

## Report on:

## Approaches

## and Methods for Evaluation of Light non-

## Aqueous - Hydrogeological

## **Assessment Tools Project**

# Submitted to: Ministry of Environment February 2006



Submitted by: Science Advisory Board for Contaminated Sites in British Columbia

## **REPORT ON**

## APPROACHES AND METHODS FOR EVALUATION OF LIGHT NON-AQUEOUS PHASE LIQUID MOBILITY – HYDROGEOLOGICAL ASSESSMENT TOOLS PROJECT

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## 1.0 INTRODUCTION

This report has been prepared for the Science Advisory Board for Contaminated Sites (SABCS) in British Columbia to evaluate approaches and methods that could be used by practitioners to evaluate the potential mobility of lighter-than-water non-aqueous phase liquids (LNAPLs) at contaminated sites in British Columbia. LNAPLs are frequently encountered at contaminated sites and include common petrochemical products such as gasoline, diesel and lubricating oils. When released to ground in sufficient quantities, LNAPL may accumulate in a porous medium near the surface of the water table as a continuous phase (often referred to as a "free-phase"). While there are several potential sources for risk associated with free-phase and residual LNAPL zones, an important consideration is the potential mobility of LNAPL. Appropriate remediation objectives and end-points must often be specified based on mobility considerations. The purpose of this report is to provide a set of useful approaches and methods for evaluation of LNAPL mobility. This guidance is not intended for sites with dense non-aqueous phase liquids (DNAPL).

The issues for assessment and management of LNAPL are complex. There is no single method to evaluate LNAPL mobility. Instead, a number of complementary approaches and tools are recommended, as subsequently described in this report. Since LNAPL mobility should be evaluated considering the broader issues for LNAPL management and decision-making, the first four sections (2 to 5) of this report provide an overview of NAPL fundamentals, regulatory context, and decision-criteria for LNAPL management. The next four sections (6 to 9) provide a conceptual model for LNAPL followed by evaluation of LNAPL mobility, providing both a detailed analysis of methods and a recommended approach.

The SABCS report on Screening Level Risk Assessment 2 (SLRA-2) Soil and Groundwater Module indicated that a precluding factor for use of SLRA-2 was "*potentially mobile non-aqueous phase liquid (NAPL) existing in soil or groundwater*". For the purposes of SLRA-2, NAPL was defined by "a) physical observations of NAPL in wells, as expressed by the presence of sheens or appreciable product thickness, and b) exceedance of the NAPL indicator standards of BC Environment." One objective of this report is to better define criteria where the presence of LNAPL should preclude the use the SLRA-2 guidance.

## 2.0 NAPL BASICS AND DEFINITIONS

Non-aqueous phase liquids (NAPLs) are liquids that exist as a separate, immiscible phase when in contact with water. The differences in the physical and chemical properties between water and NAPL result in a physical interface between the liquids which prevents the two fluids from mixing. NAPLs are typically classified as either light (*i.e.*, LNAPLs), which have densities less than that of water, or dense (*i.e.*, DNAPLs), which have densities greater than that of water. Common LNAPLs include petroleum products such as gasoline, diesel, jet fuel and lubricants. LNAPLs are commonly found at and, to some extent below, the top of water-saturated zones since the buoyancy of LNAPL in water limits the depth to which LNAPL can migrate into the groundwater zone (see Section 6.0 for additional discussion).

The movement of LNAPL through the subsurface is controlled by several processes. Upon release, LNAPL moves downward under the influence of gravity. If a small volume of NAPL is released, it will move through the unsaturated zone until its mass is immobilized within soil pores as a result of capillary forces. If sufficient volume of LNAPL is released, it will migrate until it encounters the water table, where buoyancy forces and increasing water content impede the vertical movement of LNAPL. As a result, the less dense LNAPL will migrate laterally along the water table. In general, LNAPL migration will occur in the direction of the water table gradient, although mounding of LNAPL and radial flow can occur if the rate of LNAPL movement from the surface is greater than the lateral migration.

