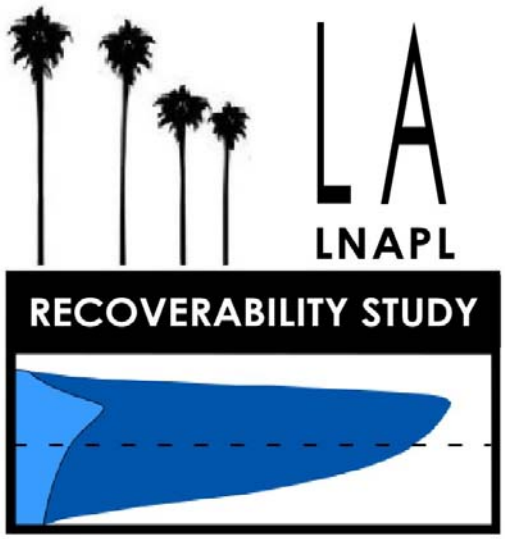
Light Non-Aqueous Phase Liquids (LNAPL)
Literature Review

Prepared by:

The Los Angeles LNAPL Working Group

October 27, 2011
VERSION 1.0



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PREPARED BY
the Los Angeles LNAPL Working Group:

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The Los Angeles LNAPL Workgroup will be working on several projects involving LNAPL until at least 2013. If you have comments or suggestions to improve the document, please send them to the Workgroup's Technical Coordinator, Dr. Charles Newell. Dr. Newell will compile the comments, and if there is time and resources, the LA LNAPL Workgroup will prepare a revised version of this document (Version 2.0) sometime in the near future.

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List of Key Terms and Definitions
LA LNAPL Literature Review

BATT	Best available treatment technology. BATT is a term used here for groundwater cleanup technologies that is similar to the concept of Best Available Technology (BAT). BAT has been employed to select water treatment technologies in California by considering the costs, benefits, and effectiveness of a particular technology. Section 1
BTEX	Benzene, Toluene, Ethyl benzene, Xylene (BTEX). These are four of the most common constituents of LNAPL that dissolve from the LNAPL and can migrate in moving groundwater. Section 2
CPT	Cone penetrometer. The CPT is a specialized geotechnical rig that is used to determine the geology of the subsurface. Section 3.1.3
Dean-Stark analysis	A chemical test to determine how much NAPL fills the pore space of a gravel, sand, or silt sample. In this method, water is first evaporated from the sample, a solvent is then used to extract any oil in the sample. Gravimetric relationships and considerations of bulk and solid density are then used to calculate total LNAPL saturation. Section 3.3.1
FID	Flame ionization detector. This is a device to determine the amount of chemical vapors that are emitted by a soil sample. Section 3.1.2
Formation LNAPL thickness	This is the actual thickness of the subsurface soil that is impacted by LNAPL, sometimes called "*True LNAPL Thickness*". Not all of the subsurface soil is filled with LNAPL. Sections 1.2, 3.3.2, 4.1
Free LNAPL	LNAPL that is hydraulically connected in the pore space and has the potential to be mobile in the environment (ASTM, 2007) Sections 1.2, 4.2.3
LIF	Laser induced fluorescence. This is a method to determine the presence of LNAPL in the subsurface. The illumination source is forced through the subsurface soil on direct-push type drilling rigs. The light causes PAH compounds to fluoresce. Section 3.1.3
LNAPLs	Light non-aqueous phase liquids. These are lighter-than-water separate phase liquids, such as crude oil, gasoline, diesel fuel, etc., that can migrate into the subsurface and form either free, mobile, or residual LNAPL. Section 1.1
LNAPL mobility	The ability of LNAPL to move in the subsurface at the local scale. It is a function of both the LNAPL fluid properties (density and viscosity) and of the intrinsic permeability of the formation. There are different methods to express mobility, including a method that calculates LNAPL "inherent mobility." Section 4.0
LNAPL relative permeability	The ratio of LNAPL permeability to intrinsic permeability of the formation. It is a measure of how mobile an LNAPL accumulation is in the subsurface. Section 4.1
LNAPL Transmissivity	(LNAPL transmissivity is a measure of how much LNAPL can be transmitted horizontally through the subsurface in an existing LNAPL zone.
Macropores	Macropores are relatively large openings in soils that can be caused by plant roots or animals. Macropores control NAPL transport in fine-grained sediments, and lead to small volume NAPL pockets isolated as "islands" within water-saturated media (Johnson and Assali, 2010). The macropores in the vadose zone are typically too small to be defined by current delineation technologies. Section 1.2
Mobile LNAPL	Free LNAPL that is moving laterally or vertically in the environment under prevailing hydraulic conditions. Sections 1.2, 4.0
Mobile Saturation	The LNAPL saturation level above which naturally occurring capillary forces prevent

	LNAPL from moving, thus the LNAPL is potentially mobile (see "Free LNAPL). Sections 1.2, 4.0
NAPLs	Non-aqueous phase liquids. Separate phase organic liquids in the subsurface. Section 1.1
NRC	National Research Council. A national research organization funded by the U.S. Federal government that publishes books and reports on a wide range of issues, including groundwater contamination. Section 7.0
NSZD	Natural source zone depletion. The process where natural processes will remove LNAPLs from the subsurface by naturally occurring physical, chemical, and biological processes. Section 4.3
PAH	Polycyclic aromatic hydrocarbons. A class of chemicals that typically have lower solubility and are heavier than the BTEX compounds. Section 3.1
PID	Photo ionization detector. This is a device to determine the amount of chemical vapors that are emitted by a soil sample. Section 3.1.2
Residual LNAPL	LNAPL that is hydraulically discontinuous and immobile under prevailing conditions. Residual LNAPL can be thought of as "individual blobs of LNAPL in individual pores" in a gravel, sand, or silt. This concept is complex, with several different conceptual models on how to apply this value, and five methods to determine a value for residual saturation. Sections 1.2, 3.3, 4.0, 5.0
Residual saturation	The LNAPL saturation level below which naturally occurring capillary forces prevent LNAPL from moving, making the LNAPL immobile. Sections 1.2, 4.0
ROI	Radius of influence. This is a general term for the radius around a treatment well or treatment point that is treated by a particular groundwater cleanup technology. Section 5.3
Specific volume	In a given area, the volume of LNAPL divided by the area. This is a calculated value of the actual amount of LNAPL present in an area divided by the area. This would be the thickness of LNAPL that would remain in an LNAPL zone if the soil and water in that area were hypothetically removed. Section 3.3
Stable body	A LNAPL body that is no longer moving laterally. Section 1.2
Submerged LNAPL	LNAPL that is found well below the water table due to a historical release, followed by a rising water table. Most submerged LNAPL is in the residual form, and conventional floating LNAPL conceptual models do not apply. Submerged LNAPL is found in the LA Basin at sites with older, historical releases of LNAPL due to rising water table since the 1950s. Sections 1.2, 3.3, 4.1
Unconfined LNAPL	LNAPL near the water table of an unconfined formation. Out-of-date conceptual models of LNAPL often referred to this as "floating LNAPL."
Well LNAPL thickness	Observed monitoring well LNAPL thickness. Terms that others have used to describe the observed monitoring well thickness are "apparent thickness" and "observed thickness" Sections 1.2, 3.3.1
WSPA	Western States Petroleum Association. A non-profit trade association that represents companies that account for the bulk of petroleum exploration, production, refining, transportation and marketing in six western states. Section 1.1

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Literature Review
LNAPL Recoverability Study

1.0 INTRODUCTION

1.1 Project Objectives

Non-aqueous phase liquids (NAPLs) are liquids that are immiscible with water so that they form a separate phase when released into the subsurface. Light non-aqueous phase liquids (LNAPLs) exhibit a liquid density less than that of water. LNAPLs can consist of one or more compounds, and are typically a mixture of petroleum hydrocarbons. LNAPLs released into the subsurface are of environmental concern because they can provide a source of long-term release of constituents of concern to the environment. Because LNAPLs form a separate phase in the subsurface, LNAPLs pose many challenges to effective characterization and remediation.

The Western States Petroleum Association (WSPA) and Los Angeles Regional Water Quality Control Board (LARWQCB) have, along with other parties, established an LNAPL Working Group to develop a cooperative approach to addressing LNAPL problems in the Los Angeles basin. The objectives of the LNAPL Recoverability Study are to:

- Establish methodologies to estimate LNAPL volume and distribution in the subsurface;
- Establish methodologies to assess LNAPL recoverability;
- Establish methodologies to assess LNAPL remediation performance; and
- Define the “best available treatment technology” (BATT) for LNAPL remediation.

This literature survey is the first step of the recoverability study. The specific objectives of this literature survey are outlined in tasks 3.1.1 and 3.2.1 of the scope of work:

Task 3.1.1:

- Characterize methodology for LNAPL volume/mobility estimation.
- Identify typical LNAPL types that may be encountered and their physical properties.
- Compile field data.
- Evaluate and select appropriate modeling program for LNAPL recovery/mobility prediction in the unsaturated and saturated zones as a function of basic soil and fluid properties.

Task 3.2.1:

- Review current and emerging removal technologies.
- Compile literature case studies that show accuracy of LNAPL recovery models from actual field sites.
- Compile data from any LNAPL recovery pilot tests performed in or applicable to the Los Angeles Basin.

The literature survey presents the combined results of these two tasks. In this review, characteristics of LNAPLs typically encountered in the LA basin are identified. A survey of methods for LNAPL characterization, determining LNAPL mobility, and assessing recoverability are then discussed and evaluated. Data on numerous LNAPL sites has been collected, along with case studies that illustrate the application of methodologies to real sites and the success of those applications.

1.2 Summary of Current LNAPL Conceptual Model

Before discussing particular models and methodologies, it is instructive to summarize the current industry paradigm of LNAPL behavior in the subsurface. Very good summaries of LNAPL behavior are contained in Newell et al. (1995), Farr et al. (1990), Lenhard and Parker (1990), USEPA (1996), Huntley and Beckett (2002), API (2004), Golder and Associates (2006), ASTM (2007), and AFCEE (2007). The short summary below is compiled from these and the other referenced sources and serves as a working conceptual model and framework for the particular methods and case studies presented in this review.

LNAPLs are typically a complex mixture of petroleum hydrocarbons, such as gasoline, diesel, or crude oil (Newell et al., 1995). These mixtures form a separate phase in the subsurface and are lighter than water. If released onto a flat surface water body, an LNAPL would float on top of the water and slowly release its more soluble components into the water. When an LNAPL is released into the subsurface, however, interactions with the soil pores in the subsurface cause LNAPL to be distributed according to principles consistent with these interactions.

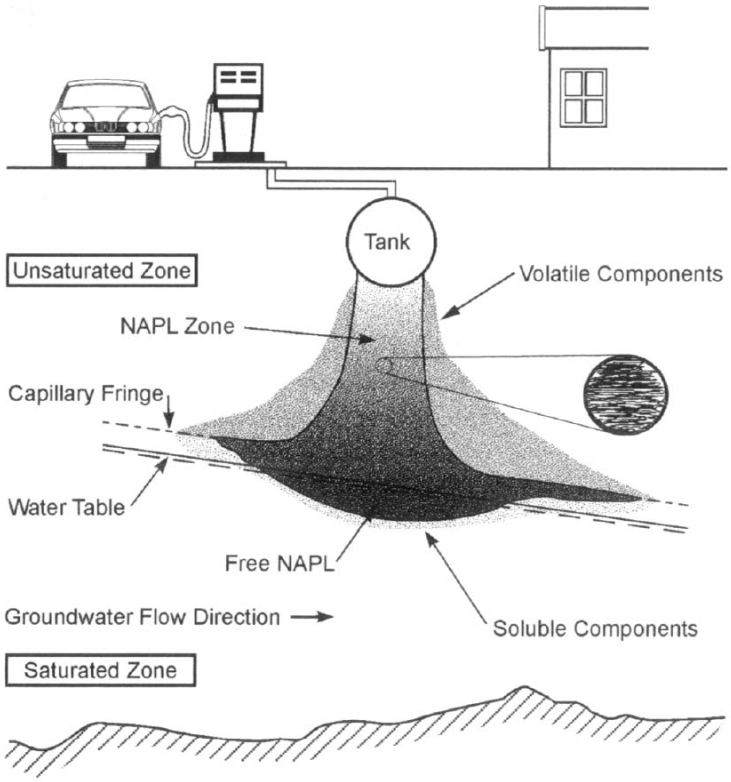


Figure 1. LNAPL idealized release conceptual model (Mayer and Hassanizadeh, 2005) shortly after release.

LNAPL does not float on top of the water table like a pancake (RTDF, 2005). Instead, LNAPL will distribute itself within the pores occupied by air and/or water. When LNAPL is released at the surface, it will flow downward under the influence of gravity until it reaches the capillary fringe (see Figure 1). As the LNAPL flows downward through the vadose zone, it leaves behind LNAPL trapped in the pore space by capillary forces (Figure 2). This residual LNAPL is immobile, so that the volume of LNAPL that reaches the water table is always less than the volume that is released at the surface. The amount of trapped LNAPL left behind at residual saturation is a function of the highest degree of LNAPL saturation experienced by the porous media

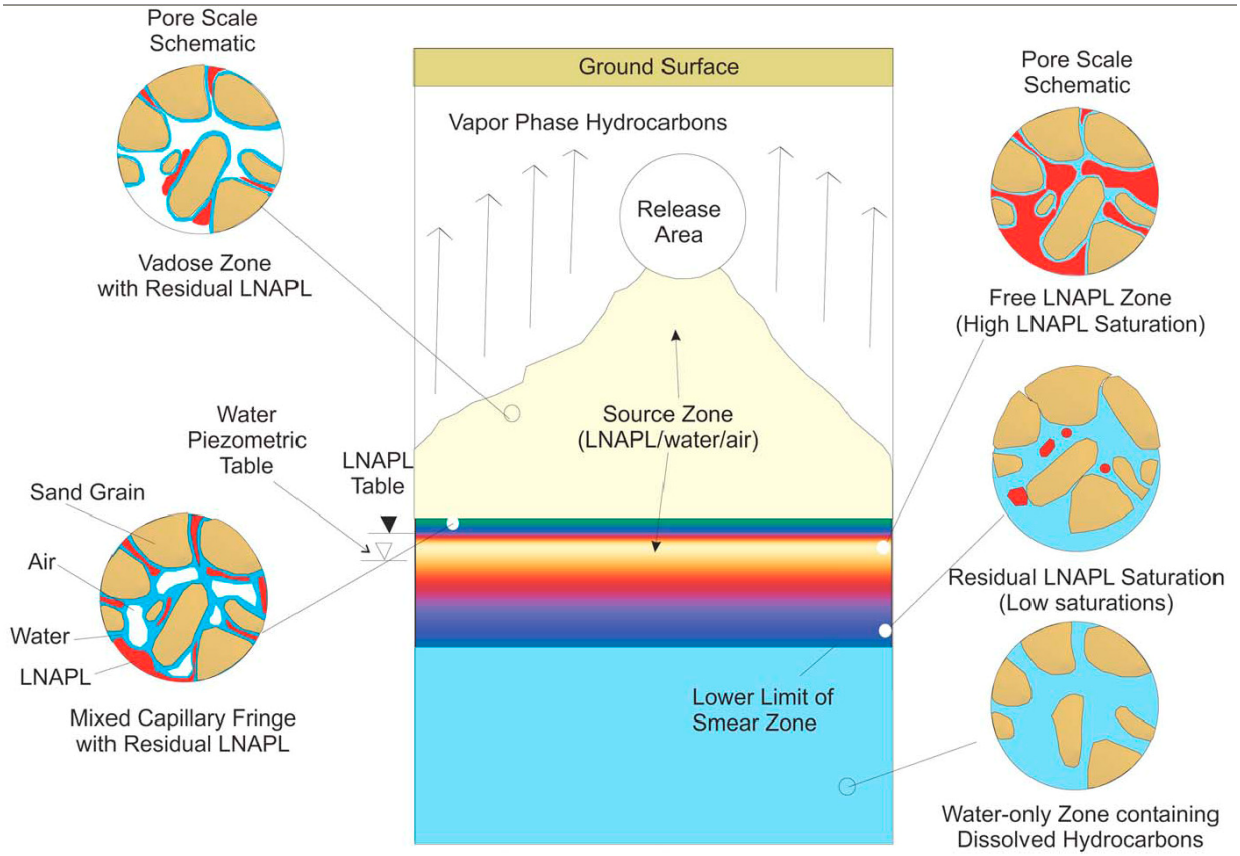


Figure 2. Distribution of LNAPL in pore space following a release (ASTM, 2007).

(Charbeneau, 2007). The greater the peak saturation of the porous media, the greater will be the residual saturation.

When LNAPL reaches the capillary fringe, it begins to spread laterally until sufficient LNAPL head develops for the LNAPL to begin displacing water. When sufficient head is developed for penetration into water-filled pores, the LNAPL will begin to displace water, causing LNAPL to flow into the pore space, while simultaneously continuing its lateral spread in a mostly radial direction. If the LNAPL release is on-going, LNAPL will continue to penetrate downward until the buoyancy and capillary forces balance the head of the LNAPL in the vadose zone, and the LNAPL will continue to migrate laterally for a time after the release ceases.

If the LNAPL is a finite source, then the LNAPL head at the source of the spill will begin to dissipate as LNAPL spreads laterally. As the LNAPL flows laterally, it first displaces water from large pores where capillary pressures are lowest (Huntley and Beckett, 2002). As the LNAPL continues to flow laterally, the LNAPL front penetrates ever decreasing pore sizes until the head driving lateral migration is unable to force water from a given size pore. At that point, the LNAPL saturation at the LNAPL front no longer increases. At the leading edge of the lateral LNAPL migration, the LNAPL saturation will be equal to the saturation corresponding to the capillary pressure equal to that needed to penetrate the largest pore size, and the LNAPL at the body edge will be immobile.

Non-viscous LNAPLs of limited volume will travel downward rapidly and reach hydrostatic equilibrium fairly quickly, typically within days to a few months. As LNAPL viscosity increases, the time for the LNAPL to reach equilibrium increases, so that releases of viscous LNAPLs such as No. 6 fuel oil may take years to reach equilibrium (Oostrom, 2006).

An LNAPL body that is no longer moving laterally is called stable. Immobile LNAPL present at or below residual saturation is termed residual LNAPL. LNAPL that is present above residual saturation is potentially capable of movement and is called free LNAPL. A stable LNAPL body will contain free LNAPL. A large stable LNAPL body can consist mostly of free LNAPL, but may not move because the LNAPL gradient is insufficient to overcome the capillary pressures that prevent LNAPL penetration of water-filled pores at the body edges (Huntley and Beckett, 2002).

After sufficient time has elapsed, LNAPL released above the water table will reach a state of vertical hydrostatic equilibrium. Under these conditions, the LNAPL does not move vertically because buoyancy and capillary forces balance the vertical force of gravity tending to force the LNAPL further downward. When LNAPL is at vertical equilibrium, the LNAPL in a vertical column both above and below the water table will form a continuous distribution of LNAPL saturation (see Figure 3). The distribution of LNAPL in the formation is a function of the LNAPL properties and of the pore size distribution of the aquifer materials (Farr et al., 1990). Note that water table fluctuations from natural hydrogeologic variability or from nearby pumping can smear the LNAPL into the vadose zone above and the saturated zone below the observed water table position.

If a monitoring well is installed at a location where mobile LNAPL exists, LNAPL will flow into the monitoring well and accumulate. Under normal conditions, the LNAPL thickness in the monitoring well will be approximately the same as the LNAPL thickness in the formation

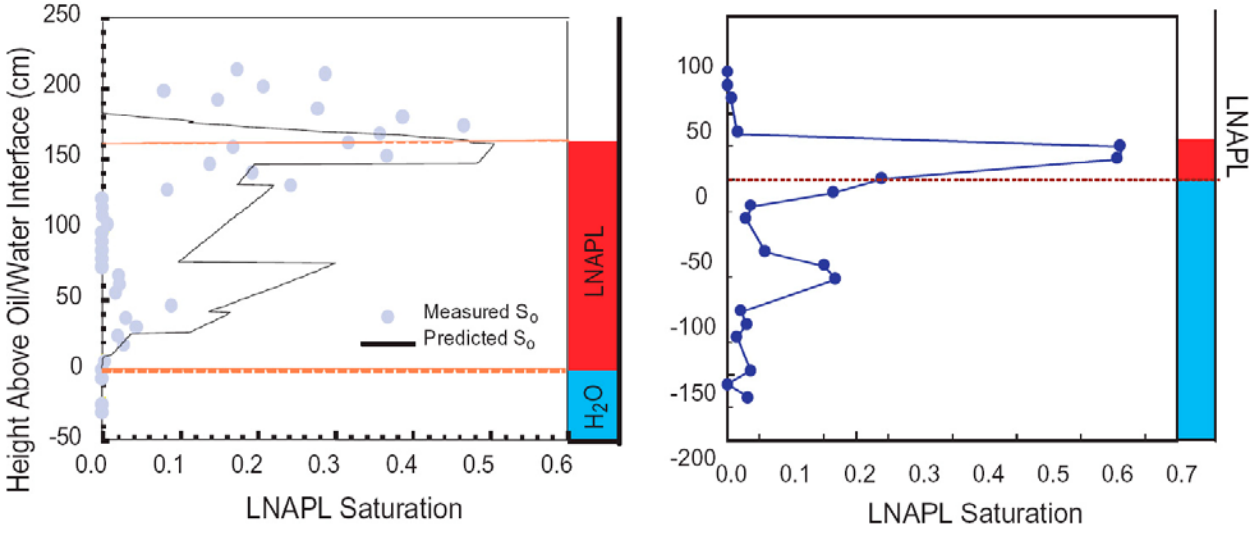


Figure 3. LNAPL saturation distribution at two sites. In the figure at left, the circles represent measurements of LNAPL saturation, while the solid black line shows saturations predicted by a vertical equilibrium model. In the figure at right, a rising water table has resulted in LNAPL entrapment below the current water table elevation. (Huntley, 1994)

(Huntley and Beckett, 2002). However, because LNAPL saturations in the aquifer are typically much less than one, and because the LNAPL saturations are not uniform in the formation, the volume of LNAPL in the aquifer will be less than the volume of a fully LNAPL-saturated media of the same thickness as the thickness of LNAPL in a monitoring well. This effect of "volume exaggeration" is illustrated in Figure 4, and is greater in fine-grained media than in coarse-grained media (Huntley and Beckett, 2002).

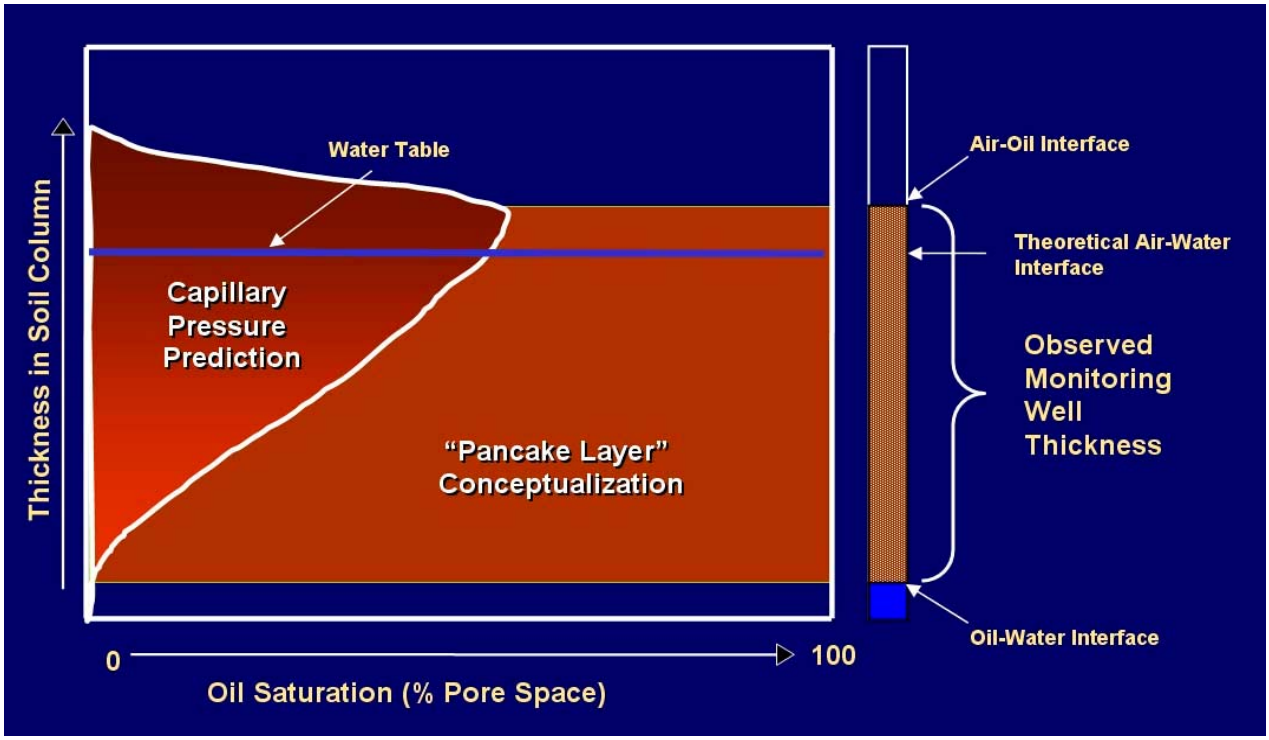


Figure 4. Comparison of LNAPL "Pancake" (Light orange) and "Shark Fin" (darker orange) subsurface conceptual models (RTDF, 2005). (Assumes same soil type).

For the same volume of mobile LNAPL present in the subsurface, the formation thickness of mobile LNAPL that resides in a fine-grained soil will be larger than the thickness of LNAPL present in a coarse-grained soil. The difference in formation thickness is a result of the greater difficulty that LNAPL has in penetrating the smaller pores of the fine-grained soil. As a result, the fraction of pore space occupied by the LNAPL in a fine-grained soil is less than the fraction of pore space occupied in a coarse-grained soil, thus the same volume of LNAPL has a smaller thickness in a coarse-grained material when compared to a fine-grained soil.

The difference in the distribution of a given volume of LNAPL has important implications for recoverability of the LNAPL. A substantial amount of LNAPL can accumulate in a monitoring well installed in a fine-grained soil, yet only relatively small quantities may be recoverable by conventional (hydraulic) means. Because the LNAPL saturation in a fine-grained soil is low, even if a substantial thickness of LNAPL is observed in a monitoring well, the LNAPL mobility is low, and the rate of LNAPL movement in the soil under an

induced LNAPL gradient will be very low relative to LNAPL flow rates in coarse-grained soils. Consequently, LNAPL recovery is most efficient in coarse-grained soils, and LNAPL recovery in fine-grained soils is frequently ineffective (Huntley and Beckett, 2002)

Not all pores are accessible to LNAPL. Dead-end pores that are isolated from LNAPL flow paths will not contain LNAPL. Because LNAPL occupies progressively larger pores as it invades unimpacted soil, the smallest pores in the soil will not be occupied by the LNAPL. In many cases, LNAPL moves mainly through macropores and secondary porosity openings rather than through the soil pore space. Secondary porosity is pore space created in the subsurface by fractures, fissures, or solution channels between consolidated or unconsolidated material. In many soils, fluid movement occurs primarily through these channels. Because macropores and secondary porosity openings are usually large in comparison to the average pore size of the soil, LNAPL readily moves through these structures, and can move quite rapidly under high hydraulic gradients. Macropores and secondary porosity are not reflected in pore size analyses performed on soils, and may be overlooked as potential LNAPL flow pathways.

Macropores control LNAPL transport in fine-grained sediments, and lead to small volume LNAPL pockets isolated as “islands” within water-saturated media (Johnson and Assali, 2010). The macropores in the vadose zone are typically too small to be defined by current delineation technologies. Elevated product thickness measurements in fine-grained units are not representative of the formation, but indicative of macropore conditions.

As LNAPL is removed from the subsurface using an LNAPL recovery well, the amount of LNAPL remaining in the formation steadily declines. This decline results in decreased LNAPL saturations, so that the LNAPL that remains flows more slowly toward the recovery well. As a result, LNAPL recovery typically follows a general declining production curve (Huntley and Beckett, 2002). It is possible to use this curve to estimate the total amount of LNAPL that was initially present in the formation.

The physical processes that are used to formulate this conceptual framework are discussed in the following sections, along with the models that are currently in widespread use to assist with LNAPL management. For clarity, the following definitions will be used to describe the state of LNAPL mobility throughout the remainder of this document:

- *free LNAPL* – LNAPL that is hydraulically connected in the pore space and has the potential to be mobile in the environment (ASTM, 2007).
- *mobile LNAPL* - free LNAPL that is moving laterally or vertically in the environment under prevailing hydraulic and soil type conditions (ASTM, 2007)
- *residual LNAPL* – LNAPL that is hydraulically discontinuous and immobile under prevailing hydraulic and soil type conditions (ASTM, 2007).
- *submerged LNAPL* – LNAPL that is found well below the current water table due to a historical release, followed by a rising or fluctuating water levels. Submerged LNAPL can be found in the LA Basin at sites with older, historical releases of LNAPL due to rising water table since the 1950s.

All mobile LNAPL is free LNAPL, but not all free LNAPL is mobile (ASTM, 2007). The thickness of LNAPL observed in a monitoring well is a second subject area for which the following definitions are presented to avoid unnecessary confusion:

- *observed monitoring well LNAPL thickness* (or simply "well LNAPL thickness") (H_o): the thickness of floating LNAPL observed in a monitoring well. Terms that others have used to describe the observed monitoring well thickness are "apparent thickness" and "observed thickness".
- *formation LNAPL thickness* (H_f) the thickness of subsurface soil that is impacted by LNAPL. This is sometimes called "*True LNAPL Thickness*".
- *specific volume (D_o)* – in a given area, the volume of LNAPL (excluding residual LNAPL above and below the LNAPL lens) divided by the area. For example, this is the number of cubic feet of LNAPL divided by the area (measured in square feet). This results in a hypothetical thickness of the LNAPL (in units of feet) if all the aquifer material (air, water, sand grains, clay stringers, etc) were hypothetically removed. Specific volume can also be reported in units of gallons per acre or some other volume per area method. DO is calculated by integrating the LNAPL saturation curve over the formation thickness, and thus represents an area under the "shark fin" multiplied by porosity.

These definitions are presented in Figure 5.

