPL in the pore space and the number of fluid phases present in further characterising what is immobile. This is because these underlying factors have important implications, including for instance, the expected magnitude of the residual and entrapped saturations (residual saturations in the vadose zone are generally lower than entrapped saturations below the water table – Charbeneau et al. 1999; Mercer & Cohen 1990; Wilson et al. 1990), how these portions of the LNAPL may be mobilised and how they may be affected by other loss mechanisms.

### 3.6.3 Capillary pressure

For mobile LNAPL, the critical state variable is the fluid pressure. It is the LNAPL pressure in relation to the other fluids that controls its distribution within a porous medium. Because of the existence of a stable interface between the fluids, the difference in fluid pressures is maintained by the interfacial forces acting on the curved interface between the fluids. For a two-fluid phase system, the difference in pressure between the non-wetting and wetting fluids is termed the capillary pressure, $P_c$:

$$P_c = P_{nw} - P_w$$  \[Equation 7\]

where $P$ is pressure and the subscripts $nw$ and $w$ refer to the non-wetting and wetting fluids respectively. In a water-wet, two-fluid phase system, water is the wetting phase.
and either air or LNAPL (whichever is present) is the non-wetting phase giving rise to the capillary pressures:

\[ P_{c,aw} \] – air-water capillary pressure
\[ P_{c,nw} \] – LNAPL-water capillary pressure.

For a three-fluid phase system, the capillary pressure is generalised to the pressure difference between any two fluid pairs with due regard to the hierarchy of wetting. Thus, a further capillary pressure may be defined:

\[ P_{c,an} \] – air-LNAPL capillary pressure.

The same capillary pressure, \( P_{c,an} \), also arises in a two-fluid phase system where LNAPL and air are the interstitial fluids. In this case LNAPL would be the wetting fluid.

The capillary pressure can be related to the characteristic radius, \( r \), of the interface and interfacial tension through the Laplace Equation of Capillarity (Corey 1990):

\[ P_c = \frac{2\sigma}{r} \]  \hspace{1cm} [Equation 8]

An illustration of the pore-scale distribution of fluid phases in relation to the wetting order, and radii of the fluid interfaces is shown in Figure 4. In this instance:

\[ P_{c,aw} = P_a - P_w = \frac{2\sigma_{aw}}{r_1} \]  \hspace{1cm} [Equation 9]

and

\[ P_{c,an} = P_a - P_n = \frac{2\sigma_{an}}{r_2} \]  \hspace{1cm} [Equation 10]

![Figure 4. Cartoon of the distribution of fluids in a porous material illustrating the conceptual model of the radius of curvature of the interfaces as a result of fluid pressure differences.](image-url)
Fluid pressures are often presented as equivalent water heads (height of a water column supported by the fluid pressure – such as would be indicated by a manometer). Fluid heads, $H$, are scaled from the pressures according to:

$$H = \frac{P}{\rho_w g}$$

[Equation 11]

where $\rho_w$ is the density of water and $g$ is the acceleration due to gravity. While many observations of hydraulic pressures are made according to equivalent water heads (for example, potentiometric heads and water table elevations), it is often more convenient to retain pressures as a primary unit of measurement where air pressures vary naturally or as a result of forced air flows as part of remediation attempts. To preserve generality and reinforce its fundamental role in capillary and hydraulic behaviour, pressure is used throughout the LNAPL flow theory that is developed below.

### 3.6.4 Saturation (volume fractions), pressure and permeability relationships

Figure 4 illustrates that the volume of the pore space occupied by various fluids is dependent on the radius of the fluid interfaces in relation to the size of pore bodies and pore throats. This is the underlying principle that gives rise to the relationships that may be used to describe the volume fractions of the fluids and their hydraulic conductivity in the porous medium. Volume fractions are usually reported as fluid saturation, $S$, the ratio of the volume fraction of the fluid to the porosity of the porous media:

$$S = \frac{\theta_v}{\phi}$$

[Equation 12]

where $\theta_v$ is the volumetric fraction (content) of the fluid and $\phi$ is the porosity of the porous media. Instead of using an absolute hydraulic conductivity, it is more usual to characterise the ease of fluid flow under a pressure gradient at the ambient conditions (of fluid saturations) as a relative permeability, $k_r$:

$$k_r = \frac{k}{k^*}$$

[Equation 13]

where $k$ is the fluid permeability for the given conditions and $k^*$ is the intrinsic permeability of the porous material, independent of the fluid viscosity (Corey 1990). The intrinsic permeability $k^*$ is computed from the empirical relationship:

$$k^* = \mu \frac{Q}{A \frac{\Delta P}{\Delta x}}$$

[Equation 14]

where $\Delta P/\Delta x$ is the fluid pressure gradient, $Q$ is the volume flux of fluid, $A$ is the cross sectional area of fluid flow and $\mu$ is viscosity. Although shown here as a scalar, $k^*$ is generally a vector, taking on different values dependent on the direction of fluid flow. The directional dependence (anisotropy) in the permeability is a consequence of structure in the porous medium, due to the orientation of individual grains, layering of different grain size material or different orientations of fracture sets and macropores.
The saturation-capillary pressure \((S - P_c)\) relationship

The saturation-capillary pressure \((S - P_c)\) relationship is a combined characteristic of the porous material and resident fluids (mainly the distribution of pore sizes and the interfacial tensions of the fluids) which describes the saturation of fluids as a function of fluid capillary pressures – i.e. denoted \(S(P_c)\). The \(S - P_c\) relationship is rather complex and a full description of the fluid saturation requires consideration of hysteresis and the history of fluid saturation changes in the porous media. An example is shown in Figure 5 which illustrates the primary drainage and imbibition curves for a two-fluid phase system along with secondary curves. The secondary curves arise where the porous material has previously been subjected to drainage and imbibition of the wetting fluid and there is a further reversal between imbibition and drainage. Note that by convention, the drainage and imbibition curve is in reference to the wetting fluid. That is, the drainage curve represents the displacement of the wetting fluid by the non-wetting fluid and the imbibition curve represents the displacement of the non-wetting fluid by the wetting fluid. Salient features of the \(S - P_c\) relationship are:

- fluid displacement pressure, \(P_d\)
- residual saturation (sometimes referred to as the irreducible saturation), \(S_r\), and
- entrapped saturation, \(S_e = (1 - S_m)\), where \(S_m\) is the critical saturation (Corey 1990).

\[
P_c(S) = \text{function of } S
\]

\[
P_d = \text{fluid displacement pressure}
\]

\[
S_r = \text{residual saturation}
\]

\[
S_m = \text{critical saturation}
\]

\[
S_e = (1 - S_m)
\]

\[
S_c = \text{entrapped saturation}
\]

Figure 5. Schematic showing the elements of the saturation-capillary pressure relationship for two fluids in a porous material. The diagram shows the relationship between wetting-phase saturation and capillary pressure. The main drainage and main imbibition relationships are shown along with the secondary drainage relationship.

It is useful to encapsulate the \(S - P_c\) relationship in a function that allows it to be summarised with a small number of parameters and also to be more easily used in mathematical models. Two popular functional relationships originally developed for soil
water applications are the van Genuchten (van Genuchten 1980) and Brooks-Corey (Brooks & Corey 1964) relationships. These are for two-phase systems, where water is the wetting phase and air is the non-wetting phase. More detail can be found in Appendix B.

The main drainage curve for the porous medium is most frequently used for characterisation and applied without regard to the hysteresis and complexities of swapping between drainage and imbibition. This may be acceptable where only the original release and spread of LNAPL is considered (i.e. LNAPL displacing water), or where hysteresis is not pronounced. A full prediction of hysteretic behaviour is usually confined to specialist simulation models. Otherwise the appropriate drainage or imbibition curve should be used for the task at hand. It should be noted that methods are available for predicting the imbibition curve (e.g. Steffy et al. 1997a) where it is not measured directly.

Research has shown that a \( S – P_c \) relationship for a particular fluid pair may be generalised to provide an adequate description for other fluid pairs and indeed for a three-fluid phase system. The \( S – P_c \) relationship can be adapted to another fluid pair through scaling using the fluid interfacial tensions as the scaling factor (Parker et al. 1987). More detail can be found in Appendix D.

**The relative permeability-saturation \((k_r – S)\) relationship**

The relative permeability-saturation \((k_r – S)\) relationship presents a description of the functional relationship between the fluid relative permeability and fluid saturation. The relationship can be most readily appreciated for a two-fluid phase system where the permeability of both fluids can be expressed as a function of the wetting-phase saturation. Figure 6 shows an example of the relative permeability relationships for the main drainage and imbibition of liquids in a saturated porous medium. In general, the \( k_r – S \) relationship is also hysteretic although mostly less so than the \( S – P_c \) relationship. Key features here are the zero wetting phase permeability at saturations less than \( S_r \) and the zero non-wetting phase permeability at saturations greater than \( S_m \). A shift in the curves is also apparent, particularly for the non-wetting fluid (LNAPL for example), once the non-wetting fluid is introduced to the system. Importantly, at the same individual fluid saturations, the non-wetting phase has a greater relative permeability. This is due to the preferential distribution of the non-wetting phase in the larger pore bodies.
The measurement of multi-phase relative permeabilities is challenging. Experimental measurements are rarely available and therefore they are usually estimated from mathematical relationships. Although, particular functional forms have been proposed for $k_r(S)$ (usually power functions of the saturations), it is much more common to estimate the fluid relative permeability from the $S – P_c$ relationship. Again, there are a range of mathematical relationships that have been proposed. However, two are usually proposed in concert with the van Genuchten and Brooks-Corey formulations of the $S – P_c$ relationship (Charbeneau et al. 1999). These are the Mualem and Burdine models. Details are given in Appendix C.

It is important to note that the relative permeability of water (the wetting fluid) only depends on its own saturation. However, the relative permeability of LNAPL depends on both the water saturation and the total liquid saturation (because it is the intermediate wetting fluid). As well as the liquid relative permeabilities, both the Mualem and Burdine models can also be used to estimate the gas permeability if that is required. However, except for active remediation using air flushing technologies, the air is generally considered as a stagnant phase.

### 3.6.5 Residual and entrapped saturations

Much of the NAPL contaminant literature takes residual and entrapped saturations as fixed-value properties of the combined system of porous-media and fluids. This is not the case.

Residual and entrapped saturations depend on the history of fluid saturations and the scale of measurement/observation. The dependence on the history of fluid saturation can be seen in Figure 7. This shows that different entrapped saturations arise from different reversal points in the drainage/imbibition process. For a range of porous materials, the entrapped saturation can be simply predicted from the LNAPL saturation at the reversal point (Johnston & Adamski 2005; Steffy et al. 1997b). In addition,
Entrapment is fundamentally a process related to pore heterogeneity. Hence the scales of heterogeneity within a porous material or geological unit will determine what may be the characteristic measurement or observation scale for its determination. In particular, it should be noted that macroscopic entrapment in variably-textured inclusions is likely (Wilson et al. 1990).

Residual saturations in the vadose zone may also vary according to the water saturation and be influenced by the history of entrapment of both LNAPL and air. For instance, air and LNAPL may be entrapped/occluded in the water as well as there being portions of the LNAPL and air that are continuous in the pore space. Equally, it is common for air to be entrapped within the liquid phases in the capillary fringe and below the water table as a result of the variation of the water table. This will also have an effect on entrapped saturations of LNAPL.

![Diagram](image)

**Figure 7.** Illustration of the dependence of entrapped saturations on the history of fluid saturation in a porous medium. The diagram shows three histories (arrows on curves show chronology) of wetting phase saturation as a function of capillary pressure – following the main drainage and imbibition curves and two other histories with different reversal points. The entrapped saturation of non-wetting phase fluid is a function of the wetting phase saturation at the reversal point.

While concepts of residual and entrapped saturations are comparatively well defined for inert fluids and the time scale of most laboratory characterisations, other processes affect what is seen in the field. The weathering processes of volatilisation, dissolution and biodegradation will not only alter some of the fluid properties controlling residual and entrapped saturations, but mass loss may appreciably reduce LNAPL saturations below those expected.
3.7 General movement of LNAPL in soils and aquifers

Releases that lead to subsurface LNAPL contamination may take many forms but usually arise through:

- leaks/spills onto the ground from above-ground storage tanks or pipes, or
- leaks directly into the subsurface from underground storage tanks or pipes.

The location of the release along with the rate and total volume of the release all have differing influences on the movement and ultimate fate of the released LNAPL. For instance, large, catastrophic releases onto the ground may allow general spreading and even ponding of the LNAPL at the ground surface. While this may lead to a more uniform infiltration of the LNAPL over a large area, it may also increase the possibility of finding preferential flow paths into the subsurface. On the other hand, leaks from subsurface sources would normally tend to be more localised and controlled by the local soil properties. A key point of differentiation for releases of LNAPL is whether they are flux controlled (i.e. the infiltration rate matches the release rate) or the release rate exceeds the local infiltration capacity of the soil and infiltration becomes driven by the pressure head of the LNAPL. An important feature of leaks from buried pipelines is the high pressures the LNAPL may be under. The high driving pressure may add considerably to the spread of the LNAPL.

Once it has entered the subsurface environment, LNAPL will redistribute under the influence of gravity and capillary forces. Gravitational forces will tend to dominate, driving the downward migration of the LNAPL through the vadose zone where air is easy to displace. However capillary forces will also enhance the downward infiltration of the LNAPL as well as lateral spreading. Dissipation of the driving pressure heads over an increasing depth mean that the rate of downward advance of the LNAPL will generally reduce over time. The ultimate depth reached by infiltrating LNAPL is influenced by many factors:

- the volume of the spill
- loss mechanisms acting on the LNAPL
- retention characteristics of the profile materials
- heterogeneity of the profile materials, and
- location of the water table.

For relatively uncomplicated granular porous media systems where the release is not ongoing, the LNAPL will tend to be left at residual saturations behind the infiltrating front. The magnitude of this residual saturation and volume of release, along with the depth of the water table, determines the potential depth of infiltration of the LNAPL.

The capillary fringe at the water table acts as an impediment to the advancing LNAPL because of the unfavourable density contrast between LNAPL and water. The greater density of water compared to the LNAPL and the absence of the lower density air means the continued advance of the LNAPL is dependent on capillary forces, specifically the LNAPL-water capillary pressure. This is balanced by the inherent displacement pressures of the porous medium.

Given sufficient pressure, the LNAPL will displace water to some distance below the capillary fringe and water table. However, the LNAPL will more easily spread laterally within the capillary fringe to the water table (Miller et al. 2004). Thus with sufficient
LNAPL volume, a plume of LNAPL will move within the aquifer to be distributed over an interval of the profile centred on the original capillary fringe to the water table (see Figure 8). An LNAPL table will also form in the aquifer where pressures of the LNAPL are above the local atmospheric air pressure. The lateral spreading of LNAPL is largely controlled by the topography of the water table away from the area of local mounding of the LNAPL. The LNAPL plume will continue to spread laterally while the saturation of LNAPL in the plume continues to be high enough to develop capillary pressures capable of displacing water from the materials at the leading edge of the plume. Thus an LNAPL plume will naturally cease spreading. And even when the LNAPL plume does cease to spread, free-LNAPL will (at least initially) remain within the body of the plume.

![Diagram of LNAPL plume development](image)

**Figure 8. Cartoon of the development of an LNAPL plume in an uncomplicated granular porous medium in relation to the water table and original capillary fringe to the water table.**

Temporal variations of the groundwater table elevation will, over time, spread LNAPL vertically in the profile from its original place of emplacement (predominantly within the capillary fringe). This process will give rise to residual saturations of LNAPL in the unsaturated zone and entrapped LNAPL in the saturated zone (see Figure 8). Varying water tables is a strong factor in reducing the spread of an LNAPL plume.

Free-LNAPL will continue to remain (and appear in wells) until LNAPL saturations are sufficiently decreased by vertical spreading of the LNAPL by water table variations (smearing) and natural LNAPL losses from the plume. As the LNAPL decreases towards residual and entrapped saturations, pressures in the LNAPL fall below atmospheric pressure and LNAPL will no longer appear in wells. However, LNAPL will remain in the aquifer.

### 3.7.1 Distribution of LNAPL in the vicinity of the water table

The distribution of LNAPL in the vicinity of the water table and where it accumulates and spreads is of critical importance in terms of the recovery of LNAPL for remediation. Figure 9 shows the expected quasi-equilibrium vertical distribution of LNAPL saturation.
in a uniform granular porous medium away from the original source. The distribution here is for a mature LNAPL release – that is, after a sufficient period of time for the water table to have varied and for the fluid distributions to be in quasi-equilibrium. Key features are:

- residual LNAPL saturations in the vadose zone above the capillary fringe
- a peak in LNAPL saturation immediately at the top of the capillary fringe
- an LNAPL table above the water table, indicating free LNAPL that will enter a screened well, and
- entrapped saturations of LNAPL below the water table.

Figure 9 shows an illustration of the vertical distribution of LNAPL saturation and associated appearance of the fluids in a fully screened well and a well screened below the interval where LNAPL is mobile. In this instance, the maximum LNAPL fluid pressure is greater than atmospheric pressure in the well, allowing the LNAPL to drain from the aquifer into the well that is fully screened. The interfaces between the fluids in the fully-screened well reflect fluid pressures within the aquifer:

- the air-LNAPL interface – which reflects where the LNAPL pressure equals air pressure \( P_{c,an} = 0 \), and shows the elevation of the LNAPL table (analogous to the water table which is where the groundwater pressure equals the air pressure), and
- the LNAPL-water interface – which reflects the elevation where the LNAPL pressure is equal to the water pressure, that is, where \( P_{c,nw} = 0 \).
The well screened below the interval where LNAPL is mobile only allows water to enter and displays another fluid interface:

- the air-water interface – which reflects where the water pressure equals air pressure \( (P_{c,aw} = 0) \), that is, the water table.

The elevation of the water table may also be calculated from the interfaces in the fully screened well according to:

\[
z_{aw} = z_{nw} + \frac{\rho_w b_n}{\rho_n} \quad \text{[Equation 15]}
\]

In some simple situations, the observed fluid interfaces and capillary pressures can be used to predict the vertical distribution of fluid saturations and relative permeability (see Appendix D). These can be useful for indicating the amount of LNAPL present and the potential for free LNAPL recovery. Examples of computed vertical distributions of capillary pressures, liquid saturations and relative permeabilities are shown in Figure 10.

![Figure 10. Theoretical equilibrium distribution of capillary pressure heads, liquid saturations and liquid relative permeabilities in the vicinity of the water table for hydrostatic conditions along with the expected observation of LNAPL in a fully screened monitoring well. Calculations using a van Genuchten \( S - P_c \) relationship for a homogeneous fine sand and characteristics of diesel fuel \( (\rho_n = 0.845, \beta_{nw} = 3.65 \) and \( \beta_{an} = 2.49) \) with an observed LNAPL table 0.2 m above the water table. See Appendix D for detailed explanations.](image-url)
3.7.2 LNAPL in wells as an indicator of the presence of LNAPL

The appearance and thickness of LNAPL in wells is a key piece of information used for contaminated site assessment and monitoring. Appearance of LNAPL in wells may often be the first indication of the presence of LNAPL at a site and may indeed become a major criterion set for site remediation. As indicated above, a lot of theory has developed around using observed LNAPL thickness in wells to infer many characteristics of the LNAPL distribution in the surrounding aquifer. This includes the mass of LNAPL in the aquifer (Farr et al. 1990; Lenhard & Parker 1990) and its recoverability (Charbeneau & Chiang 1995; Charbeneau et al. 2000). However, there are many pitfalls in using LNAPL thickness in wells as a measure of LNAPL contamination. These pitfalls are encapsulated in what the ITRC (2009a) termed the ‘in-well LNAPL dilemma’:

- the absence of LNAPL from a well does not mean LNAPL is not present in the aquifer
- the appearance of LNAPL in a well does not necessarily mean the LNAPL plume is migrating
- decreasing LNAPL thickness in a well does not necessarily mean that the remediation is working
- LNAPL thickness in a well is a not a good predictor of the potential rate of recovery
- the presence of LNAPL in a well does not necessarily indicate that the LNAPL has the potential to migrate.

It needs to be borne in mind that LNAPL in a well is only a reflection of the presence of free LNAPL (that above atmospheric pressure). That is, it is no reflection of the residual and entrapped saturations of LNAPL in the aquifer. The free LNAPL that may enter a well is usually only a small fraction of that in the aquifer. Hence the expression of LNAPL thickness in wells can change appreciably over time due to forcing by changes in the water table – without any significant lateral movement of the LNAPL or change in its mass in the aquifer. It is not uncommon for LNAPL to disappear from wells under high water table conditions as the increased groundwater pressures spread LNAPL vertically in the profile. This makes changes to LNAPL thickness over time difficult to interpret in terms of changing LNAPL mass in the aquifer. However, many wells display a characteristic relationship between LNAPL thickness in the well and elevation of the water table (Figure 11). For the well shown in Figure 11, LNAPL disappears from the well once the water table rises above an elevation of 2.2 m. Deviations from such established relationships can be used to infer other stresses on the LNAPL including increasing or decreasing mass in the aquifer.
Figure 11. Relationship between LNAPL thickness in a well, $h_n$, and the elevation of the water table, $z_{aw}$, showing seasonal changes due to rainfall recharge.

A less common variation to the behaviour depicted in (Figure 11) is where LNAPL thickness in the well increases as the water table rises. Such a ‘confined’ response is a result of the inability of the LNAPL to displace water from overlying layers. This increases pressures in the LNAPL relative to water, increasing LNAPL thickness in the well.

Another issue that can be encountered is that the LNAPL present in the well may become disconnected from that in the aquifer. This may occur in low transmissivity formations, or where the LNAPL has a low relative permeability. Rapid changes in the water table in the well may not allow equilibration of the LNAPL in the well to the conditions in the surrounding formation. If there is any doubt about whether or not the LNAPL in a well is in equilibrium with the aquifer, it is highly recommended to remove the LNAPL from the well and monitor its recovery over time.

### 3.7.3 Spreading and LNAPL mobility in plumes

The concepts of the mobility and spreading of LNAPL plumes and the mobility of LNAPL within plumes often become confused. There are a number of concepts here that have to be clearly enunciated to avoid confusion when discussing LNAPL mobility. The concepts that need to be distinguished are:

- the mobility of LNAPL within the body of an LNAPL plume
- the LNAPL that may be migrating within the LNAPL plume
- the mobility of the plume itself (i.e. spreading of the plume).

Each of these mobility parameters have different implications and are measured in different ways.

#### Mobility within the body of the plume

The mobility of LNAPL within the body of a plume is basically a measure of the rate at which the LNAPL may move within the plume under natural or applied pressure gradients. This relates directly to the relative permeability of the LNAPL in the aquifer.
Its main use is to identify the possible rates of recovery of LNAPL from the plume, particularly in the case of free-LNAPL recovery.

The usual metric for this mobility parameter is the LNAPL transmissivity. By analogy with groundwater tests, the LNAPL transmissivity can be determined by LNAPL bail-down tests or from LNAPL pumping from wells. The transmissivity of the LNAPL is more complex than that for groundwater. It is an integration of the depth-distribution of LNAPL conductivity which is the product of relative permeability and intrinsic permeability of the aquifer materials over the depth interval of mobile LNAPL. Mathematically, the LNAPL transmissivity, $T_n$, is given by:

$$T_n = \int_{z_{nl}}^{z_{nu}} k_r \frac{\rho_n g}{\mu_n} \, dz$$

[Equation 16]

In Equation 16, $z_{nu}$ is the upper elevation of mobile LNAPL, and $z_{nl}$ is the lower elevation of mobile LNAPL. The relative permeability distribution can be quite sharply peaked in the profile (see Figure 10) making $T_n$ sensitive to fine-scale variability and vertical movement of LNAPL in the profile due to varying water tables. Methods for determining $T_n$ from bail-down tests are presented by Huntley (2000).

A method has also been developed to directly measure the flow rate of LNAPL through a screened well (Sale et al. 2007). This tracer-dilution method can yield estimates of the rate of flow within the LNAPL plume by use of appropriate factors for the convergence of LNAPL flow through the well. LNAPL transmissivity in the aquifer can be inferred from these flow rates where LNAPL pressure gradients are known.

**Migrating LNAPL in the plume**

Another measure often referred to is the inherent oil mobility, designated as $M_n$, which relates to the depth-averaged velocity of the oil within the LNAPL plume. For consistency with the rest of the report, we change the terminology to inherent LNAPL mobility and notation to $M_n$. The inherent LNAPL mobility is the ratio of the LNAPL transmissivity to the specific volume of LNAPL in that part of the profile where mobile LNAPL occurs, $V_n$. That is,

$$M_n = \frac{T_n}{V_n}$$

[Equation 17]

From this definition, the depth-averaged velocity of LNAPL migrating within a plume, $\bar{u}_n$, is given by:

$$\bar{u}_n = M_n \nabla H_n$$

[Equation 18]

where $\nabla H_n$ is the lateral gradient in the LNAPL head (i.e. as indicated by the LNAPL table).

Thus the inherent LNAPL mobility within a plume depends both on the LNAPL transmissivity and the volume of LNAPL in that part of the profile where mobile LNAPL is found. A subtlety here is that the specific volume of LNAPL used in the calculation is not only that fraction which is mobile. It includes all the LNAPL that is in the interval...
containing the mobile LNAPL. This assumes all the LNAPL in that interval is moving and participates in the LNAPL migration.

**Plume mobility (spreading)**

The plume mobility/rate of spread differs fundamentally from the within-plume measures of LNAPL mobility. The rate of spread of an LNAPL plume is measured by the rate of advance of the leading edge of the LNAPL plume. This in itself may be relatively difficult to determine, particularly over relatively short time periods. The advance of a plume is likely to be sporadic due to water table fluctuations and changing hydraulic gradients. Spatial variability of the aquifer materials may also make identification of the advancing front difficult. The appearance of LNAPL in monitoring wells would be a common way to detect if an LNAPL plume was advancing (and at what speed). However, as discussed above, there are caveats around the interpretation of the appearance of LNAPL in wells.

### 3.7.4 LNAPL in finer textured unconsolidated materials

Finer textured granular materials such as those of silty or clayey textures often have low permeability, high water contents, and high displacement pressures. In many instances the displacement pressures of such materials are greater than LNAPL pressures usually encountered in the subsurface. This makes them difficult for LNAPL to invade and move through – causing them to become a barrier or restriction to LNAPL movement. Thus the general movement of LNAPL through these materials is expected to be different to that of coarser textured (sandy) materials discussed above. The limited penetration of LNAPL into the finer textured materials means that overall saturations of LNAPL would be expected to be low. It also follows that the low saturations (and hence low relative permeabilities) combined with the low intrinsic permeability of the materials means that any movement of LNAPL through fine-grained materials may be very slow.

Where such materials exist as layers within a coarser matrix in the vadose zone, these layers would be expected to cause lateral spreading and even pooling of the LNAPL on the layers (Figure 12). This would lead to LNAPL becoming perched above the general water table elevation. In these instances, the lateral spreading of the LNAPL would be dictated by the topography of the finer textured layer. Unless the topography is known, the spread of the LNAPL may be unpredictable and unrelated to the local groundwater table gradient.

Layers of finer textured materials in the vicinity of the water table may also confound the movement and general behaviour of the LNAPL. For example, water table variations may allow LNAPL spreading laterally to become confined below dipping layers of fine textured materials (see Figure 12). This situation can give rise to different responses of the LNAPL in wells to varying water tables (i.e. thickness increase with a rise in the water table). However, it may also mean that LNAPL pressures are sufficient to maintain the LNAPL at saturations that make it mobile and largely stagnant.
3.7.5 LNAPL in dual-porosity materials

A bimodal (or even multi-modal) distribution of pore sizes is often encountered in soil and aquifer materials. This can lead to complex interactions developing between domains with quite different fluid flow and retention behaviour. The complexity of these interactions may make it difficult to provide an overall description of fluid behaviour from the usual field measurements. This is largely because of the extreme and fine-scale variability that is present.

Where the vadose zone is predominantly of a finer texture, inhomogeneities and preferred flow can be very important in LNAPL movement (Tzovolou 2009). Coarser textured inhomogeneities and voids will likely be the main pathways of LNAPL movement. That is, flow through these fine textured zones would be limited to coarser inclusions as well as voids arising from plant roots, soil fauna and other pedogenic processes. Thus the overall LNAPL saturation may be low and the presence of LNAPL may be limited to coarser textured zones. In this respect, the low saturations observed at the large scale may not provide a good indicator of the potential rate of LNAPL movement and distribution of the LNAPL. However, the finer textured materials may be an important reservoir of dissolved constituents that are derived from the LNAPL.

The concentration of LNAPL movement through preferential pathways can lead to some complex behaviour in these dual porosity materials. For instance, the extension of preferential flow paths below the water table may allow LNAPL much deeper below the water table than expected. Enhanced penetration of the LNAPL may be coupled with high LNAPL pressures maintained because of the limited ability of pressures to be dissipated by lateral losses from the preferential pathway system. Where the preferential flow path system intersects coarser materials below the water table, these coarser layers may be invaded by the LNAPL. From here, the LNAPL may spread laterally below the water table and be confined by overlying finer textured materials.
It needs to be kept in mind that a range of preferential flow paths may also be introduced to the subsurface due to human activity. Sewers, pipes, tanks and a range of other services may be laid in trenches and backfilled with material more conducive to LNAPL migration than the surrounding native soils. Foundations, piles and drill holes may also provide pathways for vertical preferential flow.

Not all dual-porosity materials may effectively confine the LNAPL to the macropores. Macropores are found in materials with a range of matrix properties – some where water may be more easily displaced by the LNAPL. Some fractured and karstic limestones and sandstones would be examples. This leads to the prospect of LNAPL pervading the aquifer matrix as well as residing in a macropore network. Subsequent water flow through a macropore system may isolate and entrap the LNAPL in the matrix of the aquifer, for example, during attempts to remediate. An example of this is shown in Figure 13.

![Figure 13. Model simulation of the LNAPL invasion and recovery for a dual porosity material with an orthogonal fracture network showing LNAPL saturation – (a) after invasion of the LNAPL and (b) following the recovery of the LNAPL from the indicated screened interval (MG Trefry 2004, pers. comm.).](image)

### 3.7.6 LNAPL in fractured hard rocks

Fractured hard rock aquifers are complex environments for the movement of LNAPL. The defining characteristic here is that the LNAPL and other fluids are confined to a relatively sparse, three-dimensional network of cracks and fractures. Aspects of the movement of LNAPL through fractured rocks are described by Hardisty et al. (2003). The cracks and fractures individually and collectively transport the fluids including the LNAPL with essentially no interaction with the rock matrix other than with the faces of the fractures.

Above the water table, LNAPL will move downwards through vertical and sub-vertical fractures. In all but the largest aperture fractures, infiltrating LNAPL will displace the majority of other fluids and travel as a ‘plate’ through the fracture. The presence of sub-vertical fractures and intersections with horizontal and sub-horizontal fracture sets mean that LNAPL may move laterally from the original source before reaching the...
water table. Good characterisation of the fractured rock would be needed to predict the lateral spread. The confinement of the LNAPL to the fractures and generally low bulk lateral transmissivity (due to the small cross sectional area with the rock volume) means that fluid pressures driving the infiltration of the LNAPL may be maintained deep into the vadose zone. Maintenance of high LNAPL pressures (and hence high capillary pressures) will enhance both lateral migration and vertical penetration of the LNAPL below the water table. Indeed, much deeper penetration of the LNAPL below the water table may be encountered in fractured rocks compared to sandy aquifers. Figure 14 shows the evolution of LNAPL distribution in a fractured rock aquifer for one of many possible scenarios from a surface release of LNAPL.

Figure 14. Possible evolution of LNAPL in a fractured rock aquifer from a surface release.
The fractures themselves are complicated conduits for the transmission and retention of fluids. Typically they are rough walled, variable aperture and may contain porous materials as a result of chemical alteration of the fracture face or transport of fine materials. Fracture aperture controls the ability of LNAPL to displace resident fluids and enter the fracture. The entry of LNAPL into a fracture is controlled by the displacement pressure which may be estimated by the Laplace Equation of Capillarity (Corey 1990):

$$P_d = \frac{2\sigma \cos \theta}{b}$$  \[Equation 19\]

where $b$ is the fracture aperture and $\theta$ is the contact angle with the wetting fluid (often assumed to be zero).

The vertical extent of LNAPL in fractures across the water table can be predicted for hydrostatic situations in the same way as granular porous materials. In fact, there is a direct analogy with the analysis for a granular material with a well-defined displacement pressure.

The qualitative difference is that during the active infiltration of the LNAPL, the LNAPL pressures and LNAPL-water capillary pressure could be much higher. In effect, the top elevation of the LNAPL in the fracture is the LNAPL table.

Fracture aperture can vary at a number of scales, which means that fluid saturations and relative permeabilities vary over a range of fluid capillary pressures. Hence, fluid displacement does not occur abruptly at a single capillary pressure.

The ‘cubic law’ (Witherspoon et al. 1980) for the fluid flux between smooth parallel plates is often assumed to be a reasonable approximation for real fractures. The cubic law leads to fracture permeability being given as:

$$k = \frac{b^2}{12}$$  \[Equation 20\]

However, it has increasingly been shown that this relationship is not accurate for rough-walled, variable aperture fractures. Nevertheless these relationships continue to be useful, first-order approximations for fracture characteristics determined from borehole testing.

At the scale of a single fracture, some similarity to a granular porous media may be seen. Specifically there may be definable (non-trivial) relationships between fluid capillary pressure, fluid saturation and fluid relative permeability within the fracture. Variability of the aperture properties would suggest that similar relationships may exist at multi-fracture scales. However, it is unclear how far the analogue can be taken.

Entrapment of LNAPL in fracture networks may also be qualitatively different to granular materials. Capillary trapping may occur at the scale of individual, variable-aperture fractures (i.e. LNAPL entrapped within different areas of a fracture), or LNAPL may remain entrapped in different fractures during displacement by water depending on the contrast in fracture aperture. In the latter case, the intersection of fractures will act as the equivalent of the pore throat in granular materials in determining by-passing and macroscopic entrapment processes. Trapping of LNAPL may preferentially occur in horizontal or sub-horizontal fractures during water table fluctuations.
A major challenge for fractured rock aquifers is to characterise the connectivity of fractures. Connectivity of different fractures may dominate control of LNAPL movement and this may differ significantly from interpreted hydraulic gradients. Because of this, predictions based on concepts based on equivalent porous media may be poor and/or misleading.

Viewed at a local scale, lateral spreading of the LNAPL will be dependent on connectivity of fractures within the near-water table zone (see Figure 15). This may be a limited vertical interval, diminishing further the chance of LNAPL connectivity. As a result, the properties of some fractured rock aquifers show fairly extreme variability in both the expression and mobility of LNAPL from observations taken from wells. And indeed, there are no guarantees that LNAPL will be expressed in all wells placed within the boundaries of an LNAPL plume or that LNAPL in nearby wells is connected. The end result is that remediation efficiency will be variably and critically dependent on the particular intersections of a well with the local fracture network.