Within the subsurface environment, water typically is the wetting phase, meaning that it is preferentially attracted to solids and forms a continuous coating around soil particles, and fills the smaller void spaces. In the vadose zone, the larger pore spaces are often filled with air, and LNAPL in the vadose zone typically forms an intermediate wetting phase between the water and air, and displaces air from the larger pores. Near to the water table (*i.e.*, capillary fringe and below), the pore spaces are filled with water, and LNAPL forms the non-wetting fluid. Within this zone, LNAPL will only move into saturated pore spaces if the capillary displacement pore entry pressure is exceeded, as discussed in Section 8.5. A low permeability stratum above the water table can also act as a capillary barrier to LNAPL migration, unless the soil is dry and LNAPL is the wetting phase. A changing water table height can influence the lateral and vertical movement of NAPL through changing capillary pressure conditions.

LNAPL may occur as either *residual LNAPL* or as *free-phase LNAPL* within the subsurface environment. LNAPL that is retained by soil capillary forces and that is trapped within pore spaces is relatively immobile and termed residual LNAPL. Free-phase LNAPL occurs when the LNAPL saturation exceeds the residual saturation, and a continuous LNAPL phase exists among interconnected pores in the soil matrix. The free-

phase LNAPL volume may move vertically or laterally within soil in response to gravity or, less commonly, viscous forces. Over time, dissolution of LNAPL components and volatilization will deplete the LNAPL, reducing saturation and mobility. An excellent glossary of technical terms for characterizing immiscible fluids in geologic media is provided in ASTM (2005) (Appendix X6).

## 3.0 REGULATORY CONTEXT OVERVIEW

Historically, regulations for management of free-phase LNAPL have required the removal of LNAPL product from wells, as defined by its thickness in wells rather than its concentration in an environmental medium (*i.e.*, soil, groundwater, air). In BC, the regulatory imperative, while less specific compared to some jurisdictions, has generally been interpreted to mean that extraction and/or control of free-phase LNAPL is required at contaminated sites.<sup>1</sup> In practice, the presence of product in wells at a site has been used as both the factor driving remediation and the end-point for evaluating remediation success (*i.e.*, thickness of product in wells). In the US, federal regulations state that LNAPL must be removed to "*the maximum extent practicable*" (USEPA, 1988). State regulations are similar in terms of general principles, although some also define end-points based on various criteria including the product thickness in a well (3 mm, or 1/8 inch, Georgia), sheen (Maryland), or any measurable amount of product (Utah) (API, 2005). Until recently, there has been little evaluation or recognition of the factors that control product recovery and mobility, or consideration of risk-based approaches to define remediation objectives or end-points for free-phase LNAPL.

There are significant recent developments for LNAPL management based on work by a number of agencies and industry groups, and new paradigms for evaluating LNAPL are being developed. This has led to a better understanding of LNAPL distribution, mobility and recoverability, and related issues associated with prediction and mitigation of groundwater and vapour plumes evolving from a LNAPL source. These improvements in the science have led to a number of quantitative tools that assist in the prediction of LNAPL mobility. Furthermore, there has been a recognition of the technical impracticability or limits to removal of LNAPL (both free-phase and residual), and that partial removal of LNAPL may have a limited effect on the longevity of associated solute plumes (Huntley and Beckett, 2002).<sup>2</sup> Decision-making criteria for evaluation of LNAPL management are described in greater detail in Section 5.0.

<sup>&</sup>lt;sup>1</sup> B.C. Contaminated Sites Regulation indicates that "water must be remediated so that nonaqueous phase liquids are not present in quantities in excess of that acceptable to a director."

<sup>&</sup>lt;sup>2</sup> The effect of LNAPL removal on the longevity of associated solute plumes is a subject of on-going scientific debate. Detailed discussion on this topic goes beyond the scope of this report. The reader is referred to the LNAST software tool (API, 2000) for more information on this topic. The examples provided in the LNAST guide indicate that the plume longevity is highly site specific; however, for many scenarios presented, the longevity is several decades or longer.