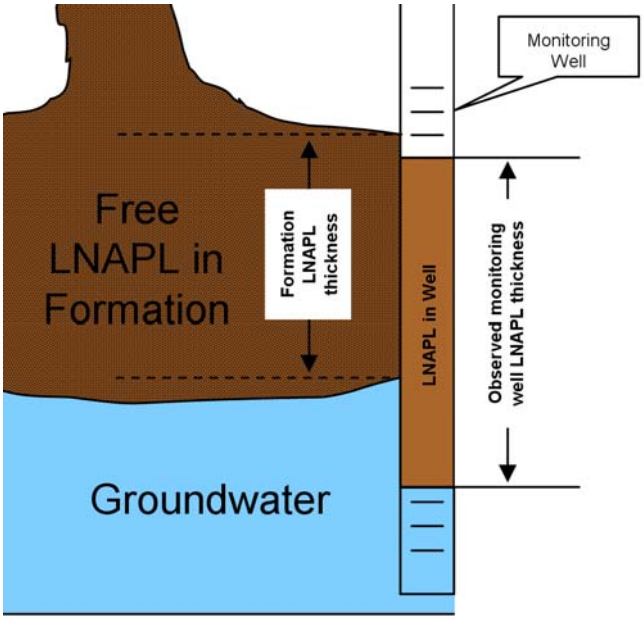


Figure 5. Definition of thickness terms used in this document. Specific volume is not shown, but would be less than the formation LNAPL thickness.

Historically the terms like "apparent thickness" and "actual product thickness" were used to describe LNAPL distribution in the field. Rules of thumb were employed in the past, where the "apparent thickness" was usually 2 to 10 times thicker than the "actual product thickness." These terms are being used less frequently as our understanding of LNAPL

and new conceptual models (e.g., the “shark fin”) of the distribution of LNAPL in the subsurface have developed. See Section 3.3.1 for more information about the history of LNAPL conceptual models.

LNAPL can act as a source of secondary impacts in adjacent soil, soil gas, and groundwater. The LA LNAPL *Conceptual Model* document provides references on how to estimate the fluxes of LNAPL constituents from the LNAPL phase to other phases. These fluxes from the LNAPL also results in Natural Source Zone Depletion (NSZD) that deplete the “source zone” (the LNAPL body) (ITRC, 2009A). NSZD, when properly understood, can be used as a comparative tool to evaluate the relative effectiveness of LNAPL remediation technologies and enhance the overall understanding of a site. The ITRC (2009A) states “since rates of destruction vary greatly from site to site, the residence times of source zone constituents in environmental media can vary greatly.” The ITRC (2009B) states that the potential time frame for NSZD is “very long”, i.e., > 10 years (see Appendix 1).

1.3 A Note on Units Used in This Document

Throughout this document, example calculations are provided for most of the equations. For simplicity, SI units are used in all equations. However, unless indicated otherwise, any consistent set of units may be used for any of the calculations illustrated in this document. Note that typical units are shown for variables and constants in these equations. As illustrated in the examples, conversion factors may be needed in the calculations with these typical units to convert to a consistent set of units.

2.0 CHARACTERISTICS OF LNAPLS POTENTIALLY PRESENT AT REFINERIES

LNAPLs potentially present at refineries and petroleum distribution facilities include feedstocks, intermediate process streams, and final products from a variety of sources. Major LNAPL types potentially present at petroleum facilities include (API, 2002):

Feedstocks:

- Crude oil
- Natural gas liquids
- Recycled oil

Intermediate Streams:

- Atmospheric gas oil (light and heavy)
- Naphtha (light & heavy from various units)
- Vacuum gas oil (light and heavy)
- Gas oil (light and heavy)
- Residuum
- Aromatics (benzene, toluene, xylenes, etc.)

Major Products:

- Gasoline
- Jet fuel/kerosene
- Diesel oil
- Fuel oil (several grades)
- Asphalt
- Lubricants
- Petrochemicals (olefins, aromatics, etc.)
- Residuum

Other Process Streams:

- Used solvent or lean oil
- Slop oil

The physical properties of streams for which data are readily available are summarized in Table 1. These properties were obtained from Jokuty (1999), Fetter (1999), Charbeneau (2003), and Charbeneau (2007). The chemical composition of refinery process streams and additional information on the properties of hydrocarbons can be found in Huntley and Beckett (2002), Newell et al. (1995), Mercer and Cohen (1990), and the Government of Canada database (http://www.etc-cte.ec.gc.ca/databases/OilProperties/Default.aspx), as well as texts in the chemical engineering literature.

The table below summarizes typical physical properties of four key LNAPL materials (Source: Table 1 and other sources as noted).

	Density @ 15°C (g/cm^3)	Viscosity (cp)	Interfacial Tension (dynes per cm)
Gasoline	0.729	0.355 – 0.659	50
Diesel	0.827	Wide range	4 - 28.2
JP A/B	0.77 – 0.79	1.18 -1.59	50 (API 4729)
Crude Oil	0.832 – 0.914	Wide range	25-30.5

These physical properties are important for estimating LNAPL volumes and LNAPL mobility (see Section 3) and are needed for evaluating some (but not all) potential remediation technologies (See Section 5).

3.0 LNAPL DISTRIBUTION

In order to determine a precise volume of LNAPL in a formation, the volume of LNAPL present in the entire vertical soil column must be known at all locations within the formation. Because it is not possible to obtain this information, methods of estimating LNAPL volume at different discrete points within the subsurface must be used to estimate a total LNAPL volume. The estimates of LNAPL specific volumes at these discrete locations can then be used to estimate the total LNAPL volume in the formation through spatial interpolation. The uncertainty in estimating these two quantities arises from the following factors related to the LNAPL and to the formation:

- The source of the LNAPL, and therefore, the original properties of the LNAPL, may not be known.
- The physical properties of the LNAPL and the LNAPL chemical composition may not have been constant during the time of release.
- The LNAPL body may consist of more than one LNAPL type.
- The amount of LNAPL weathering and the spatial distribution of this weathering is unknown.
- Properties of the formation that affect LNAPL distribution vary on the scale of centimeters and are difficult to measure accurately.
- The relationships that govern distribution of LNAPL in the subsurface are still being refined.
- Unknown water table fluctuations smear LNAPL in the formation.
- Resource limitations constrain the amount of data that can be collected at any given site.

These limitations make estimation of subsurface LNAPL volume, mobility, and recoverability imprecise. As a result, estimations of LNAPL volume typically cover a wide range of values (EPA, 1996). Due to the assumption of vertical equilibrium these volumes overestimate the actual recoverable LNAPL volume; therefore, many investigators recommend that several different methods of estimating LNAPL volumes be used in conjunction to reduce the significant uncertainty (ASTM, 2007; USEPA, 2005; USEPA, 1996; Golder Associates, 2006). See Section 3.4 for more discussion about the uncertainty involved in LNAPL volume estimation.

In estimating LNAPL volumes, the composition of the LNAPL is not an important factor except as it affects the physical properties of the LNAPL. For fluid flow rates, the density and viscosity are important, but any liquid with the same density and viscosity will flow at the same rate under the same induced gradient. Similarly, LNAPL saturation is affected by LNAPL interfacial tensions, and fluids exhibiting the same interfacial tensions will cause similar saturations in a porous media. Chemical composition can become important when the fate of the LNAPL is being assessed, since changes in the LNAPL chemical composition will affect the LNAPL mobility and persistence in the subsurface and can be used to determine the rate of natural source zone depletion (NSZD).

The process of estimating a total subsurface LNAPL volume usually involves four steps:

1. Determining LNAPL presence at specific locations;
2. Determining the areal extent of LNAPL occurrence;
3. Estimating the vertical distribution (and specific volume) of LNAPL at discrete locations; and,
4. Interpolating and extrapolating the discrete specific volume estimates to determine the total LNAPL volume.

These steps and the methods employed are described in the following sections, and the methods are summarized in Table 2.

3.1 Step 1 - Determining LNAPL Presence at Specific Locations

The first step in calculating the subsurface volume of LNAPL is to determine whether or not LNAPL is present at a specific location. There are many methods used to determine LNAPL existence. These methods include both direct methods and indirect methods, and methods that can be applied ex-situ (in samples brought to the surface) or in-situ (beneath the subsurface, often in real time). API (2007) provides more detail on methods that can be used to determine LNAPL presence.

3.1.1 Ex-Situ Direct Methods

Direct methods rely on direct examination or analysis of soil samples collected from soil borings or trenches. These methods are highly reliable because the LNAPL is observed directly, and no interpretation of data or calibration of instruments is required. Methods of ascertaining the presence of LNAPL in a soil sample are listed (ASTM, 2007) below. All of these methods require conventional drilling techniques to bring soil samples to the surface for examination.

- *Visual logging* – A soil core is examined visually for the presence of a sheen, LNAPL droplets, or major LNAPL deposits.
- *Paint filter test* (USEPA, 2004) – This method is used to determine the presence of free liquids in a representative sample of waste. A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the 5-min test period, the material is deemed to contain free liquids.
- *Shake test* – A portion of a soil sample is shaken with water to cause separation of LNAPL from the soil and water, which is then visually identified.
- *Dye testing* – This method is similar to the shake test, except that a hydrophobic dye (Sudan IV or other) is added to the sample. The dye preferentially dissolves into the LNAPL, and the LNAPL can then be identified visually.
- *UV examination* (USEPA, 2007) – A portion of a soil sample is illuminated with a UV lamp to stimulate fluorescence of petroleum compounds on or within the soil core. The fluorescence is produced when molecules of polynuclear aromatic hydrocarbons (PAHs) and other aromatics give off energy in an attempt to return to their ground state after being excited by the UV light source.

- *Photographic logging* – A photographic record of soil cores under ambient or UV light is generated to record the presence of LNAPL within the soil sample. Photographic logs of continuous cores can be assembled to form a continuous photographic record of NAPL distribution in the subsurface.
- *Dye-impregnated media* (FLUTe, 2007) – A dye-impregnated media (typically plastic) is pressed against the soil sample. The media indicates the presence of LNAPL with a color change.

3.1.2 Ex-Situ Indirect Methods

Indirect methods use physical or chemical indicators of LNAPL presence, such as the emanation of vapors, to determine whether or not LNAPL is present within a given soil sample. These methods are not as reliable as direct methods. Indirect methods must be calibrated by comparing the response of the indicator used to actual LNAPL presence determined using direct methods. Indirect methods of determining LNAPL presence in soil cores from soil borings include:

- *Headspace vapor analysis* (USEPA, 2004B) – The concentration of total vapors in the headspace of a soil core placed in a plastic bag or other container are measured with a photo ionization detector (PID) or a flame ionization detector (FID). The PID or FID readings are correlated to soil cores where LNAPL is present to determine the response at which LNAPL is likely present in the soil core.
- *Soil core chemical analysis* – Soil samples with Total Petroleum Hydrocarbon (TPH) concentrations that exceed 10,000 mg/kg are often considered to contain NAPLs. In addition, partitioning calculations can be used to determine the theoretical concentration at which LNAPL must be present in a soil sample containing a single compound or mixture of known composition (Feenstra et al., 1991; Brost and DeVaull, 2000; Pankow and Cherry, 1996; Mayer and Hassanizadeh, 2005). This concentration is called the soil saturation limit of the compound or mixture. If the total soil concentration exceeds the soil saturation limit, then the presence of LNAPL in the sample is implied. The expression for the total (dry basis) soil concentration above which LNAPL presence is implied is (Pankow and Cherry, 1996):

$$C_{sat} = \frac{S(K_d \rho_b + \theta_w + H\theta_a)}{\rho_b} \qquad \text{Equation 3.1}$$

where: C_{sat} = LNAPL component concentration in soil (dry basis; mg LNAPL/ kg soil);

S = LNAPL component solubility (effective solubility if LNAPL is a mixture; mg/L);

K_d = soil/water partitioning coefficient (L/kg);

θ_w = soil water content (L water /L soil);

H = LNAPL component Henry's Law constant (L air/L water);

θ_a = soil air content (air volume/ bulk soil volume);

ρ_b = soil bulk density (g/cm^3).

Example –Calculating C_{sat}

If an LNAPL contains benzene at a mole fraction of 0.02, then the effective solubility of benzene from the LNAPL is 2% of the pure phase benzene solubility of 1800 mg/L, or 36 mg/L. Assume that the soil has the following properties:

K_d = 0.62 L/kg;
θ_w = 0.15;
H = 0.25;
θ_a = 0.15;
ρ_b = 1.65 g/cm^3.

Then the maximum benzene concentration that can exist in the soil without the presence of a separate LNAPL phase is:

$$C_{sat} = \frac{S(K_d \rho_b + \theta_w + H\theta_a)}{\rho_b}$$

$$= \frac{36\frac{mg}{L}\cdot\left(\frac{L}{1000cm^3}\right)\cdot\left(0.62\frac{L}{kg}\cdot 1.65\frac{g}{cm^3}\cdot\left(\frac{kg}{1000g}\cdot\frac{1000cm^3}{L}\right)+0.15+0.25\cdot 0.15\right)}{1.65\frac{g}{cm^3}\cdot\left(\frac{kg}{1000g}\right)}$$

$$= 26\frac{mg}{kg}$$

Significant uncertainties using the partitioning method arise from the non-uniformity of LNAPL distribution in the sample and the value of the soil water partitioning coefficient (K_d). These uncertainties can result in a false negative indication of LNAPL presence. For example, if LNAPL is present primarily in the secondary porosity of a soil sample (e.g., in fissures within a clay), then the LNAPL concentration may be below C_{sat} because the LNAPL mass will be averaged over the entire weight of the soil core. This method must be used with care before the absence of LNAPL at a site can be erroneously inferred.

- *Dean Stark analyses.* LNAPL is directly extracted from soil cores using a solvent after driving off water. The weights of the sample before and after water and oil extraction are used to determine total LNAPL saturation (Dean-Stark method; Schlumberger, 2007). Total Petroleum Hydrocarbon (TPH) and LNAPL concentrations in soil over time can also be used as tools to determine the rate of NSZD.

3.1.3 In-Situ Direct Methods

In-situ direct methods use technologies similar to direct methods employed in for ex-situ soil samples, except that they are deployed downhole. The most important in-situ direct methods of LNAPL detection are:

- *Dye testing* – In-situ dye testing is similar to the ex-situ dye-impregnated media test, except that the media is deployed down-hole (see Figure 6). One example is the LNAPL FLUTe (Flexible Liner Underground Technologies, Ltd, Co.) system, in which a fabric is deployed downhole (FLUTe, 2007). The fabric reacts with the LNAPL to produce a very obvious stain on the fabric where it contacts the pure

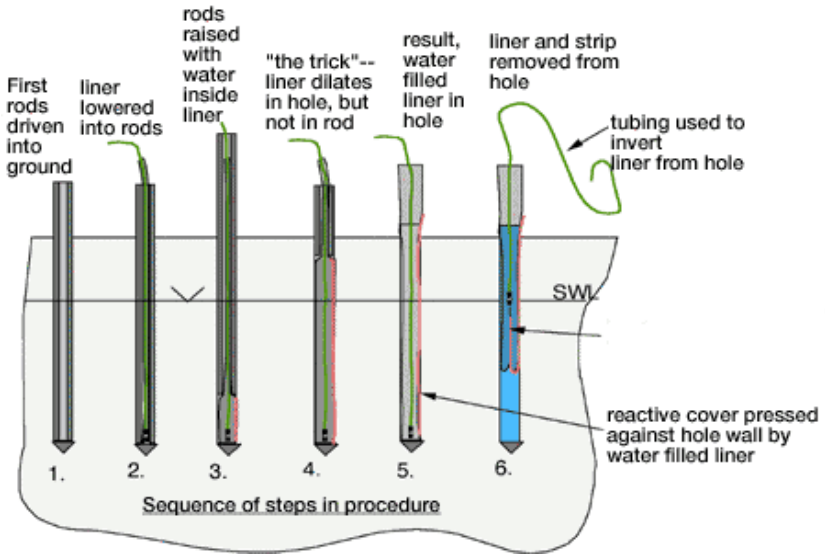


Figure 6. Down-hole dye testing concept (FLUTe, 2007).

product. The fabric is recovered by inverting the liner from the hole. As the tubing is pulled from the hole, the inverting liner follows it to the surface. After the entire liner/cover is peeled from the hole, the liner is pulled off the covering, exposing the inside surface of the cover. The stains on the inside surface are easily read for the location of the LNAPL in the hole.

- *Laser-Induced Fluorescence (LIF)* – LIF (also known as ROST or UV-ROST) is similar to UV testing of soil cores, but the illumination source is deployed downhole usually by a cone penetrometer (CPT) rig (USEPA, 2007). The system is illustrated in Figure 7. Light at a specific wavelength generated from a laser is passed down a fiber optic cable to a sapphire window in the tip of the CPT rod string as it is advanced into the subsurface. The laser light causes two- or three-ring aromatic compounds, or polycyclic aromatic hydrocarbons (PAH) in the soil adjacent to the sapphire window to fluoresce. The induced fluorescence from the PAHs is returned over a second fiber to the surface where it is quantified using a detector system. The peak wavelength and intensity provide information about petroleum product type or potential interferences. The intensity of the fluorescence is used as an indicator of the relative contaminant concentration that the soil is illuminated with light in the visible wavelength.] LNAPL is detected by direct observation of LNAPL globules.

- *Downhole video logging* – Video recording equipment mounted inside a cone penetrometer allows for real-time in-situ visualization of subsurface contaminants as the device is driven into the formation. The GeoVis video logging system was developed for the Site Characterization and Analysis Penetrometer System (SCAPS) by the U.S. Navy.

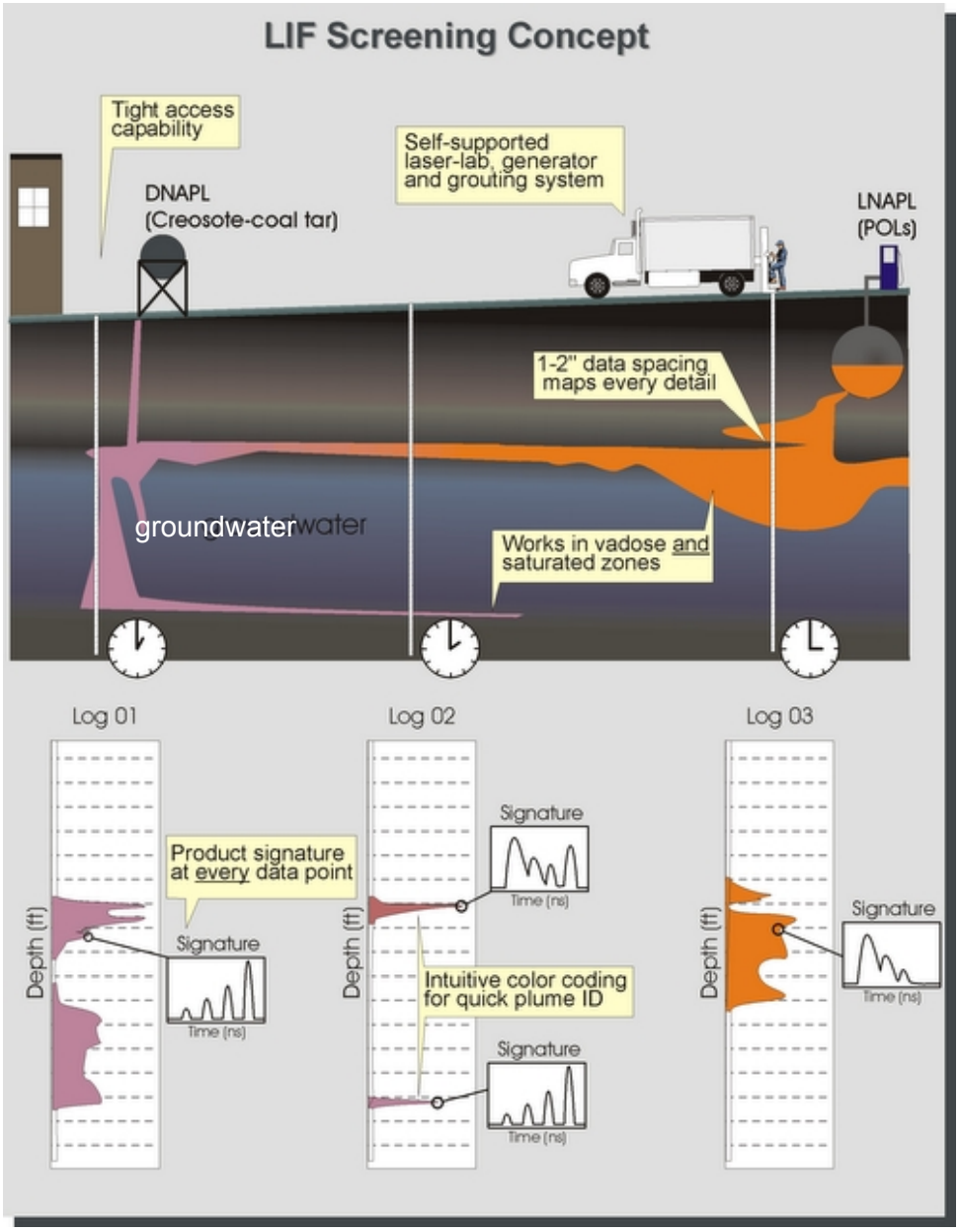


Figure 7. Laser-induced fluorescence (LIF) concept (Dakota Technologies, 2007).

3.1.4 In-Situ Indirect Methods

As with ex-situ indirect methods, in-situ indirect methods rely on indicators of LNAPL presence rather than on direct observation or evidence. The most important in-situ direct methods of LNAPL detection are:

- *Resistivity/electrical conductivity* (ASTM, 2007; Mercer and Cohen, 1993) – Geologic materials, and many LNAPLs, have geoelectric properties that vary and can be used to characterize those materials. Surface and down hole methods are available to measure resistivity or electrical conductivity. It is useful to calibrate

these readings to a few continuous cores from a site to ensure proper interpretation of the results. These methods are often very efficient, but require knowledge of the physics of the method, along with interpretive skills in data analysis. The tools can be employed down non-metallic cased holes, as well as open boreholes (often mud filled). Used more in research compared to actual field sites. Anecdotal accounts suggest this method has not been proven effective at evaluating LNAPL in the field.

- *Groundwater concentrations and moment analysis* (ASTM, 2007; Newell et al., 1995) – Concentrations of groundwater that are a significant fraction of the effective solubility of the LNAPL components are an indication that LNAPL may be present. Concentrations of dissolved constituents that do not change over time are an indication that an LNAPL body may be a continuing source of impact to the groundwater, especially if a remediation system that is recovering significant contaminant mass is in-place (ASTM, 2007). Dissolved hydrocarbon, electron acceptor reactants/products, and methane concentrations can be used to determine if biodegradation of LNAPL is occurring.

- *Membrane interface probe (MIP)* (ASTM, 2007) – The MIP generates chemical readings for volatile compounds by heating the soil materials and collecting volatized gasses through the membrane for subsequent chemical analysis. The system operation is shown in Figure 8. The amount of organic material is quantified and correlated to other direct methods to determine what MIP readings are indicative of LNAPL presence. This technology has been used frequently in the field at both LNAPL and DNAPL sites.

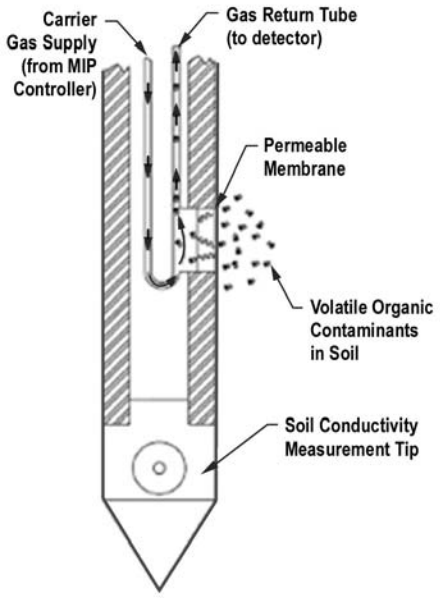


Figure 8. Functional parts of the MIP tool (USEPA, 2007).

- *Partitioning Interwell Tracer Test (PITT)* – A PITT test detects LNAPL in the subsurface based on differential partitioning of tracers, typically higher molecular weight alcohols or perfluorocarbons, between the LNAPL and water phases (National Research Council, 2005; Istok et al., 2002). The tracers are injected into the subsurface and recovered in extraction wells downgradient of the presumed LNAPL zone. Analysis of the tracer breakthrough curves provides an indication of both the presence and the quantity (saturation) of LNAPL in the subsurface. Investigations of the technique using a single well ("push-pull") technique have been developed by Istok et al. (2002). Currently, this method is relatively expensive and difficult to perform, and has been used infrequently at LNAPL sites.

- *Soil Vapor Analysis (National Academy, 2004; Cohen and Mercer, 1993, Agostino et al., 2002)* – Soil probes or passive soil-gas collectors are used to withdraw soil gas. Soil gas surveys can yield information on both the presence and extent of LNAPL, chiefly in the vadose zone. These surveys are also used to detect the

potential for impacts of vapors on surface receptors (such as indoor air quality) and to determine the rate at which NSZD is occurring through volatilization and/or biodegradation (based on vapor and carbon dioxide fluxes).

- *Other indirect methods (National Academy, 2004)* – Other indirect methods that are under development for application to LNAPL detection and determination of LNAPL extent and are not yet widely used include the following:
    - Ground-penetrating radar – use of radar signals to determine the presence and extent of LNAPL zones.
    - Seismic surveys – use of reflected sound waves to determine the presence and extent of LNAPL zones.
    - Downhole flow metering – use of downhole tools to measure vertical zones of preferential paths of groundwater inflow (Sale and McWhorter, 2001).
- Dissolved plume persistence and plume center-of-mass stability.

(Note these methods should not be considered to be proven technologies for LNAPL delineation at this point in time)

3.2 Step 2 - Determining LNAPL Areal Extent

The methods listed above can detect LNAPL presence at discrete locations. These methods can be applied across the area of interest to determine the areal extent of LNAPL. At large sites, the areal extent is usually most efficiently determined by indirect in-situ methods that have been calibrated by comparison to direct indications of LNAPL (ASTM, 2007). These in-situ methods include LIF, downhole video logging, and MIP in conjunction with conventional soil borings and advanced examination of soil cores.

Alternatively, if geophysical methods are effective in delineating LNAPL, then these may be employed directly to determine where LNAPL exists (ASTM, 2007; Cohen and Mercer, 1993). Similarly, soil gas surveys may be employed to determine the extent of volatile LNAPL bodies, especially those that are present at shallow depths below the surface (Cohen and Mercer, 1993). When survey methods are used, conventional soil borings and examination of soil cores are usually also employed to determine the survey tool responses that are indicative of LNAPL presence.

Recently, researchers have employed a moment analysis of PITT data to obtain information on the spatial distribution of subsurface LNAPL (Enfield et al., 2005; Jawitz et al., 2003).

3.3 Step 3 - Determining LNAPL Vertical Extent and Specific Volume

After defining the areal extent of LNAPL, the third step in determining the total LNAPL volume in the subsurface is to estimate the vertical extent of LNAPL, which is the volume of LNAPL present at each of the discrete locations where LNAPL is detected. The volume of LNAPL at a specific point is usually expressed as a “specific volume”, i.e., the volume of LNAPL per unit area in the entire soil column (Lenhard and Parker, 1990a; Charbeneau, 2007). The specific volume has dimensions of length and is always less than the total thickness of LNAPL within the formation. Determining LNAPL specific volume is probably the most difficult part of an LNAPL assessment, and different methods of estimation often

produce very different results (USEPA, 1996; LSPA, 2005; Ballestero et al., 1994). Methods of determining specific volume in the vadose zone and in the saturated zones are described below.

3.3.1 Methods of Determining LNAPL Specific Volume

The detection methods described above can be correlated to soil cores to relate the detection method response to LNAPL saturation. Alternatively, the TPH concentration in the soil can be used to calculate total LNAPL saturation at discrete vertical locations (USEPA, 1996), which can then be summed to determine an areal point estimate of LNAPL specific volume.

Direct Soil Measurements
When direct soil measurements are used and adsorption onto solids and dissolution into the pore water are ignored, the total LNAPL saturation in a particular soil sample can be calculated as follows (USEPA, 1996):

$$S_{NAPL} = TPH \times \frac{\rho_b}{n\rho_o} \qquad \text{Equation 3.2}$$

where: S_{NAPL} = total LNAPL saturation (L^3 LNAPL/L^3 pores);
TPH = TPH concentration in soil (mg TPH/kg soil);
n = soil porosity (L pores /L soil);
ρ_b = soil bulk density (g/cm^3); and
ρ_o = LNAPL density (g/cm^3).

Example: Estimating NAPL Saturation from TPH Data

The total petroleum hydrocarbon concentration in a soil is 20,000 mg/kg. The bulk density of the soil is 1.65 g/cm^3, the porosity of the soil is 0.3, and the density of the LNAPL is found to be 0.7 g/cm^3. Then the total LNAPL saturation is:

$$S_{NAPL} = TPH \times \frac{\rho_b}{n\rho_o} = 20000\frac{mg}{kg}\cdot\left(\frac{kg}{10^6 mg}\right)\times\frac{1.65\frac{g}{cm^3}}{0.3\cdot 0.7\frac{g}{cm^3}} = 0.16$$

A more quantitative method of estimating total LNAPL saturation is a Dean-Stark analysis. In this method, water is first evaporated from the sample. Solvent is then used to extract any oil in the sample. Gravimetric relationships and considerations of bulk and solid density are then used to calculate the total LNAPL saturation. Many environmental practitioners prefer this quantitative method over the more qualitative indirect methods.

When the LNAPL saturation in multiple soil samples are collected at a given location, a vertical profile of LNAPL saturation with depth can be created. When this vertical profile intersects the capillary fringe, the LNAPL saturation profiles resemble the characteristic LNAPL saturation profiles depicted in Figures 3 and 4. The LNAPL specific volume at the location of a single soil boring in which multiple soil samples have been analyzed is calculated by summing the individual LNAPL content values over the length of the boring

in which LNAPL was detected (Huntley et al., 1994; Lundegard and Mudford, 1998; Charbeneau, et al 1999; Charbeneau, 2007; LSPA, 2008):

$$V_o = \sum nS_{NAPL} \times dz \qquad \text{Equation 3.3}$$

where: V_o = LNAPL specific volume (m); and
dz = thickness of interval represented by S_{napl} value (m).

Example: Calculating NAPL Specific Volume from Saturation Data

Assume that three 2.5-m long soil cores each having a porosity of 0.3 contain LNAPL saturations of 0.15, 0.4, and 0.2. In this case, since the porosity and layer thickness is the same for each layer, the LNAPL specific volume is calculated as:

$$V_o = n \cdot dz \sum S_i = 0.3 \cdot 2.5m \cdot (0.15 + 0.4 + 0.2) = 0.56m$$

This can be converted to units of gallons per acre by multiplying by a conversion factor of $1x10^6$

V_o = 600,000 gallons per acre.