![Figure 15. Schematic showing the distribution of LNAPL at the water table in a fractured rock aquifer.](image)

### 3.8 Metrics for assessing the level of LNAPL contamination

The level of LNAPL contamination is described by the physical state of the LNAPL in the subsurface, primarily in terms of its distribution and mobility. Thus, there is a range of metrics for describing the physical state of the LNAPL and measurement techniques to provide information on these. However, LNAPL contamination is also evaluated in terms of a number of concerns that arise from the presence of the LNAPL (see Section 4). Thus, a full assessment of the level of the LNAPL contamination needs to provide metrics that also provide a measure of these concerns. In summary, metrics that provide quantification of the level of LNAPL contamination may be grouped according to the assessment of the LNAPL’s:

- distribution
- mobility, and
- other concerns related to the presence of LNAPL.

This section concentrates on the metrics associated with the distribution and mobility of the LNAPL. It also discusses metrics over the physical partitioning of the LNAPL to the
gas and aqueous phases that may lead to concerns over the presence of LNAPL. However, presentation and discussion of metrics for the full range of possible concerns is not attempted.

The basic metric used for characterising the spatial and temporal distribution of LNAPL is its saturation in the subsurface porous materials. This may be amenable to direct measurement but sometimes may be inferred from the LNAPL thickness in wells as described above.

The basic metrics for LNAPL mobility are the LNAPL conductivity/transmissivity (or even more fundamentally, the LNAPL relative permeability) and the LNAPL pressure gradients. The direct measurement of these metrics offers a greater challenge particularly in the face of variability at a number of scales. Thus they are often inferred through characterisation of the subsurface environment and concomitant observations of the LNAPL distribution and/or LNAPL pressures.

The metrics associated with the concerns over partitioning to the gas and aqueous phases are the spatial and temporal distributions of vapour and dissolved constituent concentrations and fluxes in the subsurface. Secondary metrics are the computed hazard and toxic risk posed by the vapours, dissolved constituents and the LNAPL itself. The computation of hazard and toxic risk are not considered further in this document. Further information may be found in vapour risk documents, water quality guidelines and soil quality guidelines.

Metrics for the more intangible factors and concerns such as aesthetic values, nuisance, business factors and intergenerational equity tend not to be generic and would generally need to be developed on a case-by-case basis. In many instances, the impairment of the beneficial use of resources and aesthetic values as well as the nuisance caused by the LNAPL may be cast in terms of a financial cost that could be used as a metric. Business factors such as community perceptions may be very difficult to quantify objectively within a metric. Cost metrics may also be used as a measure of intergenerational equity but other case-specific factors would generally also be needed to provide a more holist metric.

### 3.8.1 Methods for evaluating metrics

The methods used to evaluate particular metrics for assessing the level of LNAPL contamination are dependent on the type of aquifer. A key distinction may be made between granular (unconsolidated and consolidated materials) and fractured/dual porosity materials. This stems from the way in which the LNAPL is held and moves within these different subsurface environments. In addition, the nature of these materials largely determines the investigation, measurement and sampling techniques. Tables 8 and 9 separately present the techniques for determining the parameters relevant to LNAPL distribution and mobility metrics for granular and fractured/dual porosity materials.

Subsurface geology, stratigraphy and hydrogeology are important determinants of the general mobility of LNAPL in the subsurface as well as specific metrics for LNAPL distribution and mobility. Tables 8 and 9 include techniques for characterising these factors along with the parameters that may be quantified for determining the LNAPL-related metrics. Of course, these factors are a very important part of the LNAPL conceptual site model.
Table 8. Techniques for determining the parameters used in defining metrics associated with LNAPL distribution and mobility in unconsolidated and consolidated granular materials.

<table>
<thead>
<tr>
<th>Category</th>
<th>Technique</th>
<th>Metrics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regional geology</td>
<td>Aerial-photo and remote-sensing</td>
<td>Lineament and trends</td>
</tr>
<tr>
<td></td>
<td>Outcrop mapping</td>
<td>Stratigraphy, porosity, permeability</td>
</tr>
<tr>
<td>Local hydrogeology</td>
<td>Surface and combined down-hole geophysics (including tomography) using: seismic refraction/transmission; resistivity; electromagnetics; ground penetrating radar.</td>
<td>Stratigraphy, porosity, aquifer state (fluid saturations)</td>
</tr>
<tr>
<td></td>
<td>Coring/drilling</td>
<td>Stratigraphy, porosity, aquifer state (fluid saturations)</td>
</tr>
<tr>
<td></td>
<td>Core analysis</td>
<td>Porosity, permeability and S–P.</td>
</tr>
<tr>
<td></td>
<td>Cone penetrometry</td>
<td>Stratigraphy, porosity, permeability</td>
</tr>
<tr>
<td></td>
<td>Wellbore geophysical logging</td>
<td>Stratigraphy, porosity, permeability</td>
</tr>
<tr>
<td></td>
<td>Aquifer testing</td>
<td>Bulk and interval conductivity/permeability, storativity/specific yield</td>
</tr>
<tr>
<td>LNAPL distribution assessment</td>
<td>Coring</td>
<td>LNAPL saturation, volume, and state</td>
</tr>
<tr>
<td></td>
<td>Cone penetrometry/MIPS/LIF</td>
<td>LNAPL content</td>
</tr>
<tr>
<td></td>
<td>Well monitoring</td>
<td>Areal distribution of LNAPL, LNAPL volume</td>
</tr>
<tr>
<td></td>
<td>Short-screened/multi-level wells</td>
<td>Depth and areal distribution of LNAPL, LNAPL volume, groundwater flow systems</td>
</tr>
<tr>
<td></td>
<td>Partitioning inter-well tracer test (PITT)</td>
<td>LNAPL saturation, volume and distribution</td>
</tr>
<tr>
<td>LNAPL mobility assessment</td>
<td>Well monitoring program</td>
<td>Areal distribution of LNAPL, fluid table elevations and gradients, groundwater flow regime, system transients</td>
</tr>
<tr>
<td></td>
<td>LNAPL analysis</td>
<td>Density, viscosity, interfacial tension, composition</td>
</tr>
<tr>
<td></td>
<td>Aqueous tracer tests (single- and multi-well)</td>
<td>Groundwater flow regime, transmissivity/permeability, porosity</td>
</tr>
<tr>
<td></td>
<td>LNAPL tracer dilution tests</td>
<td>LNAPL flow rates, transmissivity</td>
</tr>
<tr>
<td></td>
<td>LNAPL bail-down tests</td>
<td>LNAPL transmissivity/permeability, LNAPL volume</td>
</tr>
<tr>
<td></td>
<td>Discrete-depth pumping tests</td>
<td>Transmissivity/ permeability, storativity/specific yield</td>
</tr>
<tr>
<td></td>
<td>Groundwater sampling</td>
<td>Presence of LNAPL, groundwater geochemistry</td>
</tr>
</tbody>
</table>
## Table 9. Techniques for determining the parameters used in defining metrics associated with LNAPL distribution and mobility in fractured systems (adapted from Hardisty et al. 2003).

<table>
<thead>
<tr>
<th>Category</th>
<th>Technique</th>
<th>Metrics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regional fracture geology</td>
<td>Aerial-photo and remote-sensing</td>
<td>Major fracture lineament and trends</td>
</tr>
<tr>
<td></td>
<td>Outcrop mapping</td>
<td>Fracture orientation, lengths, connectivity, density, roughness and character</td>
</tr>
<tr>
<td>Local fracture network</td>
<td>Surface and combined down-hole geophysics using: seismic refraction/transmission; resistivity.</td>
<td>Stratigraphy, major fractures and fracture zones</td>
</tr>
<tr>
<td></td>
<td>Coring (vertical and angled)</td>
<td>Fracture orientation, density, roughness and character</td>
</tr>
<tr>
<td></td>
<td>Core analysis</td>
<td>Rock matrix porosity, permeability and $S-P_c$</td>
</tr>
<tr>
<td></td>
<td>Borehole imaging</td>
<td>Fracture aperture, orientation, density, roughness and character</td>
</tr>
<tr>
<td></td>
<td>Wellbore geophysical logging</td>
<td>Presence of fractures and fracture zones</td>
</tr>
<tr>
<td></td>
<td>Hydraulic packer testing</td>
<td>Bulk and fracture conductivity/permeability, fracture aperture</td>
</tr>
<tr>
<td></td>
<td>FLUTe</td>
<td>Bulk and fracture conductivity/permeability</td>
</tr>
<tr>
<td></td>
<td>In situ fracture casting</td>
<td>Fracture aperture, orientation, density, roughness and character</td>
</tr>
<tr>
<td>LNAPL distribution assessment</td>
<td>Sleeved coring with in-field analysis of fluorescence</td>
<td>Fractures containing LNAPL, depth and areal distribution of LNAPL</td>
</tr>
<tr>
<td></td>
<td>Sponge coring with laboratory analysis</td>
<td>Fractures containing LNAPL, LNAPL in matrix</td>
</tr>
<tr>
<td></td>
<td>Short-screened/multi-level wells</td>
<td>Fractures containing LNAPL, depth and areal distribution of LNAPL, LNAPL pressures, LNAPL volume, groundwater flow regime</td>
</tr>
<tr>
<td></td>
<td>Partitioning inter-well tracer test (PITT)</td>
<td>LNAPL saturation/volume</td>
</tr>
<tr>
<td></td>
<td>Flexible absorbent borehole liners</td>
<td>Fractures containing LNAPL, depth and areal distribution of LNAPL, LNAPL composition</td>
</tr>
<tr>
<td>LNAPL mobility assessment</td>
<td>Well monitoring program</td>
<td>Areal distribution of LNAPL, fluid table elevations and gradients, groundwater flow regime, system transients</td>
</tr>
<tr>
<td></td>
<td>LNAPL analysis</td>
<td>Density, viscosity, interfacial tension, composition</td>
</tr>
<tr>
<td></td>
<td>Aqueous tracer tests (single- and multi-well)</td>
<td>Fracture connectivity, groundwater flow systems</td>
</tr>
<tr>
<td></td>
<td>LNAPL tracer dilution tests</td>
<td>LNAPL flow rates, transmissivity</td>
</tr>
<tr>
<td></td>
<td>LNAPL bail-down tests</td>
<td>Fractures containing LNAPL, Transmissivity/permeability, LNAPL volume</td>
</tr>
<tr>
<td></td>
<td>Discrete-depth pumping tests</td>
<td>Fractures containing LNAPL, transmissivity/permeability, storativity/specific yield</td>
</tr>
<tr>
<td></td>
<td>Groundwater sampling</td>
<td>Fractures containing LNAPL, geochemistry</td>
</tr>
</tbody>
</table>
The measurement techniques for directly determining the primary concentration and flux metrics for the vapours and dissolved constituents in the subsurface are summarised in Table 10.

**Table 10. Techniques for directly determining the primary concentration and flux metrics for the vapours and dissolved constituents.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Metric</th>
<th>Techniques</th>
</tr>
</thead>
</table>
| Vapour   | Concentration | Gas sampling:  
• in-ground samplers  
• flux hoods  
• sampling from flux hoods  
• collection on sorbent materials |
|          | Flux     |                                                                            |
| Aqueous  | Concentration | Groundwater sampling:  
• short-screened wells  
• long-screened wells  
Soil water sampling:  
• suction lysimeters  
• integral pump test (IPT)  
• passive flux meter (PFM)  
• dosimeters |
|          | Flux     |                                                                            |

Concentrations of LNAPL constituents in the gas and aqueous phases are generally determined through the collection and analysis of physical samples. A variety of collection techniques are used. For VOCs, samples may be collected from the vadose zone using short in-ground sampling screens connected to the ground surface (see Davis et al. 2009). Alternatively, flux hoods at the ground surface may be used to measure VOC concentration immediately below ground surface. The mass flux of VOCs passing across the ground surface may be measured through modification of passive flux hoods to a configuration that continuously flushes the chamber. Mass flux is then determined from concentration time series or the accumulation of the VOCs on sorbent materials. Estimates of VOC flux can also be made from the observed concentrations and spatial concentration gradients where advective volumetric air fluxes and VOC diffusion coefficients are measured or estimated.

A range of installations and sampling techniques are available for collecting groundwater samples from below the water table and soil water from the vadose zone. More or less direct measurements of the flux of dissolved LNAPL constituents in groundwater can be made using integral pump tests (Bauer et al. 2004; Bayer-Raich et al. 2004). Passive flux meters (Annable et al. 2005) and dosimeters (Martin et al. 2003) also allow flux to be determined from the cumulative mass or time-weighted concentration where corresponding measurements of groundwater velocity are available. In the case of dosimeters, an independent measurement of groundwater velocity is required. More recent developments of the dosimeter also suggest that in situ measures of the toxicity of groundwater may be possible (Bopp et al. 2007).

Constituent fluxes in the aqueous phase can also be calculated from concentrations and concentration gradients where both the water velocity is measured independently and dispersion and diffusion coefficients are known. Inversely, flux-averaged concentrations can be calculated from mass flux where the water velocity is known.
4. Defining the objectives of LNAPL remediation

The objectives for remediating LNAPL vary greatly with the particular setting and circumstances. Clearly identifying the over-arching long-term vision and goals for the site in question and remedial activities is a critical initial stage in every site’s remediation. These long-term vision and goals for the site would be formulated in consultation with stakeholders. The stakeholders usually consist of (US EPA 2005):

- the site owner(s) and occupier(s)
- regulatory agencies
- local councils
- neighbouring property owners
- special interest groups.

Each of these may have different interests and concerns over the LNAPL contamination. Regulatory requirements may have a large influence on the long-term vision and goals.

Remediation objectives to meet these over-arching goals follow naturally from identifying risks and site-specific factors that constitute the concerns over the presence of LNAPL. Inherently, the remediation objectives will define target remediation end points sufficient for satisfying the goals set for the site. The end points themselves will be developed through consideration of concerns posed by the presence of the LNAPL at the site. This chapter examines particular issues around the concerns posed by LNAPL, how these concerns determine remediation objectives and end points, and how this ultimately may guide the selection of LNAPL remediation strategies.

4.1 Framework for site management and remediation

The selection of LNAPL remediation strategies sits within an overall framework for contaminated site management and remediation. A flow chart summarising the processes and steps within this overall framework is presented in Figure 16. This flow chart emphasises a number of factors and steps that underpin the need for remediation as well as the ultimate selection and implementation of an LNAPL remediation strategy.

Inherent in the remediation selection and implementation process is a clear understanding of the occurrence and state of LNAPL in the subsurface. This primarily comes from the initial investigations used to develop a detailed conceptual site model. However, a site model will undergo improvement through the process of selecting a remediation strategy. For instance, the need to identify the concerns associated with the presence of the LNAPL is likely to drive further specific investigations at a site. In addition, the step of selecting remediation technologies would likely require specific information not necessarily sought as part of developing an initial conceptual site model.
The LNAPL remediation selection and implementation process has multiple decision points requiring re-evaluation of the long-term vision and goals for the site. Determining remediation objectives and end points as well as the selection of appropriate remediation technologies may warrant review of these, particularly in terms of what may be reasonably achieved.

There are further points where a decision is required over whether or not remediation of the LNAPL is required. The first of these (point 1 in Figure 16), naturally falls after identifying and evaluating the concerns over the presence of LNAPL. A result of the evaluation of the concerns may be that no further action is required (for example, where risks are deemed acceptable). Where that is not the case, steps to consider further risk-based management or the need for remediation are outlined.
Figure 16. Flow chart showing the selection and implementation of LNAPL remediation as part of the overall framework for LNAPL-contaminated site remediation and management.

The remediation strategy selection step may precipitate a further decision to proceed or not with the remediation (point 2 in Figure 16). The basis for a decision would be on practical experience of the remediation performance at the site in question or other
sites. Other guidance on likely performance in relation to remediation objectives may also be used for this decision. The alternatives to proceeding would include:

- returning to identify the concerns in light of a new long-term vision and goals for the site, and
- arguing for other forms of site management on the grounds of impracticability of active remediation of the LNAPL contamination.

This decision point naturally produces an internal iteration loop for selection of alternative remediation strategies based on changing vision and goals. This internal loop is not shown explicitly in the flow chart shown in Figure 16.

4.2 Impracticability considerations

The possibility of resorting to an argument for impracticability rather than remediation may occur at a number of points along the decision pathway. Where enough experience and understanding exists with remedial options in a familiar environment, technical impracticability may be able to be invoked. A number of other pieces of information and factors supporting an argument for impracticability would need to be incorporated (Table 11). A detailed and reliable conceptual site model would be a prerequisite for any argument for impracticability. Currently, experience and data is limited in a number of aquifer environments. Hence, it is more likely that technical impracticability may be invoked following remediation pilot trials or where the full-scale implementation of the remediation strategies occurs and remediation objectives fail to be met. Demonstration of a range of remediation strategies may be required.

Table 11. Information and factors supporting arguments for impracticability.

<table>
<thead>
<tr>
<th>Information and factors supporting arguments for impracticability.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detailed and reliable conceptual site model</td>
</tr>
<tr>
<td>Familiar environment and contaminant</td>
</tr>
<tr>
<td>Results from pilot trials</td>
</tr>
<tr>
<td>Results from full scale remediation</td>
</tr>
<tr>
<td>Assessment of impacts of remediation, net benefit and sustainability</td>
</tr>
<tr>
<td>Consideration of intergenerational equity</td>
</tr>
</tbody>
</table>

Updates to the conceptual site model and review of the long-term vision and goals for the site should follow the failure of remediation objectives being met. These updates would provide the foundations for a return to the process of selecting and implementing a revised remediation strategy or for determining impracticability. The re-entry point to this process would be through identifying the concerns that are driving LNAPL remediation as reassessed with updated conceptual site models and goals for the site.

It is noted that the meeting of remediation objectives is in the context of determined performance indicators and review times. Hence the iteration through the process of selecting and implementing a revised remediation strategy may be short circuited by reassessing whether a change to the performance indicators and review times are likely to achieve the remediation objectives.
The natural exit points from the overall process of LNAPL-contaminated site remediation and management are after the implementation of a selected remediation strategy and either:

- remediation objectives commensurate with the long-term vision and goals for the site are achieved, or
- impracticability of LNAPL remediation is justified.

In both instances, some form of continuing site management is likely although the intensity and duration would vary greatly according to the particular circumstances. As indicated above, other exit points to the process of LNAPL remediation also occur during the selection and implementation process.

4.3 Concerns and risks posed by LNAPLs in aquifers

The concerns associated with the presence of LNAPL in aquifers include:

- direct explosive risk from the LNAPL
- direct toxic risks to human health and the environment through contact or ingestion of the LNAPL
- indirect toxic risks to human health and the environment through contact, ingestion and inhalation of the constituents of the LNAPL in affected soil water, groundwater, soil air and other receptors
- risks of further and more problematic LNAPL contamination through its continuing movement and spread in the subsurface
- impairment of the beneficial use of resources, or aesthetic values whether or not associated with toxic risks
- societal and business factors, and
- intergenerational equity.

This classification facilitates the formulation of remediation objectives and appropriate responses.

Many of these concerns can be evaluated through a toxicological or other risk assessment performed through quantifying the occurrence of LNAPL and its constituents in the subsurface. For instance:

- Explosion and fire risks could be determined through the measurement of LNAPL vapours in relation to explosive limits and oxygen concentrations in subsurface and above-ground structures.
- Toxicological risks to humans could be determined in relation to acute and chronic health effects using various exposure models (Sanders & Stern 1994).
- For ecological risk, similar exposure models may be constructed in conjunction with accepted protective levels or specific assays.
- Risks of continued spread and movement of the LNAPL may be assessed through a variety of physical measurements of the state of LNAPL in the subsurface.

Further instruments may be available or specifically developed to assess the other concerns around impairment of beneficial resource use, aesthetic values, societal and business factors, and in terms of intergenerational equity.
A key separation of the risks is those that arise directly from the presence of LNAPL and those secondary/indirect risks from constituents of the LNAPL that have partitioned into the air and water phases. It follows that the risks summarised above can be further broken down according to the medium/phase in which the risk presents itself – soil, LNAPL, gas, water. It is often the case that indirect risks assume great significance because of the greater mobility of these phases compared to the LNAPL itself. This presents an added challenge in that toxicological and other risks need to be assessed for these phases and a link to the source LNAPL needs to be clearly established. This link is critical to determining LNAPL remediation requirements. This link entails concepts of source-pathway-receptor as well as exposure and resultant hazard. These concepts are not canvassed in detail here but the linkages are briefly discussed in later sections.

4.4 Remediation objectives and end points

Remediation objectives are formulated around the abatement of the identified LNAPL concerns that arise from the state of LNAPL contamination at the site. Thus there will be remediation objectives associated with all of the identified concerns. The long-term vision and goals for the site underlie both the concerns triggering the remediation and the objectives of remediation. On the other hand, the remediation end points are proposed to reflect the site conditions that would achieve the remediation objectives. Linkages between these elements are demonstrated in Figure 17. The key then is to select a remediation technology that for the given circumstances will provide technology end points that match the desired remediation end points and achieve the remediation objectives. So not only are remediation end points evaluated against remediation objectives to determine success, but remediation technologies and associated end points are sought to achieve the remediation objectives. As indicated in Figure 17, there is likely to be either implicit or explicit feedback between remediation end points that are feasible and the long-term vision and goals for the site. This arises in attempting to match the desired remediation end points with the end points possible with candidate technologies. The process for this can also be seen at different stages of the selection and implementation summary shown in Figure 16. A result of this is some degree of feedback between technology end points and remediation objectives.
Figure 17. Representation of the linkages between the LNAPL concerns, remediation objectives and end points, and technology end points.

Table 12 presents a listing of concerns, along with examples of possible remediation objectives and remediation end points. It should be emphasised that the entries in Table 12 are general in nature and more specific objectives and end points would usually be set for a given site.

The example objectives and end points in Table 12 do not incorporate elements around timing, budget and other effects of the remediation. These elements are important and should form part of remediation objectives and end points. The elements of timing, budget and effects of the remediation are generally incorporated at an overall level of the goals for the site. They would also need to be set in remediation objectives and end points. In this way they would carry through to the selection of specific remediation strategies.

For a particular remediation end point, there would be one or more metrics against which the state of the LNAPL contamination and remediation technology end point may be objectively evaluated. Some metrics are relatively straightforward such as:

- measured petroleum hydrocarbon vapour concentrations and fluxes
- LNAPL saturations in soil and aquifer materials
- concentration and flux of dissolved constituents in soil water and groundwater, and
- LNAPL pressure, pressure gradient, transmissivity and appearance in wells.

Other metrics may be more complex such as toxicity, risk and community perceptions. The various metrics are discussed further in Section 6.
Table 12. Summary of concerns and examples of remediation objectives and end points.

<table>
<thead>
<tr>
<th>Concern</th>
<th>Remediation objective</th>
<th>Remediation end point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explosion risk</td>
<td>Abate the generation and accumulation of explosive vapours</td>
<td>Volatile constituents removed to the extent that vapours do not accumulate above explosive limits</td>
</tr>
<tr>
<td>Toxic exposure to LNAPL</td>
<td>Eliminate toxic exposure to LNAPL in soil and water</td>
<td>LNAPL in direct contact with human, terrestrial and aquatic environment detoxified and/or removed to the extent that exposure risks are below set levels</td>
</tr>
<tr>
<td>Toxic exposure to volatile constituents</td>
<td>Eliminate toxic exposure to vapours in buildings and other structures as well as general above-ground settings</td>
<td>Volatile constituents are removed to the extent that exposure risks are below set levels</td>
</tr>
<tr>
<td>Toxic exposure to dissolved constituents</td>
<td>Eliminate toxic exposure to groundwater and surface water through ingestion and contact</td>
<td>Dissolved constituents are removed to the extent that exposure risks are below set levels</td>
</tr>
<tr>
<td>Mobile/spreading LNAPL</td>
<td>Prevent the future spread of LNAPL in the subsurface</td>
<td>LNAPL removed to be permanently below residual and entrapped saturations in the aquifer. Alternatively, mobility or spreading potential is reduced to below prescribed levels</td>
</tr>
<tr>
<td>Beneficial resource use and aesthetic values</td>
<td>Allow the use of the land, aquifer and groundwater resources for specified use</td>
<td>LNAPL removed to the extent that the presence of it and its constituents in other phases are below prescribed levels for the specified beneficial use</td>
</tr>
<tr>
<td>Societal and business factors</td>
<td>The presence of the LNAPL does not offend community expectations or adversely affect the reputation of the site owner or asset values</td>
<td>LNAPL removed to the extent that the site meets community and business expectations</td>
</tr>
<tr>
<td>Inter-generational equity</td>
<td>Ensure that the liability for the current LNAPL contamination is not transferred to the next generation</td>
<td>LNAPL removed to the extent that natural attenuation will eliminate likely concerns over the next 30 years</td>
</tr>
</tbody>
</table>

4.5 Targeting concerns

One way in which Table 12 is useful is that it highlights the exact concern and therefore target for the LNAPL remediation. A key point is whether or not it is the LNAPL as a whole that needs to be remediated or whether only specific constituents of the LNAPL need to be removed. Indeed, the removal of LNAPL mass (or specifically, reducing the LNAPL saturation in the aquifer) as opposed to particular constituents would seem to be a necessary condition to achieve only two and perhaps four of the seven remediation objectives presented in Table 12. LNAPL mass removal is clearly a
necessary condition to prevent the continued spread of LNAPL in the subsurface. Depending on the specifics of the site and targets, LNAPL mass removal may be either a necessary or sufficient condition to achieve the objectives associated with beneficial resource use and preservation of aesthetic values, societal and business factors, as well as intergenerational equity.

In terms of the risks through the exposure to toxic constituents of the LNAPL that have partitioned to the gas and water phases, it is self evident that it is those particular constituents that need to be the target of removal. While total LNAPL mass removal would be a sufficient condition to reach remediation objects, it is not a necessary condition. Importantly, those constituents that give rise to the toxicological risk may be a small fraction of the total mass. The same is true for the abatement of an explosive risk due to vapour accumulation – the volatile component of the LNAPL may be a relatively minor fraction of the total.

The targeting of toxicological risk drivers that partition to the gas and water phases is aided by the preferential selection of the partitioning process itself. Generally, a more limited number of constituents partition to a significant degree. This makes it easier to assess the risk and also target the particular risk drivers or class of constituents (for example, those with a high vapour pressure or high solubility). This is not necessarily the case where the remediation objective is to eliminate the toxic exposure to the LNAPL itself in either a soil or water matrix. While it might be possible to identify some particular risk drivers, it would generally be necessary to consider the LNAPL holistically in terms of its risk profile. This may require the LNAPL mass to be targeted for removal.

4.5.1 The effect of LNAPL mass removal on risk reduction

The extent to which risk may be reduced where the LNAPL mass is removed is a key consideration where the risks arise through LNAPL constituents that partition into groundwater and soil air. The issue is complex and influenced by:

- whether the risk is driven by constituent concentrations or fluxes
- heterogeneity within the aquifer, and
- distribution of the LNAPL in relation to aquifer heterogeneity.

Whether or not the risk is based on constituent concentration or constituent flux at the point of compliance or receptor exposure may be dictated by local site or regulatory conditions. Constituent flux is often taken as a measure because it determines whether assimilative or natural attenuation capacity within the aquifer is sufficient to mitigate risk. In addition, it is flux within groundwater that determines the ultimate concentrations in groundwater extraction wells. This is also the case for receiving surface water bodies. Similarly it is vapour flux in the vadose zone that determines concentrations in buildings and in atmospheric air. On the other hand, it is the concentration of constituents that may determine acute and chronic toxicity effects to ecosystems exposed to contaminated groundwater and soil air.

The effect of NAPL mass reduction on risk reduction has been an intense topic of research for DNAPLs. The assessment for DNAPLs is largely specific to a single-constituent NAPL and focused on the effect of heterogeneous distribution of NAPL as well as variability of permeability and resultant groundwater flow velocities in the
A key outcome is that the more uniform the flow within the aquifer the greater the mass of NAPL that has to be removed before concentrations and fluxes are appreciably reduced. This outcome, derived where NAPL is initially uniformly distributed in the aquifer, is somewhat modified in the case where there is a correlation between initial NAPL saturation and aquifer permeability (and hence groundwater velocity). A positive correlation between NAPL saturation and permeability (the most expected for newly entrapped NAPL) would also mean that a relatively greater mass would need to be removed to appreciably reduce constituent flux and concentration.

Huntley and Beckett (2002) produced an analysis of the effect of source mass reduction (through hydraulic recovery) on risk from dissolved constituents specifically for LNAPLs. This is incorporated into the LNAST assessment tool which may be accessed at the API website (http://www.api.org/ehs/groundwater/4715.cfm). Key outcomes from this analysis were that initial concentrations were not reduced and the maximum extent of dissolved plumes in groundwater was little affected by source mass recovery. Importantly, the persistence of dissolved plumes over time remained a function of the source mass. Hence, while source recovery does not reduce the immediate risk, the longevity of the risk was reduced. Huntley and Beckett (2002) also highlighted that target concentrations for particular constituents may be achieved much sooner where those individual constituents are able to be removed at much higher rates than the LNAPL as a whole.

The analyses done by Huntley and Beckett (2002) were made for a range of homogeneous aquifers and lack the processes associated with the heterogeneity which cause the variability of groundwater flow velocity and LNAPL saturation. However, some more recent work (Miles et al. 2008) has confirmed that the flux of constituents in groundwater for randomly heterogeneous aquifers is predominantly a function of the area over which the LNAPL exists rather than the mass.

The mass fluxes of volatilised constituents in the vadose zone arise mostly through diffusion and not advection as is the case for dissolved constituents. Despite this, the general conclusions from Huntley and Beckett (2002) analyses should pertain to the volatilised constituents. Without a change to the mass fraction in the LNAPL source, reducing LNAPL mass will not immediately affect the risks arising from the vapours.
To what extent does partial LNAPL removal reduce concerns?

Faced with the reality that most remediation techniques will only remove part of the initial LNAPL mass, a question arises as to what immediate and longer term benefits this may bring. Some of the concepts around this are illustrated for the case of the dissolved contaminants picked up by groundwater flowing through the LNAPL source.

Some of the underlying concepts

The diagrams below illustrate two of the many considerations that need to be taken into account. In both cases the LNAPL is uniformly distributed over the source zone before and after remediation that attempts to remove the LNAPL as a whole (such as free-phase recovery). The first case illustrates what is expected for a multi-component LNAPL where the groundwater concentrations will be controlled by the solubility and mass fraction of the components. Both solubility and mass fraction are unaffected by the remediation since it is only the saturation within the aquifer that is reduced. So there is no immediate effect on component concentrations from the source zone. However, the longevity of the concentrations is reduced according to the overall mass reduction. A similar effect is seen where groundwater flux may be unevenly distributed in different layers of the aquifer. No immediate effect is seen in concentration coming from the source, but the smaller mass means that individual layers are flushed of LNAPL sooner and the longevity of the resultant plume reduced.

Illustration of the effect of partial mass removal/saturation reduction on the component concentrations from a multi-component LNAPL. LANPL saturation and groundwater velocity are uniform through the source zone.

Illustration of the effect of partial mass removal/saturation reduction on the component concentration where groundwater velocity is spatially non-uniform. A single-component LANPL of uniform saturation within the source zone.
Application to the hypothetical recovery of LNAPL

Huntley and Beckett (2002) considered the partial recovery of LNAPL in more detail. They used the general theory of how LNAPL is distributed around the water table to compute the groundwater fluxes through a hypothetical LNAPL source. They further used this general theory to calculate exactly how much mass may be removed through free-phase recovery using a skimmer. This was done for different soil types. They also looked at different initial LNAPL masses in the aquifer, for which they used the thickness of LNAPL that would appear in a well as the indicator (the underlying theory of LNAPL distribution at the water table that was used allows a direct link between LNAPL thickness and mass but this is not generally the case).

The cases illustrated below again show that the LNAPL recovery has no immediate effect on dissolved contaminant concentrations coming from the source. The longevity of the contaminant concentrations coming from the source are an interesting demonstration of the different masses that may exist in different types of aquifer materials and the proportion that may be recovered. Notable is the lack of any significant recovery in the silty sand material even when 0.5 or 1 m thickness of LNAPL may appear in a well.

The effect of free-product recovery on predicted dissolved phase concentration of contaminant leaving an LNAPL source in a silty sand aquifer. Curves show cases with different initial LNAPL mass as would be reflected in the equilibrium thicknesses of LNAPL in a well (after Huntley & Beckett 2002).

The effect of free-product recovery on predicted dissolved phase concentration of contaminant leaving an LNAPL source in a coarse sand aquifer. Curves show cases with different initial LNAPL mass as would be reflected in the equilibrium thicknesses of LNAPL in a well (after Huntley & Beckett 2002).
4.5.2 Implications of the concerns on selecting a strategy for remediation

The concerns and remediation objectives influence the selection of a remediation strategy on a number of levels. As discussed above, the particular concerns and remediation objectives determine whether it is sufficient or necessary to use a targeted approach to remove particular constituents rather than attempt the removal of the whole of the LNAPL. An example of this is the use of air flushing remediation strategies such as soil vapour extraction and air sparging. These air flushing remediation strategies target volatile constituents and may be naturally suited to addressing concerns over vapour risks. In a similar vein, solvent flushing remediation strategies may be naturally suited where concerns arise through dissolved constituents in groundwater. Other concerns that are not based around the mobility of LNAPL constituents in other phases in the environment may equally call for total mass removal or the transformation/destruction of the LNAPL.

Naturally, these considerations lead to two types of remediation strategies:

- reducing the LNAPL saturation in the aquifer, and
- reducing the concentration of specific compounds present in the LNAPL.

Which of these types of strategies are being pursued needs to be clearly enunciated in any LNAPL remedial action plan.
5. In situ remediation technologies

This section presents a summary of remediation technologies that may be applied to the in situ removal of petroleum hydrocarbons. Although excavation of contaminated materials and in situ containment or isolation may be used in the management of LNAPL contamination, this is not universally considered as a remediation option. For completeness, excavation and in situ containment and isolation are included in the summary. Ex-situ treatment techniques are only discussed in the context of where the processes may be applied in situ.

Remediation strategies applicable to the removal of LNAPL petroleum hydrocarbons are described in a number of resources (ASTM International 2007; Charbeneau et al. 1999; ITRC 2009a; Mayer & Hassanizadeh 2005; NRC 1997; Oostrom et al. 2006; TCEQ 2008). There are further on-line resources provided by a number of organisations including the US EPA, US DoD, and API. Such on-line resources are useful to the practitioner as remediation technologies continue to be developed and existing techniques may need to be modified for specific situations.

A précis of the in situ remediation technologies considered in this study is presented below. More detailed descriptions of the technologies, including their basic principles, are presented in Appendix E. It should be noted that a range of different terminology is in use for the different technologies. Different systems for classifying the remediation technologies have also been used and a summary of these is given in Appendix F. Here the techniques are grouped according to their general method of LNAPL removal.

5.1 Précis of remediation technologies considered

5.1.1 Excavation

The approach here is to excavate and remove the LNAPL-contaminated materials from the subsurface. These contaminated materials are then either subjected to ex-situ treatment or disposed directly to an appropriate containment facility.