## 4.0 RISKS AND CONCERNS ASSOCIATED WITH LNAPL

There are a number of potential risks or concerns associated with LNAPL in the subsurface that are discussed below. These are important to consider when developing remedial objectives and end-points for management of LNAPL at contaminated sites.

**LNAPL Mobility**: LNAPL can migrate significant distances if the release source (*e.g.*, a leaking underground storage tank) is not eliminated. Depending on site conditions, migrating free-phase LNAPL may have the potential to impact surface water bodies, water supply wells, and underground utilities that intercept the release. LNAPL may be released from soil during excavations that occur within LNAPL areas. Enlargement of the LNAPL zone will affect the distribution and extent of associated solute plumes.

*Explosive Vapour Hazard*: Vapours released from LNAPL may migrate into utilities or other confined spaces and accumulate at concentrations representing an explosion hazard. Elevated vapour concentrations may also occur during excavations within LNAPL source zones.

*Vapour Health Risk*: Volatilization from LNAPL and migration into indoor or ambient air may pose unacceptable human health risks based on long-term exposure.

*NAPL Toxicity*: Direct contact with LNAPL in soil, groundwater or surface water may present human health or ecological risks.

**NAPL Dissolution**: Fluctuating water tables may act to spread LNAPL vertically within a soil, creating a "smear zone" of LNAPL which may extend below the water table. Mobile groundwater within the smear zone that comes in direct contact with LNAPL will, itself, become contaminated with the constituents of the LNAPL, be it gasoline, fuel oil, or specific distillates. This occurs in a predictable manner based on groundwater and LNAPL chemistry. Gasoline components in the dissolved-phase may migrate away from the LNAPL zone, and have the potential to contaminate surface water bodies and water supply wells, and may pose human health and ecological risks through direct exposure pathways such as ingestion or dermal contact. A dissolved plume may also act as a source of soil vapour contamination which may migrate to indoor air.

*Aesthetic and Nuisance Concerns*: The presence of LNAPL and generation of odours may, in some cases, pose an aesthetic or odour nuisance concern.

## 5.0 DECISION-MAKING FRAMEWORK FOR LNAPL REMEDIATION

There has been considerable effort in recent years directed at defining a decision-making framework for remediation of sites containing LNAPL, including protocols and guidance prepared by Aqui-Ver (2004), USEPA and RTDF (2004), Texas Commission (2004) and ASTM (2005). A common element of these protocols is a framework where remediation objectives, together with remediation end-points or metrics, are defined as part of a comprehensive NAPL management strategy. The strategy is founded on scientifically sound understanding of NAPL behaviour, potential risk and other relevant factors. This approach is in contrast with historical approaches based on undefined or unquantifiable goals, and incomplete or lack of understanding of LNAPL characteristics and behaviour.

While significant advances have been made in the development of protocols, there nevertheless is a lack of clarity and uniformity in terms of methods for identifying and quantifying appropriate remediation goals and end-points. This is understandable since the issues for LNAPL management are complex; there are typically both risk-based and non-risk based drivers that require consideration, and there is uncertainty in terms of the potential outcomes. ASTM (2005) provides guidance on development of LNAPL site objectives related to LNAPL mobility, LNAPL recoverability, LNAPL thickness, plume longegivity and flux, and remediation metrics, where specific end-points are defined that relate to both benefits and costs. Remedial alternatives are evaluated in relation to these remediation objectives. Some regulatory agencies introduce the concept of plume management zones, and define minimum requirements for remediation within such zones (Texas, 2004). Depending on the technical and cost feasibility of recovering LNAPL, there may also be the option in the US to attain an "Impracticability" waiver if there are serious constraints in terms of technical and cost feasibility.

Defining realistic end-points for LNAPL recovery can also be influenced by the significant variation in methods that can be used to recover free-phase LNAPL or remediate residual LNAPL zones. For example, free-phase LNAPL recovery methods range from passive skimming, which is a low-intensity and relatively low-cost method, to greater intensity methods such as dual-phase high vacuum extraction or techniques where surfactants or steam are used to enhance LNAPL mobility.