This method can be applied to LNAPL at any location within the soil column, including the vadose zone, saturated zone, or both.

Methods Applicable to LNAPL at the Water Table

If the LNAPL has reached the capillary fringe or water table, the method of calculating LNAPL saturation (and specific volume) from a combination of indirect and direct methods applied at soil borings can be used to determine the LNAPL specific volume. In practice, however, at sites where LNAPL has encountered groundwater, the LNAPL in the saturated part of the formation is typically quantified by installing monitoring wells at locations where detection methods indicate that LNAPL is present. The observed monitoring well LNAPL thickness can be related to the specific volume of LNAPL in the formation using models that consider LNAPL and/or soil properties. Methods of estimating LNAPL specific volumes when LNAPL has reached the capillary fringe or water table are described below. Only analytical methods are considered in this literature survey. Numerical models that can also be used to determine LNAPL specific volumes, as well as LNAPL mobility and recoverability, are not covered by this review.

Old Conceptual Model: Pancake Model

The simplest method of estimating the LNAPL specific volume is to assume that the volume of LNAPL in the formation is equal to the volume of LNAPL accumulating in a monitoring well multiplied by the formation porosity (see Figure 2). This conceptualization of LNAPL is often referred to as the “pancake model” (Huntley and Beckett, 2002), and is widely acknowledged to be an incorrect conceptualization of LNAPL distribution in the subsurface. However, because this model of LNAPL distribution requires only a

knowledge of porosity and measurements of LNAPL thickness in monitoring wells, it is simple to apply and is conservative.

If the subsurface is assumed to be completely saturated with LNAPL, then the apparent LNAPL thickness is multiplied by the formation porosity to derive the upper limit of specific volume. The apparent LNAPL thickness can be multiplied by any other factor between 0 and the formation porosity to account for LNAPL saturations less than 1. Because the pancake model is an upper limit of LNAPL specific volume, it can be used as a "reality check" for other estimates of LNAPL specific volume, and is therefore a useful quantity to calculate at any LNAPL site. It is not relevant to residual LNAPL or to vadose zone LNAPL that does cause an accumulation of LNAPL in wells, however.

New Conceptual Model: Vertical Equilibrium

Under conditions of vertical equilibrium, buoyancy, capillary and gravitational forces all balance one another so the water and oil phases exist in static equilibrium. As a result, soil moisture curves can be used to determine the free product distribution in the soil based on the observed thickness in a monitoring well (Charbeneau, 2000). The relationships describe a continuously variable LNAPL saturation in the formation (the "Shark Fin"). This saturation distribution is integrated over the vertical section of the formation occupied by the LNAPL to determine a specific LNAPL volume. This method is used by Farr et al. (1990), Leonard and Parker (1990), and Charbeneau (1999).

Farr et al. (1990) present several different models to calculate specific volume from

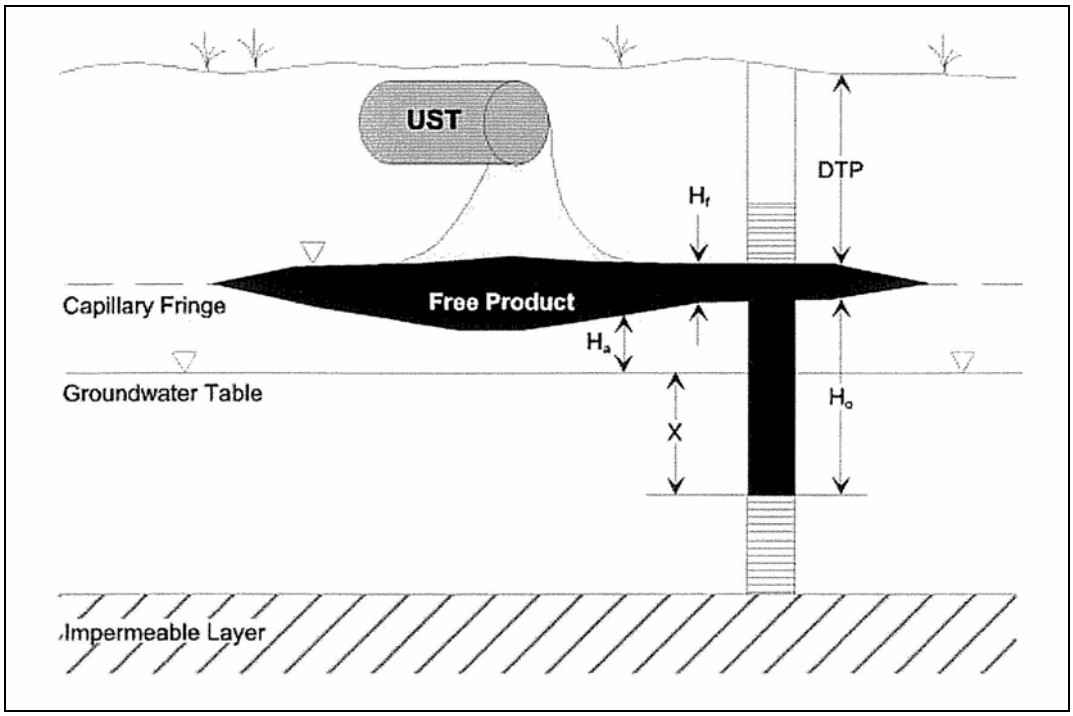


Figure 9. Definition of parameters for simple models (EPA, 1996).

observed LNAPL accumulations in monitoring wells for different soil types. For an unconsolidated sand with uniform pore sizes, the equation modified from Farr et al. (1990) is (Figure 9):

$$V_o = n(1-S_r)D\left[\left(\frac{H_o}{D}\right)-1\right]$$

Equation 3.4

$$D = \frac{P_d^{ow}}{\Delta\rho g} - \frac{P_d^{aw}}{\rho_o g}$$

where: V_o = specific volume of LNAPL (m);
S_r = reduced water saturation (L^3 LNAPL/L^3 pores);
H_o = thickness of LNAPL in monitoring well (apparent thickness; m);
P_d^{ow} = LNAPL-water displacement pressure (m-H_2O);
P_d^{aw} = air-water displacement pressure (m-H_2O);
$\Delta\rho = \rho_w - \rho_o$; and,
g = acceleration of gravity (9.81 m/ s^2).

Example: Calculating LNAPL Specific Volume From Apparent Thickness Data

Assume the following soil and LNAPL properties:

S_r = 0.045;
H_o = 0.5 m;
P_d^{ow} = 0.3 m;
P_d^{aw} = 0.069 m;
$\Delta\rho = \rho_w - \rho_o$ = 1 g/cm^3 – 0.7 g/cm^3 = 0.3 g/cm^3; and,

Then the specific volume is calculated as follows:

$$D = \frac{P_d^{ow}}{\Delta\rho g} - \frac{P_d^{aw}}{\rho_o g} = \frac{0.3m}{0.3\frac{g}{cm^3}\cdot 9.81\frac{m}{s^2}} - \frac{0.069m}{0.7\frac{g}{cm^3}\cdot 9.81\frac{m}{s^2}} = 0.092\frac{cm^3 s^2}{g}$$

and

$$V_o = n(1-S_r)D\left[\left(\frac{H_o}{D}\right)-1\right]$$

$$= 0.3\cdot(1-0.045)\cdot 0.092\frac{cm^3 s^2}{g}\left[\left(\frac{0.5m}{0.092\frac{cm^3 s^2}{g}}\right)-1\right]$$

$$= 0.12m$$

Charbeneau (1999, 2000) presents a model similar to that of Farr (1990) except that differing residual LNAPL saturations are allowed for the vadose zone and the saturated zone. The equations of the Charbeneau model are presented in Charbeneau (1999) and Charbeneau (2000). Charbeneau later updated the model with a focus on the van Genuchten soil characteristic curves and piece-wise linear equations to represent LNAPL specific volume as well as LNAPL mobility (Charbeneau, 2003). This model is used in the spreadsheet tools issued by API in API Publication 4729 (Charbeneau, 2003).

More recently, Charbeneau (2007) has worked with API to implement LNAPL volume estimation tools within the framework of stand-alone software rather than within a spreadsheet environment. The modified model allows up to three different layers to be present, and is implemented in the API LNAPL Distribution and Recovery Model (LDRM). The LDRM is documented in API Publication 4760 (Charbeneau, 2007).

Durnford et al., 2004 created a vertical equilibrium model that accounts for a historically variable water table. The model uses a comprehensive set of algorithms based on the work by Lenhard (1992). Uniquely, the model accounts for hysteresis and entrapment of nonwetting phases. Durnford et al. (2004) created an html applet that implements the model. The applet is available for online use or downloading at http://www.engr.colostate.edu/~durnford/. However, as the model is intended for student use, it has not been peer reviewed or widely distributed.

Resource & Systems International (RASI) has developed a software program called OILVOL that implements a vertical equilibrium model within a framework that can calculate a total subsurface volume of LNAPL (RASI, 1995). The software uses the Farr (1990) and Lenhard and Parker (1990) model to determine the LNAPL specific volume based on a given apparent thickness. The software is currently in version 2.0, and is distributed through Scientific Software Group (SSG, 2007). The model user's guide documents the model formulation and implementation (RASI, 1995).

The assumption of vertical equilibrium is not valid at all sites. Where vertical LNAPL gradients exist and vertical migration of LNAPL is occurring, more sophisticated models are needed to accurately represent LNAPL specific volumes from monitoring wells, and LNAPL movement in the subsurface (Sleep et al., 2000).

In studying the effect of a rising and falling water table, Liao and Aral (1999) conclude that single measurements of LNAPL thickness in wells in which LNAPL thicknesses are fluctuating leads to significant error in the estimation of LNAPL.

A major complication when using any method of estimating LNAPL volumes is water table fluctuation. When the water table rises and falls, LNAPL is smeared above and below its initial position. When the water table returns to its initial position, it will have lost LNAPL volume to the formation above and below the water table, which is trapped as residual LNAPL. The process is illustrated in Figure 10 (Fetter, 1999). When the water table falls, LNAPL occupies pores previously occupied only by water within the saturated zone. When the water table rises, this LNAPL is left behind as residual LNAPL, and the volume of free LNAPL in the formation is reduced. If water table fluctuations are large relative to the free LNAPL thickness in the formation, water table fluctuations may be sufficient to trap all of the previously free LNAPL.

Water table fluctuations can also cause LNAPL to appear and disappear from monitoring wells. If the water table rises, some previously free LNAPL will become trapped as residual LNAPL in the newly-created saturated zone. If the water table falls, LNAPL that was residual LNAPL in the saturated zone can become free LNAPL in the newly formed vadose zone, and LNAPL may then enter a well in which it was not previously observed. This process is illustrated in Figure 11.

A more detailed discussion of LNAPL mobility, residual saturation, LNAPL modeling tools and other topics is provided in Section 4.0.

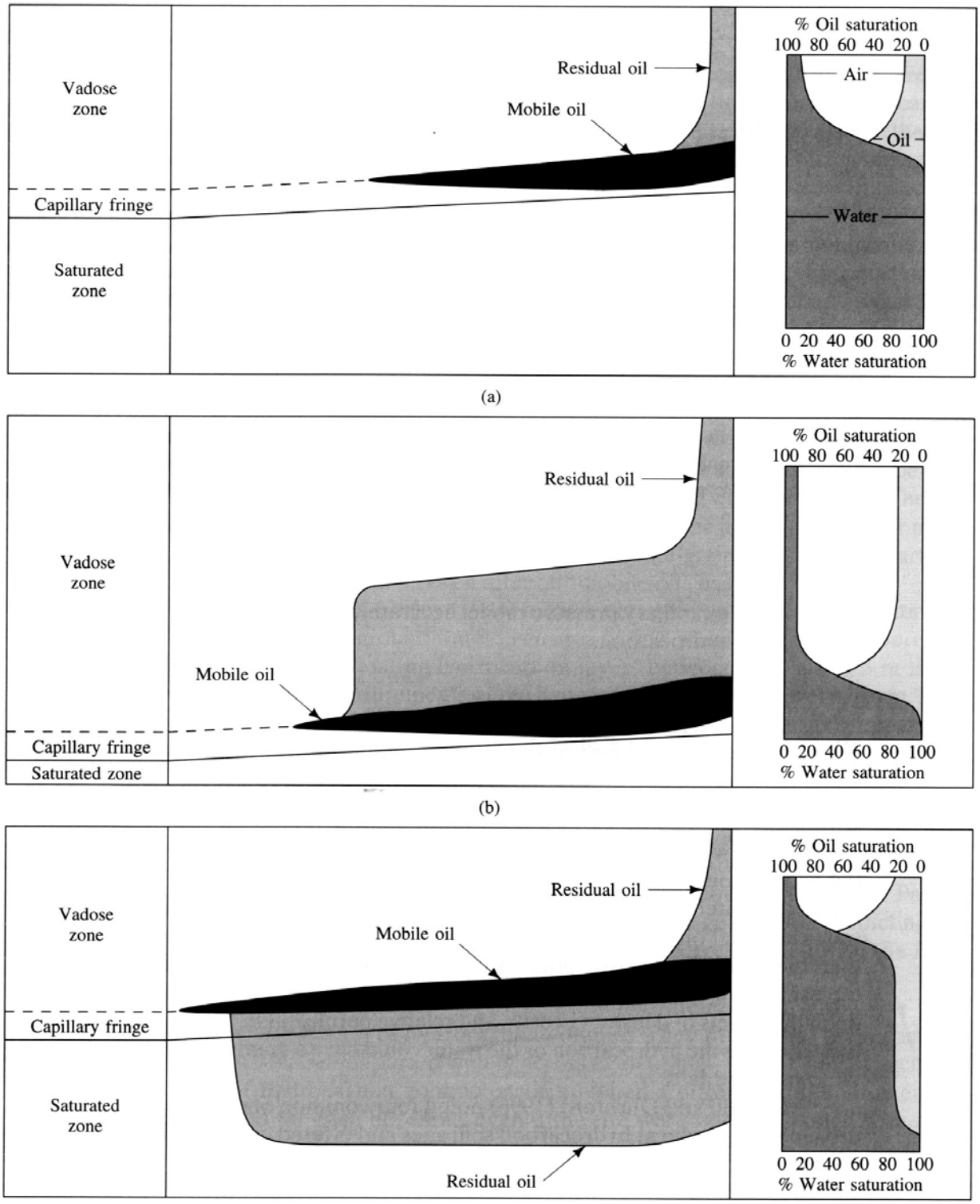


Figure 10. Effect of falling water table on LNAPL distribution (Fetter, 1999).

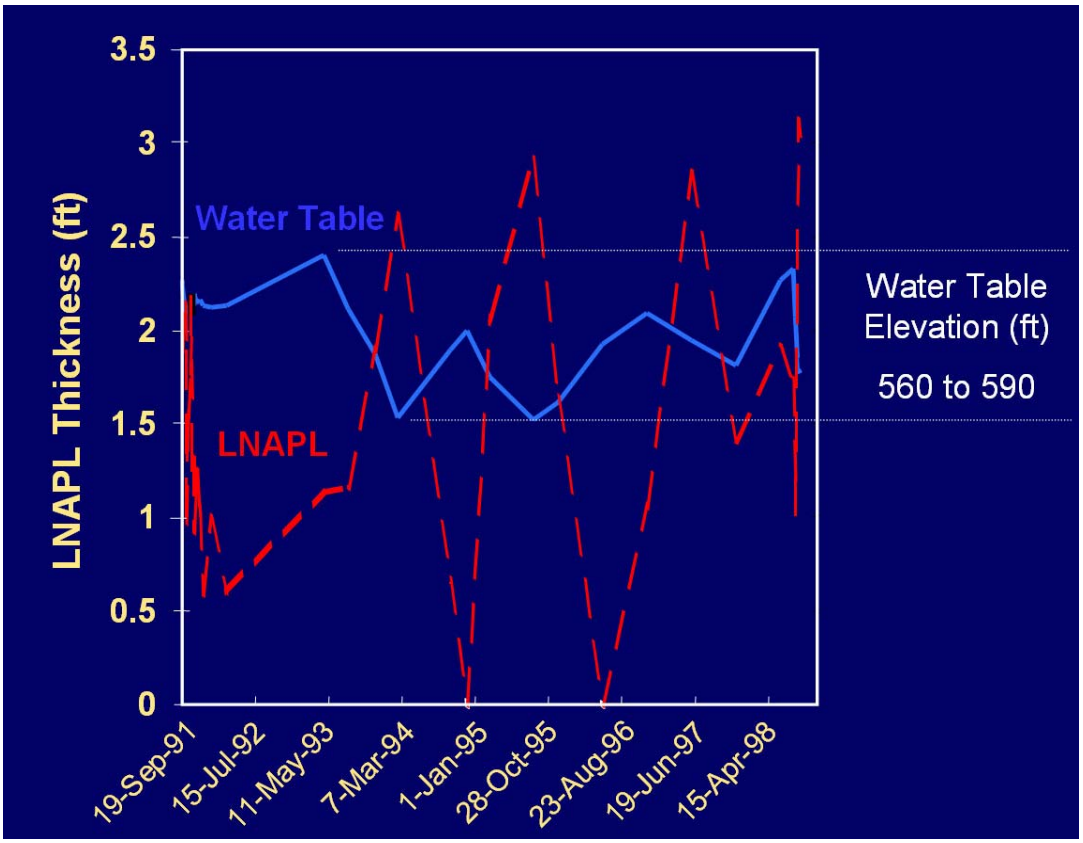


Figure 11. Change in observed monitoring well LNAPL thickness with water table fluctuations (RTDF, 2005).

Experiments and simulations performed by Oostrom et al. (2006) indicate that care must be taken with using any of these models with viscous LNAPLs. Their work showed that viscous LNAPLs may remain in the saturated zone for a significant amount of time instead of rising with a rising water table. Thus, viscous LNAPLs may be present in the formation, but may not enter monitoring wells when the water table has risen about its initial level.

It is important to note that LNAPL can still be present in a formation, even if it does not appear in monitoring wells. If the LNAPL is present below residual saturation, it will be trapped in the formation pore space by capillary forces and cannot flow. Therefore, it will be unable to enter a monitoring well.

3.3.2 Evaluation of LNAPL Volume Estimation Methods

Literature Review

The literature contains several evaluations of the different LNAPL volume estimation models. Huntley et al. (1994) compared the vertical distribution of LNAPL to LNAPL distributions predicted using the models of Farr (1990)). LNAPL saturations ranged from 5% to 50%, with apparent thicknesses ranging from 1.5 to 2.5 m. The modeled vertical saturation distribution matched the general shape of the observed saturation distribution. In the three monitoring wells where LNAPL reached equilibrium calculated LNAPL specific volumes compared favorably to the measured specific volumes, falling between the

measured total specific volume and the measured specific volume from only below the oil/water interface.

Adamski et al. (2005) used the spreadsheets developed by Charbeneau (2003) to estimate the specific volume of LNAPL from an unknown source in a fine-grained soil. Measured LNAPL saturations in the soil column were mostly non-detect, and the authors concluded that this result was due to the large-scale heterogeneity of the matrix coupled with the small sampling scale, resulting in samples that were not representative. Because of the sparse dataset, it is not possible to firmly conclude how well the Charbeneau model performed. However, using site-specific data, the Charbeneau model did predict a higher saturation near the top of the sampling interval where LNAPL saturations are expected to be highest. When vertical gradients were taken into account using a preliminary version of the Charbeneau (2007) model, the peak LNAPL saturation was slightly less than the measured peak value. Adamski et al. (2005) emphasize the importance of using site-specific data rather than literature values of key parameters.

Li and Yang (2005) utilized the Charbeneau (2003) model to estimate specific volumes at nine locations at a former refinery. Although the soils at the site are not classified, the van Genuchten parameters reported for the soils suggest that they consisted of well sorted, coarse grained material, such as a sand. The identity of the LNAPL was also unknown, although LNAPL parameters were measured for the study. The authors report that the Charbeneau (2003) model match measured specific volumes from soil cores at five of the nine locations. The authors concluded that water level fluctuations, hydraulic influence form pumping wells, and variation in fluid properties were possible causes of difference between measured and modeled specific volumes at the four locations with a poor correspondence.

Specific Volume Estimates at the Shell Carson Facility

Specific volume estimates were developed for six pilot test areas at the Shell Carson facility. Two soil cores and CPT/ROST data from each pilot test location were used to develop 12 separate specific volume estimates, which ranged from 0.05 to 2.6 feet (ft^3LNAPL/ft^2soil) (Geosyntec, 2008). Specific recoverable volume was also estimated, and ranges from 0.001 to 0.35 feet (ft^3LNAPL/ft^2soil).

Specific Volume Model Comparison

The different models for estimating either LNAPL specific volume were evaluated for a test case to determine how the models responded to different input parameters. As part of the LA LNAPL project, a hypothetical LNAPL was assumed to be a crude oil. Model calculations of LNAPL formation thickness for four different apparent LNAPL thicknesses (0.1 inch, 1 inch, 1 foot, and 5 feet) were calculated for two different soil types. A medium sand was used as a representative coarse-grained soil, and a silty sand was used as a representative fine-grained soil. The results of model comparison are shown in Table 3.

The specific volume calculations predicted by the four vertical equilibrium models differed more than expected, since all of these models share a very similar theoretical basis. The API (2004) model predicted results that are very different from the Charbeneau (2003) and Charbeneau (2007) models, predicting a specific LNAPL volume of zero when the other two models predicted a finite specific volume. Overall, the Charbeneau (2003) model predicted much higher specific volumes than the Charbeneau (2007) model at low apparent LNAPL thickness values. At higher LNAPL thicknesses, the Charbeneau (2003)

model predicted LNAPL specific volumes that were approximately 75% greater than the Charbeneau (2007) model. Predictions of LNAPL specific volume of OILVOL were comparable to the API (2004) model in the medium sand, but were close to the Charbeneau (2003) model for the silty sand.

None of the models evaluated in this review will accurately predict the LNAPL formation thickness or specific LNAPL volume under fluctuating water table conditions. The smearing of LNAPL above and below the elevations observed at the time of LNAPL measurements will add residual LNAPL in the vadose zone above the zone of mobile LNAPL and in the saturated zone below the level of mobile LNAPL. If the total fluctuations of the water table are known subsequent to the LNAPL release, then the amount of LNAPL trapped above and below the zone of mobile LNAPL can be approximated from residual saturations, and this volume must be manually added to the estimates of LNAPL specific volume to develop a total LNAPL formation volume.

3.4 Step 4 - Estimating Total Subsurface LNAPL Volume

After estimates of specific LNAPL volume have been made at discrete locations, the total volume of LNAPL in the aquifer can be estimated by interpolating and/or extrapolating the discrete estimates over the area of the LNAPL body to determine a spatial distribution of LNAPL specific volume (see Figure 12). Methods of interpolating the discrete LNAPL specific volume measurements are discussed in many texts on geostatistics, including, for example: Davis, (1986), Isaaks and Srivastava (1989), and Chiles and Delfiner (1999). Spatial interpolation methods include:

- linear;
- inverse distance weighted;
- Clough-Tocher;
- natural neighbor; and,
- Kriging.

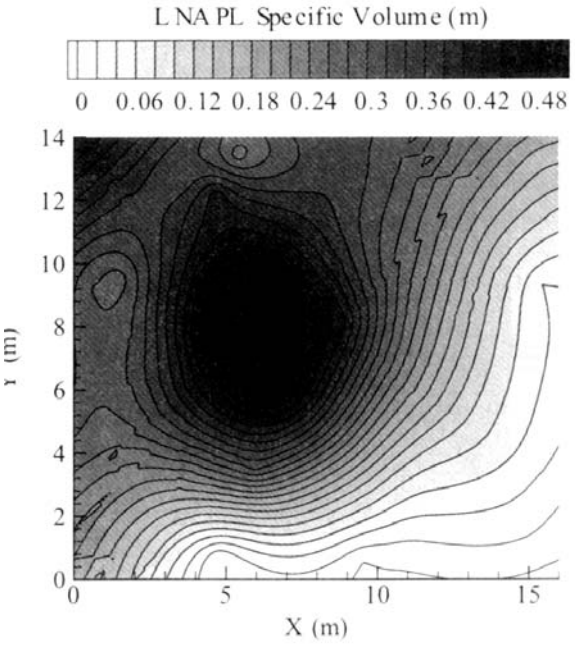


Figure 12. LNAPL specific volume contours determined through Kriging (Mayer and Hassanizadeh, 2005).

Various software programs, such as GMS (EMS-i, 2007) and Surfer (2007) are available to perform areal interpolation. The OILVOL program (SSG, 2007) performs area-wide estimates of LNAPL volume using Kriging.

Note there is considerable uncertainty in LNAPL volume estimates. Even a carefully designed LNAPL delineation study based on numerous direct measurements of LNAPL saturation can result in volume estimates that have uncertainty in the range of plus or minus of a factor of two or more (e.g., a 1000 gallon estimate could reflect an actual value of between 500 and 2000 gallons). Any volume estimate should be accompanied by an estimate of the uncertainty in the volume estimate. In general, this uncertainty means that

recovery targets should not be geared to recovering a certain volume but be more geared to what is being left behind.

4.0 METHODS TO ESTIMATE LNAPL MOBILITY AND LNAPL RECOVERY USING CONVENTIONAL TECHNOLOGIES

4.1 Overview of LNAPL Mobility

LNAPL mobility is the potential for LNAPL to move in the subsurface at the local scale. LNAPL mobility is a function of both the LNAPL fluid properties (density and viscosity) and of the soil properties (i.e., the intrinsic permeability of the formation and pore entry pressure, Charbeneau, 2000). Like other fluids in porous media, LNAPL obeys Darcy's Law, and LNAPL movement through the subsurface is dependent on the hydraulic gradient of the LNAPL. However, because the pores in the subsurface may contain LNAPL, water and/or air, LNAPL mobility is also a function of how much LNAPL is present.

LNAPL mobility is an important concept in the selection of remediation technologies for managing LNAPL releases, as "Conventional Technologies" (defined in Section 5.1), which remove LNAPL by hydraulic means (pumping or some other type of fluid extraction), are typically employed at LNAPL sites. "Post-Conventional Technologies", as defined by the LA LNAPL workgroup, are technologies that focus on residual LNAPL. The residual LNAPL can be present because of free LNAPL removal via Conventional Technologies or past lateral spreading of the LNAPL body, or it may be the result of historical releases and long-term rising water tables that create submerged LNAPL.

In the strictest sense, LNAPL is mobile even if the actual rate of movement is negligible or non-existent Similarly, if LNAPL is sufficiently mobile to enter a well, then it is "recoverable", even if the rate of recovery is negligible and/or quickly diminishes. However, as a practical matter, an LNAPL may be mobile, but if its rate of movement is negligible, then its mobility may not warrant action to control its movement. Similarly, if LNAPL is recoverable, but the rate of recovery or the recoverable volume is very small, then attempts to recover the LNAPL may not be justified technically or economically. Therefore, the degree of LNAPL mobility and recoverability are important considerations in assessing the significance of potential LNAPL migration. These considerations lead to two important questions typically posed at LNAPL sites:

- Question 1: Can the LNAPL move under the influence of a likely or prevailing hydraulic gradient (i.e., is the LNAPL "mobile")?
- Question 2: Can LNAPL be recovered using conventional pumping technologies (i.e., is the LNAPL "recoverable")?

To answer these two questions, the assessment of LNAPL mobility can be either empirical, based on observations of LNAPL in the field, or quantitative, based on calculations of LNAPL rates of movement or potential movement. Our review has led to five different methods that have been used or proposed by different groups to answer Questions 1 and 2 posed above. These methods are summarized in the table below and are described at length in the subsequent sections. At small, simple sites, a single method may provide sufficient information for moving forward, while at other larger, more complex sites a "weight of evidence" approach may be advantageous.

The five methods of assessing LNAPL migration and recoverability we found in the technical literature were:

Method	Metric	Which Question?	Where Usually Applied?	How These Methods Are Applied (or Proposed To be Applied)
1. Evaluate site temporal data	1.1 Change in LNAPL footprint over time; consistent, large-scale changes in apparent thickness in LNAPL; and changes in the dissolved plume footprint.	1	Edge of LNAPL Zone (see Figure 13)	If the data show an **expanding LNAPL footprint** then LNAPL is considered to be mobile (ASTM, 2007). If the groundwater dissolved plume is stable or shrinking then that is indirect evidence that suggest the LNAPL footprint is not expanding (LSPA, 2008)
2. Apply Darcy's Law and Related Methods	2.1 LNAPL Mobility Term (from calculations of LNAPL properties and soil characteristics)	1 or 2	Either core or edge of LNAPL Zone	If LNAPL "Practical Limit of Mobility (PLM)" defined using a Mobility Term is < **10^{-7} cm^3sec/g** then LNAPL "can be presumed to be effectively immobile" (LSPA, 2008).
	2.2 LNAPL Seepage Velocity (from calculations of LNAPL and soil properties or from LNAPL tracer tests)	1 or 2	Either core or edge of LNAPL Zone	ASTM (2007) provides example where a LNAPL Seepage Velocity > **0.3 meters per year** (1 foot per year) indicates recovery by hydraulic skimming may be feasible.
	2.3 LNAPL Transmissivity (from calculations of LNAPL properties and soil characteristics; recovery data; or from LNAPL baildown test)	1 or 2	Either core or edge of LNAPL Zone	If LNAPL **Transmissivity > 1.1 to 8.6 x 10^{-7} m^2/s (0.1 to 0.8 ft^2/day)** then area/well is above the Practical limit of hydraulic and pneumatic recovery systems (ITRC, 2009; see text box on pg 43 of this document).
3. Evaluate Pore Entry Pressure	3.1 Apparent LNAPL thickness	1	Edge of LNAPL Zone	If **apparent LNAPL thickness in well > than pore entry head**, then LNAPL has potential to move (and be removed by pumping) (Charbeneau, 2007).
4. Compare Measured LNAPL Saturation to Residual Saturation	4.1 LNAPL Saturation	1 or 2	Edge and Core of LNAPL Zone	If **saturation > residual saturation** (determined by one of several methods) then LNAPL has potential to move ASTM, 2007) (and be removed by pumping).
5. Apply LNAPL Computer Models	5.1 Computed rate of LNAPL movement or rate/volume of recovery	1 or 2	Edge and Core of LNAPL Zone	Assess significance of LNAPL movement or recovery relative to site remedial objectives (Charbeneau, 2007).

Note we are not advocating using any of the metrics above as strict numerical standards to be applied to a specific site. Site-specific issues such as risk, site status,

and other factors need to be considered in addition to these general guidelines to determine LNAPL mobility issues. This table summarizes the key methods used to define LNAPL mobility in the technical literature. The LA LNAPL Conceptual Model document has additional information about how to assess LNAPL mobility.