5.1.2 Containment

Physical containment

The LNAPL is isolated from the surrounding environment by a physical barrier. The barrier may consist of steel sheeting, constructed low permeability cut-off walls using grout or other low-permeability materials or even consist of a cut-off drain. Impermeable capping may also be used to prevent contact with contaminated material and vapours. Such a cap is also used in reducing the flux of water through the LNAPL. Continued spread of the LNAPL may also be prevented by in situ mixing of the soil.

Hydraulic containment

Hydraulic containment uses groundwater extraction or water injection to reduce or prevent the lateral spread of LNAPL. Groundwater extraction from within the area of an LNAPL plume will direct the movement of mobile LNAPL internally, thus constraining it within the existing plume. Water injected outside the LNAPL plume may be used to create a hydraulic barrier to the lateral movement of LNAPL.
5.1.3 Free-LNAPL recovery

Interceptor trenches
A high permeability material infilling an excavated trench allows the interception and removal of LNAPL through pumping of LNAPL from the trench.

Skimmer-well recovery
Skimmer pumps selectively recover LNAPL when placed in a well (or similar situation) where LNAPL floats on the surface of the water. The intake to the pump floats at the LNAPL-water interface and LNAPL enters either through a hydrophobic filter or orifice located a small distance above the LNAPL-water interface.

Single- and dual-pump recovery
Single- (total liquids) and dual-pump systems utilise the drawdown of the water table by pumped groundwater extraction to enhance the lateral movement of LNAPL during the pumped recovery of LNAPL from a well.

Water flooding
Water flooding is designed to increase the water table gradients within the aquifer to promote lateral movement of mobile LNAPL to a recovery well. It combines water injection through a nearby well or wells with groundwater extraction from an LNAPL recovery well(s) to increase hydraulic gradients above those possible with single- and dual-pump recovery. The injected water is sometimes heated to improve the mobility of the LNAPL.

Vacuum-enhanced recovery
Vacuum-enhanced recovery is a system whereby a partial vacuum is applied to the LNAPL recovery well. In the first variant, a partial vacuum is created by an air suction pump connected to the sealed well which may contain any configuration of liquid recovery pumps. The second variant uses a drop tube (also called a straw or stinger) connected to an air suction pump with the end of the tube placed such that the liquids in the sealed well are drawn (or sucked) up by the air flow by a process of entrainment. This particular variant is sometimes called total fluids pumping, MPE, MPVE, slurping or bioslurping.

5.1.4 Volatilisation and biodegradation

Soil vapour extraction and bioventing
In soil vapour extraction and bioventing, air is drawn through the vadose zone to volatilise and aerobically biodegrade LNAPL in the vadose zone. An air pump is used to extract air from wells screened in the vadose zone. In some variants of bioventing, air may also be injected into the vadose zone, generally with concomitant air extraction.

Air sparging and biosparging
Air sparging entails injecting air into the saturated aquifer through a well screened below the water table. As the injected air moves through the aquifer below the water table, volatile components are stripped from the LNAPL while at the same time delivering oxygen that can be used by aquifer microflora to degrade the LNAPL.
5.1.5 Engineered bioremediation

**Engineered bioremediation**

Engineered bioremediation is a generic term for any in situ technique focussed on degrading the LNAPL through enhanced biological activity. The underlying principle is to engineer the delivery of amendments and, in rare instances, specialist microorganisms to the LNAPL in order to remove the LNAPL by a process of biodegradation.

5.1.6 Chemical flushing

**Surfactant flushing**

In surfactant flushing, chemicals that are active at the interfaces between water, LNAPL and mineral surfaces are injected dissolved in water to deliberately mobilise the LNAPL. Mobilised LNAPL is extracted through groundwater pumping and/or hydraulic recovery of the LNAPL.

**Co-solvent flushing**

Co-solvents or co-solvent solutions are injected into the subsurface to increase the solubility of LNAPL or its constituent components. The solubilised LNAPL may then be removed through pumping of groundwater.

5.1.7 In situ chemical oxidation

Solutions and, in the case of ozone, a gaseous mixture of strong oxidants are injected into the subsurface to provide in situ oxidisation of dissolved petroleum hydrocarbons and the source LNAPL. Oxidants include:

- *hydrogen peroxide and Fenton’s reagent*
- *potassium permanganate*
- *persulphate*
- *ozone*
### 5.1.8 Thermal methods

**Steam injection**
Steam is injected into the subsurface to facilitate remediation mainly through the enhanced vaporisation of the LNAPL although the LNAPL may also be mobilised through the applied pressure and reduction of viscosity.

**Electrical resistance heating**
Electrical resistance heating uses electrodes placed in the aquifer to raise the temperature in order to volatilise the LNAPL.

**Radio frequency and microwave heating**
The subsurface is heated through the application of radio-frequency or microwave electromagnetic energy to decrease the viscosity of LNAPL in order to increase its mobility and render it more amenable to hydraulic recovery and/or volatilise LNAPL constituents.

| **Table 13** provides a summary of some of the general attributes of the remediation technologies. These attributes relate to the most applicable remediation objectives and settings, issues that may arise in their application and some of the notable strengths and weaknesses. Further details are available in Appendix E. |
Table 13. Summary of some of the general attributes of the remediation technologies. See Appendix E for detailed descriptions of the technologies.

<table>
<thead>
<tr>
<th>Remediation technology</th>
<th>Most applicable remediation objectives</th>
<th>Most applicable settings</th>
<th>Issues and impacts</th>
<th>Main strengths</th>
<th>Main weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excavation</td>
<td>Almost all</td>
<td>Shallow unsaturated zone, unconsolidated materials</td>
<td>HSE, sustainability</td>
<td>Total removal, fast, addresses fine soils and heavy LNAPL</td>
<td>Sustainability, cost</td>
</tr>
<tr>
<td>Physical containment</td>
<td>Reduce spreading, reduce exposure</td>
<td>Unsaturated and water table zone, unconsolidated materials</td>
<td>HSE during installation</td>
<td>Short times to control, controls all phases</td>
<td>Capital costs, intergenerational equity</td>
</tr>
<tr>
<td>Hydraulic containment</td>
<td>Reduce spreading</td>
<td>Water table zone, moderate permeability</td>
<td>Contaminated water waste stream, ongoing operation</td>
<td>Short times, control dissolved plumes</td>
<td>Ongoing operating costs, sustainability</td>
</tr>
<tr>
<td>Interceptor trenches</td>
<td>Reduce spreading</td>
<td>Water table zone, most unconsolidated geologies</td>
<td>VOCs, limited by site infrastructure</td>
<td>Simple, length of collection helps</td>
<td>Possible long time frames for removal</td>
</tr>
<tr>
<td>Skimmer-well recovery</td>
<td>Reduce spreading, reduce mobility</td>
<td>Water table zone, higher permeability</td>
<td>Relatively slow</td>
<td>Simple technology</td>
<td>Long time frames, pump maintenance</td>
</tr>
<tr>
<td>Single- and dual-pump recovery</td>
<td>Reduce spreading and mobility, control dissolved plumes</td>
<td>Water table zone, moderate permeability</td>
<td>Contaminated water waste stream</td>
<td>Not dependent on the initial presence of free LNAPL</td>
<td>Treatment, vertical spread of the LNAPL</td>
</tr>
<tr>
<td>Water flooding</td>
<td>Reduce spreading, reduce mobility</td>
<td>Water table zone, moderate permeability</td>
<td>Possible spreading and treatment costs</td>
<td>Improved recoverability with hot water</td>
<td>Operating costs, possible spreading</td>
</tr>
<tr>
<td>Vacuum-enhanced recovery</td>
<td>Reduce spreading, reduce mobility, addresses dissolved and VOC concerns</td>
<td>Vadose and water table zones, higher volatility LNAPLs</td>
<td>Generation and treatment of waste streams, HSE</td>
<td>Aggressive, multiple removal mechanisms, applicability to lower permeability formations</td>
<td>Operating costs, waste streams, vapour treatment</td>
</tr>
<tr>
<td>Soil vapour extraction and bioventing</td>
<td>Reduce exposure to vapours and LNAPL, reduce LNAPL saturation</td>
<td>Vadose zone, sandy materials, middle distillates and gasoline</td>
<td>Control and treatment of vapours</td>
<td>Can be low cost where no treatment, removal to very low saturations</td>
<td>Possible long time frames</td>
</tr>
</tbody>
</table>
Table 13 (cont.). Summary of some of the general attributes of the remediation technologies. See Appendix E for detailed descriptions of the technologies.

<table>
<thead>
<tr>
<th>Remediation technology</th>
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<th>Issues and impacts</th>
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<th>Main weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air sparging and biosparging</td>
<td>Reduce dissolved and vapour exposure</td>
<td>Saturated and near water table zones, sandy materials, gasoline and middle distillates</td>
<td>Control and treatment of vapours, impacts of heterogeneity, mass transfer limitations</td>
<td>Targets dissolved and volatile risk drivers, can be short times, treats saturated zone</td>
<td>Costs of off gas treatment, small radius of influence, heterogeneity issues</td>
</tr>
<tr>
<td>Engineered bioremediation</td>
<td>Reduce saturation, reduce composition-based concerns</td>
<td>Various parts of profile, moderate to high permeability, heavy and middle-distillate LNAPL</td>
<td>Increasing the spread of contaminants</td>
<td>Low cost</td>
<td>Long time frames</td>
</tr>
<tr>
<td>Surfactant flushing</td>
<td>Reduce exposure to dissolved contaminants</td>
<td>Saturated zone, sandy materials, most LNAPLs, low initial saturations</td>
<td>Effects on the host aquifer, treatment of extracted liquids, cost</td>
<td>Removal to low saturations</td>
<td>High cost, effects of heterogeneity</td>
</tr>
<tr>
<td>Co-solvent flushing</td>
<td>Reduce exposure to dissolved contaminants</td>
<td>Saturated zone, sandy materials, most LNAPLs, low initial saturations</td>
<td>Effects on the host aquifer, treatment of extracted liquids, cost</td>
<td>Removal to low saturations</td>
<td>High cost, effects of heterogeneity</td>
</tr>
<tr>
<td>Hydrogen peroxide and Fenton’s reagent</td>
<td>Reduce exposure to dissolved contaminants</td>
<td>Saturated zone, sandy materials, most LNAPLs, low initial saturations</td>
<td>HSE, effects on the host aquifer, treatment of extracted liquids, cost</td>
<td>Removal to low saturations, may tolerate heterogeneity</td>
<td>High cost, HSE, technical risk</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>Reduce exposure to dissolved contaminants</td>
<td>Saturated zone, sandy materials, low initial saturations</td>
<td>HSE, effects on the host aquifer, treatment of extracted liquids, cost</td>
<td>Removal to low saturations, may tolerate heterogeneity</td>
<td>Not appropriate for aromatics, high cost, HSE, technical risk</td>
</tr>
<tr>
<td>Ozone</td>
<td>Reduce VOC and dissolved-phase exposure</td>
<td>Vadose and saturated zones, sandy materials, most LNAPLs, low initial saturations</td>
<td>HSE, treatment of vapours, cost</td>
<td>Removal to low saturations, oxidation within the vadose zone</td>
<td>Severe HSE issues, technical risk, treatment times</td>
</tr>
<tr>
<td>Persulphate</td>
<td>Reduce exposure to dissolved contaminants</td>
<td>Saturated zone, sandy materials, most LNAPLs, low initial saturations</td>
<td>HSE, effects on the host aquifer, treatment of extracted liquids, cost</td>
<td>Removal to low saturations, may tolerate heterogeneity</td>
<td>High cost, HSE, technical risk</td>
</tr>
</tbody>
</table>
Table 13 (cont.). Summary of some of the general attributes of the remediation technologies. See Appendix E for detailed descriptions of the technologies.

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<thead>
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<th>Main strengths</th>
<th>Main weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam injection</td>
<td>Reduce VOC risks and exposure, reduce LNAPL saturation and mobility</td>
<td>Vadose zone, volatile and semi-volatile LNAPL</td>
<td>Control and treatment of vapours, mobilisation of LNAPL, energy intensive, HSE</td>
<td>Tolerant to heterogeneity, suitable for dual porosity materials, suitable for viscous LNAPL</td>
<td>Energy intensive, sustainability, cost</td>
</tr>
<tr>
<td>Electrical resistance heating</td>
<td>Reduce VOC risks and exposure, reduce LNAPL saturation and mobility</td>
<td>Vadose zone, volatile and semi-volatile LNAPL</td>
<td>Control and treatment of vapours, energy intensive, HSE</td>
<td>Tolerant to heterogeneity, suitable for fine materials, suitable for viscous LNAPL</td>
<td>Energy intensive, sustainability, cost</td>
</tr>
<tr>
<td>Radio frequency and microwave heating</td>
<td>Reduce VOC risks and exposure, reduce LNAPL saturation and mobility</td>
<td>Vadose zone, volatile and semi-volatile LNAPL</td>
<td>Control and treatment of vapours, energy intensive, HSE, effect of water content on radius of influence</td>
<td>Tolerant to heterogeneity, and suitable for fine materials</td>
<td>Radius of influence, effects of high water contents, energy intensive, sustainability, cost</td>
</tr>
</tbody>
</table>
5.2 Selection of LNAPL remediation technologies

Key factors in the selection of LNAPL remediation technologies as part of an LNAPL management strategy include:

- remediation objectives and end points
- the physical setting
- impacts of the remediation, and
- implementation factors.

The selection of a remediation technology is generally complex with many competing demands and a degree of uncertainty. Thus, remediation technology selection requires careful and well-structured processes. Examples of these are seen in the documents of ITRC (2009a), TCEQ (2008) and ASTM International (2007). Figure 18 shows a flow chart of the steps involved in the remediation selection. The shaded region in Figure 18 is an expansion of the ‘Select remediation technologies’ step within the overall framework for LNAPL-contaminated site remediation and management (Figure 16).

Figure 18 presents a step-wise approach where, after remediation objectives and end points are determined, candidates are screened and shortlisted based on their anticipated effectiveness. The screening is based on:

- the required remediation end points
- setting of the LNAPL contamination
- impacts of the remediation, and
- other implementation factors.

At this point of the selection process, it should be considered whether or not a staged/sequential remediation effort using a treatment train of different technologies may be required. If so, interim remediation end points may need to be determined for the different remediation stages and the candidate technologies identified.

Following this screening, a final list of preferred options would be decided, and an assessment made as to whether or not further site-specific information is required before implementation. Pilot testing of preferred options may then occur. Pilot testing is a valuable aid to refining options.

A decision point is included near the end of the process illustrated in Figure 18 to assess whether or not the identified preferred remediation options will likely give satisfactory performance. The performance would be assessed in terms of the remediation objectives and end points as well as the impacts of the remediation. In the case where performance seems likely to be inadequate, the following actions depend on whether remaining LNAPL candidates provide hope of attaining the current remediation objectives and end points. If so, the selection process is repeated. Otherwise the selection process is exited and moves to a review of the long-term vision and goals for the site. Such a review is also included for the case where the performance of the preferred remediation option is satisfactory. This admits the possibility that better-than anticipated remediation performance may allow alternative long-term visions for the site and goals to be adjusted accordingly.
Figure 18. Flow chart showing the steps involved in the selection of a remediation technology (shaded region) as part of the overall framework for site remediation and management.
5.3 The initial screening process

The initial screening of candidate remediation technologies would be done separately for each of the identified remediation objectives and associated remediation end points. Such a separation is suggested to allow the option of a sequential application of different remediation technologies to emerge more clearly. It also reduces some of the complexity of multiple objectives/selection criteria. The general process is summarised in Figure 19.

![Figure 19. Suggested general process for the initial screening of remediation technologies.](image)

The initial screening process ends with a comparison of the candidates across all the remediation objectives set for the site. It is here the relative rankings and likely end points of the candidate remediation technologies would be used to make a decision over whether multiple or sequential application of technologies are required or may be more efficient. This decision point is shown in Figure 18.

A tool for summarising the assessment of individual remediation technologies is presented in Table 14. This formalises the assessment against selection criteria, highlighting strengths and weaknesses of the technology and attempts to identify the likely end point that may be reached through application of the technology. The final assessed technology end point is an important outcome of the assessment tool. There is also provision for an assessment whether the technology could be used as part of increasing the efficiency of the overall remediation strategy by inclusion in a treatment train. This would occur where the technology considered is unlikely to meet the remediation end point but could be useful in making more feasible another technology that could reach the ultimate end point. The reverse situation may also occur. That is, the application of a particular remediation technology may make it more difficult for following technologies to efficiently reach desired remediation end points.

The tool also provides information for a side-by-side comparison of remediation technologies for the given remediation objective. Just what remediation technologies are included in the initial screening for a given remediation objective (rather than assessing all those available) relies on preliminary understanding of the general applicability of different technologies. Some guidance on this is provided in the following section (see specifically Table 15). The technology assessments and end points presented in the summary tool would be backed by more detailed analyses.
### Table 14. Tool for summarising the initial screening of remediation technologies.

<table>
<thead>
<tr>
<th>Remediation objective:</th>
<th>Site condition/requirement</th>
<th>Technology assessment/end point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remediation end point:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remediation technology:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remedial processes:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Assessed technology end point:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Possible use in a treatment train:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Selection criteria

<table>
<thead>
<tr>
<th>Setting</th>
<th>Geology/hydrogeology</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Location of LNAPL</td>
</tr>
<tr>
<td></td>
<td>State of LNAPL</td>
</tr>
<tr>
<td></td>
<td>Type of LNAPL</td>
</tr>
<tr>
<td></td>
<td>Built environment</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Impacts</th>
<th>HSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wastes and treatment</td>
</tr>
<tr>
<td></td>
<td>Resources/environment</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Implementation</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Timing</td>
</tr>
<tr>
<td></td>
<td>Complexity</td>
</tr>
<tr>
<td></td>
<td>Technical risk</td>
</tr>
<tr>
<td></td>
<td>Capital costs</td>
</tr>
<tr>
<td></td>
<td>Operating costs</td>
</tr>
<tr>
<td></td>
<td>Acceptability</td>
</tr>
</tbody>
</table>
5.4 Remediation selection criteria

The broad factors that need to be considered in the screening and selection of a remediation strategy or technology are, as outlined above:

- remediation objectives and end points
- the physical setting
- impacts of the remediation, and
- implementation factors.

There are a number of specific selection criteria to each of these factors that need to be evaluated. Commentary on these selection criteria are provided in the sections below. A general evaluation of LNAPL remediation strategies against these selection criteria is provided in the description of LNAPL remediation technologies given in Appendix A. The following sections expand on the selection criteria and how they may relate to the selection of particular remediation technologies.

5.4.1 Remediation objectives and end points

Separate remediation objectives and end points are derived for each of the concerns identified as a result of the presence of the LNAPL. The remediation objectives and end points vary with particular situations and they are also likely to be specific to regulatory jurisdictions and other stakeholder needs. For example, classes of groundwater, beneficial use, soil and site use criteria would likely have specific local definitions. Hence for simplicity, the discussion of the issues associated with the remediation selection for the different possible end points is presented under the heading of the concern being addressed. The general objectives and end points in Table 12 are those being addressed. An overarching consideration in the selection process is the timing within which remediation is desired. Therefore, the desired timing is a common qualifier for achieving remediation objectives and end points.

In terms of the initial screening of remediation technologies outlined above, consideration of the concerns and remediation objectives is seen as a means of shortening the list of technologies to assess against the other factors.

Explosion risk

Vapours from the LNAPL are the source of explosive risk. Therefore, remediation techniques that control vapour movement or preferentially remove or degrade the volatile constituents would be most appropriate. Containment or barrier technologies may be used to physically stop the vapours. Otherwise volatilisation and biodegradation as well as multi-phase extraction technologies would be favoured. Even thermal methods may offer advantages in volatilising the risk drivers in some particular settings. Another approach may be to submerge the LNAPL such that a water-saturated diffusion barrier is created to limit the flux of vapours. However the practicability of such an approach for this is unknown. Such a situation may arise, however, in other approaches such as water flooding and chemical flushing.

Toxic exposure to LNAPL

The technologies selected to meet remediation objectives and end points for this concern depend on the exposure pathway. Where it is from the discharge of LNAPL, either containment strategies or those that reduce the LNAPL mass (to the extent of
immobilising the LNAPL) would be possibilities for selection. In the case where the exposure is through contaminated surface soils, the options from which to select would most naturally include capping, excavation and engineered bioremediation. Soil vapour extraction and bioventing would also be worthy of close consideration.

**Toxic exposure to volatile constituents**

This concern has similarities to that of explosion risk. Again the possible remediation technologies depend on the exposure pathway. However, the most common is through diffusion of VOCs from the LNAPL or contaminated groundwater to the ground surface. So a technology that controls vapours (some containment technologies), extracts or degrades the VOCs (volatilisation and biodegradation technologies) would be clear candidates. In addition, remediation techniques that may preferentially remove the volatile components from the LNAPL (such as multi-phase extraction, air sparging and biosparging) would be candidates.

**Toxic exposure to dissolved constituents**

The most direct approach for addressing the concerns over toxic exposure to dissolved constituents is to target removal of the particular toxic constituents from the LNAPL. Chemical flushing techniques would be candidates in this respect. However the volatilisation and biodegradation techniques may be effective at targeting the toxic constituents where they also have adequate volatility. Containment methods may also have a direct and immediate impact on exposure. Methods such as free-LNAPL recovery that attempt LNAPL saturation and mass reduction are unlikely to have an immediate impact on exposure but may reduce the longevity of the exposure.

**Mobile/spreading LNAPL**

Other than containment or excavation, the primary means of mitigating the concerns of mobile or spreading LNAPL is to immobilise it by reducing it to below residual and/or entrapped saturation. Free-LNAPL recovery methods are often the most suitable for this. However other technologies may achieve the same or better LNAPL saturation reduction. The question then is the necessity of a greater saturation reduction and whether or not the free-LNAPL recovery provides certainty of immobilisation under future conditions. The possibly shorter time frames for achieving remediation objectives in the case of some other technologies may also need to be considered in the selection.

**Beneficial resource use and aesthetic values**

A large range of potentially quite disparate remediation objectives and end points may eventuate from the concerns around beneficial use and aesthetic values. Therefore a wide range of remediation technologies may result from the selection process. Where the LNAPL is seen as a contaminant of groundwater affecting its beneficial use, the LNAPL as a whole may need to be removed. Alternatively a more targeted approach may be required to remove dissolved contaminants to reduce impairment due to taste and odour, or remove the LNAPL to prevent the presence of sheens in the groundwater or LNAPL appearing in wells.
Societal and business factors

The varied societal and business factors that can arise in this concern could lead to equally varied remediation objectives and end points. So it is hard to make a general statement about which remediation technologies would be most appropriate. These would need to be selected on a case-by-case basis.

Intergenerational equity

The example remediation end point presented for the concern over intergenerational equity allows the possibility of leaving part of the LNAPL contaminant in place. Implicitly, this assumes that there are no other concerns that would dictate more extensive LNAPL removal. However, such remediation end points may not be so simply met by some of the technologies that lead to only partial removal of the LNAPL mass. The issue is largely that of the recalcitrance of the LNAPL which remains. In many instances, a generational time-scale may be short in terms of LNAPL contamination. For instance, rates of biodegradation of LNAPL entrapped below the water table may be very slow because of the limited flux of electron acceptors. The biodegradation processes that do act on the LNAPL make it more recalcitrant and the proportion of components of very low solubility and volatility mean that an appreciable amount may persist over long (greater than one generation) periods. Hence, some of the more aggressive LNAPL removal technologies may need to be selected.

Table 15 presents a summary of prime candidates to address remediation objectives. The major use of this Table is to assist in the initial screening of remediation technologies. That is, these would be the ones used for the initial screening tool described above.

Note that Table 15 should only be used as a guide for choosing which technologies to assess as part of the initial screening. Where the specific remediation objectives differ from those given in Table 15, those technologies appropriate for assessment should be reassessed. The remediation objectives for the societal and business factor concerns are most likely to be very site-specific. For that reason, no prime candidate technologies are offered in Table 15.

It also needs to be borne in mind that a sequence of different remediation technologies may be required (or would be more efficient) to reach the remediation objective. Those remediation technologies with end points not matching the required remediation end points are not included in Table 15 against the corresponding remediation objective and concern. However this possibility is specifically accounted for in the overall remediation selection process (see Figure 18). An affirmative answer regarding the use of a particular remediation technology in a treatment train in the initial screening tool would prompt assessment of other remediation technologies.
<table>
<thead>
<tr>
<th>Concern</th>
<th>Remediation objective</th>
<th>Prime technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explosion risk</td>
<td>Abate the generation and accumulation of explosive vapours</td>
<td>Excavation, Physical containment, Soil vapour extraction and bioventing, Air sparging and biosparging, Steam injection, Electrical resistance heating, Radio frequency and microwave heating</td>
</tr>
<tr>
<td>Toxic exposure to LNAPL</td>
<td>Eliminate toxic exposure to LNAPL in soil and water</td>
<td>Excavation, Physical containment, Soil vapour extraction and bioventing, Engineered bioremediation</td>
</tr>
<tr>
<td>Toxic exposure to volatile constituents</td>
<td>Eliminate toxic exposure to vapours in buildings and other structures as well as general above-ground settings</td>
<td>Excavation, Physical containment, Soil vapour extraction and bioventing, Air sparging and biosparging, Steam injection, Electrical resistance heating, Radio frequency and microwave heating</td>
</tr>
<tr>
<td>Toxic exposure to dissolved constituents</td>
<td>Eliminate toxic exposure to groundwater and surface water through ingestion and contact</td>
<td>Physical containment, Hydraulic containment, Single- and dual-pump recovery, Vacuum-enhanced recovery, Hydrogen peroxide &amp; Fenton’s reagent, Ozone, Persulphate</td>
</tr>
<tr>
<td>Mobile/spreading LNAPL</td>
<td>Prevent the future spread of LNAPL in the subsurface</td>
<td>Excavation, Physical containment, Hydraulic containment, Interceptor trench, Skimmer-well recovery, Single- and dual-pump recovery, Vacuum-enhanced recovery, Water flooding</td>
</tr>
</tbody>
</table>
Table 15 (cont.). Prime candidate remediation technologies for remediation objectives.

<table>
<thead>
<tr>
<th>Concern</th>
<th>Remediation objective</th>
<th>Prime technologies</th>
</tr>
</thead>
</table>
| Beneficial resource use and aesthetic values | Allow the use of the land, aquifer and groundwater resources for specified use | Excavation  
  Physical containment  
  Soil vapour extraction and bioventing  
  Air sparging and biosparging  
  Engineered bioremediation  
  Ozone  
  Steam injection  
  Electrical resistance heating  
  Radio frequency and microwave heating |
| Societal and business factors   | The presence of the LNAPL does not offend community expectations or adversely affect the reputation of the site owner or asset values | *Determined by more specific remediation objectives |
| Intergenerational equity       | Ensure that the liability for the current LNAPL contamination is not transferred to the next generation | Excavation  
  Vacuum-enhanced recovery  
  Soil vapour extraction and bioventing  
  Air sparging and biosparging  
  Surfactant flushing  
  Co-solvent flushing  
  Hydrogen peroxide & Fenton’s reagent  
  Potassium permanganate  
  Ozone  
  Persulphate steam injection  
  Electrical resistance heating  
  Radio frequency and microwave heating |

5.4.2 The physical setting

A detailed consideration of the physical setting in which the LNAPL remediation is to be attempted provides the foundation for the selection of a remediation strategy. It is here that the importance of a well-researched conceptual site model assumes great prominence. The specific selection criteria that need to be evaluated associated with the physical setting are provided in Table 16. Table 16 also lists specific classifications within the criteria. A discussion of the selection criteria and how the classifications within the criteria would be used are provided in the subsections below. The discussion also includes the general applicability of different remediation technologies.
Table 16. Selection criteria related to the physical setting of the LNAPL contamination.

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Classification</th>
</tr>
</thead>
</table>
| Geology/hydrogeology       | • Unconsolidated sandy materials  
                              | • Finer textured unconsolidated materials 
                              | • Dual porosity materials (consolidated and unconsolidated) 
                              | • Fractured hard rocks 
                              | • Heterogeneity                                                                 |
| Location of the LNAPL      | • Vadose zone 
                              | • Capillary fringe/near water table 
                              | • Saturated zone                                                            |
| State of the LNAPL         | • Free 
                              | • Mobile 
                              | • Immobile                                                                   |
| Type of LNAPL              | • Gasoline-range 
                              | • Middle-distillate 
                              | • Heavy, weathered                                                           |
| Built environment          | • Green fields 
                              | • Brown fields 
                              | • Operating heavy industrial 
                              | • Urban and light industrial                                                 |

Geology/hydrogeology

The underlying processes of the various remediation technologies are critically dependent on the geology/hydrogeology in which the LNAPL needs to be remediated. Thus a classification of the subsurface is a critical step in the selection process. As outlined in Section 3, it is useful to adopt the classification system of the subsurface geology that matches the likely behaviour of LNAPL to the processes used by the remediation system. A further general issue that arises in considering the subsurface environment is the presence of heterogeneity. This can have a profound effect on remediation performance, especially in terms of the uniformity and predictability of the remediation. The greatest range of remediation options is available for sandy materials. Finer textured materials pose challenges for those remediation technologies dependent on injecting or extracting fluids and may be where thermal treatments could be more effective. Similar challenges are presented by dual porosity materials. However, multi-phase extraction techniques do offer advantages in the finer and dual porosity materials in terms of the large pressure gradients that can be applied for fluid extraction. Fractured rock environments present challenges to most remediation techniques. Free product recovery methods are the most usual in situ techniques applied in this environment and the potential of other technologies is largely unexplored.

Location of the LNAPL

Where the LNAPL contamination resides in relation to the water table in the profile affects the physical remediation processes that can be brought to bear on the LNAPL contaminant. When present in the vadose zone, air-flushing technologies that either volatilise or aerobically degrade the LNAPL may be relatively easy to implement. A
different set of technologies would be selected to apply the same remediation processes below the water table. The capillary fringe/near water table zone has specific importance in terms of LNAPL distribution and behaviour as well as gaining access to the LNAPL. This zone is amenable to manipulation by fluid injection and extraction which may mean that a greater range of remediation techniques may be available. Addressing LNAPL entirely within the saturated zone naturally presents the opportunity to use liquid-based strategies to remove the LNAPL.

**State of the LNAPL**

The state of the LNAPL essentially revolves around its potential for movement and therefore physical recovery. The presence of free-LNAPL under existing site conditions means that the range of free-LNAPL recovery techniques could be suitable. Conversely, such techniques would have little or no application where the LNAPL was immobile. The presence of mobile or free LNAPL may be disadvantageous for other remediation techniques. Those that inject liquids risk further spread of such LNAPL.

**Type of LNAPL**

The different physical properties of LNAPL are encapsulated in a selection criterion based on the generalised type of the LNAPL. These generalised types can be related to viscosity, volatility and solubility. These physical properties relate directly to the potential of the different technologies. Higher viscosities associated with the heavy and highly weathered LNAPL make free-LNAPL recovery less attractive. Thermal methods may have particular application to these materials. Gasoline-range LNAPL has relatively high volatility and therefore is eminently suitable for the volatilisation-based technologies. Middle-distillate LNAPLs are generally good candidates for biodegradation, have viscosities that do not unduly limit free-LNAPL recovery and maintain some potential for volatilisation.

**Built environment**

The presence of buildings and other above-ground infrastructure can often complicate or limit the application of remediation technologies. This is especially the case for technologies that may depend on closely-spaced treatment infrastructure such as wells. Where above-ground infrastructure is present, technologies with a low spatial density of remediation infrastructure (both above- and below-ground) and with a large treatment zone may be preferred. Below-ground services and infrastructure may raise similar issues. Other factors that may be considered here are the availability of services required for the remediation systems – such as power, water, sewers and treatment systems. However, these factors would also enter into remediation selection process by way of cost.

**5.4.3 Impacts of the remediation**

Remediation operations are not without risk and commonly produce their own direct and indirect costs as well as impacts. Such risks, costs and associated impacts need to be accounted for in the selection of a remediation technology (Bracken et. 2006; CL:AIRE 2010; Hardisty et al. 2008). Discussion of these is included in the description of remediation technologies below. Broadly, the main issues relate to: health and safety considerations; production of waste streams and further spreading of the LNAPL and its constituents; impacts on other aspects of the environment and existing resources; and the overall cost/benefit.
Health and safety considerations

The LNAPL is itself a potentially hazardous substance, so its recovery as well as the generation and recovery of petroleum hydrocarbon vapours create heightened health and safety issue for operational staff as well as nearby communities and infrastructure. In some remediation technologies, hazardous and toxic chemicals are used that create further health and safety issues that need to be accounted for in the overall assessment of the technology. The remediation process and equipment will also have associated hazards that will need to be managed.

Waste streams and spreading

Many of the LNAPL remediation technologies produce waste streams contaminated with the LNAPL, its constituents and by-products or amendments that may have been used to facilitate the remediation. The handling and treatment of these waste streams will be an issue for the cost effectiveness of the particular technologies. However, there is a more general issue as to whether the created waste stream is greater in volume than that which may occur in situ.

Remediation treatments also have the potential to spread LNAPL and its constituents in other phases within the subsurface, creating more widespread impact.

Impacts on the environment and existing resources

Existing groundwater resources may be affected by LNAPL remediation through the disturbance of the existing groundwater hydraulics as well as changes to groundwater quality. These may also have flow-on effects to other aspects of the environment. Extraction of groundwater to assist LNAPL recovery may deplete available local resources while liquid injection and extraction schemes may also detrimentally influence local groundwater hydraulics.

Groundwater quality may be affected in a number of ways. Spreading of LNAPL in the aquifer may lead to the greater contamination of groundwater, while injection and extraction schemes may displace contaminated groundwater into formerly pristine parts of the aquifer. Aquifer geochemistry may also be disturbed by hydraulic manipulation. However, the injection of remediation amendments and physical treatments of the subsurface have the potential to introduce new chemicals of concern to the groundwater and affect important bio-geochemical processes. For instance, some of the treatments may suppress microbiological activity that facilitates existing and future natural attenuation processes.

Air injection as part of remediation also has the potential to spread hydrocarbon vapours in the subsurface. This may increase the volume of the subsurface contaminated and may also lead to repartitioning of vapours into groundwater.

Other environmental factors that may be included as part of the remediation selection are the CO₂ footprint of the operations as well as the more immediate effects of noise, vibration, dust and odours on local amenity. The impacts of remediation activities on local amenity can be accentuated in urban environments. Thus, those more sensitive to the surroundings and public acceptability would be favoured for selection. Formal cost benefit analyses would be made in the selection of alternative remediation technologies. However, life cycle analyses would also be usefully undertaken to assess the overall benefit of attempting the remediation.
5.4.4 Implementation

There are a number of factors around the implementation of the remediation technologies that are important criteria in the selection process. These range from those amenable to reasonably objective measurement and comparison (such as scale, timing and costs), to those of individual, public and other stakeholder perception (such as technical risk and acceptability). All of these have the potential to modify the selections from that based on physical feasibility of the remediation.