Provided below are some of the key elements of a decision framework that can be used for the evaluation and implementation of LNAPL management measures:

- 1. Conduct Initial Site Investigation.
- 2. Develop Initial Conceptual Site Model.
- 3. Determine Presence or Absence of LNAPL.
- 4. Implement Immediate Response Actions When Necessary.
- 5. Conduct Detailed Site Investigation.

- 6. Refine Conceptual Site Model.
- 7. Evaluate Potential Risks Associated with LNAPL.
- 8. Define LNAPL Remediation Objectives.
- 9. Define LNAPL Remediation End-points or Performance Metrics.
- 10. Evaluate Remediation Alternatives, Develop Remedial Action Plan and Contingency Plan.
- 11. Implement and Monitor Remedial Action.
- 12. Update Remediation Objectives and End-points If Necessary.
- 13. Implement Long-term Site Management or Site Closure.

A guiding principle of the decision-making process is that a thorough evaluation of potential risk to human and ecological health should be conducted, and that LNAPL management measures should be implemented to mitigate those risks considered unacceptable. LNAPL management measures can include recovery, which is defined here as LNAPL removal or soil decontamination, or controls, which are measures taken to address plume migration or exposure to associated solute plumes (*e.g.*, hydraulic or vapour controls).

Since continued mobility and spreading of free-phase LNAPL could, in many cases, result in adverse risks, an appropriate risk-based goal would be to reduce LNAPL mobility to "*de minimus*" levels. While the general goal is reduce mobility to low levels, specific remediation goals and end-points pertaining to the recovery of free-phase LNAPL from a site may be difficult to define. The recovery of free-phase LNAPL at some sites may be warranted to reduce LNAPL mobility to acceptable levels. However, at other sites, no recovery of LNAPL may be warranted despite appreciable thicknesses of free-phase LNAPL within the core of the LNAPL zone since the LNAPL zone may be regionally stable (*i.e.*, not expanding) due to the constraining capillary pressures at the periphery of the LNAPL zone. A framework for evaluating LNAPL mobility is discussed in detail in Sections 8 and 9.

Practically, the remediation objective and end-point may also depend on the consequences of being wrong. For example, if predictions for LNAPL mobility are wrong (*e.g.*, LNAPL continues to migrate when the measured thickness in wells was sufficiently small to infer that the LNAPL was stable) and the consequences for continued LNAPL migration are severe, then more stringent remediation end-points and performance metrics should be considered. Such situations may occur, for example, if free-phase LNAPL is observed in wells located within a few metres of a stream with sensitive aquatic habitat, or if future development may include excavations that could encounter LNAPL.<sup>3</sup>

<sup>&</sup>lt;sup>3</sup> Note that in the first condition, LNAPL located within 30 m of a sensitive aquatic habitat, SLRA-2 cannot be applied.

In addition to risk-based objectives based on LNAPL mobility, there may be other riskbased or non-risk based LNAPL remediation objectives, including:

- Reduce the longevity of compounds of concern that are present within the LNAPL body;
- Reduce the dissolved or vapour-phase chemical fluxes migrating across some specified boundary, and,
- Reduce chemical concentrations in groundwater, soil or soil vapour at some specified boundary.

Over the short-term, recovery of free-phase LNAPL using methods other than excavation or vapourization commonly does not achieve significant reductions in chemical longevity, flux or concentration since it is not possible to recover all free-phase LNAPL, and since a significant mass of residual LNAPL will remain in the subsurface. Therefore, the above objectives are typically applied from a longer-term perspective (decades) based on cost-benefit considerations. Models that can be used to predict longevity, flux and concentration are available (*e.g.*, API (2002)).

LNAPL remediation objectives that are simply statements relating to product thickness in wells (*e.g.*, "remove until less than specified thickness") or generalized recovery objectives (*e.g.*, "recover LNAPL until no longer effective") are less helpful and should, to the extent possible, be replaced with specific objectives and end-points based on risk-based considerations and cost-benefit analysis.