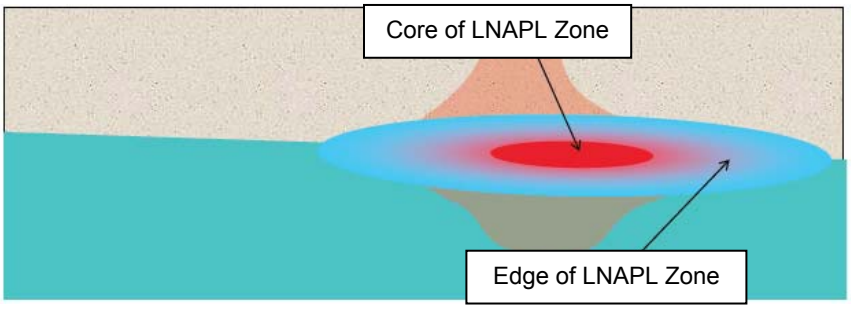


Figure 13. LNAPL Mobility Considerations in Two Different Areas of LNAPL Zone. In the core, Darcy's Law Methods are frequently used to estimate potential LNAPL recoverability at core of the LNAPL body. At the edge of the LNAPL body, pore entry pressure calculations and temporal data are often used to evaluate mobility. (Adapted from Hers et al., 2009).

The LNAPL mobility discussion in the following sections provides more detail on the five methods above. However, certain conditions can make the mobility question less important, such as when LNAPL is already in contact with a receptor (such as discharge to surface water or in the capture zone near a water supply well). Other situations make the mobility analysis more complex, and may make some of the methods listed above more difficult to apply. Examples of more complicated situations that may occur are: (Hers et al., 2009):

- LNAPL in fractured bedrock (not expected to be common in the LA Basin);
- Very steep LNAPL gradients;
- Very large water table fluctuations;
- Preferential pathways such as utility trenches or underground pipelines
- LNAPL very close to a receptor.

4.2 Method 1: LNAPL Mobility Based On Temporal Data

Temporal data include LNAPL data collected over time. Examples of how temporal data can be used to evaluate LNAPL mobility are provided below:

- LNAPL Zone footprint. LNAPL is mobile if the LNAPL zone footprint increases over time in the absence of complicating factors, such as non-equilibrium conditions or water table fluctuations. For example, if LNAPL begins to appear in wells that did not previously exhibit LNAPL, then the LNAPL is very likely to be mobile. Temporal soil sampling can also be used to evaluate LNAPL mobility. The LSPA (2008) state that: "Repeated stable measurements of LNAPL in soil at the limits of LNAPL present in soil can serve as indicators of LNAPL stability." They

recommend that sufficient data be collected to demonstrate seasonal trends, with three sets of soil data collected over at least a 2-year period.

- Dissolved plume data. A stable dissolved plume (such as BTEX from a gasoline release) over several years is supporting evidence that the LNAPL zone is not expanding and that the LNAPL source is not mobile (ASTM, 2007).
- Although not temporal data per se, the time since the likely LNAPL release together with consideration of the nature of the LNAPL can be used to evaluate the likelihood of LNAPL mobility. LNAPL is likely to be less mobile at sites where the release volumes are small and a long time period has elapsed since the last release event.

4.3 Method 2: Darcy's Law Methods

Within the subsurface, LNAPL can move only through the pores that contain a continuous, interconnected LNAPL phase. As the LNAPL saturation in the subsurface increases, an increasing fraction of the pore space contains interconnected LNAPL, and the conductivity of the formation to LNAPL increases. The ratio of permeability when LNAPL is present to the intrinsic permeability of the formation is called the LNAPL **relative permeability** (Charbeneau, 2000). Relative permeability can be measured, but is most often calculated by combining soil moisture curves with models that relate saturation to permeability (Figure 14; Huntley and Beckett, 2002).

LNAPL conductivity is also a function of the LNAPL density and viscosity. As LNAPL density decreases, LNAPL conductivity increases. Viscosity has the opposite effect, and increasing LNAPL viscosity decreases LNAPL mobility.

LNAPL mobility will vary throughout an LNAPL body, with the highest LNAPL mobility occurring where the LNAPL saturation is greatest. At the LNAPL body edges, where LNAPL is present at low saturations, LNAPL mobility will be very low. This relationship is shown in a cross-section of an LNAPL body in Figure 13. If the LNAPL body mobility at the edges is sufficiently low, the LNAPL body is called "stable," meaning that the movement of the LNAPL body as a whole is negligible (API, 2003). Stable LNAPL bodies can still contain a high volume of free LNAPL. However, the LNAPL can still be stable because the gradient is insufficient to cause LNAPL flow.

Darcy's Law methods are useful in the core of an LNAPL zone, where there is significant accumulation of LNAPL (see Figure 13), to assess LNAPL recoverability. At the edge of the LNAPL zone, Darcy's Law methods provide an estimate of the potential rate of LNAPL migration. Darcy's Law can overestimate LNAPL migration if pore entry pressure and/or residual saturation issues are not considered (Sections 4.4 and 1.2 and 4.5).

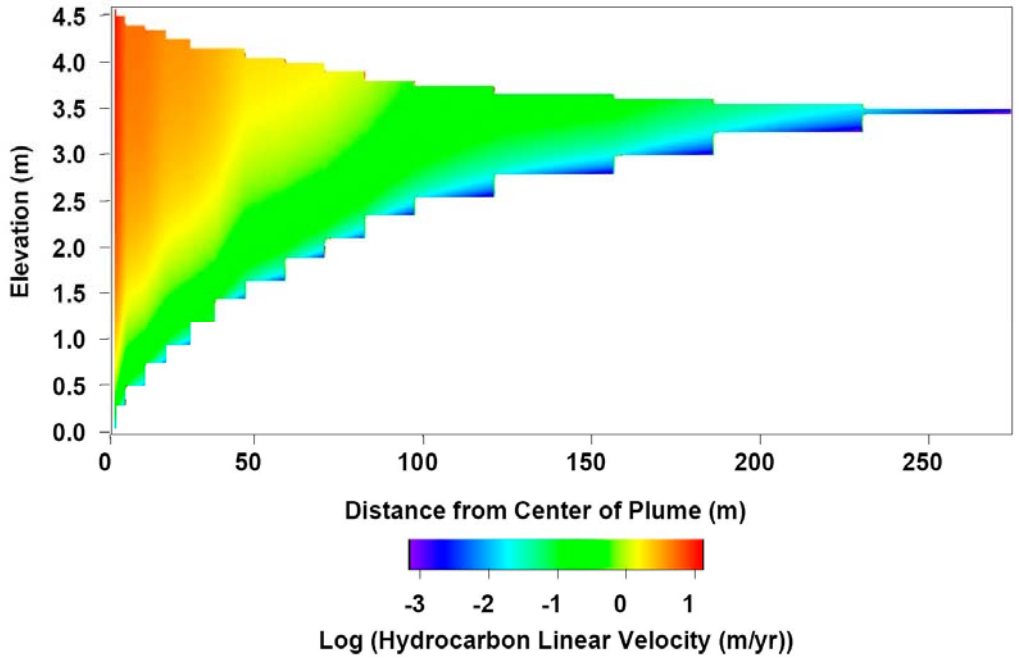


Figure 14 LNAPL zone (called plume in this figure) cross-section showing distribution of LNAPL body mobility (expressed in terms of potential LNAPL linear seepage velocity). LNAPL mobility is lowest at the edges of the body, where LNAPL thickness is thin and saturations are low (Huntley

4.3.1 LNAPL "Mobility Term"

Sale (2001) introduced an LNAPL "Mobility Term" defined as:

$$M_o = \frac{100 \cdot k_{ro} k_i}{\mu_o}$$ Equation 4.1

where: M_o = LNAPL "Mobility Term" (cm^3 s/ g) ;
k_{ro} = LNAPL relative permeability (defined below);
k_i = formation intrinsic permeability (cm^2);
μ_o = LNAPL dynamic viscosity (cP; centipoise).

The factor of 100 appearing in this expression converts meters to centimeters in the viscosity units.

Intrinsic Permeability k_i

LNAPL conductivity is a function of formation properties and chemical properties. The formation properties affect LNAPL conductivity through the formation's intrinsic permeability. Intrinsic permeability can be determined using the aqueous hydraulic conductivity as follows:

$$k_i = \frac{K_i \mu}{100^2 \cdot \rho_o g} \qquad \text{Equation 4.2}$$

where:

k_i = formation intrinsic permeability (cm^2);
K_i = hydraulic conductivity of water (cm/s);
ρ_o = density of water (g/cm^3);
g = acceleration of gravity (9.81 m/ s^2); and,
μ = dynamic viscosity of water (cP).

Example: Calculate intrinsic permeability assuming a water hydraulic conductivity of 10^{-3} cm/s (representative of a fine sand) and properties of water at 20° C:

$$k_i = \frac{K_i \mu}{100^2 \cdot \rho_o g} = \frac{10^{-3}\,\frac{cm}{s} \times 1cP}{100^2 \cdot 1\frac{g}{cm^3} \times 9.81\frac{m}{s^2}} = 1.0 \times 10^{-8}\,cm^2$$

The intrinsic permeability of $1.0 \times 10^{-8}\,cm^2$ is indicative of a very fine sand. The table below presents conversions of typical hydraulic conductivities (using a water density of 1 g/cm^3 and a dynamic viscosity of 1.0 cP for water) to formation intrinsic permeabilities for certain soil types.

	K_w	k_i
Soil Type	**(cm/s)**	**(cm^2)**
Gravel	10^{1}	10^{-4}
Coarse Sand	10^{-1}	10^{-6}
Fine Sand	10^{-3}	10^{-8}
Silt	10^{-6}	10^{-11}
Clay	10^{-8}	10^{-13}

In 2005, the Licensed Site Professionals Association (LSPA) published an LNAPL white paper that concluded that the LNAPL conceptual "pancake model" used to describe the nature, extent, migration, and risks associated with LNAPL had been shown to be invalid, and that a more accurate and useful conceptual model was available (this new model is described in Section 1.0 of this LA LNAPL Literature Review). Key points of the white

paper were that the "pancake model" should no longer be used, that apparent thickness in monitoring wells is not a meaningful indicator of risk, and that multi-phase fluid flow concepts should be employed. The LSPA followed this white paper with a "Part II" document that identifies improved methodologies for characterization and compliance purposes (LSPA, 2008).

In Part II, the LSPA illustrate how Equation 4.1 can be used for a site-specific evaluation of LNAPL mobility based only on intrinsic permeability, LNAPL viscosity, and relative permeability:

> *Site specific mobility evaluations require an understanding of the distribution of k_i, k_{ro}, and μ_o throughout the LNAPL-impacted areas of the disposal site. In many cases only a single LNAPL is present, and μ can be determined by performing a single test for dynamic viscosity at the appropriate temperature. Similarly, permeability testing is a straightforward procedure. Borehole hydraulic conductivity tests are recommended to characterize hydraulic conductivity, and intrinsic permeability can then be calculated from the hydraulic conductivity test results.*

Methods for determining relative permeability are described in the text box, but by using a value of 1.0 a conservative (i.e., overestimate) of mobility will result (LSPA, 2008). The LSPA defined a "Practical Limit of Mobility" or PLM, below which "LNAPL can be presumed to be effectively immobile." Based on an assumed hydraulic conductivity of 10^{-4} cm/sec for water, the recommended PLM for any LNAPL in any type of porous media using Equation 4.1 is **1.0×10^{-7} cm^3 s / g** (LSPA, 2008).

Example – LNAPL "Mobility Term"

Assume that a soil and LNAPL have the following characteristics:

$k_i = 10^{-11}$ cm^2 (typical permeability of a silt);
k_{ro}= 0.0625 (calculated from LNAPL saturation; see box on "Determining Relative Permeability k_{ro}");
μ_o = 0.62 cP (for gasoline; Huntley and Beckett, 2002).

Use Equation 4.1 to calculate the LNAPL "Mobility Term":

$$M_o = \frac{k_{ro} k_i}{\mu_o} = \frac{100 \frac{cm}{m} \times 0.0625 \times 10^{-11} cm^2}{0.62 \frac{g}{m \cdot s}} = 1.0 \times 10^{-10} \frac{cm^3 \cdot s}{g}$$

The example in which gasoline is present in a silt formation results in a "Mobility Term" less than the PLM ($1.0 \times 10^{-10} < 1.0 \times 10^{-7}$ cm^3 s / g). Thus the gasoline in the formation would be immobile.

Determining Relative Permeability k_{ro}

The LNAPL hydraulic conductivity is a function of saturation through the relative permeability (which is a function of soil properties). Relative permeability can be calculated by integrating the Burdine (1953) equations with the Brooks and Corey (1964) soil moisture model, or by combining the van Genuchten (1980) soil moisture function with the Burdine (1953) or Mualem (1976) equations (Charbeneau, 2003; Huntley and Beckett, 2002). The equations of Mualem (1976) generally predict larger values of LNAPL relative permeability for the same LNAPL and porous media properties (Charbeneau, 2003). Typical saturation and relative permeability curves are shown in Figure 15. As an alternative to these models, the square of the mobile LNAPL saturation (difference between LNAPL saturation and LNAPL residual saturation) can be used to approximate the average LNAPL relative permeability (Charbeneau, 2000).

Section 4.5 describes how residual LNAPL saturation is determined. Total LNAPL saturation can be obtained from the Dean-Stark method. Once values of total and residual LNAPL saturation are obtained, the mobile LNAPL saturation can be determined and the relative permeability of the LNAPL can be calculated from:

$$k_{ro} = S_{om}^{\ 2} \qquad \text{Equation 4.3}$$

where:

k_{ro} = LNAPL relative permeability (dimensionless); and,

$S_{om} = (S_o - S_r)$ = mobile LNAPL saturation (L^3 LNAPL/L^3 pores)

where:

S_o = Total LNAPL saturation in pore space (L^3 LNAPL/L^3 pores); and,

S_r = Residual LNAPL saturation (L^3 LNAPL/L^3 pores).

.

Example: Calculate relative permeability using Equation 4.3 assuming a total LNAPL saturation of 0.3 and a residual LNAPL saturation of 0.05:

$$k_{ro} = S_{om}^{\ 2} = (S_o - S_r)^2 = (0.3 - 0.05)^2 = 0.25^2 = 0.0625$$

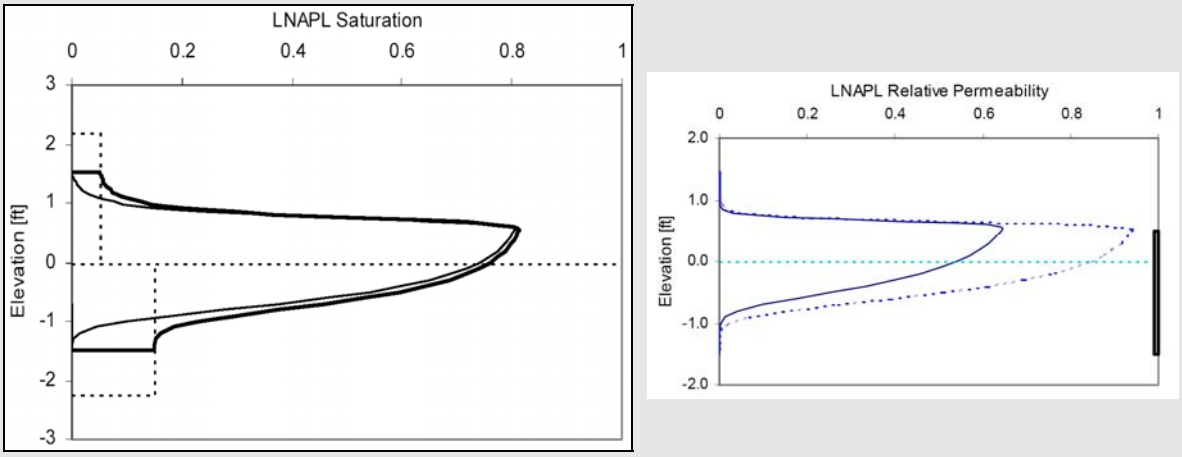


Figure 15. LNAPL saturation and relative permeability as a function of depth within the formation calculated using the Burdine (solid line) and Mualem (dashed line) expressions (Charbeneau, 2003).

4.3.2 LNAPL Seepage Velocity

Darcy's Law for LNAPL flow can be written in one dimension as (Huntley and Beckett, 2002):

$$q_o = k_{ro} k_i \frac{100^3 \cdot \rho_o g}{\mu_o} \frac{\Delta h_o}{\Delta x} \qquad \text{Equation 4.4a}$$

where: q_o = LNAPL flux (Darcy velocity, m/ s);
k_{ro} = LNAPL relative permeability (dimensionless);
k_i = formation intrinsic permeability (m^2);
ρ_o = LNAPL density (g/cm^3; can obtain from literature or experimentally);
$\Delta h_o/\Delta x$ = LNAPL gradient (slope on LNAPL surface) in x direction (m/ m);
g = acceleration of gravity (9.81 m/ s^2);
μ_o = LNAPL viscosity (cP; can obtain from literature or experimentally).

The LNAPL seepage velocity (or linear velocity) can then be calculated by dividing equation 4.4a by the fraction of porosity through which the LNAPL can move, which is the product of the porosity of the formation and the NAPL saturation:

$$V_{so} = \frac{q}{nS_o} \qquad \text{Equation 4.4b}$$

Where: n = porosity (L^3 pores/L^3 soil); and,
V_{so} = LNAPL seepage (or linear velocity; m/s);
S_o = LNAPL saturation (L^3 LNAPL/L^3 pores)

The ASTM "Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface" (ASTM, 2007) provides a detailed discussion of how to calculate and apply LNAPL seepage velocity. In section X3.2.3.2 "Multiphase Estimates of LNAPL Stability", ASTM uses an example of 10^{-6} cm/sec as an allowable seepage velocity through landfill liners. This value is then used as a "Potential Benefit Metric" and as in an example goal for LNAPL mobility reduction (ASTM, 2007). Hers et al., (2009) then calculated that the ASTM value of 10^{-6} cm/sec is equivalent to an LNAPL seepage velocity less than **0.3 meters per year (about 1 foot per year) and** is a "de minimus velocity", below which one would "not need to be concerned with LNAPL mobility."

Example – LNAPL Seepage Velocity

Calculate the seepage velocity of an LNAPL in a soil with the following LNAPL, groundwater, and soil characteristics:

$$\frac{\Delta h_o}{\Delta x} = 0.001;$$

$k_i = 10^{-10}$ m^2 (typical soil permeability of a coarse sand);
n = 0.43 (porosity of a typical sand);
S_o=0.3;
S_r=0.05;
ρ_o = 0.7 g/cm^3
μ_o = 0.62 cP (for gasoline; Huntley and Beckett, 2002)..

First, calculate relative permeability using Equation 4.3 (see text box on "Determining Relative Permeability k_{ro}":

$$k_{ro} = S_{om}^{\ 2} = (S_o - S_r)^2 = (0.3 - 0.05)^2 = 0.25^2 = 0.0625$$

Then use Equation 4.4a to calculate the Darcy velocity:

$$q_o = k_{ro} k_i \frac{\rho_o g}{\mu_o} i_o = 0.0625 \cdot 1x10^{-10} m^2 \frac{0.7 \frac{g}{cm^3} \cdot 9.81 \frac{m}{s^2} \cdot \left(\frac{100cm}{m}\right)^3}{0.62 \frac{g}{m \cdot s}} x\, 0.001 = 6.6 \times 10^{-8} \frac{m}{s}$$

Use Equation 4.4b to calculate seepage velocity:

$$V_{so} = \frac{q_o}{nS_o} = \frac{6.6 \times 10^{-8} \frac{m}{s}\left(\frac{86400s}{day} \cdot \frac{365days}{yr}\right)}{0.43 \text{ x } 0.30} = 16.2 \frac{m}{yr} = 53 \frac{ft}{yr}$$

According to the example provided by ASTM (2007) this LNAPL would be potentially recoverable.

The ASTM "Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface" (ASTM, 2007) provides a detailed discussion of how to calculate and apply LNAPL seepage velocity. In section X3.2.3.2 "Multiphase Estimates of LNAPL Stability", ASTM uses an example of 10^{-6} cm/sec as an allowable seepage velocity through landfill liners. This value is then used as a "Potential Benefit Metric" and as in an example goal for LNAPL mobility reduction (ASTM, 2007). Hers et al., (2009) then calculated that the ASTM value of 10^{-6} cm/sec is equivalent to an LNAPL seepage velocity less than **0.3 meters per year (about 1 foot per year) and** is a "de minimus velocity", below which one would "not need to be concerned with LNAPL mobility."

LNAPL Velocity Tracers

An emerging method to estimate LNAPL velocity is the use of velocity tracers in wells that contain LNAPL. Researchers at Colorado State developed a tracer-based method where a fluorescent dye that is only visible in an LNAPL is injected into a well containing LNAPL (Sale et al., 2007). The LNAPL column is intermittently agitated to obtain uniformly mixed tracer concentrations at the time of measurement. The rate of disappearance of the dye is then used to estimate the LNAPL migration rate (LNAPL Darcy velocity). To convert these LNAPL Darcy velocity to LNAPL seepage velocity one divides by the LNAPL content (mobile LNAPL saturation times porosity; see Equation 4.4b).

Mahler (2010) compiled data from LNAPL tracer tests. Seven sites, with a total of 50 wells, were evaluated, where LNAPL was present. The hydrologic setting observed at the seven sites were glacial till, silt and dense coral sand, fine sand, sand with gravel, and silty clays. The LNAPL Darcy velocities found with the hydrophobic dye ranged from 0.006 to 2.6 m/yr, with a mean and median of 0.15 and 0.064 m/yr for the LNAPL Darcy velocities, respectively. These measured LNAPL Darcy velocities are significantly less than typical groundwater Darcy velocities.

The LNAPL conductivity (K_o) can be calculated from equation 4.4a if the Darcy velocity and LNAPL gradient are known. However, it is difficult obtain and accurately apply an LNAPL gradient. Alternative approaches to obtaining K_o are employing LNAPL baildown and production tests (Sale 2001).

4.3.3 LNAPL Transmissivity

LNAPL transmissivity can be defined in the same manner that transmissivity is defined for flow of groundwater. However, as shown in Figure 16, the LNAPL saturation within the soil, and therefore, the LNAPL conductivity, changes with depth even in a homogeneous formation. The total transmissivity of the subsurface to an LNAPL is the vertical integration of the transmissivity throughout the LNAPL zone. If a soil boring is advanced through an LNAPL zone so that measures of LNAPL transmissivity can be made at multiple depths, then the LNAPL transmissivity is the sum of the transmissivities from each depth. Four methods for determining LNAPL transmissivity are described below.

LNAPL Transmissivity Method 1 (Calculated)

If LNAPL saturation data is available for multiple layers (for example, from multiple soil cores in a boring advanced through the LNAPL zone), then the Ko value calculated from the LNAPL saturation and soil properties, together with the thickness of the layers, can be used to calculate LNAPL transmissivity directly:

$$\overline{T}_o = \sum K_{o,i} b_i \qquad \text{Equation 4.5}$$

where: $\overline{T}_o$ = total LNAPL transmissivity (m^2/ s);
b_i = formation LNAPL thickness of layer i (m); and,
K_o= LNAPL hydraulic conductivity of layer i (m/ s)

The hydraulic conductivity of the LNAPL (K_o) can be calculated or found experimentally (baildown tests, production tests, etc.; see Sale, 2001). LNAPL hydraulic conductivity is:

$$K_o = k_{ro} k_i \frac{100^3 \cdot \rho_o g}{\mu_o}$$ Equation 4.6

where: k_{ro} = LNAPL relative permeability (dimensionless);
k_i = formation intrinsic permeability (m^2);
ρ_o = LNAPL density (g/cm^3; can obtain from literature or experimentally);
g = acceleration of gravity (9.81 m/ s^2);
μ_o = LNAPL viscosity (cP; can obtain from literature or experimentally).

Note: to obtain the value in ft^2/day multiply by a conversion factor of 9.3 x 10^5.

Example – LNAPL Transmissivity

Assume that three 0.1-m thick soil layers have average oil hydraulic conductivities of 4.3 x 10^{-8}, 5.2x10^{-7}, and 8.2x10^{-8} m/s respectively. These LNAPL conductivities can be calculated following Equation 4.6 or can be found utilizing baildown or production tests (Sale, 2001). The LNAPL transmissivity is then calculated as:

$$\overline{T}_o = \sum K_{o,i} b_i = \left(4.3\times10^{-8} \cdot \frac{m}{s} \cdot 0.1m + 5.2\times10^{-7} \frac{m}{s} \cdot 0.1m + 8.2\times10^{-8} \frac{m}{s} \cdot 0.1m \right)$$

$$= 6.45\times10^{-8} \frac{m^2}{s}$$

$$6.45\times10^{-8} \frac{m^2}{s} \cdot 9.3\ x\ 10^5 = 0.060 \frac{ft^2}{day}$$

Following ITRC (2009), the LNAPL in this example would not be recoverable because the calculated transmissivity of 0.060 ft^2/day is less than the range of transmissivities (0.1 to 0.8 ft^2/day) presented as the minimum necessary transmissivity to recover LNAPL using hydraulic or pneumatic recovery systems.

The method shown in the example above is based on very simple assumptions. In practice, more sophisticated methods are needed to more accurately address complex LNAPL sites. Cho et al. (2010) presents opinions/considerations on how to calculate LNAPL transmissivity by modeling from LNAPL saturation data (method 2), reviewing LNAPL recovery system data (method 3), and performing a baildown test (method 4; Huntley, 2000). *(Note Cho et al. (2010) is not a Regional Water Quality Control Board document, but a technical presentation that includes one RWQCB coauthor).*

LNAPL Transmissivity Method 2. LNAPL physical properties and soil properties are collected, and are entered into LNAPL models such as LDRM (discussed in more detail in Section 4.6, including the necessary input data) or other LNAPL models (such as

ARMOS). When using this method for calculating LNAPL transmissivity, Cho et al. (2010) gave the following opinions/considerations:

- There should be a high density (vertically in borehole) of LNAPL saturation or TPH data (i.e., >4 samples per foot of mobile interval).
- There should be multiple boring locations which represent a single point in time.
- Relative permeability and capillary pressure algorithms should be calibrated to soil core data (the API LDRM described in Section 4.6 or other similar models could be used since they already contain the necessary algorithms).
- LNAPL transmissivity may be correlated to CPT LIF – but this process requires correlating LIF / Saturation / Soil type data, which can be costly. However, the correlation may make sense if site has a large amount of existing LNAPL soil saturation / TPH data.
- It is better to have lots of LNAPL saturation / TPH data.
- This method of calculating LNAPL transmissivity is most applicable for calibration of LNAPL distribution models.

LNAPL Transmissivity Method 3 (LNAPL recovery data). This method can be used when LNAPL recovery data are available from a dual-phase water/LNAPL pumping system that is well designed and well operated. The data are plotted in a similar fashion as methods to calculate transmissivity from groundwater pumping tests (see Equation 3.37 in Charbeneau, 2007 for an explanation of the data analysis). When using this method for calculating LNAPL transmissivity, Cho et al. (2010) gave the following opinions/considerations:

- There must be a well-operated LNAPL recovery system.
- There must be a record of the volume of oil and water recovered.
- There must be adequate knowledge of the hydraulic conductivity distribution.
- There should be an adequate understanding of LNAPL distribution and thickness (b_n) of the mobile oil interval.
- This method makes sense if the site already has an LNAPL recovery system operating.

LNAPL Transmissivity Method 4 (LNAPL baildown tests). LNAPL baildown tests, described in Huntley, 2000, are used in this method. The well (particularly filter pack porosity) must be in good condition to ensure that the baildown test gives good results. When calculating LNAPL transmissivity in this manner, Cho et al. (2010) gave following opinions/considerations:

- There must be a well with considerable LNAPL apparent thickness (LNAPL thickness > 1 foot).
- There must be trained field staff to conduct and monitor recovery into the well.
- A well must return to equilibrium (or become close to it). .
- There should be an adequate understanding of LNAPL distribution and insight into geology (perched or confined conditions).

- The method requires competent data analysis.

These opinions/ considerations presented by Cho et al. (2010) are not a consensus view of every member of the LA LNAPL Workgroup, but do provide a useful perspective about how to obtain LNAPL transmissivity values.

Several methods for using LNAPL transmissivity to define LNAPL mobility have been proposed, with one value (0.014 ft^2/day) having been used for several studies (pg, 445 of Beckett and Lundegard, 1997). The ITRC LNAPL Technical Guidance (ITRC, 2009) suggests that an LNAPL transmissivity in the range of **0.1 to 0.8 ft^2/day (1.1 to 8.6 x 10^{-7} m^2/s)** is a minimum transmissivity for practicable LNAPL recovery when recovery is the only goal for an LNAPL remediation project (see text box below). ASTM (2007) includes an example "Potential Benefit Metric" of **0.014 ft^2/day (1.5 x 10^{-8} m/s)** for LNAPL transmissivity.

Insights into LNAPL Transmissivity as a Performance Metric

The ITRC's *Technical/Regulatory Guidance: Evaluating LNAPL Remedial Technologies for Achieving Project Goals* (ITRC, 2009a) document provides this explanation of how LNAPL transmissivity can be used to evaluate mobility (note that T_n in the ITRC document is T_o in this report):

> *Beckett and Lundegard (1997) proposed that appreciable quantities of LNAPL cannot be recovered and that there is little migration risk associated with a well with an LNAPL transmissivity (T_n) of 0.015 ft^2/day. However, ITRC LNAPL Team members' experience indicates that hydraulic or pneumatic recovery systems can practically reduce T_n to values between 0.1 and 0.8 ft^2/day. Sites in state regulatory programs in California, Kentucky, and Florida have been closed or granted no further action after developing comprehensive LCSMs and operating recovery systems, followed by demonstrating lack of LNAPL recoverability (irrespective of in-well LNAPL thickness) remaining. The T_n values at these sites were estimated to be between 0.1 and 0.8 ft^2/day. Lower T_n values can potentially be achieved, but technologies other than hydraulic and pneumatic recovery technologies typically need to be employed to recover additional LNAPL. Further lowering of T_n is difficult and can be inefficient; that is, it can take very long to marginally reduce T_n without much benefit in terms of reduction of LNAPL mass, migration potential, risk, or longevity. A site in Virginia was granted closure after it was demonstrated that the recoverability could not be significantly reduced by multiphase extraction technology below the current status. T_n values occurring at this site were below 0.1 ft^2/day. T_n is a relatively new metric; further study and experience may refine this T_n range.*

(Regarding the California site mentioned above, subsequent research showed that the regulatory staff had only verbally agreed to stop the use of an operating conventional hydraulic LNAPL recovery system at a recovery well location due to low recoverability).