Scale

The scale of implementation relates directly to the volume treated by an individual treatment unit (for example, an LNAPL recovery well or soil vapour extraction well) as well as the extent to which the individual treatment unit can be replicated. Mostly, the extent of replication is dictated by costs. For example, the thermal treatment technologies would be generally considered for small-scale treatment for this reason. Chemical flushing and in situ chemical oxidation may generally be better suited to small-scale application for a similar reason. Air sparging and biosparging would generally only be considered for moderate-scale applications because of the sometimes relatively small volume treated (compared to soil vapour extraction, bioventing and free-LNAPL recovery) by an individual well. Although the capital costs may be small for individual air sparging units, the number required may limit the technology’s attractiveness in the face of other alternatives.

Timing

Remediation objectives would commonly be set in terms of a time period in which they are required to be achieved. Remediation/management options like excavation and containment barriers are attractive because of the relatively short time required to achieve desired remediation objectives. However chemical flushing, as well as most of the in situ chemical oxidation and thermal treatments, could also be expected to achieve the remediation end points relatively quickly compared to other technologies. Biodegradation-based techniques as well as the less aggressive free-LNAPL recovery techniques would be expected to take appreciably longer. Dual- and multi-phase recovery can markedly increase free LNAPL recovery rates and the geometry of interception trenches could shorten times compared to skimmer wells.

Complexity

Complexity refers to the overall level of engineering, expertise and investigation that may be required to successfully implement the remediation. In many respects this is acutely dependent on the setting as well as the remediation technology involved. However, there are distinctions between the relatively simple technologies of free-LNAPL recovery and volatilisation and biodegradation, compared to the other technologies. However, that is not to say that some of these simpler technologies, such as vacuum-enhanced recovery and air sparging and biosparging, do not need additional engineering that adds to their complexity. Chemical flushing and in situ chemical oxidation have relatively high complexity mainly due to the high level of understanding of the processes needed to ensure success. On the other hand, thermal methods are high complexity, mainly due to the engineering involved.
Technical risk

Here technical risk encapsulates issues around the maturity of the technology, familiarity with its application, complexity of the processes involved, and its robustness in achieving remediation end points where there is a level of uncertainty. All these individual issues would need to be considered in remediation technology selection. Most of the free-LNAPL recovery technologies as well as soil vapour extraction and bioventing would be considered to have a low technical risk. Vacuum-enhanced recovery would probably be rated at slightly higher technical risk, mainly because it is increasingly applied to a greater range of settings. The technical risk is likely to decrease quickly as greater experience is gained. Air sparging and biosparging have an elevated level of technical risk because of the critical dependence of their success on aquifer structure. Chemical flushing, in situ chemical oxidation and thermal methods would generally have a high technical risk in response to most of the issues underlying this factor.

Capital cost

The capital costs of the remediation infrastructure can vary dependent on the location and conditions of the site. This will include the access to services. Well-based technologies such as free-LNAPL recovery, soil vapour extraction and bioventing, engineered bioremediation, chemical flushing and in situ chemical oxidation may have relatively low capital costs. However, the possible need for closely-spaced well networks may lead to high capital costs even though the individual unit price is relatively low. In addition, pumping equipment needs may add substantially to the unit prices.

Operating cost

A critical determinant of the operating costs is the need for treatment and disposal of waste streams. For instance, treatment of contaminated groundwater (including contamination by injected chemical amendments), and removal of VOCs from extracted air could add appreciably to the operating costs of most remediation technologies. Some exceptions would be the passive free-LNAPL recovery methods (interception trenches and skimming) although these still require disposal of the LNAPL. Engineered bioremediation, biosparging and perhaps ozone treatment are potentially the only remediation technologies that would not produce waste streams that may need treatment.

Operating costs for some remediation technologies would be relatively high due to the use and consumption of amendment chemicals (chemical flushing and in situ chemical oxidation) and through their energy use (thermal methods).

Acceptability

Acceptability is that to the stakeholders in the remediation activities. That is, the site owners and occupiers, regulatory bodies and both the local and general community. Acceptability to such stakeholders would be a synthesis of many selection criteria discussed here, and perceptions of the remediation and its benefits. However, some criteria not already covered may include such things as the interruptions to site operations, confidence/familiarity with the technology and detraction from amenity. For instance, technologies with a limited above-ground presence may be more acceptable in urban areas and industrial sites with continuing operations. As a selection criterion,
acceptability is intimately linked to a range of different site-specific factors. Hence it is difficult to generalise how particular remediation technologies may be ranked according to their acceptability. It is also possible that acceptability may differ between stakeholders.

5.5 General applicability

Many specific factors affect the performance and applicability of an LNAPL remediation technology to a particular situation. However it is useful to point to the anticipated relative effectiveness/applicability of different technologies. This can be of further use in preparation for the initial screening of technologies. Table 17 ranks the general effectiveness of candidate LNAPL remediation technologies in relation to the selection criteria:

- subsurface geology
- location of the LNAPL in the profile
- state of the LNAPL, and
- type of LNAPL.

In addition, Table 18 presents the generalised applicability assessment of the LNAPL remediation technologies in relation to selection criteria of:

- concerns
- impacts of the remediation
- implementation factors
- technical risk, and
- costs.

The background to the rankings in Tables 17 and 18 may be found in the sections above and in the general descriptions of the technologies in Appendix E.

There are several very important caveats about the rankings provided. First and foremost, most of the rankings are done in the absence of well-documented assessments of comparative performance. Rather, most rankings represent a general prediction based on the current understanding of the underlying processes involved.

Secondly, rankings do not relate to any specific remediation objective or end point. The rankings may change appreciably for different objectives and end points of the remediation process. There are many further dimensions to the assessment tables and what is presented can only be taken as giving an overall impression.

Thirdly, for any particular element (i.e. column of the tables) being considered, the rankings of remediation technologies are relative to each other. Hence the rankings are not absolute and columns in the table cannot be compared. For example, just because single- and dual-pump recovery is ranked as medium effectiveness for both sandy materials and fractured rock materials, it does not mean that the ease of remediation in these two geologies is the same.

Finally, there is a bias in the rankings in that the assessment is based on other conditions being favourable for the technology application.
Selecting and assessing strategies for remediating LNAPL in soils and aquifers

Table 17. Generalised effectiveness ranking of in situ LNAPL remediation technologies in relation to subsurface setting (geology and location), state of the LNAPL and the type of LNAPL. Rankings of high (H), medium (M) and low (L) under favourable conditions are relative to other technologies and do not necessarily reflect the absolute level of performance expected. n.a. = not applicable. Rankings are general in nature, and will vary dependent on particular remediation objectives.

<table>
<thead>
<tr>
<th>Geology</th>
<th>Location</th>
<th>State</th>
<th>Type</th>
<th>Type</th>
<th>Type</th>
<th>Type</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy materials</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Dual-porosity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fractured rocks</td>
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<td></td>
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<td></td>
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<tr>
<td>Heterogeneity</td>
<td></td>
<td></td>
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<tr>
<td>Vadose zone</td>
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<tr>
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<tr>
<td>Mobile</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

| Excavation          | Excavation | H | H | H | L | H | H | L | H | H | H | M | H | H |
| Containment         | Physical containment | H | H | H | M | H | H | H | H | H | H | H | H |
| Hydraulic containment |          | H | M | M | L | L | n.a. | H | H | H | H | H | H | H |
| Free-LNAPL recovery | Interceptor trenches | H | L | L | H | H | n.a. | H | L | L | L | L | L | L |
| Skimmer-well recovery |          | M | L | L | L | L | n.a. | H | L | L | L | L | L | L |
| Single- and dual-pump recovery |          | M | L | M | M | M | n.a. | H | M | H | M | L | L | L |
| Water flooding      |          | H | M | H | M | M | n.a. | H | M | H | H | L | L | M |
| Vacuum-enhanced recovery |          | H | M | H | H | H | M | H | M | H | M | M | M | L |
| Volatilisation and biodegradation | Soil vapour extraction and bioventing | H | L | M | M | M | L | H | L | n.a. | L | M | H | H | M |
| Air sparging and biosparging |          | M | L | M | M | M | H | n.a. | H | H | L | M | H | M | L |
| Engineered bioremediation | Engineered bioremediation | H | L | M | M | M | L | M | L | M | M | H | M | M |
| Chemical flushing   | Surfactant flushing | H | L | M | M | M | L | M | H | L | M | M | M | M |
| Co-solvent flushing |          | H | L | M | M | M | L | M | H | L | M | M | M | M |
| In situ chemical oxidation | Hydrogen peroxide and Fenton’s reagent | H | L | M | M | M | L | M | L | M | M | M | M | M |
| Potassium permanganate |          | M | L | M | M | M | L | M | L | L | L | L | L | L |
| Ozone               |          | H | L | M | M | H | H | H | H | L | M | M | M | M |
| Persulphate         |          | H | L | M | M | M | L | M | H | L | L | M | M | M |
| Thermal methods     | Steam injection | H | H | H | L | H | H | M | M | H | H | H | H | H |
| Electrical resistance heating |          | M | H | H | L | H | H | M | M | H | H | H | H | H |
| Radio frequency and microwave heating |          | M | H | H | L | H | H | M | M | H | H | H | H | H |
Table 18. Generalised applicability and assessment ranking of LNAPL remediation technologies in relation to the concerns/trigger being addressed, impacts, implementation and costs. Rankings of high (H), medium (M) and low (L) are relative to other technologies. Rankings of large (L), medium (M) and small (S) for scale and long (L), medium (M) and short (S) for timing. ind. = indeterminate. Rankings are general in nature and will vary dependent on remediation objectives and setting.

<table>
<thead>
<tr>
<th>Concerns Impacts Implementation</th>
<th>Expl. risk</th>
<th>Toxic exposure</th>
<th>Exposure to VOCs</th>
<th>Dissolved constituents</th>
<th>Mobile/spreading</th>
<th>Beneficial use, aesthetic</th>
<th>Societal and business fact</th>
<th>HSE</th>
<th>Wastes and treatment</th>
<th>Resource env. impact</th>
<th>Scale</th>
<th>Timing</th>
<th>Complexity</th>
<th>Technical risk</th>
<th>Capital costs</th>
<th>Operating costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excavation</td>
<td>Excavation</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td>ind.</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>M</td>
<td>S</td>
<td>L</td>
<td>L</td>
<td>n.a.</td>
</tr>
<tr>
<td>Containment</td>
<td>Physical containment</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td>ind.</td>
<td>M</td>
<td>M</td>
<td>L</td>
<td>M</td>
<td>S</td>
<td>L</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>Hydraulic containment</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>M</td>
<td>H</td>
<td>L</td>
<td>ind.</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>L</td>
<td>S</td>
<td>L</td>
<td>M</td>
<td>L</td>
</tr>
<tr>
<td>Free-LNAPL recovery</td>
<td>Interceptor trenches</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>L</td>
<td>ind.</td>
<td>M</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>M</td>
</tr>
<tr>
<td>Skimmer-well recovery</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>L</td>
<td>ind.</td>
<td>L</td>
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<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Single- and dual-pump recovery</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>L</td>
<td>ind.</td>
<td>L</td>
<td>M</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>L</td>
<td>M</td>
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</tr>
<tr>
<td>Water flooding</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>M</td>
<td>ind.</td>
<td>L</td>
<td>M</td>
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<td>L</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Vacuum-enhanced recovery</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>M</td>
<td>ind.</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td>M</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Volatilisation and biodegradation</td>
<td>Soil vapour extraction and bioventing</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>H</td>
<td>ind.</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Air sparging and biosparging</td>
<td>H</td>
<td>L</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>ind.</td>
<td>M</td>
<td>M</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Engineered bioremediation</td>
<td>Engineered bioremediation</td>
<td>M</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>L</td>
<td>H</td>
<td>ind.</td>
<td>L</td>
<td>L</td>
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<td>L</td>
<td>M</td>
<td>M</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Chemical flushing</td>
<td>Surfactant flushing</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>ind.</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>S</td>
<td>S</td>
<td>H</td>
<td>H</td>
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<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>ind.</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>S</td>
<td>S</td>
<td>H</td>
<td>H</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>In situ chemical oxidation</td>
<td>Hydrogen peroxide and Fenton’s reagent</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>ind.</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>S</td>
<td>S</td>
<td>H</td>
<td>H</td>
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<td>Potassium permanganate</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>ind.</td>
<td>M</td>
<td>L</td>
<td>M</td>
<td>S</td>
<td>S</td>
<td>H</td>
<td>H</td>
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<tr>
<td>Ozone</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>ind.</td>
<td>H</td>
<td>L</td>
<td>L</td>
<td>S</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>M</td>
<td>L</td>
</tr>
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<td>Persulphate</td>
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<td>M</td>
<td>M</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>ind.</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>S</td>
<td>S</td>
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<td>H</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>Thermal methods</td>
<td>Steam injection</td>
<td>H</td>
<td>L</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>ind.</td>
<td>H</td>
<td>H</td>
<td>M</td>
<td>S</td>
<td>S</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Electrical resistance heating</td>
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<td>L</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>ind.</td>
<td>H</td>
<td>H</td>
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<td>S</td>
<td>M</td>
<td>H</td>
<td>H</td>
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<td>H</td>
<td>L</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>ind.</td>
<td>H</td>
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<td>S</td>
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</tr>
</tbody>
</table>
6. Metrics and performance indicators for determining the success of LNAPL remediation

This section discusses the metrics and performance indicators that can be used in various stages of the remediation of an LNAPL contaminated site:

- developing an LNAPL conceptual site model
- developing a remediation action plan
- undertaking LNAPL remediation, and
- deciding when remediation should cease.

Metrics that describe the level and state of the LNAPL contamination in the subsurface would be used as part of the initial site assessment and to develop a site conceptual model (see Section 3). These same metrics would be used in determining when end points may have been reached during the remediation process. Indeed, remediation end points would generally be given in terms of metrics that allowed objective assessment. In addition, performance indicators would be used to evaluate the ongoing and overall efficiency and effectiveness of the implemented remediation strategy.

The means of obtaining the values for the various metrics and performance indicators are only briefly described here. Many of the methods used to obtain the site-specific values are presented in greater detail in documents specifically related to developing conceptual site models and characterising contaminated sites (ASTM International 2007; Clements et al. 2009; Davis et al. 2006; EA 2010).

6.1 Key performance indicators for remediation strategies

Key performance indications for any LNAPL remediation or management plan must be set in relation to site-specific goals or long-term vision. These are extremely important and need to be carefully considered on a site-by-site basis (US EPA 2005). In this regard, the long-term vision or goal may be stated in the form of some target remediation end point. This target remediation end point may in turn be cast in terms of:

- effects on the environment and human health
- risks posed to the environment and human health
- liability
- future site use
- contaminant fluxes and concentrations in aqueous and gas phases
- LNAPL mobility
- LNAPL appearance in wells
- LNAPL and/or constituent mass
- LNAPL and/or constituent saturation or content in soil
- LNAPL and/or constituent removal rate.

All but one of these end points relate to direct measurement of the static state of the contaminant and its consequent effects. That of LNAPL and constituent removal rates
differs in that it relates to the dynamics of the remediation, although such dynamics will also be controlled by the state of the contaminant in the subsurface.

The key performance indicators in evaluating a remediation technology must then be posed in relation to how the remediation technology achieves or approaches these site-specific remediation end points. Use of performance indicators in this manner has also been described as the process of verification (Defra & Environment Agency 2004). More recently, the use of multiple lines of evidence in the verification of remediation has been emphasised (EA 2010).

The set of performance indicators that would normally be assessed are:

- volume of the subsurface treated
- uniformity of the treatment
- rate and extent of LNAPL and constituent removal
- rate and extent of the mitigation of various risks and effects
- LNAPL and specific constituents remaining after remediation
- displacement and transfer of the LNAPL to other phases
- effects on groundwater and soil atmosphere receptors, and
- costs and benefits.

These performance indicators are discussed in more detail below.

**6.1.1 Volume of the subsurface treated**

The volume of the subsurface treated relates to what is often referred to as the radius of influence of the LNAPL remediation strategy. Unfortunately the concept of a radius of influence is not really well defined and generally should be related to a specific metric. Here, it is used to indicate distances over which some discernable change is made to the saturation, specific volume, mobility and composition of the LNAPL. As well, secondary effects such as changes to the concentration of LNAPL constituents in the groundwater and soil atmosphere would also be included for determining the volume treated. Within this definition, the measure of the performance indicator is the extent of the change in these metrics. Other related measures such as fluid pressures and distances over which fluids are drawn would also be included as performance indicators. Metrics and performance indicators used for assessing the volume of the subsurface that may be treated by a remediation technology are presented in Table 19 along with their measurement techniques.
Table 19. Metrics, performance indicators and measurement techniques for evaluating performance relative to the volume of the subsurface treated.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Performance indicator</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNAPL pressure</td>
<td>Drawdown in LNAPL table as a function of distance</td>
<td>Measurements in monitoring wells</td>
</tr>
<tr>
<td>Water pressure</td>
<td>Drawdown in water table and piezometric head as a function of distance</td>
<td>Measurements in monitoring wells</td>
</tr>
<tr>
<td>Air pressure</td>
<td>Decrease/increase in soil gas pressures as a function of depth and distance</td>
<td>Measurements in the vadose zone</td>
</tr>
<tr>
<td>Amendment concentration</td>
<td>Increase in concentrations of amendments or by-products in groundwater and soil gas</td>
<td>Groundwater and soil gas sampling</td>
</tr>
<tr>
<td>LNAPL saturation</td>
<td>Change in LNAPL saturation as a function of depth and distance</td>
<td>Aquifer sampling, partitioning tracer tests</td>
</tr>
<tr>
<td>LNAPL volume</td>
<td>Change in LNAPL volume in given area</td>
<td>Aquifer sampling, partitioning tracer tests, LNAPL thickness in monitoring wells</td>
</tr>
<tr>
<td>LNAPL mobility</td>
<td>Changes in LNAPL transmissivity, LNAPL pressure gradients, viscosity as a function of distance</td>
<td>LNAPL bail-down tests, LNAPL pressure and thickness in monitoring wells, analysis of LNAPL samples</td>
</tr>
<tr>
<td>LNAPL properties</td>
<td>Changes to density, viscosity, interfacial tensions as a function of distance</td>
<td>Analysis of LNAPL samples</td>
</tr>
<tr>
<td>LNAPL composition</td>
<td>Altered constituent concentrations as a function of distance</td>
<td>Analysis of LNAPL samples</td>
</tr>
<tr>
<td>Gaseous VOCs</td>
<td>Change in vadose zone VOC concentrations as a function of depth and distance</td>
<td>Soil gas sampling and analyses</td>
</tr>
<tr>
<td>Dissolved petroleum hydrocarbons</td>
<td>Change in groundwater petroleum hydrocarbon concentrations as a function of depth and distance</td>
<td>Groundwater sampling and analysis</td>
</tr>
<tr>
<td>LNAPL movement</td>
<td>Distances over which LNAPL is recovered</td>
<td>Tracer tests – analysis of recovered LNAPL</td>
</tr>
</tbody>
</table>

6.1.2 Uniformity of the treatment

Variability in aquifers can be extreme and a key performance indicator is the extent to which the remediation treatment is uniformly effective within the treatment zone. Where the treatment techniques proposed are applied through a single borehole, the uniformity is measured by the degree to which the performance indicators of the volume treated (Table 19) vary laterally. That is, as a function of direction from the treatment borehole and vertically in the profile. Uniformity also becomes an issue where the remediation is applied through deployment of a network of individual treatment units such as wells. Differences in remediation effectiveness between individual treatment units would arise through variability of subsurface conditions. However, the influence of the subsurface variability may differentially impinge on remediation technologies and need to be included as a
performance indicator. For example, thermal treatment technologies may be less influenced by heterogeneity of aquifer properties compared to free-LNAPL recovery techniques.

6.1.3 Rate and extent of LNAPL and constituent removal

Remediation objectives are often posed in terms of the time frames required to reach specified end points. In addition, rates of LNAPL removal impinge on operating cost performance. Performance on the rate of LNAPL removal may be measured directly for a number of remediation technologies (most notably those using hydraulic extraction) while indirect measures may be required in other cases (for example where LNAPL is removed through biological or chemical transformations). Examples of the possible rate performance indicators, and measurement techniques afforded by particular remediation technologies are presented in Table 20. In addition, the mass loss rate may also be determined by repeated assessments of the LNAPL and constituent mass in the aquifer. This is applicable in the case of all remediation technologies. However, the feasibility and cost varies greatly with the subsurface setting.

Table 20. Metrics, performance indicators and measurement techniques for evaluating performance relative to the rate and extent of LNAPL and constituent removal.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Performance indicator</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNAPL flux</td>
<td>LNAPL and constituent volumetric flux as a function of time</td>
<td>Measurements from recovery pumps and operating units</td>
</tr>
<tr>
<td>Water flux</td>
<td>Water volumetric flux as a function of time</td>
<td>Measurements from recovery pumps and operating units</td>
</tr>
<tr>
<td>Air flux</td>
<td>Air volumetric flux as a function of time</td>
<td>Measurements from air pumps, sparge wells and SVE units</td>
</tr>
<tr>
<td>VOC flux</td>
<td>Total and constituent petroleum hydrocarbon mass flux in extracted air as a function of time</td>
<td>TPH and constituent petroleum hydrocarbon concentrations in extracted air together with air volumetric flux</td>
</tr>
<tr>
<td>Dissolved petroleum hydrocarbon flux</td>
<td>Total and constituent petroleum hydrocarbon mass flux in extracted water as a function of time</td>
<td>TPH and constituent petroleum hydrocarbon concentrations in extracted water (e.g. extraction and drawdown pumps, MPE unit) together with water volumetric flux</td>
</tr>
<tr>
<td>LNAPL biodegradation rate</td>
<td>LNAPL biodegradation mass loss rate as a function of time</td>
<td>CO₂ mass flux in extracted air, in situ respiration tests (vadose and saturated zone)</td>
</tr>
<tr>
<td>LNAPL destruction rate</td>
<td>LNAPL mass loss rate as a function of time</td>
<td>Mass loss rates of destructive agents, evolution rates of by-products, repeated mass estimates</td>
</tr>
</tbody>
</table>

There are a number of derived measures of performance based on computed ratios of the primary performance indicators presented in Table 20. These derived measures provide further decision points on the efficacy of the remediation and may suggest a change in operating conditions or change from one remediation system to another. Some of the possible derived performance indicators are presented in Table 21.

<table>
<thead>
<tr>
<th>Performance indicator</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNAPL flux : Water flux</td>
<td>Measures efficacy of single- and dual-pump recovery systems. Supports decisions on continued groundwater extraction</td>
</tr>
<tr>
<td>LNAPL flux : VOC flux</td>
<td>Measures efficacy of VER system. Supports decision on possible utility of SVE system</td>
</tr>
<tr>
<td>LNAPL flux : Dissolved flux</td>
<td>Measures efficacy of VER and single- and dual-pump recovery. Supports decisions on continuing VER and skimming</td>
</tr>
<tr>
<td>LNAPL flux : Biodegradation rate</td>
<td>Measures efficacy of VER system. Supports decision on possible utility of SVE system</td>
</tr>
<tr>
<td>VOC flux : Dissolved flux</td>
<td>Measures efficacy of VER system. Supports decision on possible utility of SVE and single- and dual-pump systems</td>
</tr>
<tr>
<td>VOC flux : Biodegradation rate</td>
<td>Measures efficacy of VER and air sparging systems. Supports decisions on operating air flow rates</td>
</tr>
<tr>
<td>Constituent flux : Total petroleum hydrocarbon flux</td>
<td>Measures efficacy of targeting particular risk drivers. Supports decisions on operating conditions and cessation of remediation even while LNAPL removal continues</td>
</tr>
</tbody>
</table>

6.1.4 LNAPL remaining after remediation

Key measures of the performance of any remediation technology designed to remove LNAPL are the magnitude, distribution and variability of LNAPL saturation, as well as the properties of the LNAPL remaining in the aquifer following remediation. In this case, the performance indicator assesses the level of LNAPL contamination that may ultimately be expected after exhaustive application of a remediation technology. This measure is separate to the volume of the aquifer that may be effected by a single operational unit through which the remediation is applied or delivered (for example, a recovery well). As shown in Table 22, the metrics used for this performance indicator are not just those of LNAPL mass and saturation. The metrics also include properties derived from the LNAPL saturation as it exists in the aquifer (e.g. mobility), as well as other physical and chemical properties of the LNAPL that remains. These other properties have direct relations to the concerns triggering the remediation.
Table 22. Metrics, performance indicators and measurement techniques for evaluating performance relative to the LNAPL remaining after remediation.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Performance indicator</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNAPL saturation</td>
<td>Spatial distribution of LNAPL saturation</td>
<td>Aquifer sampling, partitioning tracer tests</td>
</tr>
<tr>
<td>LNAPL volume</td>
<td>LNAPL volume in given area</td>
<td>Aquifer sampling, partitioning tracer tests, LNAPL thickness in monitoring wells</td>
</tr>
<tr>
<td>LNAPL mobility</td>
<td>LNAPL flow rates, LNAPL pressure gradients, LNAPL transmissivity, viscosity and interconnectedness</td>
<td>LNAPL tracer tests, LNAPL bail-down tests, LNAPL pressure gradients, thickness in monitoring wells, analysis of LNAPL samples</td>
</tr>
<tr>
<td>LNAPL presence</td>
<td>Presence of immobile/entrapped LNAPL</td>
<td>Aquifer sampling, partitioning tracer tests, groundwater sampling and analysis</td>
</tr>
<tr>
<td>LNAPL properties</td>
<td>Changes to density, viscosity, interfacial tensions</td>
<td>Analysis of LNAPL samples</td>
</tr>
<tr>
<td>LNAPL composition</td>
<td>Concentration of contaminants of concern</td>
<td>Analysis of LNAPL samples, groundwater sampling and analysis, soil gas sampling and analysis</td>
</tr>
</tbody>
</table>

6.1.5 Displacement and transfer of the LNAPL to other phases

Remediation strategies may be designed to purposely displace LNAPL within the aquifer or transfer constituents of the LNAPL to the gas and water phases to facilitate its removal from the subsurface. However, displacement and phase transfers of the LNAPL may equally be undesirable side effects of remediation technologies. Thus it would be important to incorporate these displacements and transfers into performance indicators. For instance, injection of remedial solutions, extraction of groundwater and extraction of air may lead to the lateral and vertical displacement of LNAPL within the aquifer. This may potentially increase the difficulty of reaching remedial end points. In addition, injection or extraction of water or air may increase the volume of the subsurface contaminated by the LNAPL or produce a greater contaminated waste stream.

Hence, the displacement of the LNAPL and transfer of the LNAPL constituents to other phases is an important performance indicator of remediation technologies. Metrics associated with this performance measure are presented in Table 23. In some instances, these metrics and measurement techniques correspond to those of the rate of LNAPL removal. These instances are where the fluid phase to which the LNAPL constituents partition are extracted from the subsurface as part of the remediation.
Table 23. Metrics, performance indicators and measurement techniques for evaluating performance relative to the displacement and transfer of LNAPL to other phases.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Performance indicator</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNAPL displacement</td>
<td>Changes to the lateral and vertical distribution of LNAPL</td>
<td>Lateral LNAPL table gradients, LNAPL thickness in monitoring wells, aquifer sampling, partitioning tracer tests</td>
</tr>
<tr>
<td>LNAPL partitioning to the vapour phase</td>
<td>VOC flux in extracted air, subsequent emission to the atmosphere, and changes to VOC concentration in the soil atmosphere and fluxes to the soil atmosphere. Contamination of soil water and groundwater by VOCs</td>
<td>TPH and constituent petroleum hydrocarbon concentrations in extracted air together with air volumetric flux; soil gas sampling; gas sampling from flux hoods; soil water and groundwater sampling</td>
</tr>
<tr>
<td>LNAPL partitioning to the aqueous phase</td>
<td>Dissolved petroleum hydrocarbon flux in extracted groundwater, changes to dissolved concentrations in the groundwater, and mass flux in groundwater</td>
<td>TPH and constituent petroleum hydrocarbon concentrations in extracted water (drawdown pumps and VER unit) together with water volumetric flux; groundwater sampling, integral pump tests, groundwater passive flux meters, dosimeters</td>
</tr>
</tbody>
</table>

6.1.6 Effects on groundwater and soil atmosphere receptors

The effects of the applied remediation on groundwater and soil atmosphere receptors follow from a number of processes. Most directly, the effects follow from the displacement and transfer of the LNAPL constituents to gas and aqueous phases. Performance indicators could be posed in terms of consequential effects rather than the magnitude of the displacement and transfers (fluxes and concentrations) themselves.

In addition, effects on the groundwater and soil atmosphere are expected from a number of other mechanisms:

- displacement of existing groundwater and soil air by introduced and internally generated fluids
- changes to the aquifer hydrogeochemistry and physical properties of the groundwater by the remediation processes, and
- diminution of groundwater resources due to the extraction of groundwater.

In these instances, performance indicators would be cast in terms of a range of metrics that may have effects on the quantity, quality and ecological function of the groundwater and soil environments. A check list of metrics and examples of possible effects would include:

- **groundwater levels:**
  - resource availability
  - oxidation of reduced species formerly below the water table
  - development of water-logged and oxygen-limited conditions in the former vadose zone
- **pH and redox potential:**
  - general water quality effects
- possible dissolution/precipitation of environmentally and toxicologically significant species
- changed conditions for microbial communities that are supporting environmental functions
- effects on subsurface infrastructure

- inorganic chemistry and salinity of soil water and groundwater:
  - changes to the conditions for microbial communities that are supporting environmental functions
  - possible detrimental effects on vegetation
  - effects on subsurface infrastructure

- subsurface temperatures:
  - changes to chemical equilibria in soil water systems
  - changed conditions for microbial communities that are supporting environmental functions
  - possible detrimental effects on vegetation
  - effects on subsurface infrastructure

- soil atmosphere composition:
  - changes to the bulk composition or incorporation of trace gases in the soil atmosphere that may affect soil microbial communities and vegetation.

**6.1.7 Capital and operating costs**

The costs associated with remediation form an important performance indicator (Hardisty & Ozdemiroglu 2004). General accounting principles can be applied and overall costs broken down to (FRTR 1998):

- initial capital cost
- rate of depreciation
- fixed operating costs
- variable operating costs.

However, other externalities should also be included (Hardisty et al. 2008). Indeed, there may be a need to look further to life cycle analyses and incorporate other concepts of environmental sustainability (CL:AIRE 2010; US EPA 2008b) and carbon footprints (Bracken et al. 2006) as well as overall environmental benefit.

**6.2 Selection of performance indicators**

As indicated, there is a wide range of performance indicators available that aid the selection and operation of LNAPL remediation schemes. One challenge is to select a set of performance indicators from the available options that provides robust and insightful information while avoiding an excessive burden of measurement and analysis. Typically, multiple lines of evidence (EA 2010) would be sought from the selection of the performance indicators. Frequency of observations must also be decided as well as the means of acquiring the values of the metrics around which performance is rated.
Of course, the set of possible performance indicators described above covers sometimes disparate situations. Usually, an appropriate set of performance indicators will emerge from consideration of:

- the remediation technology being applied
- local site factors
- remediation objectives and end points.

In addition, the effort directed to the performance indicators will be moderated by the extent of the LNAPL contamination and magnitude of the issues arising. That is, the overall significance of the LNAPL contamination.

Tables 24 and 25 summarise the applicability of specific performance indicators to various LNAPL remediation technologies. In the case of Table 24, the performance indicators are those used to determine the volume of the subsurface treated and LNAPL removal rates. Table 25 presents performance indicators for relative removal rates and the possible effects of the remediation soil and groundwater receptors. Here it is noted that the performance indicators for the amount of LNAPL remaining in the subsurface (Table 22) are common to those for the volume of the subsurface treated (Table 20) and are not duplicated in Table 24.

The performance indicators selected in Tables 24 and 25 can be viewed as the basic set required for generic implementations of the remediation technologies. However, selection of the performance indicators for specific situations would be modified by the particular setting, remediation objectives and detail of the implementation of the remediation technology. For instance, measurement of LNAPL saturation may be unnecessary where the remediation objective is to reduce risk from VOCs or dissolved LNAPL constituents in groundwater.

6.2.1 Common performance indicators and metrics

LNAPL mass/saturation

As reflected in Table 24 there will be few, if any, instances where the mass/saturation of LNAPL and its mobility as well as the expression of LNAPL in wells (or elsewhere in the environment) is not of critical interest. Hence performance indicators around these metrics would almost inevitably feature in remediation evaluation. The presence of free LNAPL and therefore its appearance in wells provides relatively easily gathered metrics on LNAPL mobility and the area of influence of remediation efforts. Of course the pitfalls of using LNAPL thickness as an indicator of LNAPL in the formation needs to be kept in mind.

A relatively high intensity (spatially and temporally) of measurements of LNAPL pressures and thickness along with the groundwater potentiometric head would always provide base data for a number of performance indicators. However these measurements do not provide a reliable indication of the LNAPL mass or saturation reduction. Thus, performance in this regard should be measured through the direct or indirect measurement of the distribution of LNAPL in the subsurface. Unfortunately cost and feasibility issues arise in measuring LNAPL distribution in the subsurface which need to be addressed. In some cases it may be reasonable to use surrogates to infer either the loss of LNAPL mass or change in its risk profile. For instance, measurements of dissolved LNAPL constituents in groundwater and VOCs in soil gas may be acceptable indicators of changing LNAPL mass as well as being separate performance indicators.
LNAPL mass balance

More generally, one objective of monitoring performance could be to construct a mass balance for the LNAPL. This is useful for using the change in mass in a monitored domain to estimate the mass removed. In addition, it provides verification of individual metrics of mass change and mass removal – in essence providing multiple lines of evidence. An important point here is where the system being monitored is not closed, i.e. mass transfers can occur across system boundaries. In this case, estimates of LNAPL mass flux into the monitored domain will add uncertainty to estimates of mass removed made from changes in mass within the domain. It is for this reason that some remediation technologies are pilot tested in closed or isolated systems (for example, sheet-piling enclosed cells).

LNAPL removal rates

In determining removal rates, it can be important to include measurements of all significant removal processes, some of which may be easily overlooked. LNAPL and constituent removal may need to be estimated for all phases – i.e. NAPL, water and gas. Fluxes in the waste streams of remediation equipment are relatively easy to measure. Measurement becomes more difficult where groundwater and soil air is displaced by the remediation and remains in the subsurface. Other forms of flux measurements within the subsurface are required in this case.

Determining the removal of contaminants in situ is generally much more difficult than fluxes in extracted fluids. The main examples of these are biodegradation and abiotic oxidation using chemical oxidants. Determining the rate of consumption of the electron acceptors or oxidants is arguably the most reliable means of determining the contaminant removal rates. Such measurement avoids the complexity and expense of determining contaminant mass changes over time. In addition, measurement and interpretation of the actual end products of the biodegradation and oxidation processes and their subsequent fate is avoided. Otherwise, some relatively sophisticated geochemical modelling may also be required to correctly interpret such data, such as CO₂ production.