In summary, the key objectives for management of LNAPL at contaminated sites are to implement all necessary measures to mitigate unacceptable risk and, where practical, recover LNAPL to the extent needed to reduce LNAPL mobility to *de minimus* levels. The objectives and end-points should consider site-specific conditions including proximity to critical receptors and possible future changes to site conditions.

## 6.0 LNAPL CONCEPTUAL MODEL

The early conceptual model for LNAPL remediation developed in the 1980s was based on a "pancake" conceptualization for LNAPL distribution and migration (Ballestero et al., 1984). In this conceptualization, it was assumed that LNAPL released within the unsaturated zone migrates vertically under gravitational force until the water table is reached, at which time the LNAPL spreads horizontally as a continuous single-phase fluid. The LNAPL was assumed to "float" as a separate layer on the water table (or capillary fringe) in the shape of a "pancake" and remain as one interconnected mass. It was assumed that the LNAPL filled essentially the entire pore space (*i.e.*, near 100 percent saturation) within the porous medium over a thickness comparable to (or some percentage of) the product thickness observed in monitoring wells. This inaccurate conceptualization ignored the critical influence of capillarity and commonly resulted in over predictions of the volume of product in the formation and recoverability.

An updated paradigm that is representative of typical soil capillary conditions is termed the "multiphase model", and is based on work by Dullien (1979), Lenhard and Parker (1990) and Farr et al. (1990) (Figure 1). In this conceptualization, LNAPL does not migrate laterally as a separate layer (pancake) only above the water-saturated zone but, instead, rests like an iceberg at sea, largely submerged (API, 2003). Movement of LNAPL in the saturated zone is constrained by the capillary pressures needed to displace water from the pores at the margins of the LNAPL. Under the multiphase conceptualization, LNAPL, water and air coexist in zones of LNAPL saturation, and LNAPL saturations will decrease with depth in the porous medium, below the equilibrium elevation of the LNAPL/air interface observed in a monitoring well. Due to the presence of water in the soil, LNAPL saturations do not reach 100 percent, but may range from as little as 5 percent to over 70 percent (API, 2005). The distribution of the LNAPL saturation in the porous medium over the depth interval between the LNAPL/water interface and the air/LNAPL interface observed in a monitoring well, is a function of the water-LNAPL capillary pressure (LNAPL is generally the non-wetting fluid compared to water). The distribution of the LNAPL saturation above the air/LNAPL interface is a function of the LNAPL-air capillary pressure, where LNAPL is the wetting fluid compared to air. The complete LNAPL saturation profile can be obtained from having both the water-LNAPL and LNAPL-air capillary pressure curves.

Where LNAPL is present in the subsurface, the volume of LNAPL per unit area of aquifer will primarily depend on the properties of soil and the LNAPL. In general, for a given observed product thickness in a monitoring well, the mobile LNAPL volume is greater within a coarse-grained medium such as a gravel, than a fine-grained medium such as a silty sand. Similarly, the volume of free-phase LNAPL will depend on the product properties and composition. The multiphase model, in conjunction with measured LNAPL thickness in wells, can be used as a basis to estimate the LNAPL

saturation profile, the volume of LNAPL in soil, and potential mobility. Key aspects of the multiphase model are capillary pressure–saturation curves that are derived for an LNAPL based on soil and fluid properties. A idealized conceptual relationship between free-product thicknesses in the well and in the soil is shown in Figure 1.