4.4 Method 3: Evaluate Pore Entry Pressure

LNAPL occurrence in a monitoring well does not necessarily imply that LNAPL is able to move in the formation. LNAPL must overcome a finite pore entry pressure before it can penetrate water-filled pores (Charbeneau, 2007) and flow laterally. Using the Brooks and Corey (1964) soil moisture model, Charbeneau (2007) derives the minimum LNAPL

observed monitoring well LNAPL thickness necessary for LNAPL to flow laterally into a porous medium that has never contained LNAPL:

$$b_{n[crit]} = \left(\frac{\sigma_{nw}}{(1-\rho_r)\sigma_{aw}} - \frac{\sigma_{an}}{\rho_r \sigma_{aw}} \right) h_d$$

Equation 4.7

where: $b_{n[crit]}$ = minimum LNAPL thickness in monitoring well for LNAPL to penetrate the formation (LNAPL apparent thickness; m);
σ_{nw} = LNAPL/water interfacial tension (dyne/ cm);
σ_{an} = Air/LNAPL interfacial tension (dyne/ cm);
σ_{aw} = Air/water interfacial tension (dyne/ cm);
ρ_r = relative LNAPL density (density of LNAPL/density of water); and,
h_d = displacement pressure head (m).

Example – LNAPL Apparent Thickness

Assume that an observed LNAPL thickness in a well has been measured to be 0.1 m. In order to determine if the observed thickness in the well is sufficient to overcome the pore entry pressure and cause LNAPL migration, the minimum LNAPL thickness in a monitoring well for LNAPL to penetrate the formation ($b_{n[crit]}$) can be calculated from Equation 4.7. Assume that the soil is are sandy loam which has a water/air displacement head of 0.13 m (determined from laboratory analysis or from published values, see below table), and that the LNAPL has the following properties (See Sale (2001) for methods of how to obtain LNAPL specific parameters):

σ_{nw} = 50 dyne/cm;
σ_{an} = 25 dyne/cm;
σ_{aw} = 65 dyne/cm; and,
ρ_o = 0.7 g/cm^3

First calculate the relative LNAPL density (LNAPL/water density ratio):

$$\rho_r = \frac{\rho_o}{\rho_w} = \frac{0.7 \frac{g}{cm_3}}{1.0 \frac{g}{cm_3}} = 0.7$$

Then use Equation 4.7 to calculate the minimum apparent monitoring well thickness needed to cause lateral LNAPL migration:

$$b_{n[crit]} = \left(\frac{\sigma_{nw}}{(1-\rho_r)\sigma_{aw}} - \frac{\sigma_{an}}{\rho_r \sigma_{aw}} \right) h_d = \left(\frac{50 \frac{dyne}{cm}}{(1-0.7) \cdot 65 \frac{dyne}{cm}} - \frac{25 \frac{dyne}{cm}}{0.7 \cdot 65 \frac{dyne}{cm}} \right) \cdot 0.13m = 0.26$$

Continued

Because the critical LNAPL thickness required to overcome the pore entry pressure of the formation is greater than that observed in the well, capillary forces in the formation would prevent the LNAPL from flowing.

Common soil properties and Brooks-Corey and van Genutchen parameters (Carsel and Parrish, 1988):

		Bulk Den.		Brooks & Corey Param.		van Genuchten Param.		
Soil	**Porosity**	**(g/cm^3)**	**K_w (m/d)**	**P_c head (m)**	**λ**	**N**	**α (1/m)**	**m**
Clay	0.38	1.64	0.048	125.	0.09	1.09	0.8	0.0826
Clay loam	0.41	1.56	0.062	0.53	0.31	1.31	1.9	0.237
Loam	0.43	1.51	0.25	0.28	0.56	1.56	3 6	0.359
Loamy sand	0.41	1.56	3.5	0.081	1.28	2.28	12.4	0.561
Silt	0.46	1.43	0.06	0.62	0.37	1.37	1.6	0. 70
Silt loam	0.45	1.46	0.11	0.5	0.41	1.41	2.	0.291
Silty clay	0.36	1.70	0.0048	2	0.09	1.09	0.5	0.0826
Silty clay loam	0.43	1.51	0.017	1	0.23	1.23	1	0.187
Sand	0.43	1.51	7.1	0.069	1.68	2.68	14.5	0.627
Sandy clay	0.38	1.64	0.029	0.37	0.23	1.23	2.7	0.187
Sandy clay loam	0.39	1.62	0.31	0.17	0.48	1.48	5.9	0.324
Sandy loam	0.41	1.56	1.1	0.13	0.89	1.89	7.5	0.471

Free LNAPL can be induced to flow in the subsurface under an applied LNAPL gradient. If LNAPL is recovered in, for example, an LNAPL skimming well, then LNAPL will flow toward the well as LNAPL in the well is removed. However, as the LNAPL is drained from the formation, the LNAPL saturation decreases. The decreasing saturation reduces the mobility of the remaining LNAPL, reducing the flow of LNAPL to the well. Thus, the ability to recover LNAPL is reduced as LNAPL is removed from the formation (Huntley and Beckett, 2002). This principle of declining production is a common experience in the oil and gas production industry.

The natural limitation to LNAPL recovery ultimately limits the effectiveness of conventional hydraulic recovery of LNAPL. Huntley and Beckett (2002) report that, in five case studies of LNAPL recovery, the percent of the initial spill recovered ranged from 23 to 28 percent at four of the sites. LNAPL recovery at the fifth site was estimated to be between 30 to 60 percent.

The LNAPL pore entry pressure equations are particularly relevant at the edge of an LNAPL zone. As shown in Figures 13 and 15, mobile LNAPL can be present in the core of the LNAPL zone, but the LNAPL found on the edges of the LNAPL zone are immobile.

4.5 Method 4: Saturation vs. Residual Saturation

As defined by the LA LNAPL workgroup, residual saturation is “The LNAPL saturation level below which naturally occurring capillary forces prevent LNAPL from moving, making the LNAPL immobile.” Therefore if one measures the total LNAPL saturation in a soil sample, and has a good knowledge of the actual residual saturation for that LNAPL/soil system, then LNAPL mobility can be determined:

- If $S_o < S_{or,}$ then the LNAPL is immobile.
- If $S_o > S_{or}$ then the LNAPL is free LNAPL capable of movement.

where:

S_o = total LNAPL saturation in the soil (L^3 LNAPL/L^3 pores)
$S_{or,}$= LNAPL residual saturation in the soil (L^3 LNAPL/L^3 pores)

Total LNAPL **saturation** can be determined using the methods presented in Section 3.1.2. Methods to determine the residual LNAPL saturation are discussed in the adjacent text box.

Determining Residual Saturation

Four general methods to determine residual saturation are presented below:

1. Laboratory water flood tests (Sale, 2001). Sale (2001) presents seven methods for developing a relative permeability vs. saturation curve which will provide a value for residual saturation. These methods all involve forcing fluids into the core (water-flood methods) and measuring changes in pressure as well as other factors. Soil type can be an important parameter in determining the final residual saturation.
2. Technical literature. For example, Charbeneau (2003) and Brost and DeVaull (2000) report residual saturation for a number of different hydrocarbon LNAPLs in different soil types, and recommendations for screening residual saturations. However, there has been a recent movement away from using literature values for residual saturation in favor of actual field measurements because literature estimates don't capture important site specific data, such as the loading history of the LNAPL zone (i.e., how much pore space was originally filled by LNAPL) and the importance of large pores in the migration of LNAPL.
3. Centrifuge tests. A soil sample is spun at a high velocity to produce a high centrifugal force (1000 g), and the LNAPL saturation following the test provides an estimate for the residual saturation of the sample. The results should be considered as values that do not have a strong theoretical connection to residual saturation, but are representative of the very-hard-to-mobilize component of saturation.
4. F-Factor method. Charbeneau (2007) and Johnson and Adamski (2005) present a model for estimation of residual LNAPL saturation based on the maximum LNAPL saturation experienced by the soil (the "initial" LNAPL saturation). The model assumes that the residual saturation is linearly related to the initial saturation by:

$$S_{or} = f_r S_{oi} \qquad \text{Equation 4.8}$$

where: S_{or} = LNAPL residual saturation (L^3 LNAPL/L^3 pores);
f_r = residual f-factor (unitless); and,
S_{oi} = initial LNAPL saturation (or maximum LNAPL saturation at any time; L^3 LNAPL/L^3 pores)

Continued

Example - f-Factor Method

For a fine sand with an f-factor of 0.39 that has experienced a maximum LNAPL saturation of 0.4, the residual saturation would be:

$$S_{or} = f_r S_{oi} = 0.39 \cdot 0.4 = 0.16$$

The residual f-factor appears to vary with soil texture and may also be different for saturated and unsaturated soils (Charbeneau, 2007). Vadose zone values of the f-factor determined using a similar model are reported to be 0.2 to 0.5, with a median value of 0.3 (Charbeneau, 2007). Charbeneau (2007) also reports on laboratory work by other researchers on specific soils and fresh LNAPL that give the following residual f-factor values:

Soil Type	factor values
Ottawa sand	0.18
Fine to medium sand (Safety Bay)	0.23
Fine sand and loamy sand (Texas City)	0.39 and 0.43
Clay loam (Swan Valley)	0.56

This model is not commonly used because of the difficulty of obtaining LNAPL saturation histories.

4.6 Method 5: Models for LNAPL Mobility and Recovery Estimation

Both simple and complex models have been developed to simulate the recovery of LNAPLs from the subsurface. These models apply the fundamental equations of LNAPL flow, but differ in how the principles are applied. Simple analytical models use simplified boundary conditions and constitutive relationships to derive analytical or semi-analytical expressions that can be solved relatively easily. More sophisticated numerical models support more complex boundary conditions, use more rigorous constitutive relationships, require a large number of input parameters, and involve the simultaneous solution of many equations to simulate LNAPL transport and recovery. While numerical models can be very accurate, because of their complexity, they require a high level of training to use, and therefore, have limited potential for widespread use. Therefore, they are not discussed in this literature review, which is focused on simpler tools that can be applied by environmental professionals without extensive training.

Basically these models combine Darcy's Law calculations (Method 2), pore entry pressure effects (Method 3), and the concept of residual saturation (Method 4). The output of these LNAPL models show a simulated LNAPL footprint over time (providing simulated results for Method 1), as well as showing if LNAPL can be recovered by pumping.

In these models, LNAPL mobility is a matter of calculating the relative permeability as a function of fluid saturations, and then determining the average mobility over the interval that inherently mobile LNAPL is present. The three steps in this process are 1) estimating parameters required for the LNAPL relative permeability equations, including fluid properties and soil type, 2) calculating relative permeabilities, and 3) averaging the mobility over the LNAPL thickness. The models reviewed in this paper perform the second and third steps of this process.

4.6.1 Parameter Estimation

The parameters needed for most of the models include:

- LNAPL fluid properties (density and viscosity);
- LNAPL residual saturation in the vadose zone and saturated zone;
- Formation intrinsic permeability; and,
- Soil type information, such as moisture curve parameters.

LNAPL fluid properties can either be estimated from literature sources (see Section 2) or measured. Sale (2001) discusses methods of determining LNAPL fluid properties. Formation intrinsic permeability can be calculated from aquifer tests, determined from laboratory analyses on soils (Sale, 2001), taken from the literature based on other similar soils (Charbeneau, 2000; Charbeneau, 2003; API, 2004), or estimated from grain size data (Chapuis and Aubertin, 2003). Soil moisture curve parameters can be estimated by fitting models to measured capillary pressure/saturation data (Sale, 2001) or taken from the literature for similar soils (Carsel and Parrish, 1988; Charbeneau, 2000; API, 2004). Methods to obtain residual saturation data are presented in the previous Section (Section 4.5)

4.6.2 Evaluation of LNAPL Mobility and Recoverability Models

One commonly used LNAPL mobility and recoverability model is the API's LDRM System (LNAPL Distribution and Recovery Model; Charbeneau, 2007). This model provides information on the distribution of LNAPL in the subsurface (such as saturation, thickness, etc.) and can be used to simulate LNAPL recovery using conventional hydraulic methods are. This model is focused on unconfined water-bearing units, and special measures would be required to apply to confined systems.

The API LDRM model is essentially an updated version of the API spreadsheets, except that the model is implemented within a stand-alone Microsoft Windows GUI instead of within Microsoft Excel. The basis of the API LDRM is provided in Charbeneau (2007). The most important improvements of the API LDRM over older API spreadsheets include (Charbeneau, 2007):

- selection of either US Customary or metric units;
- soil heterogeneity may be represented through use of 1, 2 or 3 soil layers;
- soil profile data may be represented either as elevation above a datum or as depth below the ground surface;
- the capability for simulating LNAPL smearing associated with water table drawdown been added;
- three different representations for LNAPL residual saturation are available, and the user may change between representations during a modeling session;
- the effects of vertical hydraulic gradient through surface fine-grain soil layers on LNAPL distribution and recovery may be represented;
- either the Burdine or Mualem relative permeability model may be selected for individual soil layers;

- measured field data on LNAPL saturation, LNAPL thickness, LNAPL recovery volume, and LNAPL recovery rate may be added and displayed on model graphical output;
- model formulation through use of the LNAPL layer transmissibility function is both more rigorous and simpler than earlier model formulations; and,
- more extensive and useful model output capabilities are included.

The user first specifies the units, number of layers, elevation datum, whether water-table smearing is accounted for, and the LNAPL residual saturation model at a screen that appears after running the executable file (see Figure 16). The remaining parameters and the layer properties are entered into a single screen that appears after the initial screen. After clicking on this screen, the API LDRM reports the initial LNAPL mobility and recoverable volume. Menus can be accessed at the top of the GUI to enter parameters for LNAPL recovery calculations, after which the model reports recovery performance for a user-specified remediation time.

Only summary model results are output to the GUI screens that initially appear. A typical summary screen is shown in Figure 17. The program writes other calculated information to a text file that is saved in the same folder as the executable. Information in the text file is comprehensive, and includes:

- Input parameter summary and calculated parameters;
- LNAPL specific volume, LNAPL recoverable volume, LNAPL transmissivity, total LNAPL saturation, water saturation, LNAPL residual saturation, and LNAPL relative permeability as a function of depth;
- Calculated recovery system parameters;

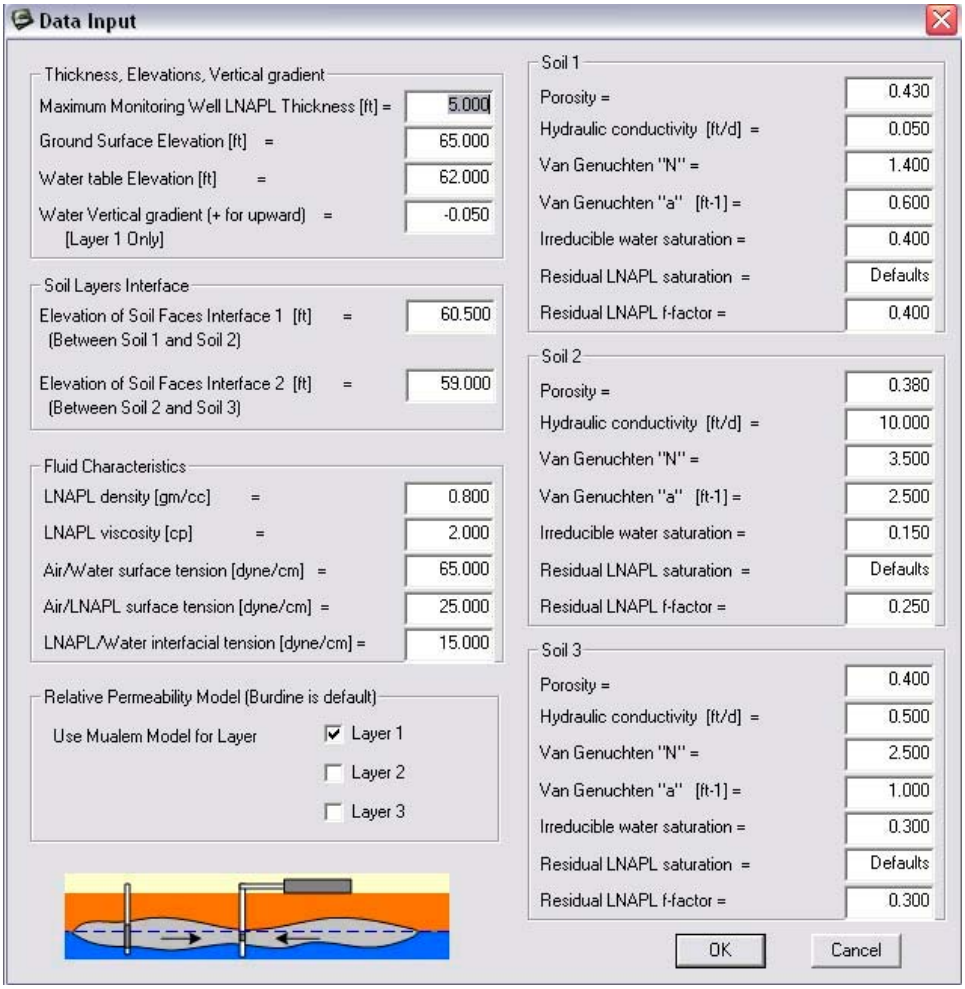


Figure 16. API LDRM input screen (Charbeneau, 2007).

- Performance of skimming wells, dual-phase extraction wells, vacuum-enhanced extraction wells, vacuum-enhanced skimming, and trenches in recovering LNAPL from an area within the influence of the remediation systems; and,
- Water table drawdown/buildup, if applicable.

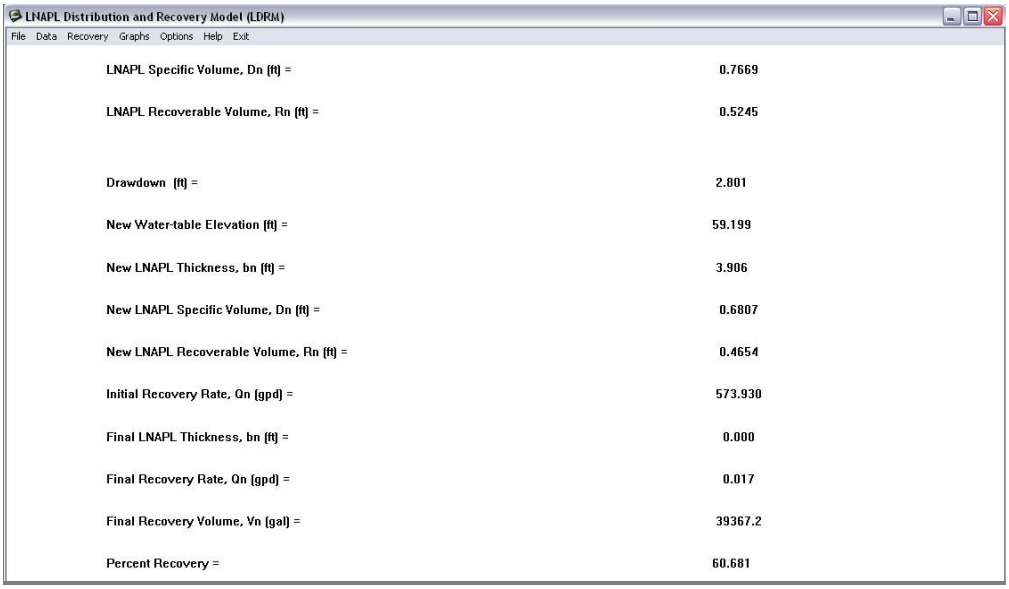


Figure 17. API LDRM model summary output (Charbeneau, 2007).

Graphic output is selected from the main menu that appears after the calculations are performed. The following information is provided in the output plots:

- Saturation profiles of LNAPL and water in all layers (see Figure 18 for an example);
- Specific LNAPL volume, recoverable LNAPL volume, and LNAPL transmissivity as a function of monitoring well thickness;
- Total LNAPL saturation, water saturation, LNAPL relative permeability, and water relative permeability as a function of elevation above the water/LNAPL interface;
- Water table drawdown/buildup, LNAPL recovery rate, cumulative LNAPL recovery volume, and thickness of LNAPL in the monitoring well as a function of time.

The model also has a sound theoretical basis, and according to the authors, it is more rigorous than earlier, similar models. The model has several features that could be important at some sites. These features include the ability to simulate LNAPL smearing during remediation, the use of the F-Factor to specify residual LNAPL, the use of up to three layers with different relative permeability models for each, and accounting for vertical water gradients.

The model is easy to use, but although the summary data is presented prominently, the saving of output data into a text file may be inconvenient for some users. Some of the output graphs are not as clean as the other models. The model is extensively documented by API Publication 4760 (Charbeneau, 2007). It is recommended that actual site data be used, if possible, to calibrate the model rather than relying exclusively on literature values for key parameters.
Charbeneau (2003) used this type of LNAPL model to compare predicted LNAPL recovery volumes to actual LNAPL volumes recovered in a skimming well pilot test. At two of the four locations evaluated, the model predictions closely matched observed results, while model predictions at a third location overestimated the actual LNAPL recovery volume by a factor of about five. The subsurface had been accurately characterized at all three of

these locations. Model predictions at the fourth skimming well, where the subsurface geology was not characterized, were significantly underestimated by the model. The authors concluded that the model provided a reasonable estimate of LNAPL recovery potential where the subsurface geology is known.

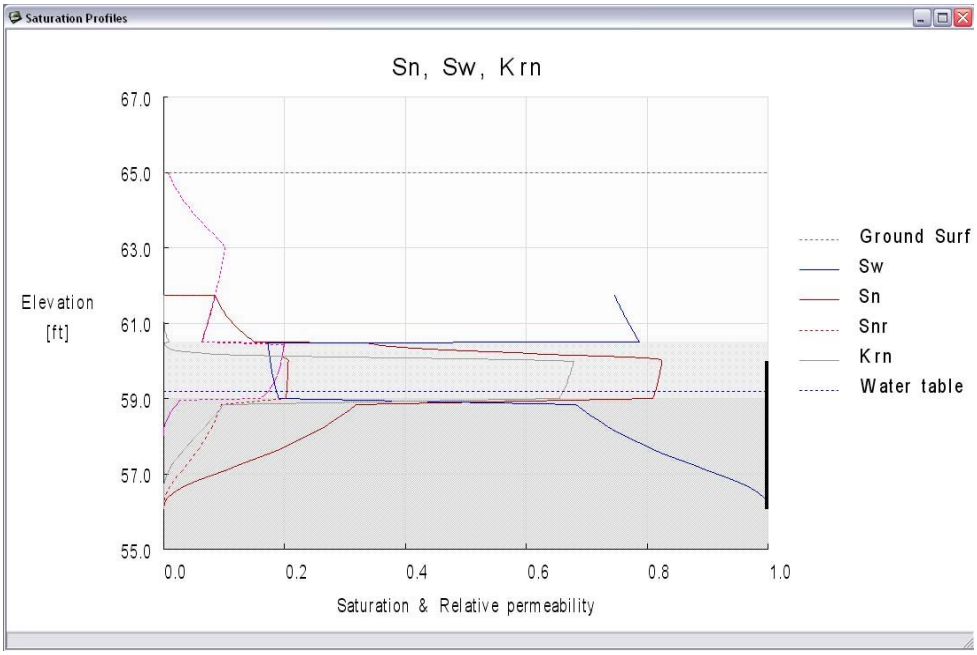


Figure 18. API LDRM graphical output: saturation profiles in the formation (Charbeneau, 2007).

4.7 Other Methods to Estimate Mobility and Recovery

4.7.1 LNAPL Inherent Mobility

Inherent LNAPL mobility is defined as the ratio of free LNAPL transmissivity to specific LNAPL volume at a given location (in other words, this is the ratio of the LNAPL conductivity averaged over the LNAPL formation thickness to the average LNAPL content over that interval) (Parker et al., 1996; API, 2004; LSPA, 2008):

$$M_o' = \frac{\overline{T}_o}{\overline{V}_o} = \frac{\overline{K}_o}{n\overline{S}_{om}} \qquad \text{Equation 4.9}$$

where: $M_{o'}$ = LNAPL mobility (m/ s);

$\overline{V}_o$ = LNAPL specific volume (m);

$\overline{K}_o$ = vertically averaged LNAPL conductivity (m/ s); and,

$\overline{S}_{om}$ = vertically averaged LNAPL saturation (L^3 LNAPL/L^3 pores).

Note that this definition s different than the LNAPL “mobility term” definition presented by the LSP (2008) and described in Section 4.2.

Example

Using the LNAPL transmissivity of 6.45 x 10^{-8} m^2/s (calculated above) and a specific volume of 0.1 m, the inherent LNAPL mobility is calculated using Equation 4.9:

$$M_o = \frac{\overline{T_o}}{\overline{V_o}} = \frac{6.45x10^{-8}\,\frac{m^2}{s}\left(\frac{86400s}{day}\cdot\frac{365day}{yr}\right)}{0.1m} = 20\frac{m}{yr} = 67\frac{ft}{yr}$$

No metric has been proposed to compare the inherent mobility of an LNAPL to the by anyone see text box on Higinbotham et al. (2003).

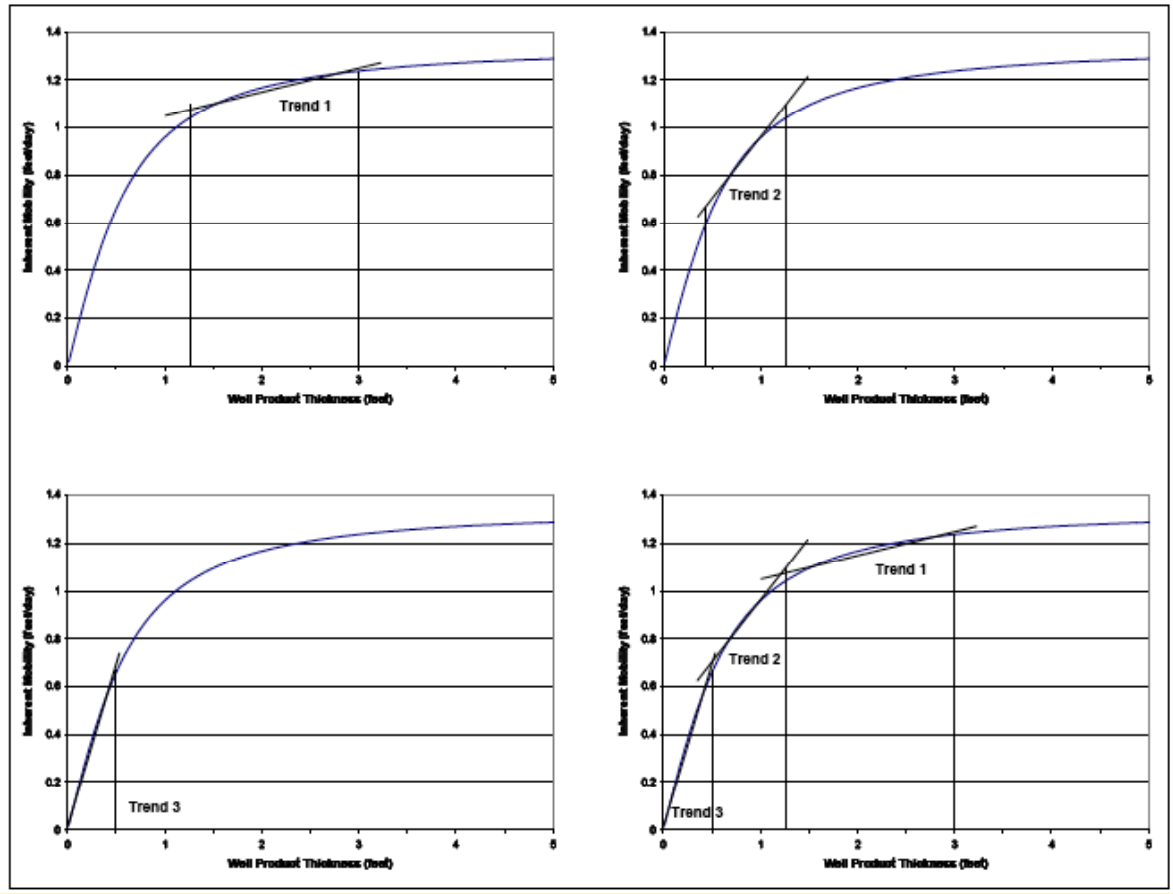
Inherent mobility is the ratio of LNAPL flow potential to and LNAPL volume. It can be calculated using Equation 4.8 or be determined from baildown tests as described by Parker, 1996. However, there is no single value of inherent LNAPL mobility that corresponds to a Practical Limit of Mobility. Higinbotham et al. (2003) present a methodology based on evaluating the *slopes* of inherent mobility versus apparent well thickness to determine a "dynamic inherent LNAPL mobility ratio" which then can be used to define practical limit of mobility (PLM; see text box).

The Higinbotham et al. (2003) method has the advantage of considering site specific conditions from a detailed multiphase fluid flow perspective, and clearly presents a logical means for determining a site-specific PLM. A disadvantage is the method has not been widely used to date.

Example of Higinbotham et al. Inherent Mobility Method

"At site C the aquifer is composed of sands and silts with minor amounts of gravel. The plume is circular in shape, covering approximately 90,000 square feet, and is composed of crude oil. Laboratory analyses indicate a product density of 0.83 g/cm3 and viscosity of 7 centipoise. The plume has been delineated and apparent well product thicknesses range from less than 0.5 feet to 4.8 feet. The average hydraulic gradient is 0.0036. Inherent mobility analyses were performed to evaluate the practical limit of mobility (PLM) of the plume to better assess remedial goals."

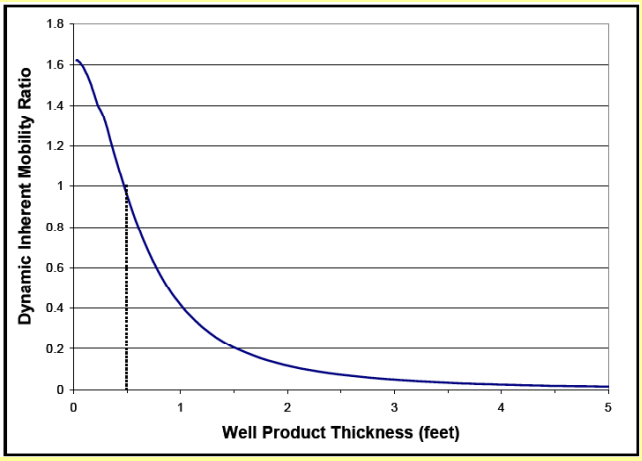
The inherent mobility vs. apparent LNAPL thickness curve was developed at the well with the largest LNAPL accumulation, and three different slopes were measured.