Costs and operational information

There are a number of other cost performance indicators that are common to all remediation technologies that are not included in Tables 24 and 25. These should be collected as a matter of course along with operational information for the plant being used. Operational information would include such things as energy use, equipment running times, reliability, and even levels of noise and vibration.
Table 24. Possible performance indicators for assessing volume of the subsurface treated, mass remaining and rates of LNAPL removal.

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<tr>
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<tr>
<td><strong>Volume treated</strong></td>
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<tr>
<td>LNAPl pressure</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<tr>
<td>Water pressure</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<tr>
<td>Air pressure</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<tr>
<td>Amendment and contaminants in water</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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</tr>
<tr>
<td>Amendment and contaminants in air</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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</tr>
<tr>
<td>LNAPl saturation</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<tr>
<td>LNAPl volume</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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</tr>
<tr>
<td>LNAPl mobility</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<tr>
<td>LNAPl properties</td>
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<tr>
<td>LNAPl composition</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<tr>
<td><strong>Rate of removal</strong></td>
<td></td>
<td></td>
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<tr>
<td>LNAPl flux</td>
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<tr>
<td>Water flux</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<tr>
<td>Air flux</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<tr>
<td>VOC flux</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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</tr>
<tr>
<td>Dissolved hydrocarbon flux</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>Biodegradation rate</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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</tr>
<tr>
<td>Abiotic destruction rate</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
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</tbody>
</table>
Table 25. Possible performance indicators for assessing relative removal rates and effects on receptors.

<table>
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</thead>
<tbody>
<tr>
<td></td>
<td>Interception trenches</td>
<td>Skimmer-well recovery</td>
<td>Single- and dual-pump</td>
<td>Vacuum-enhanced</td>
<td>SVE and biotreatment</td>
<td>Air sparging bioparging</td>
</tr>
<tr>
<td>Relative removal rates</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LNAPL flux : Water flux</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LNAPL flux : VOC flux</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LNAPL flux : Dissolved flux</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>LNAPL flux : Biodegradation rate</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>VOC flux : Dissolved flux</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>VOC flux : Biodegradation rate</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Constituent flux : TPH flux</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<td></td>
<td>✓</td>
</tr>
<tr>
<td>Effects on receptors</td>
<td></td>
<td></td>
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<tr>
<td>Groundwater levels</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Groundwater pH and redox</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Groundwater inorganic water quality</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Temperature</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Soil atmosphere</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>
7. Experience in the performance of remediation strategies

In this section, the experience that has been gained in remediating LNAPL remediation within Australian settings is examined. The objective is to highlight what gaps are present in the understanding of the performance and applicability gained in important Australian settings for the range of remediation strategies. In making such an examination, it is important to be aware of the large number of permutations that arise from the various factors of setting, remediation objectives and types of LNAPL contaminant.

7.1 Published case studies

There are a limited number of Australian case studies of LNAPL remediation that have been published (that is, presented in more readily available literature such as journal publications and conference proceedings). A listing of these publications is presented in Appendix G. Summary details of the case studies are presented in Appendix H. A key point of examining the case studies is to determine the remediation performance and remediation technology end points. The assessment of remediation technology end points is complicated because some of the case studies surveyed are pilot trials which do not attempt to reach the ultimate end point of the technology.

Table 26 tabulates LNAPL remediation case studies published in recent journal publications and conference proceedings according to the remediation technology used. It should be noted that a number of the publications report different aspects of the same case studies. For instance, Johnston et al. (2002b, 2005) present results of two series of pilot tests of free LNAPL recovery at the same site, Davis et al. (1995, 1996, 1997, 1998) report on aspects of two tests of bioventing at the same site, Johnston et al. (2000, 2002a) report on the same test of air sparging weathered gasoline and Johnston et al. (2007b, 2008a, 2008b) present results from different stages during the biosparging of weathered diesel fuel. In addition, the trials reported by Johnston et al. (2002b, 2005) were used to provide results for both free LNAPL recovery and bioventing/soil vapour extraction. Hence, Table 26 emphasises that published case studies cover a small number of the technologies that may potentially be applied to LNAPL remediation. The papers of Davis et al. (1997) and Johnston (2001) summarise other reported case studies.

The settings within which the remediation was undertaken is summarised in Table 27. This further emphasises that not only is published material limited in the range of technologies, but is also limited in the range of settings.

Aquifer materials that are obviously dual porosity in nature are poorly represented amongst the published case studies. The Tamala Limestone aquifer in which McGowan et al. (1999) undertook bioventing is known to be dual porosity. Karst and solution features were presumed (without *prima facie* evidence) to be the conduits for the remediated diesel fuel that had accumulated in the tunnels. Notably, no supporting information was provided to show any interaction between the primary and any secondary porosity. Thus the role any such interaction played in remediating the water quality and LNAPL diesel in the tunnels is unknown.
Only one published case study presents information from fractured hard rock. That case study, (Connolly et al. 1995), reports partial remediation using vacuum-enhanced recovery over a reasonably intense network of wells in fractured basalt.

Although a number of published case studies are associated with sandy materials, combined they only come from two different aquifers. All these reported case studies come from the Safety Bay Sands aquifer except for that of Weibe (1999) who presented one case study of vacuum-enhanced recovery in a dune sand aquifer in Adelaide. This is a similar setting to that of the Safety Bay Sands aquifer.

Table 26. Documented LNAPL remediation case studies summarised by technology.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Published References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excavation</td>
<td></td>
</tr>
<tr>
<td>Containment</td>
<td></td>
</tr>
<tr>
<td>Physical containment</td>
<td></td>
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<tr>
<td>Hydraulic containment</td>
<td></td>
</tr>
<tr>
<td>Free-LNAPL recovery</td>
<td></td>
</tr>
<tr>
<td>Interceptor trenches</td>
<td></td>
</tr>
<tr>
<td>Skimmer-well recovery</td>
<td>Johnston et al. 2002b, 2005</td>
</tr>
<tr>
<td>Single- and dual-pump recovery</td>
<td>Johnston et al. 2002b, 2005</td>
</tr>
<tr>
<td>Water flooding</td>
<td></td>
</tr>
<tr>
<td>Volatilisation and biodegradation</td>
<td></td>
</tr>
<tr>
<td>Air sparging and biosparging</td>
<td>Johnston et al. 2000, 2002a, 2007b, 2008a, 2008b</td>
</tr>
<tr>
<td>Engineered bioremediation</td>
<td></td>
</tr>
<tr>
<td>Engineered bioremediation</td>
<td></td>
</tr>
<tr>
<td>Chemical flushing</td>
<td></td>
</tr>
<tr>
<td>Surfactant flushing</td>
<td></td>
</tr>
<tr>
<td>Co-solvent flushing</td>
<td></td>
</tr>
<tr>
<td>In situ chemical oxidation</td>
<td>Tabor and Ho 2009</td>
</tr>
<tr>
<td>Hydrogen peroxide and Fenton’s reagent</td>
<td></td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td></td>
</tr>
<tr>
<td>Persulphate</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td></td>
</tr>
<tr>
<td>Thermal methods</td>
<td></td>
</tr>
<tr>
<td>Steam injection</td>
<td></td>
</tr>
<tr>
<td>Electrical resistance heating</td>
<td></td>
</tr>
<tr>
<td>Radio frequency and microwave heating</td>
<td></td>
</tr>
</tbody>
</table>
Table 27. Documented LNAPL remediation case studies summarised by technology and subsurface setting and geology. Case study numbers presented in the table correspond to the reference numbers in Appendix G.

<table>
<thead>
<tr>
<th></th>
<th>Vadose zone</th>
<th>Capillary fringe/saturated zone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sandy materials</td>
<td>Finer textured</td>
</tr>
<tr>
<td>Excavation</td>
<td>Excavation</td>
<td></td>
</tr>
<tr>
<td>Containment</td>
<td>Physical containment</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydraulic containment</td>
<td></td>
</tr>
<tr>
<td>Free-LNAPL recovery</td>
<td>Interceptor trenches</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Skimmer-well recovery</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Single- and dual-pump recovery</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water flooding</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vacuum-enhanced recovery</td>
<td></td>
</tr>
<tr>
<td>Volatilisation and biodegradation</td>
<td>Soil vapour extraction and bioventing</td>
<td>2, 3, 5</td>
</tr>
<tr>
<td></td>
<td>Air sparging and biosparging</td>
<td>7, 9, 12, 13, 14</td>
</tr>
<tr>
<td>Engineered bioremediation</td>
<td>Engineered bioremediation</td>
<td></td>
</tr>
<tr>
<td>Chemical flushing</td>
<td>Surfactant flushing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co-solvent flushing</td>
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<tr>
<td>In situ chemical oxidation</td>
<td>Hydrogen peroxide and Fenton’s reagent</td>
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<td></td>
<td>Potassium permanganate</td>
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<td></td>
<td>Persulphate</td>
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<td></td>
<td>Ozone</td>
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<tr>
<td>Thermal methods</td>
<td>Steam injection</td>
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<td></td>
<td>Electrical resistance heating</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Radio frequency and microwave heating</td>
<td></td>
</tr>
</tbody>
</table>
The four published case studies of LNAPL remediation in finer textured materials are from four different sites. Although this is a greater number of sites than for sandy materials, it would seem the greater range and complexity of finer textured aquifers is worthy of a larger number of studies.

A rather glaring gap is the lack of reported case studies for the remediation of LNAPL present in the vadose zone. This may be the result of a number of factors. It may be the legacy of a continued remediation approach of excavation and ex-situ treatment or disposal of contaminated material. Or it may be that LNAPL spreading in the vicinity of the water table is the major focus of attention.

### 7.2 Indications of performance

Various measures of remediation performance are reported in the published case studies. Those pilot-scale case studies that had more focus on underlying processes had the greatest range of performance indicators. Generally, the larger scale remediation efforts focused more on outcomes of the remediation and had a lower intensity of monitoring.

For the bioventing trials reported by Davis et al. (1995, 1996, 1997, 1998), aeration and oxygenation of the aquifer, in situ biodegradation rates, changes in fluid pressures, changes in groundwater chemistry and changes in the LNAPL saturation and mass in the aquifer were used to evaluate performance. In the case of air sparging a weathered gasoline, Johnston et al. (2000, 2002a) monitored air distribution and pressure in the aquifer, oxygenation of the groundwater and vadose zone, flux of extracted VOCs, changes in dissolved concentrations of petroleum hydrocarbons, and changes in LNAPL saturation, composition and mass. A slightly different approach to monitoring performance of biosparging diesel was adopted by Johnston et al. (2007b, 2008a, 2008b). Monitoring included that of air distribution and pressure in the aquifer, oxygenation of the groundwater and vadose zone, and changes in saturation and mass of the LNAPL. In addition VOC concentrations in the vadose zone profile and in flux hoods were used to measure VOC flux. Further, multiple approaches to estimating in situ biodegradation rates were used. For their free-LNAPL recovery trials, Johnston et al. (2002b, 2005) monitored LNAPL and water pressures in the aquifer, volume flux of water and LNAPL recovered, and flux of extracted VOCs. In addition, in situ biodegradation rates were determined using two techniques. Changes in saturation, composition and mass of LNAPL in the aquifer were also determined.

McGowan et al. (1999) report little detail of the performance assessment. However it seems to have been based on outcomes in terms of the LNAPL no longer being present in the tunnels and the resultant groundwater quality in the tunnels. Weibe (1999), Woods and Daud (2000) and Zafiropoulos (2007) used those performance indicators naturally suited to the vacuum-enhanced recovery technology used. Performance indicators common to the trials included VOC concentrations in the extracted air and the groundwater concentration of major petroleum fuel constituents. In addition, Weibe (1999) demonstrated the disappearance of LNAPL from monitoring wells while Woods and Daud (2000) monitored the flux of extracted groundwater and degradation of the contaminants. Zafiropoulos (2007) added monitoring of the flux of petroleum hydrocarbons dissolved in the extracted groundwater and air pressures in the aquifer to the above set of performance indicators.
The case study reported by Connolly et al. (1995) focused on operational aspects of the vacuum-enhanced recovery technology and only fluid recovery rates were monitored. This left removal through VOC extraction and biodegradation unaccounted for. However, Connolly et al. (1995) is the only sighted case study that reported the cost performance of the remediation. This aspect is poorly covered in the other published case studies.

Other externalities (such as changes to groundwater quality and quantity) that may need to be considered in the assessment of remediation performance seem to be absent from the case studies – at least in the published material examined.

7.3 Gaps in understanding of remediation performance

There appear many gaps in the understanding of LNAPL remediation performance in specific Australian settings, based on readily-available published information. The most apparent gaps are in relation to settings of particular significance in Australia as well as the range of potential remediation technologies for which experience is held.

Two questions arise as to whether these are real gaps in understanding and whether or not required understanding can be taken from experience outside Australia.

Undoubtedly, the amount of LNAPL remediation undertaken would suggest the breadth of understanding of LNAPL remediation performance must be greater than indicated by publicly available literature. However, there is also a sense that, even though the sample size is small, the gaps seen here in the published case studies are representative. Many of the identified deficiencies in understanding remediation performance also seem to exist internationally.

Somewhat surprisingly, there is a lack of case studies documenting the performance of free-LNAPL recovery systems. For the uncomplicated systems of sandy aquifers, this may be attributed to such recovery systems being relatively mature technologies (skimming as well as single- and dual-pump recovery). However, this could not be said for more complicated hydrogeological systems. Thus, the performance of free-LNAPL recovery in fractured rock, dual porosity and finer textured aquifers would seem to need an appreciably improved understanding. Equally, an adequate understanding of the performance of SVE, bioventing, air sparging and biosparging in more complex aquifers is lacking.

The lack of experience with, and understanding of, the achievable performance for chemical flushing, in situ chemical oxidation and thermal methods seems to be an additional gap. Many of these techniques have been more usually considered for chlorinated solvent DNAPLs. Applications to petroleum fuels in the near-surface environment are rarer. However, some of these technologies are utilised in petroleum reservoir engineering which provides some theoretical understanding.

In terms of the hydrogeological settings, the gaps in understanding remediation performance seem to be greatest for fractured rock and dual porosity materials. Lack of understanding of performance in these environments does not seem to be confined to the Australian environment. Fractured rocks are of significance because of their occurrence in urban and industrial areas of Victoria as well as other parts of Australia. This includes the ACT and other parts of regional Australia. However, the case of the fractured basalts in Victoria seems to warrant particular attention.
Understanding of remediation performance in important dual porosity formations also appears to be lacking. Limestone aquifers are important in various regions including suburban Perth. The significance of LNAPL contamination in the Hawkesbury Sandstone aquifer is not clear, as are indications as to which remediation technologies may perform efficiently in this setting. This would need further investigation.

There seems to be more understanding of the remediation performance in finer textured materials compared to fractured rock and dual porosity materials. However, the prevalence of these conditions warrants further improvement in understanding how LNAPL may be remediated efficiently and effectively in these settings.

The review of published cases also highlighted deficiencies in other aspects of the remediation that need better understanding. The main ones that are apparent are:

- costs of the remediation, and
- assessment of the external consequences of the remediation.

### 7.4 Other gaps

The review of case studies also suggested other gaps that may detract from the application of remediation strategies. These include:

- a lack of simulation or modelling of the LNAPL remediation that would allow a predictive capability and the option for transferring the technologies to different sites
- limited characterisation of the site and the contaminant, although this may have been a result of the form of literature available (mainly conference proceedings)
- definition of the achievability of end points for the differing technologies, and
- more innovative ways to handle and treat waste streams.
8. Pilot testing of remedial options

The initial stages of the remediation technology selection process (Figure 18) would consist of a desk-top review of available options against the various selection criteria. The outcomes of this review would be a small number of candidate technologies that should attain the desired remediation end points. The final selection of a remediation strategy would then follow from a potentially iterative procedure of:

- undertaking further site characterisation where parameters critical to the performance of the candidate technologies are lacking
- possibly conduct bench-scale tests to validate expected performance, and
- assessing the necessary implementation and performance from any available design and simulation tools.

This process is designed to narrow the range of candidate technologies in a considered and cost-effective way.

Pilot testing of candidate technologies may be a further step required before implementing the remediation strategy at full scale. ITRC (2009a) recommend pilot testing for almost all technologies. They stress the importance of gathering data to confirm the performance is as expected and will reach remediation objectives. Pilot testing is also seen as important to updating the conceptual site model.

In some cases where the setting and remediation technology selected is particularly well characterised and known (and as further experience is gained) pilot testing may not be required. Nevertheless, in many cases, the selection process leads to the conduct of pre-remediation pilot testing.

Pilot testing may be important where:

- the remediation performance at full scale is not predictable with a reasonable level of certainty
- the performance of the remediation against remediation objectives needs to be confirmed
- a preferred remediation technology candidate is not obvious, particularly because of the uncertainty of performance and multiple criteria for selection
- further site-specific operational information is required to design full scale remediation systems, and
- practicability limits to the remediation are being claimed and a demonstration is required.

Pilot testing may be for a single technology or seek to compare technologies, either side by side or sequentially at the one location. Invariably, pilot testing also provides further site assessment information.

Pilot testing needs careful design and execution to be useful and provide the desired information. Elements of a pilot testing program are discussed in the following sections.
A pilot testing case study

Pilot tests of a free-LNAPL recovery were conducted by Johnston et al. (2002b, 2005) to test the relative efficiency of the different techniques on weathered gasoline in a sand aquifer. The testing regime entailed the sequential application of different techniques in the same well:

- skimming – using a selective oil skimmer pump
- vacuum-enhanced recovery (VER) – applying different suctions to the well while skimming
- slurping – total fluids recovery through a straw, driven by air extraction
- VER plus drawdown (VER-DD) – VER was undertaken while drawdown of the water table was maintained in the recovery well by pumping groundwater.

In addition, the testing was repeated under low- and high-water table conditions.

The site of the pilot test was intensively monitored to examine the distances within the aquifer over which effects of the recovery could be detected. The intensive monitoring was also aimed at quantifying the removal rates of the LNAPL via:

- LNAPL pumped from the well (i.e. recovered as a liquid)
- mass of VOCs in the extracted air (i.e. recovered as a vapour phase)
- mass biodegraded within the aquifer.

Tests of the individual recovery techniques ran over periods of 4–14 days. Skimming on its own was repeated as a control through the sequence of testing. This was important because of the extended duration of the testing and the naturally varying water table in the aquifer. The sequence of testing is illustrated in the measured LNAPL flux pumped from the well (right, © CSIRO).

Summaries of the rate and source of LNAPL removal (see below) enabled relative performance of the different techniques to be assessed under the different conditions that may be experienced in the aquifer. Results pointed to the effectiveness of VER.
8.1 Metrics, performance indicators and controls

The key focus of a pilot testing program is to make a well documented assessment of the relative and absolute performance of candidate remediation technologies in relation to remediation objectives for the site. This is also an obvious time to gain further insights into those factors determining the performance of LNAPL remediation technologies at the site with a view for optimising the particular remediation strategies. This calls for a high level of documentation and a means of making objective comparisons between different technologies and strategies.

At the heart of making objective assessments is a clear definition of the metrics to be used in determining the levels of contamination and the concerns raised by the presence of the LNAPL. The metrics and performance indicators used for pilot testing would ideally be the same as those envisaged for full-scale operation and be appropriate for the setting and remediation strategy. However the nature of the pilot testing may mean that methods for determining some of the metrics and performance indicators need to be varied or measurements intensified. The generally limited duration and spatial scale of pilot testing means that changes to the level of contamination may be relatively small in magnitude and not extend over large areas. This makes identifying significant changes to risks and other concerns difficult – particularly where such changes are determined from differences in the state of the LNAPL in the aquifer (i.e. using before and after measurements). Some of the performance indicators related to rates that can be determined directly (rather than by changes to slowly varying state variables over time) either in the aquifer (such as biodegradation rates) or through the recovery systems (LNAPL, VOC and water flux rates) would not suffer from the same difficulties.

One of the important issues with pilot testing is that comparisons are only valid if they are made under the same conditions. This is not a trivial consideration given the natural spatial and temporal variability of site conditions as well as changes wrought by the pilot testing itself. Experimental designs that are amenable to statistical evaluation of the differences between remediation technologies in the presence of variability can reasonably be assumed to be impractical at the field scale. Consequently, it is important to include internal controls within the testing scheme and to ascertain the likely variability of performance through other means.

8.2 Dealing with issues of variability

Temporal variability of remediation performance as a result of systematic changes in the state of LNAPL in the aquifer (such as that caused by periodic changes in the water table elevation) may be relatively easy to accommodate. Pilot testing may need to be replicated only for a small number of conditions (e.g. for times of minimum and maximum water table elevation – Johnston et al. 2002b, 2005) to gain an appreciation of the range of performance. The best way to include an internal control is often to repeat the testing using the same infrastructure and operating conditions within a longer series of tests. Validation by repeating tests at one or more of the system states would also add confidence to the results.

Spatial variability offers a much greater challenge. Vertical as well as lateral variability of the aquifer materials and the distribution of the LNAPL can appreciably affect remediation performance at a range of scales. Profound effects on simple LNAPL
recovery technologies may arise even for granular porous materials with modest variability of aquifer properties (Johnston & Trefry 2009). More complex situations such as fractured rock aquifers would be expected to have an even greater range in remediation performance when applied at different locations at a particular site. An important consideration is that variability is likely to affect remediation technologies differently.

### 8.2.1 Sequential testing

A reasonable way to address the issues of spatial variability in comparing the performance of different technologies is to undertake testing as a sequential application of different remediation technologies at the one site using the same basic infrastructure. This suits (single) well-based technologies, particularly free LNAPL recovery and, to a limited extent, volatilisation and biodegradation. This sequential testing may alleviate the need for many replicates and minimise infrastructure costs. A number of forms of sequential testing may be considered:

1. A once-off pass through of technologies, of relatively limited duration (i.e. not reaching any practicability limits or specified remediation end point).

2. Continued repetition through a sequence of technologies until a practicability limit is reached for all technologies or a specified remediation end point is reached (i.e. repetition of the approach 1 above) or set number of cycles undertaken. The repetition may be punctuated by extended periods of applying a single technology in order to move to different levels of LNAPL contamination before proceeding through another sequence of candidate technologies.

3. A sequence of extended testing of increasing aggressive technologies where each technology is taken to its practicability limit before progressing to the next.

An illustration of these alternatives for sequential pilot testing is presented in Figure 20.

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**Figure 20. Schematic illustration of possible alternatives for sequential pilot testing of remediation technologies.**
A selection from these alternatives would be made according to the objectives of the testing, available time frames, specific site conditions and operational considerations.

For all the alternatives of sequential testing, it would be good experimental design to include a control treatment between successive remediation technologies to detect effects of changing aquifer and LNAPL conditions.

The free LNAPL recovery technologies as well as volatilisation and biodegradation technologies fairly naturally allow assessment of their performance to be made from instantaneous recovery rates or instantaneous in situ measures of LNAPL mass loss. Such instantaneous measures allow relative assessment from comparatively short tests thereby limiting the total mass removal. This means the underlying conditions may not change appreciably over a significant period of testing, allowing application of different remediation technologies under similar conditions. However an internal control technology could be repeated between different technologies to detect changes in the underlying conditions.

It would also generally be desirable to repeat the sequence of testing for different levels of contamination. That is, sequential testing repeated at different times over the course of LNAPL removal. Appropriate LNAPL removal may be achieved with intervening periods of sustained remediation using one or more particular technologies. A similar outcome could be achieved by repeating the sequence of testing different technologies to some specified end point. A confounding effect for this strategy is that other conditions (e.g. water table elevations) may change over extended periods. In such a strategy, there may be a reduced need to include a control treatment between the individual technologies in the sequence.

It should be noted that the third alternative mentioned above does not allow a strict quantitative comparison between different technologies. This is because different technologies are applied under different conditions within the aquifer. However it should confirm a relative ranking of technologies. A limitation is that this relative ranking needs to be determined *a priori* for the gained information to be of maximal use. For instance, no information on the relative performance is gained if there is no advance past the remediation end point or performance of the preceding technology.

### 8.2.2 Spatial variability of remediation performance

Sequential application facilitates the comparison of remediation technologies by attempting to exclude the effects of spatial variability. However, it may be important to understand how spatial variability affects absolute and comparative performance. The scale of the site and expected remediation effort would dictate the extent to which performance testing needs to be repeated at different locations. Sequential application at a number of sites with the full set of candidate technologies could be costly and onerous, but where the underlying conditions varying strongly this may need to be considered. Where the underlying conditions are known to vary in a modest fashion, testing may be with a subset of the most promising remediation technologies.

### 8.2.3 Once-off remediation trials

Some technologies such as in situ flushing, in situ chemical oxidation and soil heating are not suited to comparison through successive evaluation at the same location. These remediation technologies generally need to be run to their natural end point in order to make an assessment. Thus comparative testing is forced to be conducted at
different locations. In this case, a sound comparison must be achieved through careful selection of the sites on the basis of similarity of subsurface conditions. It may also be appropriate and/or necessary to pre-treat the site with another remediation technology (such as free LNAPL recovery) to ensure similarity of the initial state of LNAPL contamination.

8.3 Durations and end points for pilot testing

One of the main objectives of pilot testing is to compare a number of technologies within a reasonable time frame and cost. This particular objective must be balanced against other objectives which may be aimed at evaluating remediation technology end points – something that may only be achieved with considerably greater time and effort. Indeed, where remediation technology end points or practicability limits are to be identified, extended testing would be required. This would essentially amount to full-scale application, limited only by the spatial scale of the application. Here, some consideration needs to be given to the scale of the pilot test in relation to the size of the LNAPL plume. It is possible that pilot tests of limited spatial scale (compared to the size of the LNAPL contamination) may not reach remediation technology end points or practicability limits within desired time frames. Even if remediation technology end points are reached, they may not be representative of those under full-scale conditions.

Some specific features that would be sought in selecting the duration of a pilot testing program include:

- a measurable/significant change is detectable in metrics selected for evaluation
- the sphere of influence of the remediation is fully or adequately developed, perhaps signalled by asymptotic or predictable behaviour
- some point of diminishing performance or critical control on the LNAPL remediation is reached
- external forcing does not materially change the state of LNAPL contamination over the course of the test, and
- LNAPL removal does not interfere with comparative assessment.

The last point, that of the extent of LNAPL removal not interfering with comparative estimates, is specific to the situation where testing of different remediation technologies are undertaken successively at the same (or very close by) location. This potentially conflicts with the other features sought in a pilot test, some of which attempt to stress the system to identify changing and limiting controls on removal of LNAPL. There is some prospect that the LNAPL contamination at a particular location will return to close to previous conditions following the application of one technology before subsequent testing of another. This would be one reason to scan through increasingly aggressive techniques in a sequence of tests. Otherwise, strategies may be available to overcome this conflict where successive testing of different technologies (see above).

8.3.1 Characteristic times

As a matter of principle, the duration of individual tests should be in line with characteristic times for fluid pressure responses, fluid redistribution and transport, biogeochemical kinetics and heat transport in the subsurface. The ultimate aim is to mimic conditions that will develop during full scale operations. These characteristic
times will vary for different systems and in many instances may be readily estimated. For instance:

- simple tools are available to estimate the drawdown of water and LNAPL tables to guide the time for capture zones to develop during free LNAPL recovery
- fluid travel times may be adequately estimated from simple models and estimates of subsurface transport properties
- acclimatisation times and biodegradation rates can be estimated within a useful range from laboratory measurements or literature values, and
- thermal properties of subsurface systems can also be estimated within a useful range from literature values to predict heating in the subsurface.

In terms of liquid pressures and distributions, hours to days may be required to establish quasi-steady conditions that may be more typical of full-scale conditions. On top of this establishment phase, a further period would be required for the LNAPL contamination to be stressed such that time trends in remediation are discernable. So for free LNAPL recovery systems, pilot testing times of (at least) the order of days would generally be called for.

For soil vapour extraction and bioventing systems as well as air sparging and biosparging systems, the establishment phase for the air pressure and air flow responses is generally fairly rapid compared to that of liquid hydraulics – of the order of minutes to hours. Induced response of the liquid distribution would be longer (hours to days). This would also need to be accounted for in the establishment phase. However, the kinetics of biological systems may be even longer still. Acclimation periods of aquifer microorganisms may be days or even weeks. Even past the establishment phase, the kinetics of microbial degradation may be relatively slow so pilot testing of bioremediation technologies may be required over a period of weeks or even months. The kinetics of volatilisation from the LNAPL are generally much faster than those of biodegradation. However mass transfer limitations would be expected to develop and increase characteristic times. The time for mass transfer limitations to develop is an important parameter in itself.

Technologies dependent on liquid delivery into the aquifer have scale dependent characteristic times. Testing times would depend on the hydraulic conductivities of the formation. Appropriate spatial scales are required for pilot tests that account for aquifer variability and the transients of the underlying processes. Hence pilot tests may need to be conducted over a period of days and testing times may be significantly longer in some cases. Characteristic times for testing may have to be increased several fold over that indicated from averaged measures of hydraulic conductivity because of heterogeneities in geological materials. The reaction kinetics of chemical oxidants, surfactants and co-solvents are rapid compared to the fluid flow so do not impinge materially in calculating testing times.

Thermal treatment systems range in nature from those dependent on the transport of liquids and gases in the subsurface to those relying on the diffusivity of heat in porous materials. Times to achieve remediation technology end points are scale-dependent and therefore varying the scale can be used to derive practical testing times. However, the inherent spatial variability of aquifer properties and the spatial scales of the underlying processes involved will constrain the extent to which testing times can be selected.
8.4 Characterisation for up-scaling and extrapolation of results

Pilot testing, by its nature, provides results specific for a particular site, for the period of the remediation test and for the specific state of the fluids in the subsurface. Thus, pilot testing generally needs to be up-scaled to larger spatial dimensions, extended over longer times and even extrapolated to sites with conditions of different subsurface geology and contamination. A process-based model of the remediation – either a qualitative conceptual model or quantitative model – is needed for such up-scaling and extrapolation. At their core, such process-based models need two elements:

- identification of critical processes controlling the LNAPL remediation, and
- parameterisation of these processes.

To maximise benefits for full-scale applications these two elements are key to a pilot testing program. Many of the elements of the process-based models (basic hydrogeological properties of the subsurface materials and groundwater systems, fluid characteristics and chemical composition of the LNAPL, biogeochemistry of the groundwater, rate coefficients and other process descriptors) would normally be obtained through more general site assessment activities (and used in the selection of candidate remediation technologies). These may be further confirmed by the pilot testing. The pilot testing also allows the opportunity to extend the characterisation to more specific parameters related to candidate remediation technologies where such parameterisation had not already been anticipated. Additionally, remediation process parameters are mostly only obtainable at an appropriate scale through field scale measurements.

Most of the processes associated with specific technologies are known with a reasonable level of certainty (e.g. fluid extraction, biodegradation, geochemical reactions). However, their particular expression in different settings is less understood. Hence pilot testing will involve some aspects of process identification as well as the straightforward characterisation of known processes.

Empirical observations of the relative performance of different remediation technologies provide useful information. However, increased uncertainty would be associated with extrapolation of such results without proper process identification and quantification.
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstract Service</td>
</tr>
<tr>
<td>CIRIA</td>
<td>Construction Industry Research and Information Association</td>
</tr>
<tr>
<td>CL:AIRE</td>
<td>Contaminated Land: Applications in Real Environments</td>
</tr>
<tr>
<td>CUTEN</td>
<td>Clean up to the extent necessary</td>
</tr>
<tr>
<td>CUTEP</td>
<td>Clean up to the extent practicable</td>
</tr>
<tr>
<td>DEC – NSW</td>
<td>Department of Conservation and Environment, New South Wales</td>
</tr>
<tr>
<td>DNAPL</td>
<td>Dense non-aqueous phase liquid</td>
</tr>
<tr>
<td>DTSC</td>
<td>Department of Toxic Substances Control (California EPA)</td>
</tr>
<tr>
<td>EA</td>
<td>Environment Agency (United Kingdom)</td>
</tr>
<tr>
<td>EPA SA</td>
<td>Environmental Protection Authority, South Australia</td>
</tr>
<tr>
<td>EPA Victoria</td>
<td>Environmental Protection Authority, Victoria</td>
</tr>
<tr>
<td>FLUTe</td>
<td>Flexible Liner Underground Technologies Ltd</td>
</tr>
<tr>
<td>FRTR</td>
<td>Federal Remediation Technologies Roundtable</td>
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<tr>
<td>ISCO</td>
<td>In situ chemical oxidation</td>
</tr>
<tr>
<td>ITRC</td>
<td>Interstate Technology and Regulatory Council</td>
</tr>
<tr>
<td>LNAPL</td>
<td>Light non-aqueous phase liquid</td>
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<tr>
<td>NAPL</td>
<td>Non-aqueous phase liquid</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>RBCA</td>
<td>Risk-based corrective action</td>
</tr>
<tr>
<td>ROST</td>
<td>Rapid optical screening tool</td>
</tr>
<tr>
<td>MIP</td>
<td>Membrane interface probe</td>
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<tr>
<td>MPE</td>
<td>Multi-phase extraction</td>
</tr>
<tr>
<td>MTBE</td>
<td>methyl tert-butyl ether</td>
</tr>
<tr>
<td>SRC</td>
<td>formerly Syracuse Research Corporation</td>
</tr>
<tr>
<td>SVE</td>
<td>Soil vapour extraction</td>
</tr>
<tr>
<td>TCEQ</td>
<td>Texas Commission on Environmental Quality</td>
</tr>
<tr>
<td>TI</td>
<td>Technical impracticability</td>
</tr>
<tr>
<td>TPHCWG</td>
<td>Total Petroleum Hydrocarbon Criteria Working Group</td>
</tr>
<tr>
<td>US EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>VER</td>
<td>Vacuum-enhanced recovery</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile organic compounds</td>
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</table>
### Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$A$</td>
<td>Area</td>
</tr>
<tr>
<td>$b$</td>
<td>Fracture aperture</td>
</tr>
<tr>
<td>$b_n$</td>
<td>LNAPL thickness in a well</td>
</tr>
<tr>
<td>$C_e$</td>
<td>Concentration in the effluent</td>
</tr>
<tr>
<td>$C_{i,a}$</td>
<td>Concentration of the $i$-th compound in air</td>
</tr>
<tr>
<td>$C_{i,w}$</td>
<td>Concentration of the $i$-th compound in water</td>
</tr>
<tr>
<td>$C_{i,w}^*$</td>
<td>Solubility of the $i$-th compound in water</td>
</tr>
<tr>
<td>$H$</td>
<td>Head</td>
</tr>
<tr>
<td>$h_d$</td>
<td>Fluid displacement head</td>
</tr>
<tr>
<td>$g$</td>
<td>Acceleration due to gravity</td>
</tr>
<tr>
<td>$H_n$</td>
<td>LNAPL head</td>
</tr>
<tr>
<td>$k$</td>
<td>Permeability</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Relative permeability</td>
</tr>
<tr>
<td>$k^*$</td>
<td>Intrinsic permeability</td>
</tr>
<tr>
<td>$k_H$</td>
<td>Henry’s coefficient</td>
</tr>
<tr>
<td>$k_{H,i}$</td>
<td>Henry’s coefficient of the $i$-th compound</td>
</tr>
<tr>
<td>$K_{ow}$</td>
<td>Octanol-water partitioning coefficient</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Inherent LNAPL mobility</td>
</tr>
<tr>
<td>$M_o$</td>
<td>Inherent oil mobility</td>
</tr>
<tr>
<td>$n$</td>
<td>van Genuchten parameter</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$P_a$</td>
<td>Air pressure</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Capillary pressure</td>
</tr>
<tr>
<td>$P_{c,am}$</td>
<td>Air-LNAPL capillary pressure</td>
</tr>
<tr>
<td>$P_{c,aw}$</td>
<td>Air-water capillary pressure</td>
</tr>
<tr>
<td>$P_{c,mw}$</td>
<td>LNAPL-water capillary pressure</td>
</tr>
<tr>
<td>$d$</td>
<td>Displacement pressure</td>
</tr>
<tr>
<td>$p_i$</td>
<td>Partial pressure of the $i$-th compound in air</td>
</tr>
<tr>
<td>$P_n$</td>
<td>LNAPL pressure</td>
</tr>
</tbody>
</table>
$P_{nw}$  Non-wetting phase pressure
$P_w$  Water/wetting phase pressure
$P^*$  Pure compound vapour pressure
$Q$  Volume flux of fluid
$r$  Radius of curvature
$R$  Universal gas constant
$S$  Fluid saturation
$S^*$  Scaled fluid saturation
$S_e$  Entrapped saturation
$S_m$  Critical saturation
$S_r$  Residual saturation/irreducible saturation
$S_{rw}$  Residual saturation of water
$T$  Temperature
$T_{boil}$  Boiling point
$T_n$  LNAPL transmissivity
$T_{triple}$  Triple point
$V_n$  Specific volume of LNAPL
$x$  Distance
$z$  Elevation
$z_{an}$  Elevation of the air-LNAPL interface (LNAPL table)
$z_{aw}$  Elevation of the air-water interface (water table)
$z_{nl}$  Elevation of the lower extent of LNAPL in the aquifer
$z_{nu}$  Elevation of the upper extent of LNAPL in the aquifer
$z_{nw}$  Elevation of the LNAPL-water interface
$\alpha$  van Genuchten parameter
$\beta_{an}$  Air-LNAPL interfacial tension scaling factor
$\beta_{nw}$  LNAPL-water interfacial tension scaling factor
$\gamma_{i,n}$  Activity coefficient of the $i$-th compound in the LNAPL
$\gamma_{i,w}$  Activity coefficient of the $i$-th compound in the water
$\theta$  Contact angle
$\theta_v$  Volumetric fraction of the fluid
$\lambda$  Brooks-Corey soil parameter
\( \mu \)  
Viscosity

\( \mu_n \)  
LNAPL viscosity

\( \rho_n \)  
LNAPL density

\( \rho_{r,n} \)  
LNAPL relative density

\( \rho_w \)  
Density of water

\( \sigma \)  
Interfacial tension

\( \sigma_{an} \)  
Air-NAPL interfacial tension

\( \sigma_{nw} \)  
LNAPL–water interfacial tension

\( \overline{u}_n \)  
Depth-averaged velocity of LNAPL

\( \phi \)  
Porosity

\( \chi_i \)  
Mole fraction of the \( i \)-th compound in the NAPL

\( \omega_i \)  
Molecular weight of the \( i \)-th compound
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APPENDIX A.