**FIGURE 1:** Idealized Conceptualization of LNAPL in a well and adjacent formation (from API, 2003).

Given that most common LNAPLs are oils, the upper surface of the LNAPL layer is termed the "air-oil interface" and the lower surface of the oil is termed the "oil-water interface". The actual elevation of the water potentiometric surface cannot be physically measured in the well, but must be calculated using the relative density of the oil to water ( $\rho_{ro}$ ), the elevation of the water-oil interface ( $Z_{ow}$ , m), and the LNAPL thickness measured in the well ( $H_o$ , m). The theoretical air-water interface ( $Z_{aw}$ , m) in a well containing LNAPL can be estimated as follows:

$$Z_{aw} = Z_{ow} + (\rho_{ro}Ho) \tag{1}$$

The multiphase model for estimating LNAPL volume and mobility, described in greater detail in Section 8, assumes vertical static equilibrium (gravity forces are balanced by capillary forces). The accuracy of the model increases when there is no longer an active LNAPL release, when the permeability of the soil is relatively high, and when water table fluctuations are small. Fluctuations in the water table complicate the estimation of product volumes due to hysteresis (*i.e.*, capillary pressure-saturation curves are non-unique and depend on whether there is drainage or wetting of LNAPL in the porous

medium). Vertical hydraulic gradients can also reduce the accuracy of predictions using the multiphase model.

Water table fluctuations are important to consider when using the multiphase model since a falling water table typically results in greater observed thickness of LNAPL in wells, and an increased volume of mobile product. As the water table falls, oil is commonly released from the saturated zone until the LNAPL saturations approach the lower saturations that are present in the portion of the LNAPL smear zone within the unsaturated zone. Studies suggest that the effect of a falling water table is more pronounced for coarser-grained than finer-grained soils (Parcher et al., 1995).

Geologic heterogeneity can also result in non-ideal conditions, and reduce the accuracy of predictions based on the multiphase model and vertical static equilibrium. Several possible scenarios where the measured LNAPL in wells would result in biased estimates are illustrated in Figure 2. Additional information on LNAPL distribution in secondary features is provided in Adamski et al. (2005).



FIGURE 2: Conditions effecting thickness of LNAPL in Wells (from API, 2003).

Additional Notes:

- *Scenario 1*: Monitoring well is completed into underlying gravel with lower hydraulic head. The low pressure in the underlying layer draws LNAPL down the well.
- *Scenario* 2: The LNAPL pressure in an underlying layer is insufficient to displace water from overlying fine-grained sediments; however, LNAPL is present at higher elevations in the well due to absence of resistance in well (*i.e.*, the well is open and not plugged).
- *Scenario 3*: LNAPL only occurs in sparse secondary features such as joints, sand seams, root casts or animal burrows. The LNAPL thickness in well can not be related to thickness in the formation.

## 7.0 LNAPL CONDUCTIVITY, MOBILITY AND STABILITY CONCEPTS

When evaluating the potential mobility of free-phase LNAPL, it is helpful to view the movement of LNAPL at different scales, from the small "representative elementary volume" scale to the macroscopic plume scale.

## 7.1 Small-Scale Mobility

At the local (*i.e.*, centimeter) scale, the LNAPL (oil) seepage velocity can be estimated through Darcy's Law, or the mathematical product of the LNAPL conductivity and gradient divided by the effective oil porosity:

$$V_{local-scale} = K_o / (\phi S_o) * (\Delta H / \Delta X)_o$$
<sup>(2)</sup>

where,

 $K_o = \text{LNAPL}$  conductivity at a single point (cm/sec),

 $(\Delta H / \Delta X)_o = \text{LNAPL gradient (m/m)},$ 

 $\phi$  = Total porosity, dimensionless,

 $S_o = \text{NAPL}$  saturation.

The LNAPL conductivity is a function of permeability, relative permeability, saturation, and fluid properties:

$$K_o = \frac{\rho_o}{\mu_o} k_{ro} k_i g \tag{3}$$

where,

 $\mu_o$  = dynamic viscosity of the oil (g/cm-sec),

 $k_{ro}$  = relative permeability to oil (dimensionless),

 $k_i$  = intrinsic permeability of the matrix (cm<sup>2</sup>),

 $g = \text{gravitational constant (cm/sec}^2).$ 

In multiphase systems, the fluid conductivity is not only a function of the aquifer properties, but also varies with respect to the physical properties of the fluid and the fluid saturation. For example, LNAPL conductivity generally increases with LNAPL saturation and decreases with LNAPL viscosity.