Example of Higinbotham et al. Inherent Mobility Method

(Continued)

These slopes were then plotted to show a "dynamic inherent LNAPL mobility ratio", shown below. With this curve, a Practical Mobility Limit (PLM) of 0.5 feet of apparent LNAPL thickness in the well was defined.



4.7.2 Maximum Recoverable LNAPL Volume

A method of determining the total maximum recoverable subsurface volume using decline curve analysis is described by Sale (2001). The method is illustrated in Figure 19. If the decline in LNAPL production is first-order, then the slope of the semi-log recovery curve can be used to determine the maximum recoverable LNAPL. To use this method, the decline curve must be approximately first-order, the LNAPL production must be constant and continuous, and LNAPL recovery wells must be spaced such that all parts of the LNAPL body are under the influence of a recovery well.

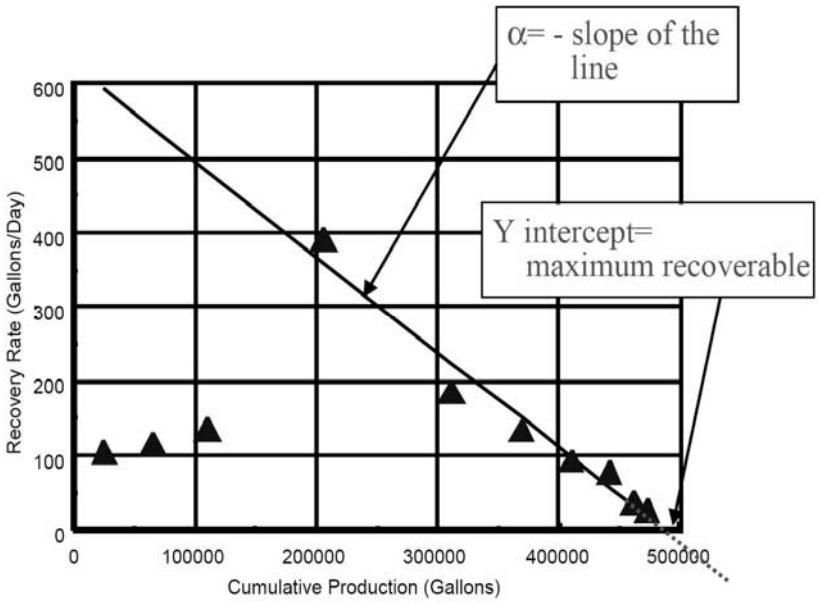


Figure 19. Decline curve analysis (Sale, 2001).

5.0 CURRENT AND EMERGING LNAPL TREATMENT AND RECOVERY TECHNOLOGIES

This section provides an overview of key LNAPL treatment and recovery technologies. It describes how these technologies are classified, how they differ, and describes their reach ("radius of influence") for treating areas containing subsurface LNAPL.

5.1 Overview

For ease of reference, LNAPL Treatment/Recovery technologies for the treatment of LNAPL have been divided into general categories used by the Texas Commission on Environmental Quality (TCEQ) NAPL workgroup:

- **Current, conventional** technology – A proven technology that removes LNAPL by physical means, including excavation, hydraulic, or pneumatic remedial measures.
- **Current, alternative** technology – A technology that removes, mobilizes, or destroys LNAPL using biological, chemical, electromagnetic, or thermal processes. Some of these technologies have not been proven at the field scale. Alternative technologies are often used as **Post-Conventional** technology for removing residual LNAPL.
- **Containment t**echnology – A technology that contains, rather than destroys or removes, LNAPL and/or an associated dissolved phase plume.
- **Assisting** technology – A technology that is used to enhance the effectiveness of another remedial technology.
- **Emerging** technology – A technology that is under development for LNAPL remediation, but has not been proven to be effective on a large scale. Some emerging technologies can also be used as a **Post-Conventional** technology for removing residual LNAPL.

The LA LNAPL Workgroup is primarily interested in testing Post-Conventional technologies that address residual LNAPL, either as LNAPL left after conventional recovery efforts are no longer efficient; or as residual in the form of submerged LNAPL.

5.1.1 Technology Overview

A number of Conventional and Post-Conventional LNAPL remedial technologies are listed by these categories in Table 4. Where available, the limitations, general cost and/or efficiency, and additional technical notes about each technology are provided in the table. The Interstate Technology & Regulatory Council (ITRC) team led by Pam Trowbridge (Pennsylvania Dept. of Environmental Protection) and Lily Barkan (Wyoming Dept. of Environmental Quality) developed a Technical/Regulatory Guidance document "Evaluating LNAPL Remedial Technologies for Achieving Project Goals." (ITRC, 2009) and also provided a summary of remediation technologies; these are provided in Appendix 1.

Tables 5a and 5b show the Technology Evaluation Matrix for LNAPL Sites developed as part of this project for evaluating Post-Conventional remediation technologies.

5.1.2 Natural Source Zone Depletion Benchmark

The ITRC (2009A) discussed how Natural Source Zone Depletion (NSZD) can serve as a *control* or benchmark when comparing the effectiveness of remediation actions. NSZD is also important to consider as a solution to residual hydrocarbons that are likely to be left behind after treatment (ITRC, 2009A).

Accurate information on LNAPL distribution, LNAPL composition, and site hydrogeology are needed to evaluate NSZD. It may be helpful to consider NSZD processes when initially creating a site conceptual model to ensure that the site characterization includes the necessary data. Mass depletion calculations vary based on the location of the LNAPL; therefore, separate estimates of LNAPL in the vadose zone and in the saturated zone are necessary. The exposed portion of the mobile LNAPL body within the vadose zone is exposed to volatilization and biodegradation. The LNAPL in the saturated zone is only exposed to dissolution and biodegradation, which will affect the mass depletion calculations that are used. (ITRC, 2009 A).

The table below lists the methods available to determine the different NSZD processes that may be occurring at a site (ITRC 2009A).

More detailed information concerning NSZD data requirements, calculations, and available software can be found in the ITRC guidance: “Evaluating Natural Source Zone Depletion at Sites with LNAPL” (ITRC, 2009A).

An emerging technology for direct measurement of NSZD attenuation rates at LNAPL sites has been developed based on carbon dioxide (CO_2) flux meters. These flux meters (developed by Colorado State University and other researchers) have been used at several refinery sites and have shown that NSZD rates on the order of thousands of gallons per acre per year at some locations (personal communication, T. Sale, CSU).

As background, recent work by Lundegard and Johnson, 2006, indicates that NAPL losses to the gas phase may be up to 2 orders of magnitude larger than those due to dissolution into groundwater. Additionally, biodegradation can become the dominant LNAPL mass loss process over time. Molins et al., 2010, estimate that greater than 98% of the carbon produced by biodegradation exits the ground surface as CO_2. (The CO_2 flux meter technology consists of traps, placed at grade to capture CO_2 leaving the subsurface using an adsorbent. Atmospheric CO_2 and barometric pumping can cause an increased measurement of CO_2, therefore a layer of the CO_2 adsorbent is placed at the top of the trap to account for this potential source of error. Removing the background CO_2 soil respiration, an accurate rate of CO_2 leaving the subsurface due to natural attenuation of LNAPL can be determined.

Although several case studies emphasize natural attenuation of fuel hydrocarbons dissolved in ground water (see literature review by Wiedemeier et al., 1999), the LNAPL source zone decay was not quantitatively investigated until a few years ago (Amos et al., 2005; ITRC, 2009; Johnson et al., 2006; Lundegard and Johnson, 2006; Molins et al., 2010; and ongoing research at Colorado State University). From the literary review three studies were selected (Lundegard and Johnson, 2006; Molins et al., 2010; and ongoing research at Colorado State University) and brief summaries of these studies are presented below.

- Oil field site with petroleum distillate release had NSZD rates of 134 to 1340 gal/acre/yr depleted using a concentration gradient calculation (Lundegard and Johnson, 2006).
- Ruptured underground pipe with crude oil release had an NSZD rate of 824 gal/acre/yr depleted using a model calibration calculation (Molins et al., 2010), and 1600 gal/acre/yr using carbon dioxide traps (Sihota et al., 2011).

NSZD process	Supporting data	Purpose
Source zone dissolution to groundwater	Static water elevations at groundwater monitoring wells	Determine the hydraulic gradient and groundwater flow direction (needed to properly interpret dissolved concentration data)
	Dissolved hydrocarbon concentrations in groundwater up- and downgradient of source zone	Increases in dissolved-phase hydrocarbon concentrations between up- and downgradient wells are evidence that dissolution is occurring
Biodegradation of dissolved source zone mass	Dissolved electron acceptor reactant (e.g., O_2, NO_3^-, SO_4^{2-}) and product (e.g., Fe^{2+}, Mn^{2+}) concentrations in groundwater up- and downgradient of the source zone	Decreases in dissolved O_2, NO_3^-, and SO_4^{2-} and increases in Fe^{2+} and Mn^{2+} between up- and downgradient wells are evidence that biodegradation is occurring
	Dissolved methane (CH_4) concentrations in groundwater up- and downgradient of the source zone	Increases in dissolved CH_4 between up- and downgradient wells are evidence that anaerobic biodegradation is occurring via methanogenesis
Source zone volatilization to vadose zone	Hydrocarbon soil-gas concentration profiles	Decreasing hydrocarbon concentrations in soil gas with distance from the source zone are evidence that volatilization of source zone is occurring
	Total petroleum hydrocarbon (TPH) composition in soil, unweathered (''fresh'') LNAPL-containing soils (or free product)	Changes in the hydrocarbon composition in soil relative to the initial hydrocarbon composition could also be evidence of NSZD and could reflect the combined effect of mass loss mechanisms
Biodegradation of volatilized source zone mass	Respiration and biogenic soil-gas concentration profiles (O_2, CO_2, CH_4)	Soil-gas profiles with decreasing O_2, increasing CO_2, or increasing CH_4 concentrations with depth to the source zone are consistent with the occurrence of biodegradation (CH_4 can also be produced by natural sources and may be distinguished by carbon stable isotope fractionation or background soil-gas profiles collected away from source zones)
	Soil TPH concentrations with time	May not be practicable—long-term monitoring and large numbers of samples may be necessary to observe trends

Source: Adapted from Johnson, Lundegard, and Liu 2006.
From ITRC, 2009a

- A refinery in the Midwest had NSZD rates between 300 to 3,200 gal/acre/yr depleted using a calculation based on carbon dioxide traps at grade (Sale personal communication, 2011).

This technology could be used in a benchmark mode by comparing natural degradation rates vs. active removal rates. For example, if attenuation rates determined from CO_2 measurements indicate that NSZD is responsible for removing LNAPL quantities which are

much higher than those removed by actively engineered remedies; a case could be made for discontinuing the active treatment. On the other hand, projected removal rates from a in-situ technology that are much higher then NSZD rates would indicate that in-situ remediation may be merited. Although, at this time the CO_2 flux meter method is in the emerging technology stages, much work is going proceeding at this time, and soon they could potentially be an important LNAPL site management technology.

5.1.3 Screening Technologies and Key Performance Metrics

The Interstate Technology & Regulatory Council (ITRC) developed a Technical/Regulatory Guidance document (ITRC, 2009) that provided a screening matrix for comparing technologies based on the following decision making criteria:

- LNAPL Remedial Objective
- LNAPL Remediation Goal
- Technology Group
- Example Performance Metrics
- LNAPL Technology and LNAPL/Site Conditions

The screening matrix included 17 different LNAPL remediation technologies, and is reproduced in Appendix 2 of this document.

5.2 LNAPL Mass Removal vs. Composition Change Technologies

In addition to the categories developed by the TCEQ, LNAPL remediation technologies can be divided into those that are implemented for the purpose of: (i) mass-recovery, (ii) mass-control, and (iii) phase-change (ITRC, 2009B). Mass-recovery and mass-control strategies are mainly aimed at addressing remedial objectives defined by the LNAPL saturation goals. Phase-change approaches focus on targeting the composition of the LNAPL and "exploit the tendencies of LNAPLs to partition to other phases by increasing the rates of volatilization or dissolution of the LNAPL constituents" (ITRC, 2009B). Degradation of the LNAPL fractions also affects LNAPL composition and weathering. Biodegradation of LNAPL constituents in the groundwater and vapor phase (volatilized components) has been widely accepted. Direct biodegradation of LNAPL, although likely to be a slow process in part due to microbial toxicity effects, has also been suggested as a mechanism for LNAPL composition change in source zones (see ITRC, 2009B for a more detailed discussion).

Active engineered LNAPL remediation technologies and their remedial objectives, including composition changes are described in the table shown below. Even though NSZD has not traditionally been thought of as a standalone remediation technology for application at LNAPL sites, the processes involved in the physical redistribution (dissolution and volatilization) and breakdown (biodegradation) of LNAPL constituents are integral part of this technology and are thus included in the discussion. NSZD is also significant "because engineered remedial actions typically do not always completely remediate soil and NSZD may be useful to address the residual hydrocarbon" (ITRC, 2009B). The supporting data necessary for determining the different NSZD processes is discussed in detail in Section 3.5 of this document.

LNAPL remediation technologies and remedial objective type targeted	
Technology	**Remedial Objective (primary shown in bold)**
Excavation	**Saturation** + Composition
Physical or hydraulic containment	**Saturation** + Composition
In-situ soil mixing	**Saturation** + Composition
Natural source zone depletion (NSZD)	**Composition** + Saturation
Air sparging /soil vapor extraction	**Composition** + Saturation
LNAPL skimming	**Saturation**
Bioslurping/enhanced fluid recovery	**Composition** + Saturation
Dual-pump liquid extraction	**Saturation**
Multiphase extraction (single and dual pump)	**Saturation** + Composition
Water flooding	**Saturation**
In-situ chemical oxidation	**Composition**
Surfactant enhanced subsurface remediation*	**Saturation** + **Composition**
Cosolvent flushing	**Saturation** + **Composition**
Steam/hot-air injection	**Saturation** + **Composition**
Radio frequency heating	**Saturation** + Composition
Three-and-six phase electrical resistance heating	**Saturation** + **Composition**
Source: ITRC, 2009B	

* Note there are two main surfactant technology variants: 1) surfactant addition for LNAPL mobilization (often an anionic surfactant); and 2) surfactant addition of LNAPL solubilization (often a non-ionic surfactant). See Table 4 for more discussion of these two methods.

5.3 RADIUS OF INFLUENCE BY TECHNOLOGY

The radius of influence (ROI) is the area that is affected by a particular remediation technology or treatment. The ROI will vary widely according to the remediation technology used and the specific site characteristics. This is why the ROI is usually measured during a pilot or small scale test of a particular technology at a given site. The ROI determines the spacing of injection points and is also an important factor in determining the total cost of treatment at a site.

5.3.1 Air Sparging

According to Leeson et. al. (2002),

> "The standard design approach includes injection wells on 15 ft centers; however wells may be spaced closer or further based on data recovered during the pilot test and economic feasibility" (Pg 12).

With certain site conditions and accurate characterizations of the site it may be possible to increase injection well spacing.

> "All other factors being equal, remediation is more effective in settings having a higher density of air channels in the treatment zone" (Pg 4)

> "Distances between injection wells at the full-scale level can be optimized (and the number of wells minimized) when the air distribution is more fully characterized at the pilot scale level" (Pg 5)

If the 15ft spacing is not economically feasible then, "the smallest well spacing that is not cost prohibitive should be determined" (Pg 12). This being said, it is likely that the effective reach of an injection well will be 10 ft or less at sites with less than ideal conditions.

> "Generally the lateral extent is not much more than 10 ft in any direction away from the injection well" (Pg 12, A-7)

Good candidate sites for air sparging are "aquifers found at medium to shallow depths (<50 ft below ground surface [bgs]) and sandy/silty soils" (Pg 8). This technology would not perform as well in sites that are deep and clayey.

> "Air sparging is not expected to be effective in clayey settings" (Pg 8)

Key Points

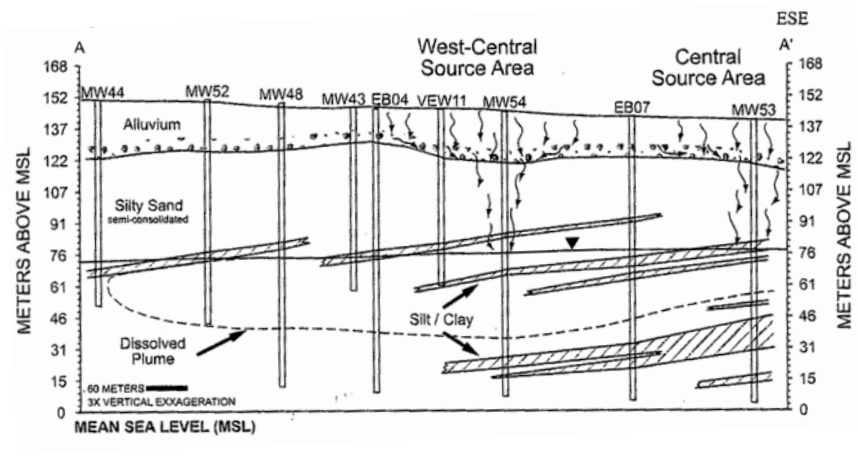
- Generally, well spacings should be 15 ft; although ROI may be < 10 ft in many cases.
- Air sparging is not appropriate for clayey soils.

5.3.2 Deep Air Sparging

According to Klinuchuch et. al. (2007), air sparging can also be used 15 to 46m beneath the water table (bwt) although it is more challenging than air sparging at shallower depths. Their paper describes the application of air sparging to an impacted aquifer at depths greater than 76 m below ground surface (bgs) and up to 40 m thick.

> "The ZOI, inferred from tracer gas and pressure in the saturated zone, increased with depth and was approximately 24 m for a sparge depth of 15 bwt, greater than 31m for a sparge depth of 31 bwt, and greater than 46 m for a sparge depth of 46 bwt." (Pg 123)

The subsequent well spacing to manage the full dissolved plume included dual-nested air sparge wells placed 46 m apart.



Site conceptual model presented in cross section

Pilot tests were conducted to determine the suitability of deep air sparging in a mixed silty sand and clay area. The stratigraphy of this study area is shown in the figure to the left. The site stratigraphy is especially important for deep air sparging as soils with low hydraulic conductivities, even thin soils, can have very high entry requirements and impede the flow of air (Pg 119). Tracer gas studies suggest that the air was moving into the saturated zone despite the layered stratigraphy that may have impeded the air flow (Pg 122).

Key Points

- Air sparging is a feasible option for aquifers up to 46 m below the water table, although it is more challenging than sparging at shallower depths.

5.3.3 In-Situ Chemical Oxidation (ISCO)

The persistence varies according to oxidant and as a result the radius of influence depends on the type of oxidant used as well as site conditions (ITRC, 2005, pg 18). Therefore, each oxidant should be examined separately. However, the following general information may also be useful:

> "Pilot scale studies provide necessary information to determine appropriate well/ point spacing as well as to determine the radius of influence and other parameters necessary to determine cost" (Pg 41).
>
> "Oxidant transport can be reaction limited because the oxidants are being depleted as they move through the subsurface. Therefore, the effective radius of oxidation treatment may be substantially less than the hydraulic (or pneumatic in the case of ozone gas) ROI. Faster rates of oxidant reaction (i.e., shorter half-lives) lead to more limited transport distances" (Pg 46)
>
> "Typical ROIs for injections range from 2.5 ft for tight clays to 25 ft in permeable saturated soils. In addition to lithology, the ROI varies based on the oxidant properties, the injection technique, and pressure . . . The hydraulic ROI will overestimate the actual oxidant dispersal for faster reacting oxidants" (Pg 48)

> "Because the oxidant can enter the sand zone easier than the silty clay zone, the ROI will be greater in the sand." (Pg 48)

For batch delivery strategies the formula below can be used to calculate ROI. However, it is important to note that this is the hydraulic ROI and the effective ROI may be less (Pg 52).

$$ROI = \sqrt{\frac{V}{n * \pi * t}}$$

Where, ROI = Radius of Influence (m)
V= Volume of oxidant solution (m^3)
t= Thickness of treatment zone (m)

Example

For example, if 2 million liters of oxidant is used to treat a 5-m thick zone with a porosity of 0.3, then the radius of influence would be:

$$ROI = \sqrt{\frac{V}{n * \pi * t}} = \sqrt{\frac{2x10^6 L\left(\frac{m^3}{1000L}\right)}{0.3 * \pi * 5m}} = 21m$$

Most oxidants must be applied to a saturated or near saturated soil matrix with the exception of ozone, which is gaseous (Pg 21). To determine the dispersion of ozone through the soil and the necessary spacing of injection points the soil permeability of the site is necessary for both the saturated and vadose zones (Pg 29). It may be necessary to space the injection points so that the zones of influence overlap (Pg 41).

> "Some ozone generators inject less than 1 scfm, which may result in very limited (<5-ft) influence areas at each injection well" (Pg 46)

The limited zone of influence combined with the need to overlap zones results in very closely spaced injection wells, which may not be feasible for a large site. Other oxidants that are aqueous and persistent are likely to have larger zones of influence.

> "Permanganate is more persistent in the subsurface than H_2O_2 or ozone, so the ultimate ROI in highly permeable saturated soils can be >100 ft." (Pg 51)

> "Persulfate is more persistent in the subsurface than H_2O_2, or ozone, so the ultimate ROI in highly permeable saturated soils will be greater." (Pg 52)

Many oxidants can react with various components naturally found in site soils in a way that decreases permeability and reduces the radius of influence.

> "Background measurements of manganese concentration should be collected to establish existing conditions prior to injection of permanganate. The potential for manganese dioxide precipitation and clogging of aquifer pore space should also be evaluated" (Pg 27)

Determining the ROI is very important in determining the necessary application of oxidant as too little will not be effective, but too much will increase costs and also reduce the cost effectiveness. This is especially true for both persulfate and peroxide.

> "Overdosing of iron can reduce the aquifer permeability due to formation of iron oxides" (Pg 27-8)

Key Points

- Pilot tests are very useful as ROI varies widely between different solvents and site characteristics.
- Generally, more persistent oxidants in permeable and saturated soils will have greater ROIs.
- ROIs generally range between 0.75 m (2.5 ft) and 7.5 m (25 ft).
- An equation to determine the hydraulic ROI is available above.
- Determining the correct oxidant and the correct amount is important to avoid interactions with site soils that will decrease effectiveness.

5.3.4 Surfactant Flushing

According to AATDF (1997), surfactant systems with a greater distance between injection/withdrawal wells take more time to complete than systems with smaller spacings (Pg 2-5, 2-6). The spacing between injection and recovery wells can be from 0 to 30 m (Pg 5-10) depending on the desired time frame and cost requirements. The time it takes to cycle 1 pore volume can take days to years depending on site conditions and well spacing (Pg 5-10).

> "The applicability and likelihood of success of a surfactant/cosolvent flood is inversely proportional to the degree of heterogeneity at a site."(Pg 5-31)

This technology has been applied at a number of LNAPL sites with LNAPL near the water table. Laboratory and field tests should be conducted to determine the correct surfactants or if the site characteristics even make this technology feasible for a given location.

An example design for a large LNAPL site (27 acres) involves 60 m (197 ft) injection drain lines spaced 30 m (98 ft) apart (Pg 6-16). With this spacing it is estimated that it will take a total of 6 years for remediation. Smaller sites are likely to use closer spacings and injection wells.

Key Points

- Larger spacings between injection points correspond to longer times to cycle one pore volume.
- Treatment is more likely to be successful at homogeneous sites.
- This technology is experimental, but 30 m (98 ft) spacing could be used as a guideline for a larger site.

- An above ground treatment system is often required.

5.3.5 Thermal Conductive Heating

According to Terratherm (2007) the typical spacing for wells is ranges from 7 to 20 ft.

"The deepest full-scale application to date is to 105 ft." (FAQ section)

This technology is considered economically feasible for sites between 1,000 and 1,000,000 cubic yards of soil. Generally, full remediation would take 2 months to 2 years varying according to soil moisture and contaminant types.

Key Points

- Conductive heating typically requires well spacing between 7 and 20 ft.
- Full treatment can take as little as 2 months or as long as 2 years.
- Significant above ground infrastructure is required.

5.3.6 Thermal Steam Heating (Dynamic Underground Stripping)

According to DOE (2000):

"Well spacings of ~40 ft should be used for the final design to optimally deliver steam to the finer grained materials." (Pg B-4)

Although this technology is able to treat contamination in interbedded sands and clays, it is not as effective in clayey soils (Pg 11). Therefore, it is recommended that electrical heating be used to supplement steam injection in heavy clay areas. Steam injection to vaporize trapped liquids can take weeks to months (Pg 7). The minimum depth for this treatment to be cost effective is 5 ft (Pg 11).

Key Points

- Well spacing should be around 12m (40 ft) depending on site conditions.
- This technology is not as effective in heavy clay or shallow (< 1.5 m) depths.

5.3.7 Summary

The radius of influence varies widely between different technologies and within a particular technology according to site characteristics. Site characterization is very important for determining the ROI at a particular site and allows decision makers to choose the most effective and cost efficient well spacings for final remediation. See Figure 20 for a visual representation of well spacing ranges (note that the design spacing of 98 ft for surfactant flushing represents an estimated 6 year remediation time).

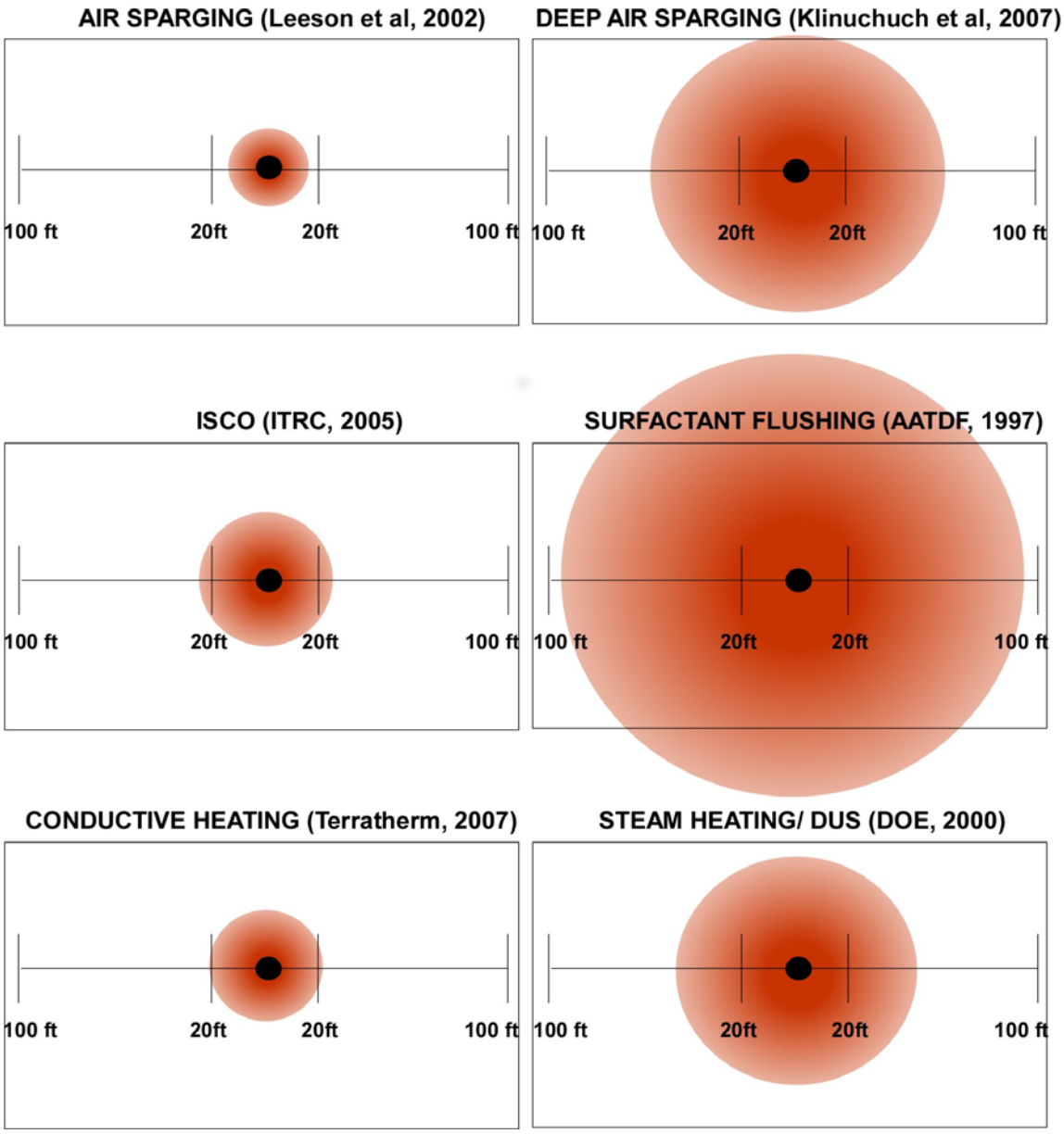


Figure 20: Well Spacing Distances by Technology

6.0 FIELD DATA AND CASE STUDIES

6.1 LNAPL Site Compilation

A search of the technical literature has identified information about 120 sites that can be analyzed for use in developing general conclusions about LNAPL behavior in the subsurface. These sites represent a variety of soil types, LNAPL types, and climatic conditions. The amount of information available for the site is highly variable. Some sites are extensively documented in site investigation and remediation reports, while other sites are described only in the technical literature. Work is on-going to extract key information from these sites that will be useful for developing a general LNAPL site conceptual model.

6.2 LNAPL Model Evaluation Case Studies

Only a few technical papers have been identified that compare LNAPL volume, mobility, and/or recovery models to measured data. Wilson et al. (2005) used the API (2004) model to a petroleum refinery site with a mixed LNAPL containing gasoline, jet fuel, kerosene, diesel, and other petroleum compounds. The site consists of artificial fill material underlain by fluvial, estuarine and salt-march deposits, and is hydrogeologically complex. Soils in the study area consisted of coarse to fine sands mixed with some gravel, silt layers and clay stringers. Groundwater was unconfined at most of the study locations. They reported that at three of the four locations where representative model parameters were obtained, the model predictions of LNAPL recovery by skimming and multi-phase extraction matched pilot testing well. At the fourth location, borings advanced during the pilot testing phase of the project encountered soils different from those used for the model evaluation, and the model results differed considerably from the pilot test results. Wilson et al. (2005) stress that accurate data on soil properties are essential for model accuracy.

As discussed in Section 3, Huntley et al. (1994) compared hydrocarbon saturations to those predicted by the Farr (1990) and Lenhard and Parker (1990) model. Huntley et al. (1994) also used the van Genuchten (1980) soil moisture model with the Mualem (1976) model to estimate average LNAPL conductivity. The LNAPL conductivities predicted by the model matched measured values of LNAPL conductivity from a pump test within a factor of 2, indicating very good accuracy considering the significant uncertainties (e.g., residual oil saturation, small scale soil property variability, in-situ LNAPL properties) involved in these types of calculations.