Typical Australian soils and aquifers

In reviewing the soils and aquifers in Australia which are important to consider in relation to LNAPL contamination, emphasis is placed on those found in major urban and industrial areas. These areas generally equate to the state and territory capitals where the vast majority of petroleum fuels are refined, stored and distributed. In addition, it is these population centres where human health and other concerns are likely to be most pressing. Such emphasis allows some focus within the otherwise vast range of different soils and aquifers that may be encountered in Australia. Here, soil and aquifer systems are discussed for different states.

A.1 Western Australia

The greater Perth metropolitan area is located on the Late Tertiary – Quaternary sediments of the Perth Basin (Playford et al. 1976). The superficial aquifers are assemblages of unconsolidated sandy materials and lithified carbonate sands, as well as finer textured clays and silts (Davidson 1995).

The two major sand units of interest are the coastal Safety Bay Sands and Bassendean Sands which are encountered further inland on the coastal plain. Both are reasonably uncomplicated aeolian sands. The Safety Bay Sands are calcareous sediments that may display partial cementation in places and have discernable layering of different grain-sized material. The Bassendean Sands are leached quartz sands that may contain layers of iron-organic material in the vicinity of present or past water tables. The heterogeneities within both the Safety Bay Sands and the Bassendean Sands have the potential to complicate the movement and remediation of LNAPLs but their basic unconsolidated, granular nature simplifies the understanding of LNAPL behaviour and offer scope for a range of remediation strategies.

The Tamala Limestone calcarenite occupies a significant portion of the coastal margins of the Perth Basin and offers a more challenging environment for both understanding and remediating LNAPL. The limestone is mostly blanketed by the leached yellow sands of the Spearwood dunes. The limestone has varying degrees of cementation, contains sub-horizontal bedding planes, solution channels and root channels. It is known to be karstic, particularly in the vicinity of the water table, and its high transmissivity is presumed to mainly arise from secondary porosity. However, the limestone matrix has a reasonably high porosity and significant hydraulic conductivity. Overall the Tamala Limestone would be viewed as a dual porosity unit.

Silty and sandy clays of the Guildford Clay unit are encountered on the inland (eastern margin) of the coastal plain and could be considered as fairly typical of what would be expected of finer textured unconsolidated materials. The Guildford Clay is heterogeneous with lenses of coarser and finer textured materials and inter-bedded with other sand sequences commensurate with its fluvial origins. Heterogeneity would be important for understanding the distribution and movement of LNAPL and the fine textured nature of the materials would impinge on the range of appropriate remediation technologies.
A.2 Victoria

The urbanised and industrialised areas around Melbourne stretch in an arc with little interruption around Port Phillip Bay from Geelong in the south west to Portsea to the south of Melbourne on the Mornington Peninsula. The surface hydrogeology is varied (Leonard 1992).

The fractured basalt aquifers of the Pleistocene Newer Volcanics Province dominate the region from the Melbourne CBD to Geelong in the southwest. In particular, the basalts are derived from the Werribee Plains lava flow fields of the Western Plains Sub-province (Hare & Cas 2005) and overlie the Brighton Group sediments of the Port Phillip Basin. The basaltic plains have developed from an extended period of discrete flows which have produced lateral and vertical variability in the basalts. This has led to complex hydrogeology, particularly as fluid flow occurs through joints and fractures, vesicular openings and between flows (Leonard 1992). The upper horizons of the basalt flows are more highly fractured and jointed. Hydraulic properties vary widely at a small scale. This is expected to make predicting LNAPL movement within a relatively narrow interval of the profile around the water table very challenging.

The heterogeneous (sand, gravel, silt, clay and calcarenite) Brighton Group (Fyansford Formation) aquifer is extensive over the area to the southeast of Melbourne with the aquifer characterised by the coarser sediments forming lenticular sequences in the sheet-like deposits. The Brighton Group aquifer also outcrops to be the water table aquifer in the Geelong area and the Bellarine Peninsular area. Here it is slightly different in nature being described as sand, clayey sand, sandy clay, gravel, quartzite and sandy limestone. The heterogeneous layering of the aquifer and presence of finer textured sequences have important implications for the heterogeneity of LNAPL distributions and remediation potential.

Other sedimentary water table aquifers include dune deposits southeast of Melbourne (Brighton – Beaumaris area) which form an unconfined sand aquifer; the Bridgewater Formation which also forms an unconfined sand aquifer on the Nepean Peninsula; and the Werribee Delta aquifer which consists of sand and other coarser sediments inter-layered with clays and silts.

Basement rocks (mudstone, sandstone, greywacke and shale) that outcrop mostly in the upland regions north east of Melbourne form fractured rock aquifers.

A.3 Tasmania

Maps from Lau et al. (1987) suggest Hobart is located on the Tasmania Basin. This consists of Triassic sandstone containing Permian coal seams. Intrusive dolerite sills are an important feature of this sedimentary basin.

A.4 South Australia

The Adelaide metropolitan area is located on the Tertiary and Quaternary sediments of the Adelaide Plains. The Adelaide Plains are bounded by the Gulf of St Vincent and the Proterozoic rocks of the Mt Lofty Ranges. The near surface geology is characterised by deltaic alluvial deposits together with aeolian dune deposits near the coastal margin.
(Daily et al. 1976). Surface soils generally reflect the underlying fine textured surface geology and show a complex spatial distribution (Northcote 1976). The most extensive soils are red-brown earths, and others present include alluvial soils, coastal dune sands and cracking black earths. The water table in the surficial aquifer generally intersects clay materials. This would infer that LNAPL movement in such materials may be largely controlled by secondary features and heterogeneities of coarser textured sequences in the profile. This and the low permeabilities of such clay materials would add complexity and may limit the applicability of some of the remediation technologies.

The water table lies in sandy material over at least part of the Adelaide metropolitan area. Much of this is below an upper sequence of clay. However, in coastal regions, the upper clay sequences may be absent and the sand aquifer unconfined. While this means the sand aquifer may be more vulnerable to contamination by petroleum fuels, a greater range of remediation options may be viable.

**A.5 Queensland**

The urban and industrial areas of south east Queensland are centred around the city of Brisbane as well as the Gold Coast to the south and Noosa (Sunshine Coast) to the north. The surficial aquifers vary from Quaternary valley fill and coastal sand masses to Palaeozoic sedimentary and metamorphic rocks (Environmental Hydrology Associates 2006; Helm et al. 2009).

As well as the sand masses on North and South Stradbroke Islands, Quaternary dune sands form unconfined aquifers along much of the coastal strip between Noosa and the Gold Coast. These are generally fine to medium-grained sands with medium to high permeability and shallow water tables.

In addition, there are a number of Quaternary-age valley infill aquifers associated with major rivers in the region – including that of the Brisbane River. These aquifers were produced by fluvial and alluvial processes and thus would be expected to be somewhat heterogeneous in nature. On the coastal plain, estuarine deposits are also associated with these rivers. Again, these are heterogeneous consisting of mud, silt, sand and gravel.

The sedimentary and metamorphic basement rocks of the Palaeozoic Neranleigh Fernvale Beds are relatively extensive in the area and outcrop between Brisbane and the Gold Coast. The characteristics of these materials vary considerably because of their differing nature. However, the materials are generally fine grained and lack appreciable porosity and permeability.

Mesozoic and Tertiary sediments are also expressed around Brisbane and environs. The Mesozoic sandstones, shales, coals and some interbedded volcanics of the Mesozoic Ipswich Basin outcrop to the west of Brisbane. Bore yields suggest hydraulic conductivities of these materials are relatively low, at least in some of the upper units. Differing Tertiary sedimentary basins also outcrop around the area and vary in nature between interbedded basalts and sediments (Petrie Basin); sand, weakly cohesive clayey sandstone, gravel, silty clay, clayey mudstone, siltstone and shale (Sunnybank Formation of the Oxley Basin); and basalt claystone, siltstone and sandstone (Amberley and Booval Basins).
A.6 Northern Territory

Maps from Lau et al. (1987) suggest Darwin is located on northern fractured rock province of mainly Proterozoic metamorphic rocks. These have the characteristic of fractured hard rock aquifers with groundwater confined to the fracture network.

A.7 New South Wales

The Hawkesbury Sandstone dominates the geology of the Sydney area (Russell et al. 2009) and is the dominant aquifer in the Sydney Basin. However, the aeolian and marine Botany Sands, Ashfield and Bringelly Shales and alluvial sediments around the Parramatta and Georges Rivers are also important groundwater systems in relation to potential LNAPL contamination.

The Hawkesbury Sandstone is a fractured quartz sandstone and constitutes a dual porosity aquifer system (Tammetta & Hewitt 2004). Flow through the sandstone is generally dominated by the fracture network and the properties of the fracture networks have been studied in some detail (see also De Castro et al. 2009). These properties would be important for understanding the movement of LNAPL in this aquifer along with the interaction of the LNAPL with the matrix of the sandstone.

The Botany Sands are an important unconfined sand aquifer around the rim of Botany Bay and are most extensive to the north of the Bay (Hatley 2004). This sand aquifer is comprised of aeolian and marine deposits in incised valleys within finer textured materials (clays and stiff sand) on top of the Hawkesbury Sandstone. The unconsolidated sands contain minor clay and peat layers.

In Western Sydney the Hawkesbury Sandstone is overlain by the Ashfield and Bringelly Shales also known as the Wianamatta Group (which are assumed to be of marine origin) and surficial deposits of alluvium and colluvium (McNally 2009). These surficial deposits along with weathered shales form the water table aquifers. They are composed mainly of clays and are extremely variable in permeability. Permeability is also contributed through fractures and bedding planes in the upper part of the underlying shales.

A.8 Australian Capital Territory

Canberra and neighbouring Queanbeyan in NSW are located on the Canberra Lowlands physiographic region (Jenkins 2000), which is described as having subdued relief compared to surrounding terrain. The subdued relief of the Canberra Lowlands is attributed to the properties of the underlying shales, siltstones and interbedded volcanic sediments. However, prominent hills and mountains punctuate the plain.

A range of geology forms the basis of mainly fractured rock aquifers in the area (Evans 1987). Metamorphosed and bedded sequences of quartz arenite, siltstone, shales and sandstone make up the oldest Ordovician and Early Silurian sequences in the Canberra region. However, middle and late Silurian mudstone, siltstone, ignimbrite, bedded tuff, minor ashstone and minor limestone are found under most of the urban and industrialised areas (Evans 1987). The fractured rocks form regional aquifers, however local superficial unconsolidated aquifers are also present (Evans 1987). There
are notable alluvial and colluvial deposits in eastern and north-eastern parts of suburban Canberra consisting of layered gravel, sand, silt and clay.

The overlying soils typically show topographic gradations within the landscape units (Jenkins 2000). Shallow lithosols are generally found on hills and near rock outcrops while podsol developed over red and yellow earth soils are found on slopes. Poorly drained solodic and solodised solonetz soils as well as podsol, earths and alluvial soils are found in valleys. Even on slopes, the soils are prone to water logging and subsoils have low permeability.
APPENDIX B.
Saturation-capillary pressure relationships

The van Genuchten and Brooks-Corey relationships are particular functional approximations to experimentally observed dependence of the wetting phase liquid saturation on the capillary pressure between the wetting and non-wetting phases. The relationships are for a porous material with two fluids. Typically, measurements are made with water (the wetting phase) and air (the non-wetting phase).

The van Genuchten function gives the wetting phase saturation as:

$$ S = S_r + (1 - S_r) \left[ 1 + (\alpha P_c) \right]^{\left( \frac{1}{n} \right)} $$  \hspace{1cm} [Equation B1]

where $\alpha$ and $n$ are fitted parameters.

The Brooks-Corey relationship is given by:

$$ S = \begin{cases} S_r + (1 - S_r) \left( \frac{P_d}{P_c} \right)^\lambda, & P_c > P_d \\ 1, & 0 \leq P_c \leq P_d \end{cases} $$  \hspace{1cm} [Equation B2]

where $\lambda$ is the fitted soil parameter.

The two functions usually provide a reasonable fit to observed data and differ mainly in the region where $P_c$ approaches zero. The van Genuchten function approaches $S = 1$ smoothly and full saturation is only reached at $P_c = 0$. On the other hand, the Brooks-Corey relationship assumes that the porous media remains fully saturated until the capillary pressure exceeds the positive displacement pressure. It follows from this that predicting the distribution of fluids in a particular porous material may be quite different depending on which of the functional forms are used. Many favour the Brooks-Corey relationship because a discrete, non-zero displacement pressure is often observed in the case of LNAPL displacing water. However, the van Genuchten relationship has other advantages and in many cases, a preferred relationship is not evident in simulating NAPL distribution and movement (Fagerlund et al. 2006).

Research has shown that a $S - P_c$ relationship for a particular fluid pair may be generalised to provide an adequate description for other fluid pairs and indeed for a three-fluid phase system. The $S - P_c$ relationship can be adapted to another fluid pair through scaling using the fluid interfacial tensions as the scaling factor (Parker et al. 1987). In this regard, the air-water $S - P_c$ relationship is used as a reference due to its greater ease of determination and more general availability.

In addition, for a three-fluid phase system, the water saturation is determined by the LNAPL-water capillary pressure and the total liquid (water + LNAPL) is determined by the air-LNAPL capillary pressure.
By defining a scaled fluid saturation, $S^*$:

$$S^* = \frac{(S - S_{rw})}{(1 - S_{rw})} \quad [Equation \ B3]$$

with $S_{rw}$ the residual water saturation, the scaling can be stated as the following functional relationships for situations where LNAPL is present:

$$S^*_w = S^* \left( \beta_{nw} P_{c,nw} \right) \quad [Equation \ B4]$$

$$S^*_i = S^* \left( \beta_{ni} P_{c,ni} \right) \quad [Equation \ B5]$$

In these equations, the appropriate capillary pressure is multiplied by the ratio of interfacial tensions, $\beta_{nw}$ and $\beta_{ni}$:

$$\beta_{nw} = \frac{\sigma_{nw}}{\sigma_{nw}} \quad [Equation \ B6]$$

$$\beta_{ni} = \frac{\sigma_{ni}}{\sigma_{ni}} \quad [Equation \ B7]$$
APPENDIX C.
Relative permeability-saturation relationships

Mathematical equations are used to predict the relative permeability of the fluids in a porous medium from the saturations of the fluids. In the saturated zone, where there are two (liquid) fluid phases, different equations for the relative permeability are used depending on the functional relationship assumed between fluid saturation and capillary pressure.

The Mualem models are applied with the van Genuchten \( S - P_c \) relationship. In the case of water as the wetting fluid the relative permeabilities of water and LNAPL are given as:

\[
k_{rw} = \left(S_w^*\right)^{0.5} \left\{ 1 - \left[ 1 - \left(S_w^*\right)^\frac{1}{\gamma} \right]^{\gamma} \right\}^2
\]  
[Equation C1]

\[
k_{rn} = \left(S_n^*\right)^{0.5} \left\{ \left[ 1 - \left(S_w^*\right)^\frac{1}{\gamma} \right]^{\gamma} - \left[ 1 - \left(S_l^*\right)^\frac{1}{\gamma} \right]^{\gamma} \right\}^2
\]  
[Equation C2]

where \( S_w^* = (S_w - S_{wr})/(1 - S_{wr}) \), \( S_n^* = S_n/(1 - S_{wr}) \) and \( S_l^* = S_n^* + S_w^* \) is scaled total liquid saturation. In addition:

\[
\gamma = 1 - \frac{1}{n}
\]  
[Equation C3]

The Burdine model is usually applied with the Brooks-Corey model. This gives the liquid phase relative permeabilities, again with water as the wetting fluid, as:

\[
k_{rw} = \left(S_w^*\right)^{\frac{1 + 2}{\lambda}}
\]  
[Equation C4]

\[
k_{rn} = \left(\frac{S_n^* - S_{nr}}{1 - S_{nr}}\right)^2 \left(\frac{S_l^*}{\lambda} \right)^{\frac{1 + 2}{\lambda}} - \left(\frac{S_w^*}{\lambda} \right)^{\frac{1 + 2}{\lambda}}
\]  
[Equation C5]
APPENDIX D.

Estimating the vertical distribution of fluid saturations and relative permeability

The assumption of equilibrium hydrostatic conditions allows the vertical distribution of fluid pressures to be computed along with the capillary pressures. Hydrostatic conditions imply:

\[ P_w(z) = P_a(z_{aw}) + \rho_w g (z - z_{aw}) \]  \hspace{1cm} [Equation D1]

and

\[ P_n(z) = P_a(z_{an}) + \rho_n g (z - z_{an}) \]  \hspace{1cm} [Equation D2]

where, by definition of the liquid tables,

\[ P_a(z_{aw}) = P_a(z_{aw}) \quad \text{and} \quad P_a(z_{an}) = P_a(z_{an}). \]

(Liquid tables are the elevation where the liquid pressure is equal to the air pressure). This allows simplified expressions of the gauge pressures of the liquids (i.e. relative to air pressure) where the air pressure is constant and equal to atmospheric pressure in the subsurface. In the formulation of the equations above, gravity, \( g \), is acting in the opposite direction (downwards) to \( z \) and therefore has a negative value.

From this it follows that:

\[ P_{c,aw}(z) = g(\rho_w - \rho_a)(z - z_{aw}) \]  \hspace{1cm} [Equation D3]

\[ P_{c,an}(z) = \rho_n g (z - z_{an}) \]  \hspace{1cm} [Equation D4]

Capillary theory would then allow the vertical distribution of water, LNAPL and total liquid saturation to be computed from the \( S - P_c \) constitutive relationship for the soil. This fact has been used by many (firstly by Lenhard & Parker 1990 and Farr et al. 1990) to interpret the volume and distribution of LNAPL in the aquifer from its thickness in a well. Indeed, this analysis forms the basis of tools for evaluating LNAPL recovery schemes and their predicted benefits (API 2007; Huntley & Beckett 2002) as it also allows the prediction of the relative permeability of the fluids in the aquifer. However, the underlying assumptions and consequent limitations need to be recognised. Most importantly it assumes equilibrium hydrostatic conditions (rarely found) and does not account for residual saturations developing in the aquifer.

Because residual and entrapped saturation is neglected, prediction of LNAPL saturations from LNAPL thickness in a well would be most applicable to the recent lateral emplacement of LNAPL in the aquifer. That is, prior to the development of residual and entrapped saturations due to water table variations. Cases for van Genuchten and Brooks-Corey \( S - P_c \) relationships and associated \( k_r(S) \) function are shown in Figures D1 and D2. These illustrate a number of key points:

- For a van Genuchten \( S - P_c \) relationship, the LNAPL water interface in the well indicates the lower extent of the LNAPL, \( z_{nl} \), in the surrounding aquifer. For a Brooks-Corey relationship, the lower extent of LNAPL is located a distance above the LNAPL-water interface – the distance related to the displacement head.
Thus:

\[
Z_{nl} = \begin{cases} 
Z_{nw} & \text{(van Genuchten)} \\
Z_{nw} + \frac{h_d}{\beta_{nw}\left(1 - \frac{\rho_a}{\rho_w}\right)} & \text{(Brooks-Corey)}
\end{cases}
\]  \[\text{[Equation D5]}\]

- The maximum LNAPL saturation occurs immediately above the capillary fringe – above the LNAPL table.
- The mobile LNAPL extends to an elevation, \(z_{na}\), where the total liquid saturation determined by the air-LNAPL capillary pressure equals the water saturation determined by LNAPL-water capillary pressure. The elevation, \(z_{na}\), is independent of the particular \(S - P_c\) relationship and calculated directly from:

\[
Z_{na} = \frac{Z_{nw}\beta_{an} \frac{\rho_a}{\rho_w} - Z_{nw} \beta_{nw} \left(1 - \frac{\rho_a}{\rho_w}\right)}{\beta_{an} \frac{\rho_a}{\rho_w} - \beta_{nw} \left(1 - \frac{\rho_a}{\rho_w}\right)}
\]  \[\text{[Equation D6]}\]

- The change from a two- (air-water) to a three-fluid phase system (air-LNAPL-water) in the vadose zone is associated with an abrupt change in the total liquid saturation.

\[\text{Figure D1. Theoretical equilibrium distribution of capillary pressure heads, liquid saturations and liquid relative permeabilities in the vicinity of the water table for hydrostatic conditions along with the expected observation of LNAPL in a fully screened monitoring well. Calculations using a van Genuchten } \ S - P_c \ \text{relationship for a homogeneous fine sand and characteristics of diesel fuel } (\rho_a = 0.845, \beta_{nw} = 3.65 \text{ and } \beta_{an} = 2.49) \ \text{with an observed LNAPL table 0.2 m above the water table.}\]
Figure D2. Theoretical equilibrium distribution of capillary pressure heads, liquid saturations and liquid relative permeabilities in the vicinity of the water table for hydrostatic conditions along with the expected observation of LNAPL in a fully screened monitoring well. Calculations using a van Genuchten $S - P_c$ relationship for a homogeneous fine sand and characteristics of diesel fuel ($\rho_n = 0.845$, $\beta_{nw} = 3.65$ and $\beta_{an} = 2.49$) with an observed LNAPL table 0.2 m above the water table.
APPENDIX E.

Description of remediation technologies

A description of LNAPL remediation technologies is provided below with general commentary about the physical setting in which it is commonly applied, its likely performance in relation to remediation objectives and other issues associated with the technology.

E.1 Excavation

The approach here is to excavate and remove the LNAPL-contaminated materials from the subsurface. These contaminated materials are then either subjected to ex-situ treatment or disposed directly to an appropriate containment facility.

Process

Excavation involves the removal of the LNAPL-contaminated materials through mechanical excavation. It may also be possible to remove material using large-diameter borings. Once removed, the excavated material is either subjected to ex-situ treatment or disposed to an appropriate landfill facility. The ex-situ treatment may be undertaken on-site or at some off-site treatment facility. The excavation would be refilled with either fresh, uncontaminated material or the excavated material after treatment.

Remediation objectives and end points

As the ultimate objective is to remove all the LNAPL present, this remediation technology could be applied to the remediation objectives associated with almost all potential concerns. The end point of the remediation could be zero LNAPL saturation in the volume of the subsurface excavated where fresh, uncontaminated material replaces that removed. Alternatively, where treated material is returned to fill the excavation, a target LNAPL saturation or content of particular contaminants of concern could be stipulated as the end point. One of the attractive features of excavation is that it promises a quick removal of the contamination.

Physical setting

Excavation is best suited to relatively shallow unconsolidated materials of the vadose zone. The type of unconsolidated material is typically not a factor. However, excavation would offer advantages for finer textured materials which are problematic for a range of other technologies. Deep excavation is also possible but will incur increased engineering controls. Excavation below the water table is possible with dewatering. The high groundwater extraction rates needed for de-watering in high permeability materials may make the excavation of these materials below the water table less attractive and limit the depth of excavation. Although excavation is possible in consolidated materials, including fractured hard rocks, the practicability would need to be closely examined.

The success of excavation of the contaminated materials is independent of the type of LNAPL present so this is not a consideration in reaching remediation objectives. For this reason, excavation may be a prime candidate for heavy, high viscosity materials.
On the other hand, highly volatile LNAPLs may not be such attractive candidates because of the VOCs that would be released during the excavation.

Excavation can be very disruptive to the local environs and therefore may be limited in application where there is subsurface and surface infrastructure. Buffer zones and setbacks from the excavation may also limit where excavations may take place.

**Associated issues and impacts**

Technical risks involved in excavation include the failure to identify the location of all the LNAPL, particularly in heterogeneous environments where LNAPL movement and distribution is hard to predict. Alternatively it may not be practicable to excavate all the contaminated material. For instance it may be inaccessible under infrastructure or below the water table. There are a range of issues around the technical implementation and impact of excavation. Technical issues that may be encountered include the problems of collapse when excavating very poorly consolidated materials and the necessity for retaining or stabilising the walls of the excavation. Significant waste streams may be produced. As well as the contaminated material itself, contaminated groundwater may be produced and VOCs generated from the material during excavation and transport. LNAPL may be produced during dewatering requiring recovery and other management controls. The generation of VOCs may be particularly problematic because they are largely uncontrolled and could pose a hazard to human health. The generation of dust which may also be contaminated would be another hazard that needs to be controlled on and off site. There are a number of other health safety and environment issues that rank the technology moderate to high in this regard.

Other than hazards of the excavation itself, there are possible explosion risks from the presence of the LNAPL and vapours and the high level of vehicle movements. Amenity of the local area may also be adversely affected by noise, vibration and traffic movements. Risks of subsidence or settlement as a result of the excavation and dewatering would also need to be considered. The CO₂ emissions of intensive machinery use would need to be accommodated in assessing the overall environmental benefit. The use of landfills for off-site disposal may also be questioned in some jurisdictions. Costs for excavations may be large and restrict the size of the contamination that may be treated.

**Reference**

ITRC 2009a

**E.2 Containment**

**E.2.1 Physical containment**

**Process**

Physical containment attempts to isolate the LNAPL from the surrounding environment. The barrier may consist of steel sheeting, constructed cut off walls or capping using grout or other low-permeability materials. The containment may even consist of a cut-off drain. Vertical barriers attempt to stop the lateral spread of LNAPL. Vertical barriers may also be emplaced to stop or limit the lateral flux of dissolved LNAPL constituents in groundwater and VOCs through the vadose zone. Impermeable or low-permeability capping may also be used to prevent contact with contaminated material and vapours.
Such capping may also be used to reduce the flux of water through the LNAPL to reduce the flux of contaminants to groundwater. Continued spread of the LNAPL may also be prevented by in situ mixing. This distributes the LNAPL over a larger volume, reducing its saturation to below the level of at which it is mobile.

Vertical barriers to stop the lateral spread of LNAPL would need only to be of the form of a ‘hanging curtain’. That is, the barriers need only extend a relatively short distance below the water table to the bottom elevation of the LNAPL contamination in the profile. Practically, this would be only a short distance below the historical minimum of the water table. In this way a cut-off drain also acts as an effective barrier to lateral LNAPL movement. But in this case, LNAPL would have to be collected and removed from the drain. By comparison, barriers need to extend over the entire saturated thickness to stop the lateral movement of dissolved contaminants. Effectively, the barrier needs to be keyed into any underlying confining layer or aquitard. In the absence of such a feature, a deep hanging curtain barrier will reduce but not eliminate the dissolved contaminant flux. Similarly, a barrier to cut off lateral VOC movement needs to extend from the ground surface to below the water table.

**Remediation objectives and end points**

By effectively isolating the source LNAPL and interrupting the exposure pathways of VOCs and dissolved contaminants, physical containment addresses most of the concerns associated with the presence of the LNAPL. Where low permeability barriers are used, their permeability may be designed to reduce contaminant fluxes in air and groundwater to required remediation end points. Concentrations may not be reduced but the lower fluxes may allow natural attenuation to more rapidly reduce concentrations.

Remediation objectives related to societal and business factors concerns may not necessarily be addressed by physical containment. Objectives related to intergenerational equity are unlikely to be met. In fact, isolation and containment is likely to increase the longevity of the LNAPL contamination.

**Physical setting**

Other than for the control of VOCs, physical containment is generally directed to the saturated zone. Shallow applications are favoured. Aquifer materials of low strength are suited to driven sheet piles. Where trenching is used for cut-off walls, cohesive or consolidated materials offer the advantage of increased stability of the excavation allowing easier and more reliable emplacement. However, consolidated materials and particularly fractured hard rocks are hard to excavate. Surface and subsurface infrastructure can be a major impediment to the application of this technology. Physical containment is applicable to all LNAPL types.

**Associated issues and impacts**

While this technology offers immediate isolation of the LNAPL, effects on existing dissolved contaminant plumes will be delayed. Faster response times would be expected for VOCs emanating from the LNAPL. Health and safety concerns would arise through the use of heavy equipment for the excavation and emplacement of the barriers; exposure to contaminated materials and VOCs during the emplacement; and hazards related to the geotechnical stability of trenches that may be excavated. Where driven sheet piling is used, noise and vibration may be on-site hazards as well as being...
a nuisance to neighbouring communities. Trenching and emplacement can be a large energy user and therefore CO₂ producer. Overall costs may be large.

References
USACE 1994; US EPA 1998

E.2.2 Hydraulic containment

Process
The objective of hydraulic containment is to manipulate the water table gradients so that lateral LNAPL movement is controlled. The water table is manipulated by extracting groundwater and/or injecting water into the aquifer. Where groundwater is extracted from within the area of the LNAPL plume, the cone of depression produced in the water table will direct the movement of mobile LNAPL to the centre of the cone of depression. The spreading of the LNAPL plume will cease while water table gradients at the boundary of the plume are directed internally to the plume. Injection of water outside the LNAPL plume may also reverse gradients that are driving the lateral movement of LNAPL, thus preventing its continued spread. Placement of a number of injection wells may be needed to produce the geometry of the water table required for the desired effects on LNAPL movement. In the case of groundwater extraction, the pumping would also control the plume of dissolved contaminants from the LNAPL.

Remediation objectives and end points
This technology is specifically targeted for remediation objectives associated with the concern over a spreading LNAPL plume. The potentially attainable remediation end point would be to stop the advance of the LNAPL plume. The generally fast response of the water table means that control of LNAPL spreading could be gained quickly. Where groundwater was extracted, the technology may also be applied where the objective of remediation was to control the exposure to dissolved contaminants. In some cases, this hydraulic containment may meet objectives related to societal and business factor concerns. Since LNAPL is not removed from the aquifer, and LNAPL contamination remains within the original area of the plume, objectives associated with other concerns are not addressed. However, hydraulic containment may be very suitable as a precursor to the application of other remediation strategies.

Physical setting
Hydraulic control is applicable to the saturated zone and is not limited by LNAPL type. This control measure is best applied where the radius of influence of the groundwater extraction and water injection is large relative to the size of the LNAPL plume. This would minimise the number of wells needed for the control. Higher permeability aquifers would be most suitable in this regard. However, higher permeability carries the drawback of large pumped volumes of water. Because the pumping wells could be made relatively unobtrusive, it would find advantages in areas with appreciable above- and below-ground infrastructure.
**Associated issues and impacts**

An ongoing waste stream of contaminated groundwater is a significant issue to be faced where containment is achieved through groundwater extraction. In the case of water injection, there is a potential for creating a larger flux of contaminated groundwater which either spreads within the aquifer or is extracted as part of the containment. Because there is no LNAPL removal other than through dissolution, pumping will need to continue over long times to maintain control. This would accumulate high operating and energy costs. Without addressing the removal of the LNAPL contaminant, this technology may find it difficult to gain acceptance and would likely not be viewed as a sustainable remediation.

**E.3 Free-LNAPL recovery**

*E.3.1 Interceptor trenches*

**Process**

A high permeability material infilling an excavated trench allows the interception and removal of LNAPL through pumping from the trench. Its function is analogous to collection and pumping from a well but allows an extensive linear interception feature. The high permeability means that liquids including the LNAPL are attracted to it. Liquid levels in the trench may be manipulated to enhance fluid flow to the trench. Where LNAPL does not exist down gradient, the trench could act as a barrier to flow provided the LNAPL does not accumulate in the trench.

One of the significant advantages of an interception trench is its linear geometry. This is compared to the point collection of fluids from a vertical well.

**Remediation objectives and end points**

Interceptor trenches find application where the remediation objectives are to stop the continued spread of LNAPL and remove mobile LNAPL from the aquifer. The natural end point for the remediation (under favourable conditions) is for LNAPL to be reduced to residual and entrapped saturations in the aquifer. In this instance LNAPL would be absent from wells screened across the water table which may be a sufficient end point for objectives associated with societal and business factors. Otherwise, LNAPL may continue to appear in screened wells but with limited transmissivity or potential to spread.

**Physical setting**

Conceivably, an interceptor trench may be placed in the full range of hydrogeological settings but the depth of the water table would be an important criterion. It may also offer advantages in lower permeability materials, fractured and dual-porosity materials where flow to a well is limited or connectivity of the conducting pore system is problematic. The likely low permeability of the materials would lead to long times for LNAPL recovery but would not diminish effectiveness in intercepting and preventing the spread of free LNAPL.

Trenches target free LNAPL in the capillary fringe/near-water table zone of the aquifer. The technology would have particular application to triggers of the LNAPL being either mobile or spreading within the aquifer.
Associated issues and impacts

Because of the need for significant excavation, application of trench technology may be limited by surface and subsurface infrastructure. It also has the potential to be expensive in some settings. Although the natural end point for such hydraulic recovery is to residual and entrapped saturations in the aquifer, these may only occur over long time frames (particularly without drawdown of water levels in the trench) which will be influenced by the aquifer characteristics. Final disappearance of LNAPL from monitoring wells may be ultimately dependent on other mass loss or vertical spreading processes. LNAPL that collects in the trench may also pose an explosion risk through the presence of vapours. The presence of the trench may also create a pathway for the exposure to VOCs.

References

Charbeneau et al. 1999, 2000

E.3.2 Skimmer-well recovery

Process

Skimmer pumps selectivity recover LNAPL when placed in a well (or similar situation) where LNAPL floats on the surface of the water. The intake to the pump floats at the LNAPL-water interface and enters through a hydrophobic filter or orifice located a small distance above the interface. A pneumatic collection and discharge pump connected to the intake recovers the LNAPL. In another variation, a system that senses the presence of LNAPL may be used to control a fluid recovery pump.

Skimmer pumps recover free LNAPL that drains into the well. Recovery causes a drawdown in the LNAPL table at the well generally without affecting the elevation of the water table. The drawdown in the LNAPL table promotes LNAPL movement towards the recovery well but the magnitude of the drawdown possible is relatively small – limited to the LNAPL-water capillary pressure head.

Remediation objectives and end points

Skimmer pumps would be deployed where stopping the continued spread of the LNAPL and removal of the mobile fraction of the LNAPL were the remediation objectives. Removal of mobile LNAPL to the extent that its mobility and potential to spread is lowered below set levels would be a natural end point. Removal to the extent that LNAPL only remains at residual and entrapped saturations in the aquifer would be a most optimistic end point as hydraulic recovery cannot on its own reduce saturations to below residual and entrapped levels. To the extent that residual and entrapped saturations were achieved, this would mean the absence of LNAPL from wells screened across the water table, which in turn may meet some elements of the objectives and end points associated with societal and business factors.

Physical setting

Skimmer pumps may be applied to any hydrogeological setting that allows free drainage of LNAPL into a well. Thus it targets LNAPL from the capillary fringe/near water table zone. While highly permeable aquifers would suit the relatively small draw downs achievable, skimmer pumps are also commonly applied to situations where the
induced LNAPL inflow to the well is slow and recovery is expected over a relatively long duration.

Because it targets free LNAPL, skimming has particular application in response to concerns of the LNAPL being either mobile or spreading within the aquifer.

**Associated issues and impacts**

Skimming is a relatively low intensity technology and can be a slow recovery process. Proper maintenance of the skimmer is crucial to operation as it is often subject to fouling. Skimming may also have low efficiency in situations where LNAPL is not always present in the well. The low intensity of the recovery may not be adequate to control recent releases. In other situations, it may be difficult to reach an end point where the LNAPL is permanently at or below residual and entrapped saturations even locally around the recovery well.

**References**

Charbeneau et al. 1999, 2000

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**E.3.3 Single- and dual-pump recovery**

**Process**

Single- (total liquids) and dual-pump systems utilise the drawdown of the water table to enhance the lateral movement during the recovery of LNAPL from a well. Where a single total fluids pump (generally top loading) is set in a well below the water table elevation, both free LNAPL and water will enter the well and be non-discriminately collected and recovered by the pump. The dual-pump system uses a water-only pump set low in the well to recover groundwater at the same time that a skimmer or other type of hydrocarbon pump is set above the water pump to recover only LNAPL.

This technology enhances LNAPL recovery in four ways. Firstly, the lateral groundwater pressure gradients in the aquifer are imparted to the LNAPL producing much greater LNAPL pressure gradients than possible through skimming. Secondly, lowering the LNAPL table promotes the downward migration of mobile LNAPL to create a larger pool of free LNAPL that may enter the well. Thirdly, lowering the water table may at least temporarily allow greater capillary pressures within the aquifer in the vicinity of the well thereby increasing saturations and LNAPL relative permeability. Lastly, this technology acts as a pump and treat system where groundwater moving past the LNAPL in the aquifer dissolves soluble compounds which are then recovered. This is in addition to the recovery of already contaminated groundwater.

**Remediation objectives and end points**

As with other hydraulic recovery strategies, single- and dual-pump recovery systems would normally be instigated where the remediation was to meet objectives of stopping the continued spread of the LNAPL and removal of the mobile fraction of the LNAPL. The more aggressive processes compared to skimming means that removal of LNAPL to the extent that it only remains at or even below residual and entrapped saturations in the aquifer would be a more realistic end point. Dissolution of the soluble components of the LNAPL could drive LNAPL saturations below residual and entrapped saturations. The alternative end point of lowering the LNAPL’s mobility and potential to spread to
below set levels would be expected to be reached sooner than with skimming. In the case that LNAPL no longer appeared in wells or demonstrably had insignificant mobility, single- and dual-pump recovery may also meet some objectives and endpoints associated with societal and business factors. Capture of contaminated groundwater and controlling the spread of contaminated groundwater may also contribute to achieving objectives of eliminating toxic exposure to groundwater and surface water and to allowing the use of the groundwater resources for specified use.

Physical setting

Single- and dual-pump systems are most appropriately applied to hydrogeological settings where the hydraulic conductivity is not too high. This is mainly to avoid the treatment of large volumes of contaminated water. Even though draw downs may be small in high permeability settings, the relative permeability of the LNAPL would also be high allowing LNAPL recovery rates to be proportionately increased. However, situations where the LNAPL-contaminated interval has appreciably lower permeability than the underlying aquifer would be ones to avoid.

This remediation technology targets LNAPL from the capillary fringe/near water table zone. Because the processes are designed to transform mobile LNAPL into free LNAPL, this technology is not limited to where free LNAPL enters wells under natural conditions and is appropriate to where LNAPL may be ephemeral in wells.

Because it targets mobile and free LNAPL, single- and dual pump systems have particular application in response to concerns of the LNAPL being either mobile or spreading within the aquifer.

Associated issues and impacts

Several issues arise in single- and dual-pump recovery systems. For single-pump systems there may be issues related to the separation of the LNAPL and water for appropriate disposal of the recovered liquids. The production of contaminated water that needs appropriate treatment and disposal is an issue in both types of systems. Indeed the volumes of contaminated water created through pumping may need to be weighed against what may be created under natural conditions. Additionally, the recovery of groundwater and drawdown of the water table may impinge on the use of that resource remote for the site of contamination. A further issue is the vertical movement of LNAPL in response to the lowering of the water table. Where the water table is drawn down below historical levels, then the LNAPL would be expected to invade previously uncontaminated parts of the aquifer. This LNAPL would remain entrapped after the cessation of recovery and present a challenge to further remedial efforts.

References

E.3.4 Vacuum-enhanced recovery

Process

Vacuum-enhanced recovery is a system whereby a partial vacuum is applied to the recovery well. The partial vacuum is applied in either of two ways, thus creating two variants of this recovery technology. In the first variant, a partial vacuum is created by an air suction pump connected to the sealed well which may contain any configuration of liquid recovery pumps. In such systems, the suctions applied may be modest (<10 kPa), although significantly higher suctions may be applied in the case of fine textured materials. The second variant uses a drop tube (also called a straw or stinger) connected to an air suction pump with the end placed such that the liquids in the sealed well are drawn (or sucked) up by the air flow and recovered. This particular variant is sometimes called slurping or bioslurping. The suctions applied to produce the air flow velocity required to lift the liquids may be relatively high (>>10 kPa).

The partial vacuum applied to the well is transmitted through the well screen to the surrounding aquifer inducing a lateral gradient in the air pressure within the vadose zone and prompting air flow through the vadose zone to the well. These pressure gradients are also transferred to the LNAPL, enhancing its movement towards the recovery well. Moreover, by reducing air pressure in the aquifer, a greater fraction of the LNAPL may become free to drain into the well and be recovered. A further effect of lowering air pressures is to raise the elevation of the LNAPL and water tables (not to be confused with absolute fluid pressures) causing LNAPL and water to move upwards in the profile. This is seen as a counter to the downward displacement and further entrapment of LNAPL by water table draw down from groundwater extraction.

The induced air flow through the aquifer associated with vacuum-enhanced recovery introduces further elements of LNAPL removal – that of volatilisation and aerobic biodegradation. Thus these systems combine soil vapour extraction and/or bioventing systems with hydraulic recovery.

Remediation objectives and end points

As potentially the most aggressive free-LNAPL recovery techniques, vacuum-enhanced recovery systems are suited to the remediation objectives and end points associated with mobile and spreading LNAPL. Mass removal through volatilisation and biodegradation contributes further to preventing the future spreading of LNAPL in the subsurface. The hydraulic recovery of LNAPL that is not normally free as well as mass removal through enhanced volatilisation and biological degradation means that remediation end points of LNAPL saturations permanently below residual and entrapped saturations are potentially more achievable. Removal through volatilisation and biodegradation are important in this context as they are independent of the liquid hydraulics and can reduce LNAPL saturations to below residual and entrapped levels. The extraction of petroleum-vapour laden soil air would also contribute directly to meeting objectives on: abating the generation and accumulation of explosive vapours; and eliminating the toxic exposure to vapours in buildings and elsewhere. The associated end points of the non-accumulation of vapours above explosive limits and risks of inhalation to human health may well be reached. Further, the vacuum-enhanced recovery may indirectly address the objectives of eliminating the toxic exposure to LNAPL; eliminating toxic exposure to groundwater and surface water; and even potentially that of allowing the use of land, aquifer and groundwater resources for
specified uses. This would occur through the removal of volatile constituents with a high risk profile, effectively detoxifying the LNAPL. The extent to which exposure risk level end points would be achieved would be dependent on the nature and physical setting. No volatilisation of risk drivers would occur from within or below the capillary fringe limiting the potential of risk reduction in these cases.

**Physical setting**

Vacuum-enhanced recovery systems would be applicable to all those hydrogeological settings suitable for skimmer well, single- and dual-pump systems. However, vacuum-enhanced systems have further advantages in lower permeability settings because of the large air pressure gradients that may be developed.

This remediation technology targets LNAPL from the capillary fringe/near water table zone as well as the vadose zone. Because the processes are designed to transform mobile LNAPL into free LNAPL (by lowering air pressures as well as water pressures), this technology is not limited to where free LNAPL enters wells under natural conditions and is particularly appropriate to where LNAPL may be ephemeral in wells.

Because it targets mobile and free LNAPL, vacuum-enhanced recovery systems have particular application in response to concerns over the LNAPL being either mobile or spreading within the aquifer. In addition, it may be specifically applied to concerns associated with LNAPL in soils and the generation of vapours.

**Associated issues and impacts**

The issues associated with vacuum-enhanced recovery are similar to those of single- and dual-pump recovery – production of contaminated groundwater, separation of LNAPL and water, and effects on the groundwater resource off-site. Separation of the LNAPL and water is often more difficult when slurping. In addition, enhanced biological activity by aeration commonly increases the frequency of the fouling of pumps. In the case of highly volatile LNAPLs such as fresh gasoline, most of the LNAPL may be volatilised during recovery. This may avoid problems in separating LNAPL and water.

However, a major issue is the generation of volatile organic compounds and almost certain need to remove them from the exhaust air stream. Volatile organic compounds are generated from volatilisation within the aquifer and from the recovered fluids in their passage through the recovery equipment. Treatment of the exhaust gases can be financially expensive and resource intensive as well as having attendant health and safety risks.

**References**

**E.3.5 Water flooding**

**Process**

Water flooding is an enhancement of the single- and dual-pump recovery process. Injection of water at the same time as groundwater extraction further increases hydraulic gradients towards the LNAPL recovery well. These increased hydraulic gradients promote a greater driving force behind the movement of LNAPL towards the recovery well than would be achieved by draw down of the water table at the LNAPL recovery well on its own. The increased water pressures around the injection well provide a positive LNAPL displacement process, decreasing LNAPL towards entrapped saturations. The injected water may also be heated to reduce the viscosity and interfacial tensions of the LNAPL and thereby improve its recoverability. Although hot water flooding has a reasonably long history in oil reservoir engineering, hot water flooding for LNAPL remediation is an emerging remediation technology. Injection and extraction schemes may be of varying geometries to suit the distribution of LNAPL in the subsurface. For example, a repeated multi-spot injection and extraction pattern may be repeated over the area of an extensive LNAPL plume. Lines of injection and extraction wells may be placed either side of an elongated plume. The extracted groundwater may be reinjected with or without treatment. Groundwater extraction and LNAPL recovery would be most efficiently undertaken in the dual-pump mode (i.e. separate pumps for groundwater and LNAPL) where groundwater was to be reinjected. This would assist in the treatment and handling. Balanced injection and extraction schemes would avoid a waste stream of contaminated groundwater. However a scheme where extraction was greater than injection may avoid spreading LNAPL higher in the profile around the injection well as well as providing some control over the LNAPL and dissolved contaminant plume. This would be at the expense of possibly greater downward spreading of the LNAPL around the recovery well and the creation of a waste stream that would need disposal.

**Remediation objectives and end points**

Water flooding would be used to counter concerns over the presence of mobile and spreading LNAPL. It would be applied to meet objectives of stopping the continued spread of the LNAPL and removal of the mobile fraction of the LNAPL. The end point of the recovery would be LNAPL at or even below residual and entrapped saturations in the aquifer. Some reductions below entrapped saturations may be achieved through dissolution of the soluble components of the LNAPL particularly in this case with recirculation of the groundwater. The volume fluxes of groundwater flushed through the LNAPL would have greater potential for dissolution than for the single- and dual-pump recovery. The injection/extraction scheme is similar to that of a pump and treat system. The greater hydraulic gradients and reduced viscosity when heated water is used would be expected to reduce the time needed to reach specified end points. For instance, end points of lowering the LNAPL’s mobility and potential to spread to below set levels would be expected to be achieved sooner. In addition, end points of reduced LNAPL mobility and elimination of the appearance of LNAPL in wells could match those remediation objectives associated with societal and business factors concerns. Remediation objectives related to reducing or eliminating concerns over dissolved contaminants would only be addressed in the case of there being a net extraction of groundwater. Similarly, net extraction of groundwater would be required for this
technology to contribute to remediation objectives of allowing the use of the groundwater resources for specified use.

**Physical setting**

Water flooding is applicable to the saturated zone and the LNAPL present in the capillary fringe to the water table. Little benefit is likely in attempting to address LNAPL appreciable above the capillary fringe where LNAPL should be close to or below entrapped saturations in any case. Materials with moderate hydraulic conductivity are probably best suited to the technology because the volumes of water needed to be injected and extracted would be more easily handled. LNAPL recovery in high permeability materials should also be effective but at the cost of having to pump greater volumes of water to achieve required hydraulic gradients. However, the efficiency (particularly the rate) of LNAPL recovery on the aquifer permeability, hydraulic gradients and required pumping rates needs to be further documented. Low permeability materials would have a reduced radius of influence that would entail appreciably greater numbers of wells and associated infrastructure. Heterogeneous aquifers may not be so suitable with the possibility of bypassing and entrapment of LNAPL in the aquifer. Low permeability confining layers above the capillary fringe and LNAPL contamination would offer advantages, however. Restriction of the upward movement of LNAPL by such layers during water injection could prevent undesirable vertical redistribution of the LNAPL and improve the efficiency of the displacement process. The use of heated water offers advantages in remediating viscous LNAPLs compared to other free-LNAPL recovery methods. The effects though would not be as strong as chemical flushing technologies, but potentially at a lower cost and effort. The presence of above- and below-ground structures may not be so restrictive in the application of water flooding when compared to some other remediation techniques.

**Associated issues and impacts**

An issue that arises with water flooding is the possible spreading of LNAPL into uncontaminated parts of the aquifer. Mounding around injection wells has the potential to vertically displace the LNAPL higher into the vadose zone. Equally, drawdown around the extraction well will allow LNAPL to move downwards and be entrapped deeper below the water table. Considerate design of the pumping rates may be able to minimise these effects. Many issues arise over the handling and treatment of the extracted groundwater. The need to treat the groundwater before being re-injected needs to be evaluated, including regulatory requirements. Re-injection of untreated groundwater would offer cost advantages but careful assessment would be required of the overall effect on the flux and distribution of contaminated groundwater in the aquifer. Increased exposure to dissolved contaminants and further loss of beneficial use of the groundwater resource would need to be avoided. If fresh groundwater from an uncontaminated aquifer (or part of the same aquifer) is used, then this use of the groundwater may also affect beneficial use of the aquifer in question. Other issues related to the handling and treating of the recovered LNAPL and groundwater would be similar to those of the other free-LNAPL recovery methods. Enhanced costs of treatment would be anticipated where heating of the injected water was undertaken. This is likely to increase energy use and impact on the overall environmental benefit.

**References**

Fulton et al. 1991; ITRC 2009a; O’Carroll & Sleep 2007, 2009; US EPA 2000
E.4 Volatilisation and biodegradation

E.4.1 Soil vapour extraction and bioventing

Process

In soil vapour extraction and bioventing, air is drawn through the vadose zone to volatilise and aerobically biodegrade LNAPL in the vadose zone. The advective flux of air increases the rate of volatilisation greatly over that of the natural situation which is limited by diffusion. In addition, the advective air flux provides oxygen directly to the LNAPL rather than relying on diffusion from the ground surface. Particular remediation systems may be designed to achieve a particular balance between volatilisation and biodegradation. Some applications of bioventing have injected air into the subsurface. Passive bioventing systems, which rely on barometric pressure variations and wind turbines, have also been instituted.

Remediation objectives and end points

As vadose-zone based remediation technologies, soil vapour extraction and bioventing are primarily used where the objectives are to eliminate toxic exposure to LNAPL in soil and allow the use of the land resources for a specified use. For many types of petroleum hydrocarbons, essentially complete removal of the LNAPL may be possible admitting end points where exposure risks and mass contents are below required levels. The soil vapour extraction may be more effective in targeting particular risk drivers where they are more volatile than the LNAPL as a whole, alleviating the need for total mass removal to risk targets and avoiding complications of the toxicity or of some specific risk drivers to soil microflora. Soil vapour extraction would also be employed for the specific objectives of abating the generation and accumulation of explosive vapours as well as eliminating the toxic exposure to vapours in buildings and other structures. A secondary benefit of soil vapour extraction and bioventing remediation strategies would be through reducing LNAPL mobility in the vadose zone. This follows directly through reductions in LNAPL saturation. However, they would not be considered as an emergency or rapid response to the release of LNAPL into the subsurface. Further indirect benefits would accrue from soil vapour extraction and bioventing through the removal of soluble components that may present concerns over toxic exposure to some dissolved constituents and the beneficial use of groundwater resources.

Physical setting

Soil vapour extraction and bioventing are better suited to unconsolidated sandy materials with efficiencies expected to decline as the materials become finer textured. Secondary porosity in such materials may assist. The application is limited to the vadose zone where there is adequate air permeability and therefore largely targets residual LNAPL and some of the mobile LNAPL. Some schemes have purposely exposed LNAPL in the capillary fringe and below the water table using water table drawdown.

The technologies could specifically be considered where the concerns for remediation are the generation of vapours and presence of LNAPL in soils. Soil vapour extraction would often be a first response where explosive vapours needed to be controlled and risks from the inhalation of vapours.
Higher volatility LNAPLs such as gasoline are particularly suited to remediation by soil vapour extraction whereas middle-distillate and heavier petroleum hydrocarbons are more thoroughly addressed with bioventing.

**Associated issues and impacts**

A major consideration in the application of soil vapour extraction and bioventing systems is the likely need for treatment of the extracted air to remove the volatile hydrocarbons. Treatment has attendant issues of cost, and resource utilisation, as well as the process having health and safety aspects. Where air is injected into the subsurface for bioventing, it may be difficult to control the vapours that are generated and a complementary soil vapour extraction system would generally be required.

With bioventing, nutrients, water and temperature may also control rates of biodegradation as well as the supply of oxygen. Rates of removal of the LNAPL may be low without suitable amendment. In many cases, it may be cost effective to rely on natural conditions, although the need for amendment should be considered in respect to the required timing for remediation objectives.

Where groundwater is extracted as part of this remediation approach, issues of further contamination of groundwater, cost and resource utilisation associated with necessary treatment and effects of off-site groundwater resources need to be considered.

**References**


**E.4.2 Air sparging and biosparging**

**Process**

Air sparging and biosparging are an extension of soil vapour extraction and bioventing approaches to remediation below the water table. Air sparging entails injecting air into the saturated aquifer through a well screened below the water table. As the injected air moves through the aquifer below the water table, volatile components are stripped from the LNAPL while oxygen is delivered to aquifer microflora to use in degrading the LNAPL. The instability of air flow below the water table makes for complex (channelling for instance) and often hard to predict aeration of the formerly saturated zone – rendering the air sparging treatment less efficient than that in the vadose zone. Heterogeneity in the subsurface may also have a profound effect on the air distribution. The operation of spargling systems may be adjusted to emphasise either the volatilisation or biodegradation aspects of removal. High air injection pressures and flow rates favour greatest treatment zones and highest removal rates. However, high air injection rates tend to produce a large flux of volatile components that would generally need to be captured and treated by a soil vapour extraction system. Lower air injection rates may allow the generated volatile compounds (as well as the LNAPL) to be degraded in the subsurface thus avoiding the need for collection and treatment of fugitive vapours.
Remediation objectives and end points

The remediation objectives of air sparging and biosparging would generally include those based on mass reduction as well as those directed towards risks from specific components of the LNAPL. In terms of the reducing mobility of the LNAPL, air sparging would only normally be considered where the LNAPL saturation in the aquifer was already near residual and entrapped levels. Further mass loss below these levels through volatilisation and biodegradation would therefore contribute to the achievement of remediation objectives of preventing the future spread of LNAPL in the subsurface and potentially some specific objectives arising from societal and business concerns. However, the preferential removal of volatile constituents of the LNAPL contributes to more specific risk-based objectives such as abating the generation and accumulation of explosive vapours and eliminating toxic exposure to vapours. Where the more volatile components also present a specific risk in the dissolved phase, air sparging would also assist with meeting objectives of eliminating the toxic exposure to groundwater and surface water as well as allowing the use of the groundwater resources for specific uses. The relevant end points in these vapour- and groundwater-based objectives could potentially be achieved without the total removal of the LNAPL mass.

Physical setting

Air sparging systems are most frequently applied to unconsolidated sandy materials. The lateral distribution of air below the water table in uniform sands, particularly coarse sands, may be little more than a couple of metres. However, layering (both finer and coarser textured materials) above the depth of air injection can cause appreciable lateral spreading of air, but generally at the cost of a loss in the efficiency of removal. Finer textured and dual porosity materials are less frequently considered as suitable for air sparging. This is because of the difficulty of displacing liquids from the materials and the channelling of air flow through a small volume of the subsurface. In cases, this may still be of advantage because the same parts of the porous materials occupied by the LNAPL will be that preferentially accessed by the air. However benefits may be disguised because of the large mass of dissolved constituents poorly accessed in the finer textured matrix. A similar scenario may prevail for fractured rock aquifers where sparged air would be forced into intimate contact with LNAPL also in the fracture network. Access of the air to the LNAPL may not be assured, however, because of limited connectivity of fractures and the secondary porosity in case of dual porosity materials.

Air sparging is arguably one of the few LNAPL remediation strategies that addresses LNAPL present below the water table, in the capillary fringe/near water table zone and the vadose zone. It can potentially be applied to a wide range of concerns. It would not be considered for addressing spreading LNAPL and would generally be considered as a follow up to free-LNAPL recovery.

Higher volatility LNAPLs such as gasoline are particularly suited to remediation by air sparging. Middle-distillate petroleum hydrocarbons are candidates for biosparging where the generation of volatile compounds may be within the assimilative capacity of indigenous microorganisms in the vadose zone.
**Associated issues and impacts**

The control and treatment of generated volatile organic compounds via a soil vapour extraction is generally required. Such treatment has attendant issues of cost and resource utilisation, as well as having health and safety aspects.

Removal rates through volatilisation may initially be high due to the LNAPL spreading on the air interface created in the saturated zone. However, mass transfer limitations may be appreciable for entrapped LNAPL, particularly where channelling of air flow occurs.

Nutrients and temperature may also control rates of biodegradation in addition to the supply of oxygen. Removal rates of the LNAPL through biodegradation therefore may be low without suitable amendment. The need for amendment needs to be considered in respect to the timing to achieve remediation objectives.

**References**

Benner et al. 2002; Johnston et al. 2002a, 2008a

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**E.5 Engineered bioremediation**

**E.5.1 Engineered bioremediation**

**Process**

In this instance, engineered bioremediation is a generic term for any in situ technique focused on degrading the LNAPL through enhanced biological activity. The underlying principle is to engineer the delivery of amendments and, in very rare instances, specialist microorganisms to the LNAPL in order to remove the LNAPL by a process of biodegradation. Bioventing and biosparging are specific forms of engineered bioremediation that focus on gaseous oxygen delivery for aerobic bioremediation. More generally, molecular oxygen in gases or aqueous phases may be added for aerobic biodegradation. Alternatively, other electron acceptors such as sulphate and nitrate may be added for anaerobic biodegradation. A feature of engineered bioremediation is the addition of nutrients and other amendments as well as other manipulation of the subsurface environment (such as temperature manipulation) to optimise biological activity. An example would be land farming for contaminated surface soils. Systems for delivery of amendments at greater depths in the vadose zone and saturated zone are possible. In some approaches, biodegradation promoted in the water phase enhances dissolution of constituents from the LNAPL leading to a greater rate of removal.

**Remediation objectives and end points**

Engineered bioremediation would generally be used as a tertiary LNAPL mass removal strategy with remediation objectives of: preventing the future spread of LNAPL in the subsurface; allowing the use of the land, aquifer and groundwater resources for beneficial use; and those objectives around societal and business factors. The biodegradation is a discriminatory process with sequential and preferential removal/transformation of biodegradable constituents of the LNAPL. The sequence and preference for degradation may not correspond to risk drivers that may be specific targets of other remediation objectives. Indeed there may be a negative correlation between biodegradability and toxicity to human health as well as the greater
environment. Nevertheless, biodegradation is often observed to reduce the LNAPL saturation and specific constituent contents to levels where risk end points may be reached.

**Physical setting**

By their nature, engineered bioremediation schemes attempt to develop methods specifically tailored to a particular setting. However, a fundamental aspect is the efficient delivery of amendments through a carrier fluid (gas and/or water) meaning that finer textured and dual porosity materials, as well as those with a high degree of heterogeneity, pose appreciable challenges. Fractured rock aquifers would also normally not present a sufficient LNAPL-water contact area for high biodegradation rates. Particular schemes may be targeted to all areas of the profile – from the vadose zone to the saturated zone. Enhanced bioremediation would generally be considered in response to concerns over aesthetics and nuisance, LNAPL in soils and sediments and LNAPL in contact with groundwater. It would not be suited to responding to triggers of spreading or mobile LNAPL. Rather, it would be used after attempts at hydraulic recovery. And it is suited to addressing middle-distillate and heavier petroleum hydrocarbons.

**Associated issues and impacts**

A number of issues may arise through the use of amendments and carrier fluids in addressing the LNAPL pollutants. Some of the amendments such as nutrients may need to be controlled themselves to avoid adverse impacts on groundwater and receiving environments for instance. The carrier fluids for the amendments may also cause displacement of the LNAPL, potentially spreading the contaminant or adding to the dissolved constituent flux in groundwater and soil atmosphere if not controlled. Biodegradation is likely to be a relatively slow removal process and recalcitrant compounds may remain.

**References**

Davis et al. 1998; Seagren et al. 2002

**E.6 Chemical flushing**

**E.6.1 Surfactant flushing**

**Process**

In surfactant flushing, chemicals that are active at the interface between water and LNAPL are injected dissolved in water to deliberately mobilise the LNAPL. The surfactants reduce the interfacial tension and thereby reduce the capillary trapping of LNAPL in the porous materials. This enables the hydraulic recovery of the mobilised LNAPL. Where concentrations of the surfactants are optimised, micelles are produced which converts the LNAPL to a dispersed phase in the water (emulsion). Thus the LNAPL may be removed by the extraction of the water through pumping. Usually, a total liquids pump would be used to accommodate both groundwater and mobilised LNAPL.
Remediation objectives and end points

Surfactant flushing achieves remediation objectives through LNAPL mass reduction and does not target specific risk drivers within the LNAPL. Thus the remediation end points for specific risks from volatile and dissolved constituents would need to be assessed around issues of required mass reduction to produce acceptable concentrations and fluxes. In this regard, the LNAPL saturations remaining after surfactant flushing may be extremely low. Based on the amount of reagent necessary, surfactant flushing would be applied where the LNAPL was already around residual/entrapped saturations in aquifers. As such, it may not be a particularly efficient means of preventing the future spread of LNAPL in the subsurface. However, it still may be very effectively applied to meet objectives of allowing the use of land, aquifer and groundwater resources for specified use.

Physical setting

As with other flushing technologies, surfactant flushing is most often applied to unconsolidated sandy materials where fluid displacement is most efficient. Surfactant flushing may also be effective where LNAPL resides in finer textured materials provided heterogeneity and the presence of secondary porosity does not diminish the flushing efficiency too adversely. At least in principle, surfactant flushing could be effective in fractured rock aquifers given sufficient fracture connectivity. Surfactant flushing would most usually be applied to LNAPL in the capillary fringe and below the water table and, potentially, shallow vadose zones. The need for extraction of the flushing solution and mobilised LNAPL would make addressing LNAPL in deep vadose zones more problematic. The injection and extraction scheme would also need to be carefully designed to target LNAPL in and immediately above the capillary fringe where wells were used rather than vertical infiltration of a surfactant solution. A wide range of LNAPL petroleum hydrocarbons may be addressed through surfactant flushing. The technology could be used for most of the concerns for remediation save for that of a spreading LNAPL.

Associated issues and impacts

The addition and extraction of surfactant solutions raise a number of issues related to associated effects on the groundwater and the aquifer. Treatment of extracted fluids is another critical issue. For instance, the injection and extraction system needs to be engineered to insure capture of the surfactant (which may pose its own risks) and mobilised LNAPL. Effects of the surfactants on the indigenous microbial communities may need to be assessed where it is planned to rely on natural biodegradation processes after LNAPL recovery. Manipulation of the groundwater system may also produce further mobilisation and entrapment of LNAPL remote from the immediate site of the flushing. A key issue is the treatment and ultimate disposal of the produced liquids – potentially a mixture of groundwater, water-LNAPL emulsion and LNAPL. For this, there are attendant issues of cost and resource utilisation, as well as having health and safety aspects.

References

Chevalier 2003; Couto et al. 2009; Falta et al. 1999; Jayanti et al. 2002; Londergan et al. 2001; Palomino & Grubb 2004
E.6.2 Co-solvent flushing

**Process**

Co-solvent flushing increases the solubility of LNAPL or its constituent components. The solubilised LNAPL may then be removed through pumping of groundwater. Most commonly, alcohols are used as co-solvents. In addition, some co-solvents such as alcohols would decrease the viscosity of LNAPL making it more amenable to hydraulic recovery.

**Remediation objectives and end points**

Co-solvent flushing follows a slightly different process to that of surfactants. Because it is based on the dissolution of individual constituents in the LNAPL it may be used to reach end points where soluble constituents are targeted for reduction without needing total LNAPL removal. However, co-solvents, like surfactants, also provide a means of reducing the total LNAPL mass. Hence they may directly address the remediation objectives of preventing the future spread of LNAPL (although co-solvents would generally be used where LNAPL was already removed to around residual and entrapped saturations), allowing the use of the land, aquifer and groundwater resources to be used for beneficial use and those related to societal and business factors. In many instances, the degree of LNAPL removal expected to be attained would be sufficient to reach specific risk based end points such as those related to the toxic exposure to the LNAPL, accumulation of explosive vapours, exposure to toxic vapours, and exposure levels for dissolved constituents.

**Physical setting**

The physical setting for the use of co-solvents is essentially the same as that for surfactants. That is, predominantly simple hydrogeology where flushing is reasonably efficient, and is addressing LNAPL below the water table, in the capillary fringe and shallow vadose zones. A large range of LNAPL petroleum hydrocarbons could be addressed for most LNAPL triggers. An exception may be the deliberate treatment of high viscosity LNAPL to increase the potential for hydraulic recovery.

**Associated issues and impacts**

Co-solvent flushing has similar issues and potential impacts as surfactants in regard to effects on the groundwater and aquifer along with the treatment of the extracted liquids.

**References**

Imhoff et al. 1995; Rao et al. 1997; Sabatini et al. 1996; Simpkin et al. 1999

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E.7 Chemical oxidation

**E.7.1 Hydrogen peroxide and Fenton’s reagent**

**Process**

Hydrogen peroxide ($\text{H}_2\text{O}_2$) and Fenton’s reagent (a mixture of $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ salts) are used to chemically oxidise hazardous organic compounds in water treatment systems. A similar approach can be used for the in situ oxidation of dissolved petroleum hydrocarbons and the source LNAPL. Treatment solutions would typically be injected through wells or an infiltration gallery. Hydrogen peroxide is a strong oxidant and the
presence of \( \text{Fe}^{2+} \) improves the kinetics of the oxidation process. The reaction kinetics of direct oxidation by \( \text{H}_2\text{O}_2 \) is slow relative to the rate at which it decomposes reducing the efficiency of the process. Ferrous iron in solution reacts with the hydrogen peroxide to form hydroxyl free radicals – as part of a chain-propagating reaction (under favourable conditions). Modified systems may use chelating agents to stabilise the \( \text{Fe}^{2+} \) or use heat instead of \( \text{Fe}^{2+} \) for activation to produce hydroxyl free radicals. The oxidation can lead to the complete mineralisation of petroleum hydrocarbons or produce lower molecular weight organic compounds that are more amenable to biodegradation. Because of the stoichiometry of the oxidation reaction large amounts of \( \text{H}_2\text{O}_2 \) may be required in addressing LNAPL. Hence the aim of the remediation may be to transform recalcitrant compounds to ones more readily biodegraded or to enhance the dissolution of the LNAPL by reducing aqueous phase concentrations. In a variant of the Fenton’s chemistry, calcium peroxide (\( \text{CaO}_2 \)) may be used instead of \( \text{H}_2\text{O}_2 \).