Adamski et al. (2005) used the Charbeneau (2003) and Charbeneau (2007) models to estimate LNAPL recovery from a three-phase recovery system. The Charbeneau (2003) model estimated 530 gallons of recoverable LNAPL, while actual recovery volume was 151 gallons. The Charbeneau (2007) model predicted a total LNAPL recovery volume of 290 gallons. The authors attribute the model overestimates of recoverable volume to site heterogeneity and the use of a large representative apparent LNAPL volume for the modeling calculations.

Many of the other case study sites identified have sufficient information for application of the analytical models discussed in this review, albeit with literature values of key parameters. In a recent literature review, Oostrom et al. (2006) also identifies multi-phase flow experiments, some of which may provide additional data for model evaluation.

7.0 HYDROGEOLOGIC SETTINGS

The following are Hydrogeologic settings that from the National Research Council (NRC, 2004). These settings were developed to evaluate the effectiveness of a particular remediation technology for a particular zone or area. Two of the five are particularly relevant to sites in the Los Angeles Basin:

- *Type I – Granular Media with Mild Heterogeneity and Moderate to High Permeability*

  Type I media include systems with porosities that are consistent with typical granular media (e.g., 5 percent to 40 percent), with permeabilities that are consistent with sand or gravel deposits (>10^{-14} m^2 or hydraulic conductivity >10^{-7} m/s), and mild heterogeneity (less than three orders of magnitude). As conceptualized here, this material is about as uniform as it can be in nature and thus is relatively uncommon. Deposits of this nature are encountered in association with windblown sands and beach deposits. Examples include beach sands at the Canadian Forces Base Borden, Canada, and dune deposits at Great Sand Dunes National Park, Colorado. Due to its mild heterogeneity and moderate to high permeability, all portions of this media type can transmit groundwater.

An example of this type of hydrogeologic setting is found at the Chevron El Segundo facility.

- Type III – Granular Media with Moderate to High Heterogeneity

  Type III encompasses systems with moderate to large variations in permeability (greater than three orders of magnitude) and porosities that are consistent with granular media (e.g., 5 percent to 40 percent). Given large spatial variations in permeability (at the scale of centimeters to meters), portions of the zone are comparatively transmissive while others contain mostly stagnant fluids. For the purpose of this report, the more transmissive zones in Type III media have a permeability greater than 10^{-14} m^2 (K > 10^{-7} m/s). Near-surface deposits of this nature are common due to the abundance of alluvium with large spatial variations in permeability and are encountered in either rock or alluvium associated with deltaic, fluvial, alluvial fan, and glacial deposits. Examples include the Garber-Wellington Aquifer in central Oklahoma, the Chicot Aquifer in Texas and Louisiana, and varved sediments near Searchmont, Ontario.

An example of this type of hydrogeologic setting is found at the Shell Carson Terminal.

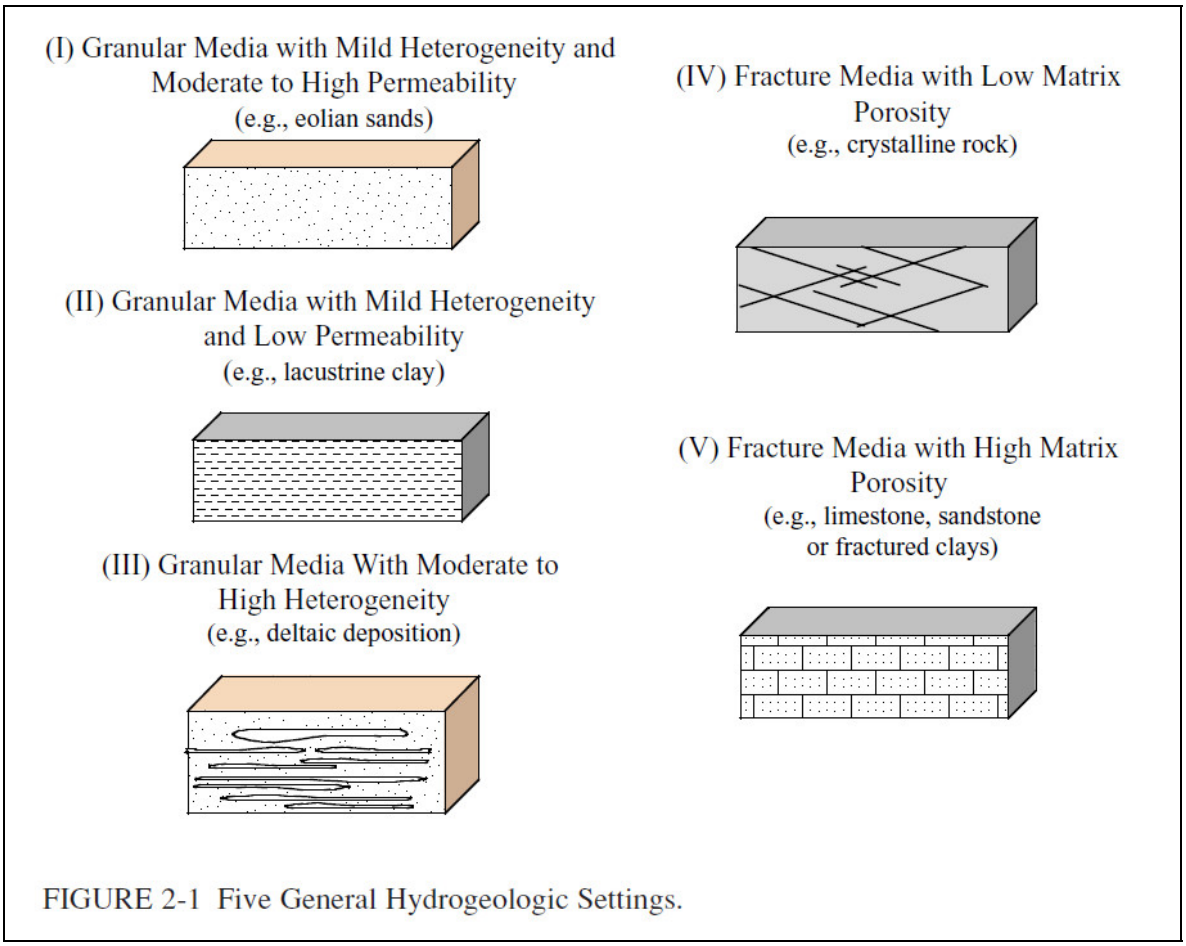


FIGURE 2-1 Five General Hydrogeologic Settings.

NRC, 2004.

Three other types of sites have less applicability to the Los Angeles Basin:

- Type II – Granular Media with Low Heterogeneity and Low Permeability

  Type II settings have porosities that are consistent with typical granular media (e.g., 5 percent to 40 percent), low spatial variation in permeability (less than three orders of magnitude), low permeability consistent with silt or clay deposits ($k < 10^{-14}$ m^2), and low hydraulic conductivity ($K < 10^{-7}$ m/s). An example is a clay deposit with no significant secondary permeability features (such as fractures, root holes, animal borrows, or slickenslides). These systems are somewhat uncommon (especially in the near-surface environment where releases typically occur), although some examples include TCE-contaminated clays at the Department of Energy's Savannah River Site in South Carolina. More typically, low-permeability materials contain significant secondary permeability features and thus fit better into the Type V setting description

- Type IV – Fractured Media with Low Matrix Porosity

  Fractured media with low matrix porosity are common in crystalline rock including granite, gneiss, and schist. Examples include bedrock in the Piedmont and Blue Ridge Mountain region of the southeastern United States and plutonic cores of mountain ranges in the western United States. The primary transmissive feature in Type IV settings is secondary permeability caused by fractures, because little to no void space

exists in the unfractured matrix. The permeability of the unfractured matrix is considered to e less than 10^{-17} m^2 ($K < 10^{-10}$ m/s). However, the bulk permeability of the media is dependent on the frequency, aperture size, and degree of interconnection of the fractures, such that the anticipated range of bulk permeability values is 10^{-15}–10^{-11} m^2 ($K = 10^{-8}$–10^{-4} m/s). The porosity of both the matrix and the fractures is typically small—less than 1 percent. However, in regions where crystalline rock has been extensively weathered (e.g., at the top of bedrock), the bulk media can behave more like a porous medium than what would be expected from a fractured rock type setting. A primary feature that differentiates Type IV from Type I is that contaminants in Type IV will occur in a sparse network of rock fractures that may or may not be hydraulically interconnected. In general, sources zones in fractured media with low matrix porosity are less commonly encountered than sources zones in Type III and Type V settings. This reflects the fact that many surface releases never reach bedrock and, in the United States, crystalline bedrock occurs less frequently than sedimentary bedrock (Back et al., 1988).

- Type V – Fractured Media with High Matrix Porosity

  This setting includes systems where fractures (secondary permeability) are the primary transmissive feature and there is large void space in the matrix. The permeability of the unfractured matrix is considered to be less than 10^{-17} m^2 ($K < 10^{-10}$ m/s). The anticipated range of bulk permeability values is 10^{-16}–10^{-13} m^2 ($K = 10^{-9}$–10^{-6} m/s). The porosity of the fractures relative to the total unit volume is small (e.g., <1 percent). However, unlike Type IV, in Type V hydrogeologic settings the porosity of the unfractured matrix is anticipated to fall in the range of 1 percent to 40 percent. Fractured media with high matrix porosity are commonly encountered in sedimentary rock (e.g., limestone, dolomite, shale, and sandstone) and fractured clays. Examples include the Niagara Escarpment in the vicinity of the Great Lakes (see Figure 2-7) and fractured lake-deposited clay in Sarnia, Ontario, Canada.

  An important variant of the Type V setting is karst, which is common in carbonates (e.g., limestone or dolomite). In this scenario, transmissive zones include sinkholes, caves, and other solution openings that vary widely in aperture and have the potential to store and transport significant contaminant mass (see Figure 2-8). Permeability in karst terrains varies over tens of orders of magnitude from low permeabilities between fractures to open channel flow in channels and caves (Teutsch and Sauter, 1991; White, 1998, 2002). Karst is characterized by both rapid transport along sparse dissolution features and a high ratio of stagnant to transmissive zones. As such, it is one of the most challenging hydrogeologic settings to characterize and manage.

8.0 REFERENCES

AATDF. Technology Practices Manual for Surfactants and Cosolvents. February 1997. Rice University, Houston, TX.Adamski et. al., 2005. LNAPL in Fine Grained Soils: Conceptualization of Saturation, Distribution, Recovery, and Their Modeling. Ground Water Monitoring & Remediation, 25 (1), 100-112.

AFCEE, 2007. NAPL Source Zone Treatment, www.afcee.brooks.af.mil/products/techtrans/NAPLSourceZoneTreatment/NAPLOverview.asp, Air Force Center for Environmental Excellence, accessed May 7, 2007.

Agostino et al., 2002. Assessment of subsurface hydrocarbon contamination resulting from multiple releases at six former bulk fuel storage and distribution terminals, Austin, Texas: a case study, P.N. Agostino, R.J. LeBlanc, Jr., V.T. Jones, III, in AAPG Studies in Geology No. 48 and SEG Geophysical References Series No. 11, Surface Exploration Case Histories: Applications of Geochemistry, Magnetics and Remote Sensing, D. Schumacher and L. LeShack, ed.

American Society for Testing and Materials (ASTM), 2007. Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface guide (ASTM E 2531-06, 2006).

Amos, R. T., K. U. Mayer, B. A. Bekins, G. N. Delin, and R. L. Williams, 2005. Use of dissolved and vapor phase gases to investigate methanogenic degradation of petroleum hydrocarbon contamination in the subsurface, *Water Resour. Res.,* 41, W02001, doi:10.1029/2004WR003433.

API, 2002. Refinery Stream Specification, API PUBL 4723, November 1, 2002.

API, 2003. Answers to Frequently Asked Questions About Managing Risk at LNAPL Sites. API Soil and Groundwater Research Bulletin, Number 18.

API, 2004. "API Interactive LNAPL Guide, Version 2.0.4", prepared by Environmental Systems and Technologies and Aqua-Ver, Inc., July 2004.

Aral, M. M. and Liao, B. (2000), LNAPL Thickness Interpretation Based on Bail-Down Tests. Ground Water, 38: 696–701. doi: 10.1111/j.1745-6584.2000.tb02705.x

ASTM, 2007. ASTM E 2531 – 06, Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface, February, 2007.

Ballestero et al., 1994. An investigation of the relationship between actual and apparent gasoline thickness in a uniform sand aquifer, Ground Water 32(5), 708-718.

Bear, J., *Dynamics of Fluids in Porous Media*, American Elsevier, New York, NY, 1972.

Beckett, G. D., and P. Lundegard. 1997. "Practically Impractical—The Limits of LNAPL Recovery and Relationship to Risk," pp. 442–45 in *Proceedings, Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation Conference*. Houston: Ground Water Publishing Company.

Blake and Hall, 1984. Monitoring petroleum spills with wells: some problems and solutions, Proceedings, S.B. Blake and R.A. Hall, Fourth National Symposium on Aquifer Restoration and Groundwater Monitoring, National Water Well Association, Columbus, OH, pp. 305-310.

Brooks and Corey, 1964. Hydraulic Properties of Porous Media, R.H. Brooks, and A.T. Corey, Hydrology Papers 3, Colorado State University, Fort Collins, Colorado.

Brost and DeVaull, 2000. Non-Aqueous Phase Liquid (NAPL) Mobility Limits in Soil, E.J. Brost and G.E. DeVaull, Equilon Enterprises LLC, in API Soil and Groundwater Bulletin No. 9, American Petroleum Institute, June, 2000.

Burdine, 1953. Relative permeability calculations from pore-size data, N.T. Burdine, A.I.M.E. 198, 71-77.

Carsel and Parrish, 1988. Developing Joint Probability Distributions of Soil Water Retention Characteristics. Water Resources Research 24 (5), 755-769.

Chapuis and Aubertin, 2003. On the use of the Kozeny-Carman equation to predict the hydraulic conductivity of soil, R.P. Chapuis and M. Aubertin, Ca. Geotech, J., 40, 616-628.

Charbeneau, R.T. Johns, L.W. Lake and M.J. McAdams III, 1999. Free Product Recover of Hydrocarbon Liquids, API Publication Number 4682, American Petroleum Institute, Washington, D.C., June 1999.

Charbeneau, 2000. Groundwater Hydraulics and Pollutant Transport, Randall J. Charbeneau, Prentice Hall, Upper Saddle River, N.J.

Charbeneau, 2007. LNAPL Distribution and Recovery Model (LDRM), Randall J. Charbeneau, API Publication 4760, American Petroleum Institute, Washington, D.C., January 2007.

Charbeneau, R. J., Models for Design of Free- Product Recovery Systems for Petroleum Hydrocarbon Liquids, API Publication 4729, American Petroleum Institute, Washington, D.C., 2003.

Chiles and Delfiner, 1999. Geostatistics; Modeling Spatial Uncertainty, J. Chiles and P. Delfiner, John Wiley and Sons, New York.

Cho, P., M. Adamski, and A. Kirkman, 2010. LNAPL Transmissivity as a Metric: The Future in Tracking LNAPL Recovery Progress. Presented at ASTSWMO Conference, June 8-9 2010, San Diego.

Cohen and Mercer, 1993. DNAPL Site Evaluation, Robert M. Cohen and James E. Mercer, U.S. EPA, EPA/600/R-93/022, February, 1993.

Dakota Technologies, Inc., 2007. http://www.dakotatechnologies.com/?content=templates/news_detail.tpl&id=44, accessed 1 Aug 2007.

Davis, 1986. Statistics and Data Analysis in Geology, 2nd Ed., J.C. Davis, John Wiley and Sons, New York.

de Pastrovich , 1979. Protection of ground water from oil pollution, T.L. de Pastrovich, Y. Baradat, R. Barthel, A. Chiarelli, and D.R. Fussell, CONCAWE, The Hague, Netherlands.

DOE. Hydrous Pyrolysis Oxidation/ Dynamic Underground Stripping: Subsurface Contaminants Focus Area. February 2000. Innovative Technology summary report, DOE/EM-0504.

Durnford et al., 2004. Interpreting LNAPL Monitoring Well Data for Estimating Specific Oil Volumes and Mobility, D.S. Durnford, F. Marinelli, and C.D. Miller. Proc. 2004 API/NGWA Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Assessment, and Remediation, Baltimore, MD. pp. 179-186.

EMS-i, 2007. Environmental Modeling Systems, Inc., http://www.ems-i.com/, accessed 19 September 2007.

Enfield et al., 2005. Design of aquifer remediation systems: (1) Describing hydraulic structure and NAPL architecture using tracers, C.G. Enfield, A.L. Wood, F.P. Espinoza, M.C. Brooks, M. Annable, and P.S.C. Rao, Journal of Contaminant Hydrology, 81, 125-147.

Farr et al., 1990. Volume estimation of light nonaqueous phase liquids in porous media, A.M. Farr, R.J. Houghtalen and D.B. McWhorter, Ground Water, 28(1), 48-56.

Feenstra et al., 1991. A Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples, S. Feenstra, D.M. MacKay, and J.A. Cherry, Ground Water Monitoring Review, 11(2), 128–136.

Fetter, 1999. Contaminant Hydrogeology, 2nd Ed., C.W. Fetter, Prentice Hall, Upper Saddle River, New Jersey.

FLUTe, 2007. Flexible Liner Underground Technologies, Ltd, Co. website, http://www.flut.com/sys_3.html, accessed July 24, 2007.

Geosyntec Consultants and URS Corporation. (2007). *Light Non-Aqueous Phase Liquid (LNAPL) Investigation. Shell Oil Products Carson Terminal, Carson, California*. Prepared for Equilon Enterprises LLC. December 2007.

Geosyntec Consultants and URS Corporation. (2008). *Light Non-Aqueous Phase Liquid (LNAPL) Recovery Pilot Test and Recovery modeling Report. Shell Oil Products Carson Terminal, Carson, California*. Prepared for Equilon Enterprises LLC. May 2008.

Golden Software, 2007. Golden Software, Inc., http://www.goldensoftware.com/, accessed 19 September 2007.

Golder Associates, 2006, Report on: Approaches and Methods for Evaluation of Light non-Aqueous – Hydrogeological Assessment Tools Project, Submitted to the Ministry of Environment, British Columbia, Canada, February, 2006.

Gruszczzenski, 1987. Determination of a realistic estimate of the actual formation product thickness using monitor wells: A field bailout test, T.S. Gruszczzenski, In Proceedings of Conference on Petroleum Hydrocarbons and organic Chemicals in Ground Water: Prevention, Detection and Restoration, Dublin, Ohio: National Ground Water Association, pp. 235-253.

Hall et al., 1984. Determination of hydrocarbon thickness in sediments using borehole data, Proceedings, R.A. Hall, S.B. Blake, and S.C. Champlin, Jr., Fourth National Symposium on Aquifer Restoration and Groundwater Monitoring, National Water Well Association, Columbus, OH, pp.300-304.

Hers, I., M. Malander, P. Miasek, 2009. New Approaches and Tools for Evaluating LNAPL Mobility. Remtech 2009, Oct. 14-16, 2009, Banff, Alberta.

Higinbotham, J., M. A. Parcher, J. A. Johnson. 2003. " The Importance of Understanding Inherent LNAPL Mobility in Characterizing and Remediating Sites." *Proc. Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation*, Costa Mesa, CA API/NGWA.

Hughes et al., 1988. Two techniques for determining the hydrocarbon thickness in an unconfined sandy aquifer, J.P. Hughes, C.R. Sullivan, and R.E. Zinner, In Proceedings of Conference on Petroleum Hydrocarbons and organic Chemicals in Ground Water: Prevention, Detection and Restoration, Dublin, Ohio: National Ground Water Association, pp. 235-253.

Huntley and Beckett, 2002. Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Magnitude, D. Huntley and G.D. Beckett, API Publication 4715, American Petroleum Institute, Regulatory Analysis and Scientific Affairs Department, 2002.

Huntley et al, 1994. Nonaqueous phase hydrocarbon in a fine-grained sandstone: 1. comparison between measured and predicted saturations and mobility, D. Huntley, R.N. Hawk and H.P. Corley, Ground Water, 32(4), 626-634.

Huntley, 2000. Analytical determination of hydrocarbon transmissivity from baildown tests, D. Huntley, Ground Water 38(1), 46-52, January/February 2000.

Isaaks and Srivastava, 1989. An introduction to Applied Geostatistics, E.H. Isaaks and R.M. Srivastava, Oxford University Press, New York.

ITRC, Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated soil and Groundwater, Second Edition. January 2005. In Situ Chemical Oxidation Team.

ITRC 2009a, Technology Overview: Evaluating Natural Source Zone Depletion at Sites with LNAPL. April 2009. The Interstate Technology and Regulatory Council LNAPLs Team.

ITRC 2009b, Technical/Regulatory Guidance: Evaluating LNAPL Remedial Technologies for Achieving Project Goals. December 2009. The Interstate Technology and Regulatory Council LNAPLs Team.

Istok et al., 2002. Single-well "push-pull" partitioning tracer test for NAPL detection in the subsurface," Jonathan D. Istok, Jennifer A. Field, Martin H. Schroth, Brian M. Davis, and Varadarajan Dwarakanath, Environmental Science and Technology, 36(12), 2708-2716.

Jawitz et al., 2003. Estimating nonaqueous phase liquid spatial variability using partitioning tracer higher temporal moments, J.W. Jawitz, M.D. Annable, G.G. Demmy, and P.S.C. Rao, Water Resources Research, 39(7), 1192.

Jokuty et al., 1999. Properties of Crude Oils and Oil Products, P. Jokuty, S. Whiticar, Z. Wang, M. Fingas, B. Fieldhouse, P. Lambert, and J. Mullin, "Manuscript Report EE-165, Environmental Protection Service, Environment Canada, Ottawa, Ontario,1999. Internet Version (October, 2000) also available at http://www.etc-cte.ec.gc.ca/databases/OilProperties/Default.aspx.

Johnston, C.D. and Adamski, M. (2005). "Relationship saturation for different soil types." Petroleum Hydrocarbons Association, Costa Mesa, CA, August 17-19, pp 29-42.

Johnson, J.A. and H. K, Assali. 2010. LNAPL in Fine Grain Sediments: Characterization and Recovery, Are Standard Goals Practicable? National Ground Water Association Conference, December 2010, Houston, TX.

Johnson, P. C., P. Lundegard, and Z. Liu, 2006. Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites: I. Site-Specific Assessment Approach, Ground Water Monitoring and Remediation 26: 82–92.

Klinuchuch et. al. Deep Air Sparging – 15 to 46 m beneath the Water Table. Summer 2007. Groundwater Monitoring & Remediation 27, no. 3, pgs 118-126.

Leeson et. al. Air Sparging Design Paradigm. August 12, 2002. Battelle Memorial Institute. Columbus, OH.

Lenhard and Parker, 1990a. Estimation of free hydrocarbon volume from fluid levels in monitoring wells, R.J. Lenhard and J.C. Parker, Ground Water, 28(1), 57-67.

Lenhard and Parker, 1990b. Discussion of estimation of free hydrocarbon volume from fluid levels in monitoring wells, R.J. Lenhard and J.C. Parker, Ground Water, 18(5), 800-801.

Lenhard, R. J., 1992. Measurement and modeling of three-phase saturation-pressure hysteresis, Journal of Contaminant Hydrology, Volume 9, Issue 3, March 1992, Pages 243-269, ISSN 0169-7722, DOI: 10.1016/0169-7722(92)90007-2.

Lenhard et al., 2004. A constitutive model for air-NAPL-water flow in the vadose zone accounting for residual NAPL in strongly water-wet porous media, R.J. Lenhard, M. Oostrom and J.H. Dane, Journal of Contaminant Hydrology, 71, 261-282.

Lundegard, P.D. and B.S. Mudford, 1998. LNAPL Volume Calculation: Parameter Estimation by Nonlinear Regression of Saturation Profiles, Groundwater Monitoring and Remediation, Summary 1998.

Lundegard, P. D., and P. C. Johnson, 2006. Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites: II. Application to a Former Oil Field," Ground Water Monitoring and Remediation 26(4): 93–106.

Li and Yang, 2005. Modeling of LNAPL distribution and recovery at a former refinery site, T. Li and X. Yang, 2005.

Liao and Aral, 1999. Interpretation of LNAPL thickness measurements under unsteady conditions, B. Liao and Mustafa M. Aral, Journal of Hydrologic Engineering, 4(2), 125-134, April, 1999.

LSPA, 2005. LNAPL and the Massachusetts Contingency Plan Part I, prepared by the Licensed Site Professional Association Technical Practices Committee, April, 2005.

LSPA, 2008. LNAPL and the Massachusetts Contingency Plan Part II, prepared by the Licensed Site Professional Association Technical Practices Committee, July, 2008.

Mahler, N.T., 2010. A *Mass Balance Approach to Resolving the Stability of LNAPL Bodies*, Masters Thesis, Colorado State University, Fort Collins, Colorado.

Mayer and Hassanizadeh, 2005. Soil and Groundwater Contamination: Nonaqueous Phase Liquids, Alex S. Mayer and S. Majid Hassanizadeh, Ed., American Geophysical Union Water Resources Monograph 17, Washington, D.C.

Molins, S., K.U. Mayer, R.T. Amos, B.A. Bekins, 2010. Vadose zone attenuation of organic compounds at a crude oil spill site – Interactions between biogeochemical reactions and multicomponent gas transport, J. Contam. Hydrol., 112: 15-29.

Mercer and Cohen, 1990. A review of Immiscible fluids in the subsurface: properties, models, characterization, and remediation, J. W. Mercer and R. M. Cohen, Journal of Contaminant Hydrology, 6(2), 107–163.

Mualem, 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media, Y. Mualem, Water Resources Research, 12, 513-522.

National Research Council, 2005. Contaminants in the Subsurface: Source Zone Assessment and Remediation, Water Science and Technology Board (WSTB), The National Academies Press.

Newell et al., 1995. Light Non-Aqueous Phase Liquids, , C. J. Newell, Acree, S. D., Ross, R. R., and Huling, S. G ,EPA-540-5-95-500, United States Environmental Protection Agency, Office of Research and Development, Robert S. Kerr Laboratory, Ada, OK, 1995.

Oostrom et al., 2006. LNAPLs do not always float: an example case of a viscous LNAPL under variable water table conditions, M. Oostrom, C. Hofstee, and T.W. Wietsma, Hydrology Days 2006.

Oostrom et all, 2005. A comparison of models describing residual NAPL formation in the vadose zone, M. Oostrom, M.D. White, R.J. Lenhard, P.J. Van Geel, and T.W. Wietsma, Vadose Zone Journal, 4,163-174.

Pankow and Cherry, 1996. Dense Chlorinated Solvents and other DNAPLs in Groundwater, James F. Pankow and John A. Cherry, Waterloo Press, Portland, OR.

Parker et al., 1996. *UST Corrective Action Technologies: Engineering Design of Free Product Recovery Systems,* United States Environmental Protection Agency, Risk Reduction Engineering Laboratory Report, Contract No 68-C2-0108, p.82.

RASI, 1995. Technical Documentation and User's Guide, OILVOL Oil Volume Estimator, Resources & Systems International, Inc., Blacksburg, Virginia, 1995-07.

RTDF, 2005. "The Basics:" Understanding the Behavior of Light Non-Aqueous Phase Liquids (LNAPLs) in the Subsurface, Remediation Technologies Development Forum (RTDF) Non-Aqueous Phase Liquid (NAPL) Cleanup Alliance, February, 2005.

Sale and McWhorter, 2001. Steady-state mass transfer from single-component dense nonaqueous phase liquids in uniform flow fields, T.C. Sale and D.B. McWhorter, Water Resources Research, 37(2), 393-404, February, 2001.

Sale, 2001. Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and Recovery Models, Tom Sale, API Publication Number 4711, July, 2001.

Sale, T., G. Taylor, G. Iltis, and M. Lyverse. 2007. Measurement of LNAPL Flow Using Single-Well Tracer Dilution Techniques. Ground Water Vol. 45, No. 5, pp. 569–578

Sale, T., 2007. Personal Communication.

Sale, T., 2011. Personal Communication.

Schiegg, 1985. Considerations on water, oil, and air in porous media, H.O. Schiegg, Water Science and Technology, 17, 467-476.

Schlumberger, 2007. http://www.glossary.oilfield.slb.com/Display.cfm?Term=Dean-Stark%20extraction, accessed 10 September 2007.

Sleep et al., 2000. A modeling and experimental study of light nonaqueous phase liquid (LNAPL) accumulation in wells and LNAPL recovery from wells, B.E. Sleep, L. Sehayek, and C.C. Chien, Water Resources Research, 36(12), 3535-3545, December 2000.

SSG, 2007. Scientific Software Group, http://www.scientificsoftwaregroup.com/pages/detailed_description.php?products_id=154, accessed July 26, 2007.

Terratherm. http://www.terratherm.com/technology/faq.htm#2.6 Accessed December 20, 2007.U.S. EPA, 1996. How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites: A Guide for State Regulators. NRMRL, Washington, DC, September 1996. www.epa.gov/oust/pubs/fprg.htm

US EPA, 2004. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, U.S. EPA Office of Solid Wastes, November, 2004.

US EPA, 2004b. Site Characterization Technologies for DNAPL Investigations, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, EPA 542-R-04-017, September, 2004.

US EPA, 2005. A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL), Office of Solid Waste and Emergency Response, EPA 542-R-04-011, March, 2005, www.clu-in.org.

US EPA, 2007. Hazardous Waste Cleanup Information Web Site, http://www.clu-in.org/, accessed July 24, 2007.

Van Geel and Roy, 2002. A proposed model to include residual NAPL saturation in a hysteric capillary pressure-saturation relationship, P.J. Van Geel and S.D. Roy, Journal of Contaminant Hydrology, 58, 79-110.

van Genuchten, 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soil, M.T. van Genuchten, Soil Science Society of America Journal, 44, 892-898.

Wilson et al., 2005. A comparison of light non-aqueous phase liquid (LNAPL) recovery results by numerical modeling and field pilot testing, K.B. Wilson, D.R. Law and A.C. Hari, Ground Water On-Line, 2005.