**Remediation objectives and end points**

Although \( \text{H}_2\text{O}_2 \) and Fenton’s reagent are capable of oxidising the complete LNAPL mass, cost and health and safety issues would mostly dictate that it would not be used for the objectives addressing LNAPL at high saturation in the subsurface (such as preventing the future spread of LNAPL). These remediation technologies are more naturally suited to addressing the objective of eliminating the toxic exposure to groundwater and surface water. This is because the \( \text{H}_2\text{O}_2 \) and Fenton’s reagent oxidise the dissolved petroleum hydrocarbons in groundwater as well as the LNAPL meaning that end points requiring stringent dissolved constituent concentrations and fluxes may be achievable. Other specific risk-based end points associated with the toxicity of the LNAPL, toxic exposure to vapours and generation of explosive vapours may also be achievable because of the very low LNAPL saturations that may be reached under favourable conditions.

**Physical setting**

The need for intimate contact between the oxidising solution and the target LNAPL suggests that settings where solution delivery is not overly complicated by heterogeneities and low permeabilities are most appropriate. Unconsolidated sandy and other granular materials would offer potential for effective treatment. The ability for the oxidant to diffuse into lower permeability parts offers hope that more heterogeneous and dual porosity materials may benefit from such treatment. Hydrogen peroxide and Fenton’s reagent may also be effective in fractured rock settings subject to important caveats regarding the connectivity of fracture networks and predictability of flow. Aquifers with appreciable soil organic carbon would be less suitable for in situ chemical oxidation using \( \text{H}_2\text{O}_2 \) and Fenton’s reagent. Also, reduced minerals in the aquifer (such as sulphides) would add to the natural oxidant demand and reduce effectiveness. LNAPL within the liquid-saturated part of the aquifer would most usually be targeted and special hydraulic engineering (infiltration galleries or groundwater mounding) may be required to access LNAPL immediately above the capillary fringe. Treatment in the vadose zone by infiltration of \( \text{H}_2\text{O}_2 \) and Fenton’s reagent solutions would also be possible subject to the ability to recover any unspent solution and by products where necessary. Also, a wide range of LNAPL petroleum hydrocarbons may be addressed.
Associated issues and impacts

In the use of Fenton’s reagent, favourable hydro-geochemical conditions need to be maintained in the subsurface for efficient treatment. For instance, appropriate concentrations of \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \) need to be maintained and the oxidation is favoured by low pH conditions and a particular temperature range. Maintenance of favourable conditions and maximum efficiency may be difficult. Natural organic matter may also lessen the efficiency of the treatment through its non-discriminate oxidation. The presence of hydroxyl scavengers such as carbonates and dissolved metals (including \( \text{Fe}^{3+} \)) will also reduce efficiency and terminate chain reactions of hydroxyl production. Oxidation of reduced metal sulphides in the aquifer has the potential to release toxic metals such as arsenic into groundwater. An important issue is the endothermic nature of the oxidation and there is potential for the explosive generation of gases. Health and safety issues would arise generally in the use of such a strong oxidising agent. Cost would also be a major consideration in the use of \( \text{H}_2\text{O}_2 \) and Fenton’s reagent. As with all flushing technologies, control of the impacts of the remediation on the aquifer and groundwater need to be maintained. Heating may increase the generation of VOCs and these may need to be controlled in the vadose zone. A particular issue is the creation of oxidation products.

References

ITRC 2005; Jonsson et al. 2006; Mater et al. 2007; Neyens & Baeyens 2003; Tsai et al. 2009); US EPA 2004

E.7.2 Permanganate

Process

Permanganate supplied as either the potassium (\( \text{KMnO}_4 \)) or sodium (\( \text{NaMnO}_4 \)) salt is another strong oxidising agent that can be used for the in situ chemical oxidation of organic compounds. \( \text{KMnO}_4 \) is more commonly used and has been most intensively studied in relation to DNAPLs and may have some applicability to the situation of LNAPLs. It is generally used because of its ability to break carbon-carbon double bonds but is generally unable to attack aromatics and saturated aliphatics. This makes its application to LNAPL petroleum hydrocarbons questionable. The application of the potassium permanganate treatment solution would be similar to that of Fenton’s reagent – through wells or infiltration galleries. Potassium permanganate is slower reacting in the subsurface compared to \( \text{H}_2\text{O}_2 \) and Fenton’s reagent offering advantages in its wider distribution and lesser infrastructure requirements.

Remediation objectives and end points

The similarity of the underlying process in using \( \text{KMnO}_4 \) to that of \( \text{H}_2\text{O}_2 \) and Fenton’s reagent mean that it would be used to attain similar remediation objectives and end points. Potassium permanganate would most usually be applied to eliminating the toxic exposure to dissolved LNAPL constituents groundwater and surface water through their oxidation in the LNAPL and aqueous phases. However, \( \text{KMnO}_4 \) is not generally considered capable of oxidising benzene and polyaromatics. The very low LNAPL saturations that may be reached under favourable conditions would also mean that specific risk-based end points associated with the toxicity of the LNAPL, toxic exposure to vapours and generation of explosive vapours may also be achievable. The
objectives requiring large reductions in LNAPL saturation would be less efficient. In particular, KMnO$_4$ would not normally be considered for the objective of preventing the future spread of LNAPL.

**Physical setting**

Potassium permanganate would offer the greatest potential for effective treatment in granular, particularly sandy, materials where the delivery of the solution is not overly complicated by heterogeneities and low permeabilities. The diffusion of the KMnO$_4$ into lower permeability parts of the aquifer could mean that more heterogeneous and dual porosity materials may be beneficially treated. Again, subject to important caveats regarding the connectivity of fracture networks and predictability of flow KMnO$_4$ may potentially be effective in fractured rock settings. The effectiveness of the KMnO$_4$ would be expected to diminish as the soil organic carbon and reduced mineral content of the aquifer increased. LNAPL below the water table and within the capillary fringe would most usually be targeted. LNAPL immediately above the capillary fringe would require special hydraulic engineering to be accessed. Infiltration of the KMnO$_4$ solution would also be possible to treat other parts of the vadose zone. However, this would be subject to the ability to recover any unspent solution and by-products where necessary. Also, a wide range of LNAPL petroleum hydrocarbons may be addressed although its inability to oxidise benzene may limit its application to gasoline-range products.

**Associated issues and impacts**

An important issue with the use of KMnO$_4$ is the insoluble oxidation product MnO$_2$. Not only does this have the potential to clog the aquifer and reduce permeability, but it also has the potential to encapsulate the LNAPL source, reducing mass transfer rates and possibly isolating the LNAPL from further treatment. While laboratory studies have demonstrated such effects, some field-based studies have also shown little evidence of such adverse effects. It should be noted that there has been limited application of this remediation technology to LNAPLs. Again, control of the impacts of the remediation on the aquifer and groundwater need to be maintained in a similar manner to other flushing technologies. Specific aesthetic issues may arise through the colouration of groundwater and aquifer materials. Acidic conditions in the aquifer would also contribute to the long term release of Mn$^{2+}$ which could be detrimental to groundwater quality. The use of such aggressive oxidising agents also requires heightened measures to address heath and safety concerns.

**References**

ITRC 2005; Thomson et al. 2007; US EPA 2004; West et al. 2008

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**E.7.3 Ozone**

**Process**

The gas ozone provides chemical oxidation of organic carbon contaminants through direct and indirect pathways. Ozone itself is a strong oxidiser and is relatively stable in the subsurface ensuring good potential for distribution. However the reaction of ozone with water also produces the hydroxyl radicals which have even greater oxidation potential and faster reaction rates. Although the hydroxyl radicals are less stable, chain-propagating reactions with the reactants may deliver a continuing supply of
radicals in a similar fashion to that for hydrogen peroxide. Indeed some applications may utilise hydrogen peroxide in conjunction with ozone. The combination of ozone and hydrogen peroxide probably offers the greatest oxidation potential of the common chemical oxidation techniques. The aquifer may contain compounds that interfere with the production of the hydroxyl free radicals, diminishing the effectiveness of the technique. This is the same situation that arises for hydrogen peroxide with the key element of concern being Fe$^{2+}$. In addition, other species in the aquifer may scavenge the free radicals and reduce the overall effectiveness. The oxidation process is also non-specific so that natural soil organic matter will reduce the overall removal efficiency for the target organic contaminants. Molecular oxygen is a by-product of the decomposition of the ozone and radical formation which is often viewed as beneficial in stimulating complementary aerobic biodegradation of the target LNAPL. This is in addition to O$_2$ that may be injected along with the ozone. However, ozone also destroys aquifer microflora so biodegradation may only be possible away from the immediate area of injection or some extended period after the use of ozone. Ozone is notable amongst the chemical oxidants in that it is a gas. Delivery is mostly via vent wells into the vadose zone or sparge wells below the water table with the ozone being generated on-site using air or oxygen. Where it is co-mingled, there is potential for ozone to decompose VOCs directly in the gas phase.

**Remediation objectives and end points**

Ozone would be considered in the case where there was a need to eliminate the toxic and other detrimental exposure to dissolved LNAPL constituents in groundwater and surface water through their oxidation in the LNAPL and aqueous phases. Very low LNAPL saturations may be achieved under favourable conditions so risk-based end points associated with the toxicity of the LNAPL, toxic exposure to vapours and generation of explosive vapours may also be achievable. The direct action of ozone on gas-phase constituents of LNAPL means that this may be a specific target. However, practicability limits may be an issue when remediation objectives are to remove large LNAPL volumes and reduce very high saturations. Hence it may not usually be considered as the most efficient means to address mobile LNAPL and prevent its continued spread.

**Physical setting**

The delivery of ozone as a gas phase dictates that it is best suited to those conditions favourable to bioventing and air sparging. That is, unconsolidated sandy conditions. Efficiency will be lost as the subsurface materials become finer because of the loss of pathways for air movement and the longer residence times during which the ozone may decompose. This may appreciably limit the volume that may be treatable. Oxidation using ozone is most popularly used for contaminants in the vadose zone because of the inherent gas permeability. However it has also been applied to the saturated zone. Here the same physical hydraulic/pneumatic considerations need be considered in relation to the effective distribution of ozone in the carrier gas. However some benefit may be achieved by the fact that hydroxyl radical and molecular oxygen produced may be transported in the aqueous phase. Some of the limitations of bioventing and air sparging systems due to the generation and possible discharge of VOCs may be overcome by the use of ozone due to its direct oxidation of the VOCs. In terms of aquifer geochemistry, the major concerns in relation to the use of ozone are the presence of soil organic carbon, humic acids, Fe, Mn, hydrogen sulphide and
carbonates. These may reduce the effectiveness by reducing the oxidant available to decompose the target contamination, either by being oxidised itself, scavenging the free radicals or terminating the free-radical chain reaction.

There have been a lot of investigations to validate the use of ozone to oxidise PAHs however it is generally viewed to largely not discriminate between different forms of organic carbon, and by inference petroleum hydrocarbons. Indeed, ozone does not seem to show an appreciable preference for alkanes of different carbon number and studies have shown the effectiveness in decomposing diesel fuel.

**Associated issues and impacts**

Ozone presents serious issues of toxicity risk and can be dangerously explosive. Stringent health and safety measures are required. Even for relatively short exposure times (30 mins – 2 hours), ozone is indicated as being both toxic and lethal at low parts per million levels in some literature. Organic material such as oil and grease in distribution systems may pose a risk of explosion. The toxicity of the ozone to the aquifer’s microbial communities tends to sterilise the soil so benefits of the aeration of the contaminated aquifer may not be fully realised. However, studies have shown that microbial communities may recover and the recovery time is extended with increasing exposure times. The different reactions involved mean that ozone does not generally have a profound effect on pH in the groundwater system, reducing the risk of metal mobilisation. However, the potential for mobilisation of toxic metals in the aquifer due to pH and redox changes remains. The volatilisation of VOCs from the LNAPL and their discharge to below- and above-ground structures needs to be considered. These risks may be mitigated by the possible presence of ozone in the air phase. The possibility of unintended exposure to ozone in fugitive emissions also needs to be ruled out or effectively managed. The mass flux rates achievable with ozone injection and the stoichiometry of oxidation means that treatment times are generally longer than other chemical oxidation methods.

**References**


**E.7.4 Persulphate**

**Process**

Persulphate, $\text{S}_2\text{O}_8^{2-}$, is another strong oxidant (stronger that hydrogen peroxide) that can oxidise organic carbon including petroleum hydrocarbons. It is added as an aqueous solution most commonly of the sodium salt because of its higher solubility. The ammonium salt has similar solubility but the addition of ammonium may be subject to other considerations. The decomposition of the $\text{S}_2\text{O}_8^{2-}$ in the aquifer is dependent on pH, presence of oxygen and the concentration of the solution – affecting the functional oxidation process. Generally though, the kinetics are slow and persulphate is mostly used with some form of activation. On activation by heat or $\text{Fe}^{2+}$, persulphate produces the sulphate free radical $\text{SO}_4^- – a very strong oxidant (similar in effect to the hydroxyl free radical produced from ozone and hydrogen peroxide) that reacts very rapidly. $\text{Fe}^{2+}$ concentrations need to be carefully controlled because it also plays a role in terminating the production of the free radical. Also, acidic conditions need to be
maintained within the aquifer for the Fe$^{2+}$ to remain in solution although chelating agents may assist in this regard. Persulphate also may be activated at high pH to produce the hydroxyl radical. A feature of persulphate is that it is more stable than peroxide and ozone and less influenced by natural soil organic matter than other oxidants. The application of persulphate is similar to the other aqueous chemical oxidants – that is through the addition of a solution via wells or infiltration galleries depending on the location of the target LNAPL.

**Remediation objectives and end points**

Similar to the other chemical oxidants, persulphate would be considered to eliminate the toxic and other detrimental exposure to dissolved LNAPL constituents groundwater and surface water through their oxidation in the LNAPL and aqueous phases. Specific risk-based end points associated with the toxicity of the LNAPL, toxic exposure to vapours and generation of explosive vapours may also be achievable because of the potential to reach very low LNAPL saturations under favourable conditions. The objectives of removing large LNAPL volumes and reducing very high saturations would likely be beyond the practicability limits of the technology. Hence it would not usually be considered to address mobile LNAPL and prevent its continued spread.

**Physical setting**

The predictability and ease of amendment solution movement make sandy aquifer materials the best prospect for the application of persulphate. Heterogeneities and low permeability strata may complicate delivery of the solution and limit the penetration of amendment solution, and require a higher intensity of injection points to achieve the desired coverage. In the case of dual porosity aquifer materials, the diffusion of the oxidant into lower permeability layers offers potential for treatment in such settings. In addition, there are proponents of the use of electrokinetics with persulphate to specifically target organic contaminants in lower permeability materials. At least in principle, there seems little to suggest that persulphate would not be effective in fractured rock environments. However, injected solutions would also have the potential to displace the LNAPL away from the treatment zone. Persulphate is sensitive to geochemical conditions in the aquifer and consideration should be given matching those that are favourable. As well as the persulphate, appropriate conditions are needed for the Fe$^{2+}$ activating agent. High concentrations of chloride, carbonate and bicarbonate can reduce effectiveness by scavenging the free radicals. Aquifers with these characteristics may not be favourable to the use of persulphate. Natural soil organic matter will detrimentally utilise some of the oxidation capacity of the persulphate. However, persulphate seems less affected than some of the other chemical oxidants (mainly because of its slower kinetics) making it a possible preferred option for aquifers with elevated levels of natural soil organic carbon. Infiltrated and injected solutions of persulphate could target LNAPL petroleum hydrocarbons suspended in the vadose zone, within the capillary fringe and below the water table given appropriately engineered infrastructure. The type of LNAPL petroleum hydrocarbon is not expected to limit the use of persulphate.
Associated issues and impacts

As a strong oxidant, heightened measures are required to address health and safety concerns. Adequate controls would also need to be maintained on the distribution of the oxidant and activators within the groundwater system as well as by-products of the process. Acidification of the aquifer and mobilisation of metals in groundwater is a specific concern that needs to be addressed. The activation and oxidation reactions may produce very low pH in poorly buffered systems leading to the mobilisation of metals. The geochemistry and mineralogy of the aquifer materials need to be evaluated for the possibility of adverse outcomes. Intentional acidification of the groundwater to preserve Fe$^{2+}$ in solution may lead to similar outcomes. The oxidation process produces sulphate which may be a secondary groundwater contamination issue. Ammonium may be a further issue if the ammonium persulphate salt is used. In addition, persulphate may have a detrimental effect on soft metals such as copper and brass so subsurface infrastructure may need to be protected.

References


E.8 Thermal methods

E.8.1 Steam injection

Process

Steam injection facilitates remediation mainly through the enhanced vaporisation of the LNAPL. The heating of the subsurface by injecting steam through wells increases the rate of vaporisation by increasing vapour pressures. The thermodynamics of the liquid mixture also allows complete vaporisation of the LNAPL even though its boiling point may be above that of water. This allows very effective removal at temperatures around and just above the boiling point of water. The high velocity of the steam also raises the effectiveness. A soil vapour extraction system would be included in a steam injection scheme to capture and treat the generated vapours. Other factors that contribute to the removal of the LNAPL are the increased capillary pressures which, in conjunction with the reduction in viscosity, allow the LNAPL to be displaced. Reductions in interfacial tensions also reduce capillary trapping in the porous materials. In this respect, the displacement and condensation of the volatilised petroleum hydrocarbons at the steam condensation front may increase LNAPL saturations and LNAPL mobility to the extent that it spreads vertically or laterally. This may facilitate (or trigger) further hydraulic recovery. In many cases a range of air injection schemes may be instituted to prevent the further spread of LNAPL, particularly under gravitational forces. The effects of elevated temperature on sorption, solubility and Henry’s coefficient would also aid LNAPL constituent removal.

Remediation objectives and end points

Steam injection has the potential to reduce LNAPL saturations to relatively low levels within aquifers, possibly to the extent that a range of specific risk-based end points are reached. However, the process of volatilisation involved in the steam injection naturally addresses remediation objectives around toxic and explosive vapours. Where the
remediation objective is to prevent the future spread of LNAPL, the further mobilisation produced by the steam injection may render this technology less attractive. However, the enhanced mobility may be viewed as a positive attribute in some circumstances, for instance, low viscosity LNAPL.

Physical setting

The application of steam injection is suitable in a range of hydrogeological settings with the primary constraint being an adequate permeability to distribute the steam through the subsurface. Heterogeneity is less of an issue than other fluid-based remediation strategies because of the ubiquitous transfer of heat, even in the presence of low permeabilities. Of course some permeability is required for the efflux of the vapourised LNAPL but gas phase permeability is created by the boiling of the interstitial liquids at high temperature. Sometimes, heterogeneity in the form of lower permeability layers is advantageous in controlling the movement of steam and volatilised LNAPL. Remediation with steam injection has been attempted in dual porosity materials, even fractured limestone. Steam injection can be undertaken above and below the water table but is not naturally suited to the shallow vadose zone. It is appropriate for volatile and semi-volatile LNAPL and would be considered for those concerns other than that of spreading LNAPL.

Associated issues and impacts

Control of the generated vapours and any mobilised LNAPL are significant issues when considering steam injection. As indicated, some form of soil vapour extraction system would generally be part of the remediation design. Treatment of the collected vapours would be a significant cost. The possible mobilisation and spread of LNAPL may be addressed according to the setting of the treatment. Where the treatment is focused at or below the water table, hydraulic recovery may be appropriate. However, if the LNAPL is appreciably above the water table, further downward migration would need to be controlled. Control measures based on the injection of air (as in the case of DNAPLs) may be appropriate here and perhaps where the LNAPL is far below the water table. The application of steam injection near ground surface is somewhat problematic. Containment of the steam, collection of the vapours and avoidance of elevated temperatures present logistical challenges, especially in relation to health and safety. The heating from steam injection may also have significant effects on the biological and geochemical properties of the aquifer. A prime consideration would be the suppression of microbiological communities that may be relied on as part of the natural attenuation of the pollutants. The period over which the aquifer is effectively sterilised needs to be evaluated. Finally, steam injection is energy intensive and overall benefits through a lifecycle analysis may need to be confirmed.

References

**E.8.3 Electrical resistance heating**

**Process**

Electrical resistance heating uses electrodes placed in the aquifer to raise the temperature in order to volatilise the LNAPL. It is a similar process to that of steam injection but relies on the thermal conduction of the heat from the electrodes to raise the temperature of the surrounding aquifer. Thus it lacks aspects of the displacement and flushing of the injected steam. However, the reliance on thermal conduction means that it can be more appropriately targeted to finer textured materials. The volatilisation of the LNAPL means that the heating is run in conjunction with a soil vapour extraction system. Increases in water and LNAPL vapour (in some applications boiling of the liquids) would provide a mechanism for displacement of the LNAPL which would then be available for hydraulic recovery. As with steam injection, the displacement would be facilitated by reductions in viscosity and interfacial tension of the LNAPL. Condensation of the LNAPL at temperature fronts would also provide LNAPL that may be hydraulically recoverable.

**Remediation objectives and end points**

The remediation objectives and end points targeted using electrical resistance heating are essentially the same as that for steam injection. The process of volatilisation naturally addresses remediation objectives around toxic and explosive vapours. The extent to which these coincide with major risk drivers in the dissolved phase and the LNAPL as a whole, means that electrical resistance heating may enable a wider range of specific risk-based end points to be reached. Reaching these end points would be assisted by the relatively low LNAPL saturations that potentially may be achieved. This also means that other largely LNAPL mass-reduction objectives such as allowing the use of the land, aquifer and groundwater resources for specified uses and some objectives related to societal and business factors would admit electrical heating as an appropriate technology. While electrical heating may be feasible where the remediation objectives is to prevent the future spread of LNAPL, relative cost may render this technology unattractive compared to other technologies. However electrical resistance heating suffers less of the drawbacks of further mobilisation compared to steam injection.

**Physical setting**

Electrical resistive heating would find its greatest applicability in finer textured materials. Heterogeneities and dual porosity would not necessarily detract from its application. In addition, electrical resistance heating undertaken above and below the water table is appropriate for volatile and semi-volatile LNAPL. It would not usually be considered where the spreading of the LNAPL is the concern driving the remediation.

**Associated issues and impacts**

The possible mobilisation of the LNAPL and need to control the generated vapours are the main issues to be considered for this remediation strategy. These considerations are similar to those for steam injection. The particular safety issues associated with the electrical energy being used would need to be included in the assessment and design of the remediation strategy.
References
Buettner & Daily 1995; Davis 1997; Heron et al. 1998, 2005, 2009; McGee et al. 1998

E.8.4 Radio frequency and microwave heating

Process
Heating of the subsurface can also be achieved using the electromagnetic radiation in the radio and microwave frequency range. Such heating is achieved through the electromagnetic radiation inducing rotation of polar compounds (most notably water). The consequent intermolecular friction produces heat. The electromagnetic energy is dissipated by the heat production but essentially the energy is simultaneously applied over the soil volume without any over-riding need for thermal conduction or advection of the heat. The electromagnetic fields are generated by placing appropriate antennas in the subsurface.

There are some competing processes that require optimisation of the frequency of the electromagnetic radiation – that is, using either radio frequencies or frequencies in the microwave range. The heat generated is directly proportional to frequency which favours the use of microwaves where intense heating is sought. However, as a consequence, the depth of penetration is inversely proportional to the frequency. Thus for too high frequency, the heating effect may be limited to the near vicinity of the antennas. The relative costs of the generators for the radio waves and microwaves would also be an important consideration in selecting between forms of electromagnetic energy.

The removal processes are a combination of volatilisation of the LNAPL and increase in the mobility of the LNAPL (through decreases in viscosity and interfacial tension) so that it is more easily recovered. Volatilisation of the LNAPL means that such systems would be run in conjunction with a soil vapour extraction system. Decoupling, to a large extent, of the heating process from the permeability of the subsurface materials means that applicability of the technology to finer textured materials becomes more feasible. However, the water content of the subsurface materials affects the dissemination of the electromagnetic energy as well as the rate of heating.

Remediation objectives and end points
The temperatures targeted influence the remediation objectives and end points that would be matched to electromagnetic heating. The increased volatilisation naturally addresses remediation objectives around toxic and explosive vapours and the major risk drivers from the presence of these in the dissolved phase and the LNAPL as a whole. Hence end points related to risk-based end points for some specific compounds may be reached. Relatively low LNAPL saturations that potentially may be achieved with these techniques also means that other objectives such as allowing the use of the land, aquifer and groundwater resources for specified uses and some objectives related to societal and business factors may be within the reach of the techniques. However, radio frequency and microwave heating technologies would not be a first consideration for remediation to achieve objectives addressing the spreading of the LNAPL.
Physical setting

Radio frequency and microwave heating would not be strongly disadvantaged by the presence of finer textured materials because of the mode of transmission of the heat energy and subsequent redistribution of heat. However, water contents do influence the volume of the subsurface heated and the rate at which temperatures may be raised. Higher water contents reduce the volume influenced and increase the rate of temperature increase. Lithification of the porous materials would not present any additional impediments to the technology in itself. Some higher permeability elements of the formation would provide some advantages in facilitating efficient liquid recovery and extraction of contaminant vapours. However, reduced liquid saturations from the vaporisation of water and LNAPL may enable movement and collection of gas-phase contaminants, even in finer textured materials. In addition, dual porosity and heterogeneous materials would not pose as much of a limitation as for some other remediation techniques. With some caveats about the possible effects of high water saturations, there are no inherent limitations of radio frequency and microwave heating to above or below the water table. The technology would be more naturally suited to the vadose zone however. Volatile and semi-volatile LNAPLs would be good subjects for the technology where volatilisation was the objective. However, highly viscous LNAPLs are also targeted where the raised temperatures are used to improve mobility of the LNAPL to the extent that it may be recovered hydraulically.

Associated issues and impacts

The possible mobilisation of the LNAPL and need to control the generated vapours are important issues to be considered for this remediation strategy. These considerations are similar to those for steam injection. Also, the heat generated may damage infrastructure or need to be appropriately managed. Waste streams of extracted soil vapours and liquids from condensation of extracted gases as well as any direct liquid recovery would also need treatment and/or disposal. The particular safety issues associated with the electrical and electromagnetic energy being used would need to be included in the remediation assessment and design. The comparative rarity of applications may increase costs and reduce overall acceptability. The energy use and cost need careful attention although they may be less than those for electrical (ohmic) heating.

References

Edelstein et al. 1994; Kawala & Atamanczuk 1998; Li et al. 2008; Price et al. 1999
APPENDIX F.

Previous classification of remediation technologies

In situ remediation technologies have previously been identified and classified in various ways. Mainly they have been classified according to:

- the processes that they utilise to remove the LNAPL
- the setting in which they may be applied, and
- the objectives that are being sought.

Some of the classifications are discussed here along with the remediation technologies that have been identified.

It is notable that in the presentation of some specific LNAPL remediation technologies, associated bioremediation aspects are not highlighted. In effect, any of the air-flushing technologies or those that manipulate air pressure in the subsurface very likely induce removal of petroleum hydrocarbons through aerobic biodegradation (Johnston 2001).

F.1 NRC (1997)

The NRC (1997) classified general remediation strategies according to process:

- solidification, stabilisation and containment
- chemical and biological reaction, and
- separation, mobilisation and extraction.

A listing of the technologies falling into the categories of chemical and biological reaction as well as separation, mobilisation and extraction appropriate to in situ removal is presented in Table F1. This classification is high level and lacks further demarcation according to specific process and setting.

<table>
<thead>
<tr>
<th>Chemical and biological reaction</th>
<th>Separation, mobilisation and extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biosparging</td>
<td>LNAPL recovery (skimming)</td>
</tr>
<tr>
<td>Bioventing</td>
<td>Vacuum-enhanced recovery</td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>Multi-phase extraction</td>
</tr>
<tr>
<td>Engineered bioremediation</td>
<td>Soil flushing (water, steam, surfactants, co-solvents)</td>
</tr>
<tr>
<td>Land farming</td>
<td>Sparging (air, steam, ozone)</td>
</tr>
<tr>
<td>Passive reactive barriers</td>
<td>Thermal desorption</td>
</tr>
<tr>
<td>Thermal destruction</td>
<td>Soil vapour extraction (thermally enhanced)</td>
</tr>
<tr>
<td></td>
<td>Solvent extraction</td>
</tr>
</tbody>
</table>
F.2 Charbeneau et al. (1999)
Charbeneau et al. (1999) focused on the free-LNAPL recovery (hydraulic removal) technologies. Those technologies covered are presented in Table F2.

Table F2. Free-LNAPL recovery technologies as presented by Charbeneau et al. (1999).

<table>
<thead>
<tr>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interceptor trenches</td>
</tr>
<tr>
<td>Skimmer well recovery</td>
</tr>
<tr>
<td>Single- and dual-pump recovery</td>
</tr>
<tr>
<td>Vacuum-enhanced recovery</td>
</tr>
</tbody>
</table>

F.3 Oostrom et al. (2005)
Oostrom et al. (2005) identified hydraulic removal, pump-and-treat and soil vapour extraction as the most frequently applied remediation techniques for NAPL contamination. Notice that pump-and-treat was included in their assessment due to its application to DNAPLs. This technology has more limited application to LNAPLs. Oostrom et al. (2005) also grouped a number of in situ remediation technologies according to the underlying process (Table F3) but at a lower level than the NRC (1997).

Table F3. In situ LNAPL remediation technologies grouped by process (Oostrom et al. 2005).

<table>
<thead>
<tr>
<th>Process</th>
<th>Technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal</td>
<td>Pump and treat</td>
</tr>
<tr>
<td>Interception</td>
<td>Permeable (reactive) barrier</td>
</tr>
<tr>
<td>Induced phase transfer</td>
<td>Soil vapour extraction</td>
</tr>
<tr>
<td></td>
<td>Air sparging</td>
</tr>
<tr>
<td>Chemical flushing</td>
<td>Surfactant flushing</td>
</tr>
<tr>
<td></td>
<td>Co-solvent flushing</td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>Chemical oxidation</td>
</tr>
<tr>
<td>Thermally enhanced extraction</td>
<td>Steam injection</td>
</tr>
<tr>
<td></td>
<td>Electrical resistance heating</td>
</tr>
<tr>
<td>Thermally enhanced chemical oxidation</td>
<td>Hydrous pyrolysis oxidation</td>
</tr>
<tr>
<td>Bioremediation</td>
<td>Engineered bioremediation</td>
</tr>
<tr>
<td></td>
<td>Natural attenuation</td>
</tr>
</tbody>
</table>
F.4 TCEQ (2008)

TCEQ (2008) took a different approach and classified the remediation technologies as ‘conventional’ and ‘alternative’ according to the requirements for site-specific modifications and the processes involved. They defined a conventional technology as one that may be taken essentially ‘off the shelf’ and easily matched to site conditions. In addition, these conventional technologies are based on the hydraulic removal of the LNAPL or removal of the LNAPL as a vapour phase. Alternative technologies are those that may require significant design development and based on transforming the LNAPL or site conditions to aid LNAPL removal. The notion of conventional and alternative technologies is also taken into consideration in assessing the practicability of remediation. The conventional and alternative technologies presented by TCEQ (2008) are shown in Table F4.

Table F4. Conventional and alternative LNAPL recovery technologies as classified by TCEQ (2008).

<table>
<thead>
<tr>
<th>Conventional</th>
<th>Alternative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil vapour extraction</td>
<td>Soil flushing</td>
</tr>
<tr>
<td>Floating LNAPL extraction</td>
<td>In situ oxidation</td>
</tr>
<tr>
<td>Shallow liquid-only extraction</td>
<td>Electrical heating (+ SVE)</td>
</tr>
<tr>
<td>Dual-pump liquid extraction</td>
<td>Air sparging (+ SVE)</td>
</tr>
<tr>
<td>Low-vacuum dual phase extraction</td>
<td>Steam injection (+ SVE)</td>
</tr>
<tr>
<td>High-vacuum dual phase extraction</td>
<td>Electrokinetics</td>
</tr>
<tr>
<td>Two phase extraction</td>
<td></td>
</tr>
</tbody>
</table>

F.5 ITRC (2009a)

ITRC (2009a) divided remediation technologies into three groups:

- LNAPL mass recovery technology
- LNAPL mass-control technology
- LNAPL phase change technology.

The purpose of grouping the remediation technologies was to provide context to the basic processes through which the LNAPL remediation is achieved. The technologies presented are listed in Table F5.
Table F5. LNAPL remediation technologies as presented by ITRC (2009a).

<table>
<thead>
<tr>
<th>Technology</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excavation</td>
<td></td>
</tr>
<tr>
<td>Physical or hydraulic containment</td>
<td></td>
</tr>
<tr>
<td>In situ soil mixing</td>
<td></td>
</tr>
<tr>
<td>Natural source zone depletion</td>
<td></td>
</tr>
<tr>
<td>Air sparging/soil vapour extraction</td>
<td></td>
</tr>
<tr>
<td>LNAPL skimming</td>
<td></td>
</tr>
<tr>
<td>Bioslurping/enhanced fluid recovery</td>
<td>Vacuum-enhanced recovery through a drop tube to entrain water and LNAPL</td>
</tr>
<tr>
<td>Dual-pump liquid extraction</td>
<td>Separate pumps for LNAPL and groundwater</td>
</tr>
<tr>
<td>Multi-phase extraction – dual pump</td>
<td>Separate pumps for LNAPL and groundwater, vacuum enhanced</td>
</tr>
<tr>
<td>Multi-phase extraction – single pump</td>
<td>Single pump for the combined recovery of LNAPL and water</td>
</tr>
<tr>
<td>Water flooding</td>
<td>Including hot water flooding</td>
</tr>
<tr>
<td>In situ chemical oxidation</td>
<td></td>
</tr>
<tr>
<td>Surfactant-enhanced subsurface remediation</td>
<td></td>
</tr>
<tr>
<td>Co-solvent flushing</td>
<td></td>
</tr>
<tr>
<td>Steam/hot air injection</td>
<td></td>
</tr>
<tr>
<td>Radio-frequency heating</td>
<td></td>
</tr>
<tr>
<td>Three- and six-phase electrical heating</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX G.

Reported Australian case studies

Conference and journal papers


## APPENDIX H.
### Summary of case studies

Table H1. Summary of case studies in Appendix G. Refer to Appendix G for the case index.

<table>
<thead>
<tr>
<th>Case index</th>
<th>Site identifier</th>
<th>Aquifer name</th>
<th>Aquifer type</th>
<th>LNAPL type</th>
<th>Age</th>
<th>Size of release</th>
<th>Full/Pilot</th>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Melbourne - 01</td>
<td>Newer Volcanics</td>
<td>Fractured rock</td>
<td>Gasoline and diesel</td>
<td>u.s.</td>
<td>15 – 25 m$^3$</td>
<td>Full</td>
<td>VER</td>
</tr>
<tr>
<td>2</td>
<td>Swan Coastal Plain - 01</td>
<td>Safety Bay Sands</td>
<td>Sand</td>
<td>Diesel</td>
<td>old</td>
<td>large</td>
<td>Pilot</td>
<td>Bioventing</td>
</tr>
<tr>
<td>3</td>
<td>Swan Coastal Plain - 01</td>
<td>Safety Bay Sands</td>
<td>Sand</td>
<td>Diesel</td>
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Table H1 (cont.). Summary of case studies in Appendix G. Refer to Appendix G for the case index.

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*Note: u.s. = unspecified*