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TABLE 1
Physical Properties of Selected LNAPLs
Likely to be Encountered at Petroleum Facilities

LNAPL	Density at 0C[1,3] (g/cm^3)	Density at 15C[1,3] (g/cm^3)	Density at 20 C[1,3] (g/cm^3)	Density at 25C[1,3] (g/cm^3)	Viscosity[3] (cP)	Boiling Range[2] (^{o}C)	Interfacial Tension[1,3] (dyne/cm)	Surface Tension[1,3] (dyne/cm)
Benzene		0.882 [4]	0.876 [4]		0.683 [4]		35 (2.7 [4])	28.9 (27.9 [4])
Crude oil	0.845- 0.923	0.832 – 0.914		0.829 – 0.908	8 – 87		16.9 – 24.2	24 – 38
Diesel fuel	0.838	0.827			1 – 7	260 - 360	22.3 – 32.5	25
Ethylbenzene							35.5	29.3
Fuel oil no. 1					1 – 2.3		32.8 – 50	27
Fuel oil no. 2	0.874	0.866	0.840		4 – 8		14.7 – 15.1	26 – 29
Fuel oil no. 4	0.914	0.904	0.900	0.898	23 – 47			32.1
Fuel oil no. 5	0.932	0.923		0.917	44 – 215			
Fuel oil no. 6 (bunker C)	0.986	0.974		0.964	3180 – 7.35 X 10^7		40	27
Gasoline	0.746	0.729			0.4 – 1	20 – 190	50	19 – 23
Gasoline (casing head)					0 – 1		49 – 51	19 – 23
Gas oil (heavy)						360 - 530		
Jet A/B	0.77-0.84				1 – 3		10.8 – 39.8	23 – 27.1
Jet fuel (JP-1)					1 – 2		47-49	
Jet fuel (JP-3)			0.800		1			
Jet fuel (JP-4)	0.804	0.799		0.790	1		32.8 – 50	
Jet fuel (JP-5)		0.844	0.82		2 – 3			
Kerosene	0.842	0.839		0.835	1 – 2.3	190 - 260	47 – 49	23 – 32
Lubricating oil (hydraulic, Esso XD3-10)	0.833	0.811			102 – 253		8.8 – 10.9	21.4 – 22.5
Lubricating oil (mineral)		0.828					17.3,2.5	
Naphtha							45	20
o-Xylene							36.1	30.3
Petroleum distillates							50	21
Toluene							36.1	28.5

Notes:
1 Charbeneau, 2003.
2 Fetter, 1999.
3 API, 2004.
4 BP field site with neat benzene release; benzene in subsurface for 10 years at time of analysis; natural bio believed to have impacted IFT

Table 2
Summary of LNAPL Detection Methods

Method	Description	Reliability	Frequency of Use	Relative Cost
Ex-Situ Direct Methods				
1. Visual logging	A soil core is examined visually for the presence of a sheen, LNAPL droplets, or major LNAPL deposits.	Moderate. LNAPL is observed directly, but LNAPL may be difficult to find or identify.	High	Low
2. Paint filter test	A representative sample of material is placed in a paint filter. II any portion of the material passes through and drops from the filter in a 5 min period, then the material contains free liquid.	Low. Although LNAPL is observed directly, LNAPL may not drain freely from the soil.	Low	Moderate
3. Shake test	A soil sample is shaken with water causing separation of LNAPL allowing visual identification	Moderate. Low LNAPL saturations may prevent LNAPL from separating into the liquid phase and being observed. Liquid phase LNAPL may be difficult to observe.	High	Low
4. Dye testing	Similar to the shake test, except that a hydrophobic dye is added, which preferentially dissolves into the LNAPL, which can then be identified visually.	Moderate. Hydrophobic dyes work well for identifying LNAPL that is not readily observable by the naked eye.	High	Low
5. UV examination	A sample is illuminated with a UV lamp to fluoresce petroleum compounds on or within the soil core. Fluorescence is produced when molecules of PAHs etc. give off energy to return to their ground state after being excited by the UV light.	Moderate. Not all LNAPL compounds fluoresce under UV light. LNAPL in the soil must be exposed to the light.	High	Low
6. Photographic logging	A photographic record of soil cores under ambient or UV light is used to record the presence of NAPL within the soil sample, these can be assembled to form a continuous photographic record of NAPL distribution.	Low. LNAPL may not be visible in soil core.	Low	Low
7. Dye impregnated media	A dye-impregnated media (typically plastic) is pressed against the soil sample, LNAPL presence is indicated with a color change.	Moderate. LNAPL must be present on the soil core surface or squeezed out to appear on the media.	Low	Moderate
8. Laboratory analyses	LNAPL is directly extracted from soil cores using a solvent after driving off water, and the weights of the sample before and after water and oil extraction saturation are used to determine LNAPL saturation (Dean-Stark analysis).	High. Any oil in the sample is usually detected if a representative sample of the soil is used.	Moderate	High
Ex-Situ Indirect Methods				
1. Headspace vapor analysis	A soil core placed in a plastic bag or other container is measured with a PID or FID, the readings are correlated to soil cores where LNAPL is present to determine if LNAPL is present in the core.			
2. Soil core chemical analysis	Partitioning calculations can be used to determine the theoretical concentration at which NAPL must be present in a soil sample containing a single compound or mixture of known composition, if the total soil concentration exceeds the soil saturation limit, then the presence of NAPL in the sample is implied.			

Table 2
Summary of LNAPL Detection Methods

Method	Description	Reliability	Frequency of Use	Relative Cost
In-Situ Direct Methods				
1. Dye testing	In-situ dye testing is similar to the ex-situ dye-impregnated media test, except that the media is deployed down-hole, then the media is removed from the hole and a stain indicated the presence of LNAPL.			
2. Laser-induced florescence	LIF is similar to UV testing of soil cores, but the illumination source is deployed downhole, light generated from a laser is passed down a fiber optic cable into the subsurface. The induced fluorescence from the PAHs is returned over a second fiber to the surface where it is quantified using a detector system.			
In-Situ Indirect Methods				
1. Resistivity/ conductivity	Surface and down hole methods are available to measure resistively or electrical conductivity and characterize geologic materials and many LNAPLs that have varying geologic properties.			
2. Groundwater conc./ moment analysis	Groundwater concentrations that are a significant fraction of the effective solubility of the LNAPL components are an indication that LNAPL may be present.			
3. Membrane interface probe	Generates chemical readings for volatile compounds by heating the soil materials and collecting volatized gasses through the membrane for subsequent chemical analysis.			
In-Situ Indirect Methods (cont.)				
4. Partitioning interwell tracer test	A PITT test detects NAPL in the subsurface based on differential partitioning of tracers (between LNAPL and water phases) that are injected into the subsurface, typically higher molecular weight alcohols or perfluorocarbons.			
5. Soil vapor analysis	Soil probes or passive soil-gas collectors are used to withdraw soil gas. Soil gas surveys can yield information on both the presence and extent of LNAPL, chiefly in the vadose zone			
6. Ground-penetrating radar	Use of radar signals to determine the presence and extent of LNAPL zones			
7. Seismic surveys	Use of reflected sound waves to determine the presence and extent of LNAPL zones			
8. Downhole flow metering	Use of downhole tools to measure vertical zones of preferential paths of groundwater inflow			

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Table 3
Comparison of Analytical Model Predictions
of True LNAPL Thickness and Specific Volume

Monitoring Well LNAPL Thickness (cm)	Specific Volume (cm)			
	Charbeneau (2003)	API (2004)	Charbeneau (2007)	OILVOL (1995)
Medium Sand				
0.25	0.49	0.00	0.01	0.00
2.54	0.58	0.00	0.09	0.00
30.48	1.74	0.04	1.01	0.02
152.40	9.72	3.78	5.11	2.45
Silty Sand				
0.25	0.00	0.00	0.00	0.00
2.54	0.79	0.00	0.01	0.00
30.48	0.94	0.00	0.14	0.04
152.40	2.80	0.05	1.63	3.24

Notes:
1. For the Hall method, fine sand F was used for silty sand.

Table 4
Current and Emerging LNAPL Remediation Technologies

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Physical excavation	Contaminated soil is removed by an established excavation method and disposal or treatment of soil.	Current Conventional	Frequent	F,C/ S,U	Very short (<1 year)	Recover all LNAPL in excavation zone (typically in vadose zone)	High initial cost, but no operation/maintenance costs; established and proven method . Reliable method for removing all LNAPL from excavation zone. In practice, limited to zones above the water table with contamination in upper 40 feet.
Soil vapor extraction	Also called SVE or soil venting. A vacuum is applied to the subsurface to remove volatile constituent vapors. One of the most commonly used techniques and can be used in combination with other technologies (air sparging, steam injection, surfactant flushing, dense brine containment and others)	Current Conventional	Frequent	C / S, U	Short to medium (1-5 years)	Remove volatile constituents in LNAPL in vadose zone	Proven technology and best remedy for LNAPL in the vadose zone in most hydrogeologic settings. Limited by low-permeability, high-soil water content and heterogeneities. High initial recovery rates followed by long periods of low recovery.
Bioventing/ biosparging	A form of bio-stimulation that enhances natural in-situ biodegradation of aerobically degradable compounds in NAPL by providing additional oxygen to soil microorganisms	Emerging Technology	Moderate	C / S, U	Short to medium (1-5 years)	Remove/ destroy volatile components from free and residual LNAPL in the vadose zone	Can indirectly destroy LNAPL so no surface treatment is necessary. Reduced or no vapor treatment cost. Slower technology than SVE.
Combined fluids	One pump that removes both LNAPL and water phase	Current Conventional	Frequent	C / S, U	Medium (2-5 years)	Recover free LNAPL	Well-understood technology. Most commonly used technology with reliable design tools. Limited by low permeability, high soil water content and heterogeneities. Relatively slow technology.

Table 4
Current and Emerging LNAPL Remediation Technologies

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Floating LNAPL extraction	FLE uses an LNAPL skimming pump with LNAPL inlet set at the water-LNAPL interface for removal	Current Conventional	Frequent	F, C/ S	Long to very long (5 to 10+ years)	Recover free LNAPL	Well understood technology with reliable design tools. May be limited by site geology.
Dual-pump liquid extraction	DPLE uses two pumps, one set below the water table to create drawdown, and a second pump set at the water-NAPL interface to recover NAPL.	Current Conventional	Frequent	C / S	Long to very long (5 to 10+ years)	Recover free LNAPL	Well-understood technology. Most commonly used technology with reliable design tools. Limited by low permeability, high soil water content and heterogeneities. Relatively slow technology. Dewatering is one variant, but there are limitations to the degree of dewatering that can be achieved.
Multi-phase extraction (Dual phase extraction variant)	Uses one pump below the water table and a suction-tube from vacuum pump set above the cone of depression to remove LNAPL	Current Conventional	Frequent	C / S	Medium (2-5 years)	Recover free LNAPL	Effective method for increasing LNAPL flow rate to well when available water drawdown is limited. Vacuum increases hydraulic head without increasing drawdown. Removes NAPL, and water simultaneously. Vapor treatment is expensive.
Multi-phase extraction (Two-phase extraction variant)	Also called Bioslurping. Uses a single high-vacuum pump, suction-tube set at air-liquid interface for removal of undifferentiated LNAPL and vapor phase LNAPL	Current Conventional	Infrequent	F,C/ S,U	Long to very long (5 to 10+ years)	Recover free LNAPL; remove volatile constituents in LNAPL in vadose zone and dewatered sat. zone	Well-understood technology. Addresses capillary fringe, lower vadose zone, and upper saturated zone simultaneously. Relatively high cost due to need to separate LNAPL and water, and need to treat both water and vapor streams. Energy intensive. Vapor treatment is expensive.
Waterflood	Extraction of NAPLs via waterflood with wells or trenches, using fluid gradients to push NAPLs toward an area for extraction	Current Conventional	Infrequent	C / S	Short (1 to 3 years)	Recover free LNAPL	Not effective when available drawdown is small and/or permeability of formation is low. Produces large quantities of groundwater that require treatment.

Table 4
Current and Emerging LNAPL Remediation Technologies

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Low permeability barriers and containment	Uses trenches, chemical, or physical barriers to isolate or limit NAPL sources and reduce risks by managing the plume	Containment Technology	Infrequent	F,C/ S	Very long (10+ years)	Stop or reduce mobile LNAPL	Only addresses dissolved phase. Passive technology that can be less expensive than active technologies.
Natural Source Zone Depletion	Physical, chemical and biological processes that under the right conditions will reduce the mass, volume, toxicity or concentration of a contaminant in the soil/groundwater without human intervention	Containment Technology*	Infrequent	F,C/ S,U	Very long (10+ years)	Remove volatile/soluble components from LNAPL via volatilization and (indirectly) aerobic biodegradation	Destroys LNAPL indirectly by biodegrading soluble components. Cost is low. Likely to be much slower than most other remediation technologies. Not effective for long-chained hydrocarbons (i.e., C-20 and higher).
Air sparging	The injection of clean air into the saturated zone of a porous medium to volatilize and transport contaminants for removal by SVE The SVE prevents the contaminated air from reaching uncontaminated areas Used for LNAPL and DNAPL	Current Alternative	Infrequent	C / S, U	Short to medium (1-5 years)	Remove volatile/ soluble components from saturated zone LNAPL via volatilization and (indirectly) aerobic biodeg.	Proven technology. Uses two processes to remove volatile/soluble compounds: volatilization and biodegradation. Commonly combined with SVE to capture vapors. Inexpensive. Limited by low permeability, high soil water content and heterogeneities. Relatively low radius of influence (15 feet).

*Note: The LA LNAPL Working Group is evaluating NSZD.

Table 4
Current and Emerging LNAPL Remediation Technologies

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
In-situ chemical oxidation	Increases the mass flux from a source zone by breaking up organic chemicals in place Can provide rapid containment and destruction of readily oxidized contaminants	Current Alternative	Infrequent	C / S, U (ozone oxidant)	Very short to short (< 1 to 3 years)	Destroy LNAPL in residual and free phases (as well as dissolved and sorbed constituents). Used primarily for saturated zone but some vadose zone applications	Addresses both residual and free phase. Can destroy LNAPL but large quantities of oxidant is needed. May result in further cleanup issues (such as elevated metals). Success depends on the degree of contact of the NAPL solution and the injected substance. Limited effectiveness in low permeability settings. Typical spacing for injections range from 2.5 feet for tight clays to 25 feet in permeable saturated soils. Also done with soil mixing.
Thermal remediation	Involves the injection of steam, electromagnetic energy, or conductive heat to heat the NAPL zone and volatilize contaminants. Often used in combination with SVE to capture vapors	Current Alternative/ Emerging technology	Infrequent	F,C/ S,U	Very long (10+ years)	Volatilize and destroy free and residual LNAPL for both vadose and unsaturated zone	Relatively high removal performance if high temperature can be maintained. More effective in low-permeability media than most other technologies. High water inflow can compromise project effectiveness. Careful monitoring is required. Not typically performed at retail sites due to health/safety concerns. High cost. Typical well spacing for conductive heating: 7 to 20 feet. Energy intensive.
Surfactant flushing for LNAPL Mobilization	Surfactants (typically anionic) are delivered to pooled or trapped NAPL. Primary purpose is to decrease NAPL-water interfacial tension , which promotes mobilization	Current Alternative	Infrequent	C / S	Very short to short (< 1 to 3 years)	Remove free LNAPL and some residual LNAPL from saturated zone	Removes LNAPL through mobilization and demobilization in the subsurface. Success depends on contact. Relatively expensive technology. Difficult to apply on large scale.

Table 4
Current and Emerging LNAPL Remediation Technologies

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Surfactant flushing for LNAPL Solubilization	Surfactants (typically non-ionic) are delivered to pooled or trapped NAPL. Primary purpose is to increase solubility of LNAPL constituents and extract resulting dissolved phase mass	Current Alternative	Infrequent	C / S	Very short to short (< 1 to 3 years)	Remove free LNAPL and some residual LNAPL from saturated zone	Removes LNAPL through solubilization. May be inefficient for removing significant LNAPL mass due to need to solubilize LNAPL. Success depends on contact. Relatively expensive technology. Difficult to apply on large scale.
Alcohol flushing	Similar to surfactant flushing. Derived from a crude oil recovery technique in which miscible, low-molecular weight alcohols are delivered to NAPL regions to solubilize and mobilize pure phase NAPLs. Alcohols are also used as co-solvents with other surfactants	Emerging Technology	Very few applications nationwide	C / S	Very short to short (< 1 to 3 years)	Remove free LNAPL and some residual LNAPL from saturated zone	Addresses both residual and free phase. Addition of chemicals that may require further cleanup. Success depends on the complete contact of the NAPL solution and the injected substance. High cost.
Electrokinetics	A DC electrical field is established in the NAPL zone that induces water and NAPL migration to a recovery area. NAPL flow through a treatment zone can be induced	Emerging Technology	Very few applications nationwide	F / S, U		Recover free LNAPL and some residual LNAPL from vadose zone	In theory, can mobilize some residual LNAPL. Designed for fine-grained soils where other technologies are ineffective. Oxidation/ reduction reactions can form undesirable products. Not proven effective at many sites.

Table 4
Current and Emerging LNAPL Remediation Technologies

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Denitrification	Soybean oil coated particles can be used to denitrify NO2 and NO3. Particles can be used as a permeable barrier in a trench. Oils can also be injected through a well to avoid digging trenches.	Emerging Technology	Very few applications nationwide			Remove and destroy soluble components from free and residual LNAPL in the saturated zone	Can indirectly destroy LNAPL so no surface treatment is necessary. Most effective during the first 10 weeks then declines in efficiency, Very limited field data.
Dense brine strategies	Displacement or containment using dense brines Used primarily for DNAPL	Emerging Technology	Very few applications nationwide			Remove free LNAPL and some residual LNAPL from saturated zone	Displacement technologies are well understood. Likely not to be applicable to most LNAPL sites. Brine can cause secondary water quality impact.
Humic acid enhanced remediation	Humic acid solutions can be used to increase the solubility of petroleum derived compounds	Emerging Technology	Very few applications nationwide			Remove free LNAPL and some residual LNAPL from saturated zone	Based on natural compounds. May be some problems with clogging. Only addresses soluble LNAPL constituents.
Fracturing	Not a clean-up method in itself; used to break up dense soil or clay below ground to assist other cleanup methods	Assisting Technology	Infrequent			Increase permeability for both vadose and unsaturated zone	Can help address problems with clean-up of low permeability units. Cannot be used in high seismic activity areas where it might open up new pathways for contaminants.

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Table 5
List of Technologies Considered for LA LNAPL Pilot Tests

TECHNOLOGY	KEY DATA SOURCE	CASE STUDY	GENERAL UNIT COST ($ per cubic yd)	TYPICAL SPACING FOR VERTICAL WELLS (ft)	DOES TECHNOLOGY REMOVE FREE PRODUCT?	DATA POINT ON HOW MUCH LNAPL IS REMOVED? (gallons per sq. ft)	WHAT IS TYPICAL REDUCTION IN LNAPL MASS? (%)	WHAT IS TYPICAL REDUCTION IN VOC GW CONC. (%)	FOR LA LNAPL PILOT TEST			NOTES
									OPERATIONAL CONCERNS?	DESIGN, ACCESS CONCERNS?	GENERAL TIME-FRAME	
Surfactant	Surbec	Golden case study	$56 (range: $16 to $256)	30	YES	0.16 (from presentation case study)	> 85% (NRC); >95% (Harwell)	~ 90% (Case Study)	Moderate	Moderate, possible to apply w/ horizon. well	Weeks or Months	Technology from one vendor: Surbec
Thermal Conductive	Terratherm	Eugene case study	$60 (range: $40 to $129)	7-20	YES	1.2 (from presentation case study)	90% to 99% (est.)	90% to 99% (est.)	High	High	Months	Guadalupe data could be reanalyzed in lieu of pilot test? Vendor estimate for pilot test costly.
Deep Sparging	Chevron/ URS	GWMR Paper	$1.5* (range: $0.5 to $5	90	Partially- soluble constituents	0.1 (from presentation case study)**	-	> 99% (Case Study)*	Moderate	Moderate, possible to apply w/ horizon. well	Year or more	May require expensive SVE component for projects in LA Basin
Pulsed Pure Oxygen Biosparging	XDD	New Jersey	$10 (range: $3 to $30)	15 - 35	Partially- soluble constituents	0.8 (from presentation case study above)		85% (Case Study)	Low-Moderate (No SVE)	Moderate, difficult to apply w/ horizon. well	Year or more	Some safety issues, may not require SVE
ChemOx	CSM	CSM data mining study	$300 for LNAPL sites (range: $100 to $900)	-	-	-	-	95% (CSM)	High	High, possible to apply w/ horizon. well	Weeks or Months	LNAPL not typical application for chemox; high unit cost; safety concerns by some group members
Deep Soil Mixing/Chemox	CSU	Conceptual Design	240 (range: $112 to $525)	-	-	-	72% (Pilot Test)	99.4% (Pilot Test)	High	Very High	Months	Only one pilot study to date; high cost; need complete access; high oxidant demand.
Biosparging	Earth Tech	Czech Rep. study	$10 (range: $3 to $30)	-	-	-	54% (Case Study)	-	Moderate	High, possible to apply w/ horizon. well	Year or more	Replaced with pure-oxygen biosparge to eliminate need for SVE
Steam Treatment	Lundegard	Guadelupe Site	$200 (range: $190 to $260)	-	-	-	54% (Case Study) (?? For stream treated zone)	81% (Case Study)	High	Moderate, possible to apply w/ horizon. well	Months	Already performed extensive pilot at Guadelupe; expensive.
Natural Source Zone Depletion	GSI	AFCEE, GSI	-	-	SLOWLY, INDIRECTLY	0.02** (theoretical; assumes on 5 year treatment period)	-	44%** empirical; assumes 5 year treatment period)	Low	Low	Years	Use as a control for each pilot test?

Notes:
1) Technology application and performance data are very general and were only used for the evaluation of potential pilot test technologies.
2) Information compiled from a variety of sources and members of the LA LNAPL Workgroup.

* *no NAPL in treatment zone*
** *Theoretical calculation over 5 year period - see slides for detail.*

APPENDIX I

ITRC 2009 B Table 5.2

Table 5-2. Summary information for remediation technologies

LNAPL technology	Advantages	Disadvantages[a]	Applicable geology (fine, coarse)[b]	Applicable to unsaturated zone, saturated zone[c]	Applicable type of LNAPL[d]	LNAPL remedial objective type (saturation, composition)[e]	Potential time frame[f]	Appendix A reference table numbers
Excavation	100% removal, time frame	Accessibility, depth limitations, cost, waste disposal	F, C	U + S	LV, LS, HV, HS	**Sat** + Comp	V. short	A-1.x
Physical or hydraulic containment (barrier wall, French drain, slurry wall)	Source control, mitigation of downgradient risk	Hydraulic control required, site management, cost, depth and geologic limitations	F, C	S	LV, LS, HV, HS	**Sat** + Comp	V. long	A-2.x
In situ soil mixing (stabilization)	Time frame, source control	Accessibility, required homogeneity, depth limitations, cost, long-term residual management	F, C	U + S	LV, LS, HV, HS	**Sat** + Comp	V. short to short	A-3.x
Natural source zone depletion	No disruption, implementable, low carbon footprint	Time frame, containment	F, C	U + S	HV, HS	Sat + **Comp**	V. long	A-4.x
Air sparging/soil vapor extraction	Proven, implementable, vapor control	Does not treat heavy-end LNAPLs/low-permeability soils, off-gas vapor management	C	U + S	HV, HS	Sat + **Comp**	Short to medium	A-5.x
LNAPL skimming	Proven, implementable	Time frame, limited to mobile LNAPL, ROI[g]	F, C	S	LV, LS, HV, HS	**Sat**	Long to v. long	A-6.x
Bioslurping/ enhanced fluid recovery	Proven, implementable, vapor control	Time frame, limited to mobile LNAPL, ROI	F, C	U + S	LV, LS, HV, HS	Sat + **Comp**	Long to v. long	A-7.x
Dual-pump liquid extraction	Proven, implementable, hydraulic control	Time frame, limited to mobile LNAPL, ROI	C	S	LV, LS, HV, HS, > residual	**Sat**	Long to v. long	A-8.x
Multiphase extraction (dual pump)	Proven, implementable, hydraulic control	Generated fluids treatment	C	S	LV, LS, HV, HS, > residual	**Sat** + Comp	Medium	A-9.x

APPENDIX II

ITRC 2009 B Table 6.1

Table 6-1. Preliminary screening matrix

LNAPL remedial objective	LNAPL remediation goal	Technology group	Example performance metrics[a]	LNAPL technology and LNAPL/ site conditions[b,c]
LNAPL saturation-based remedial objectives				
Reduce LNAPL saturation when LNAPL is above the residual range	Recover LNAPL to maximum extent practicable	LNAPL mass recovery	• LNAPL transmissivity • Limits of technology • Limited/infrequent well thickness • Decline curve analysis • Asymptotic performance of the recovery system • Cost of mass removal • Soil concentration at regulatory standard	• DPLE C, S, LV, LS, HV, HS • MPE (dual pump) C, S, LV, LS, HV, HS • MPE (single pump) C, S, LV, LS, HV, HS • Water flooding C, S, LV, LS, HV, HS • LNAPL skimming F, C, S, LV, LS, HV, HS • Bioslurping/EFR F, C, U, S, LV, LS, HV, HS • Excavation F, C, U, S, LV, LS, HV, HS
Reduce LNAPL when LNAPL is within residual saturation range	Further abate LNAPL beyond hydraulic or pneumatic recovery	LNAPL mass recovery	• Limits of technology • Asymptotic mass removal • Cost of mass removal • Soil concentration at regulatory standard	• Cosolvent flushing C, S, LV, LS, HV, HS • SESR C, S, LV, LS, HV, HS • AS/SVE C, U, S, HV, HS • ISCO C, U**, S, HV, HS • RFH F, U, S, LV, LS, HV, HS • Three- and six-phase heating F, U, S, LV, LS, HV, HS • Steam/hot-air injection C, U, S, LV, LS, HV, HS • NSZD F, C, U, S, HV, HS
Terminate LNAPL body migration and reduce potential for LNAPL migration	Abate LNAPL body migration by sufficient physical removal of mobile LNAPL mass	LNAPL mass recovery	• Total system recovery rate vs. background LNAPL flux • LNAPL saturation profile • LNAPL footprint/center of mass stabilization • Stable dissolved-phase plume concentrations, dissolved-plume shape	• Excavation F, C, U, S, LV, LS, HV, HS • DPLE C, S, LV, LS, HV, HS • MPE (dual pump) C, S, LV, LS, HV, HS • MPE (single pump) C, S, LV, LS, HV, HS
	Stop LNAPL migration by physical barrier	LNAPL mass control	• No first LNAPL occurrence downgradient	• Physical containment (barrier wall, French drain, slurry wall) F, C, S, LV, LS, HV, HS
	Sufficiently stabilize mobile LNAPL fraction to prevent migration	LNAPL mass control	• Stable dissolved-phase plume, dissolved-plume shape • No first LNAPL occurrence downgradient in LNAPL-unaffected soils	• In situ soil mixing (stabilization) F, C, V, LV, LS, HV, HS

APPENDIX II

ITRC 2009 B Table 6.1 (Continued)

LNAPL remedial objective	LNAPL remediation goal	Technology group	Example performance metrics[a]	LNAPL technology and LNAPL/ site conditions[b,c]
LNAPL compositional-based remedial objectives				
Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source[d]	Abate unacceptable vapor accumulations by sufficient depletion of volatile constituents in LNAPL	LNAPL phase change and LNAPL mass recovery	• LNAPL composition change • Soil volatile organic compound (VOC) concentrations to below regulatory standard • Soil vapor plume concentrations to below regulatory standard • Asymptotic performance of the recovery system • Cost of mass removal	• AS/SVE C, U, S, HV, HS • RFH F, U, S, LV, LS, HV, HS • Three- and six-phase heating F, U, S, LV, LS, HV, HS • Steam/hot-air injection C, U, S, LV, LS, HV, HS
	Abate unacceptable soil vapor concentrations by physical barrier or containment	LNAPL mass (vapor) control	• Soil VOC concentrations to below regulatory standard	• Physical or hydraulic containment (vapor barrier, barrier wall) F, C, S, LV, LS, HV, HS • SVE (vapor management and collection) C, U, S, HV, HS
	Control or treat soluble plume to abate unacceptable dissolved-phase concentrations at a specified compliance point	LNAPL mass control (interception of dissolved-phase plume)	• No first constituent occurrence at unacceptable levels downgradient • Dissolved-phase regulatory standard met at compliance point • Reduced dissolved-phase concentrations downgradient of the barrier	• Modified AS for enhanced biodegradation (e.g., oxygen injection) C, U, S, HV, HS, LS, LV • Physical or hydraulic containment (barrier wall, French drain, slurry wall, wells, trenches) F, C, S, LV, LS, HV, HS • DPLE C, S, LV, LS, HV, HS • MPE (dual pump) C, S, LV, LS, HV, HS • MPE (single pump) C, S, LV, LS, HV, HS • NSZD F, C, U, S, HV, HS
Reduce constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source	Further reduction of groundwater and vapor concentration beyond acceptable levels	LNAPL phase change		• NSZD F, C, U, S, HV, HS

APPENDIX II

ITRC 2009 B Table 6.1 (Continued)

LNAPL remedial objective	LNAPL remediation goal	Technology group	Example performance metrics[a]	LNAPL technology and LNAPL/ site conditions[b,c]
LNAPL aesthetic-based remedial objectives				
Aesthetic LNAPL concern abated (saturation objective)	Geotechnical soil instability abated	LNAPL mass recovery	• Specific soil concentration that results in desired soil stability	• Excavation F, C, U, S, LV, LS, HV, HS • NSZD F, C, U, S, HV, HS
		LNAPL mass control	• Soil concentrations remain stable or decreasing • Acceptable structural strength	• In situ soil mixing (stabilization) F, C, U, S, LV, LS, HV, HS • NSZD F, C, U, S, HV, HS
Aesthetic LNAPL concern abated (composition objective)	Offensive odors abated	LNAPL mass (vapor) control	• Vapor concentrations (to below odor threshold) • Specific soil concentration	• Physical containment (barrier wall, French drain, slurry wall) F, C, S, LV, LS, HV, HS • SVE (vapor management and collection) C, U, S, HV, HS • AS (addition of oxygen)/SVE C, U, S, HV, HS • NSZD F, C, U, S, HV, HS

[a] Overall, until such time as the risks are mitigated by the LNAPL remedial technology(ies), risks should be managed via engineering or institutional controls.
[b] C = coarse soils, F = fine-grained soils, S = saturated zone, U = unsaturated zone, U** = unsaturated zone with ozone oxidant; LV = low volatility, LS = low solubility, HV = high volatility, HS = high solubility.
[c] If explosive conditions exist, emergency response approach is assumed to mitigate risk (i.e., immediate engineering control and abatement of vapors is assumed to reduce risk).
[d] Considered potentially most effective technology, without significant underutilization of technology capability.