It is important to recognize that a gradient is required for potential LNAPL migration. The LNAPL gradient may differ from the hydraulic gradient if LNAPL migration is occurring. It is also important to recall that LNAPL migration is subject to pore entry pressures that must be overcome and will limit migration near the periphery of the plume. Pore entry pressures for LNAPL displacing water can be overcome by increasing LNAPL pore pressure or reducing water pore pressure (*i.e.*, falling water table).

## 7.2 Plume-Scale Mobility

*"Stability"* is a term often used when describing the lateral expansion or migration of LNAPL beyond the limits of the LNAPL zone or plume. The LNAPL plume will migrate and expand when LNAPL is being released to the subsurface and contributing mass to the plume. When the source of LNAPL is stopped, the plume will come to a stable configuration or footprint after some period of time. While vertical redistribution of LNAPL within the core of the plume can continue to occur, no further expansion of the LNAPL plume occurs when stability is achieved. The relationship of LNAPL plume mobility and stability is illustrated below in Figure 3.



FIGURE 3: Conceptual Relationship Between Plume Stability and Mobility (from API, 2005)

LNAPL plume stability refers to the movement of an oil plume as a whole. In an approximate sense, the plume stability can be quantified using the effective conductivity to derive a macro-scale LNAPL velocity (the term "plume-scale" velocity is not used since the "entire" plume may not be mobile). The terminology described in (API, 2005) is adapted<sup>4</sup> here, in that the conductivity divided by the effective porosity in Equation 2 is replaced with a mobility term, as follows:

$$V_{macro-scale} = M_o * (\Delta H / \Delta X)_o \tag{4}$$

where  $V_{macro-scale}$  is the average or effective velocity over the vertical interval with mobile LNAPL and  $M_o$  is the inherent oil mobility.

The inherent oil mobility was defined by Parker (1996) as the ratio of free oil transmissivity to specific oil volume at a given location. The inherent mobility is similar to the effective (or "average") relative permeability concept described by Charbeneau (2003).

The inherent oil mobility is equivalent to the ratio of the average oil conductivity to the effective free oil porosity, as shown below:

$$M_o = \frac{T_o}{V_o} = \frac{b_o \overline{K_o}}{b_o \phi \overline{S_o}} = \frac{\overline{K_o}}{\phi \overline{S_o}}$$
(5)

where,

 $M_o$  = Inherent oil mobility (m/day),

 $T_o = \text{LNAPL}$  (oil) transmissivity, integrated along the oil saturation profile (m<sup>2</sup>/day),

- $V_o =$  Specific oil volume per unit area (m<sup>3</sup>/m<sup>2</sup>),
- $b_o =$  Free oil thickness in the well at static equilibrium (m),
- $\overline{K_o}$  = Mean oil conductivity, averaged along the oil saturation profile below the air-oil interface in the well (m/day),
- $\overline{S_o}$  = Mean oil saturation, averaged along the oil saturation profile, dimensionless.

<sup>&</sup>lt;sup>4</sup> Aqui-Ver, Inc. (2004) use the terminology "plume-scale velocity" in place of "macro-scale velocity".

## 8.0 EVALUATION OF LNAPL MOBILITY

The objective of this section is to discuss approaches, methods and issues for the evaluation of LNAPL mobility. A recommended framework for evaluation of LNAPL mobility is provided in Section 9.0.

## 8.1 General Considerations

There are several possible approaches or methods that can be used to evaluate LNAPL mobility. These include the following:

- (i) **Observational Approach:** Observations over time of LNAPL and dissolved plume characteristics;
- (ii) **LNAPL Recovery Analysis:** An analysis of LNAPL recovery data indicating declining yields (*i.e.*, recovery analysis);
- (iii) Theoretical Methods to Estimate LNAPL Plume Mobility: Theoretical methods to estimate LNAPL plume mobility, supported by field and laboratory measurements to obtain model input parameters;
- (iv) **Evaluation of LNAPL Pore-Scale Movement at Plume Front**: Theoretical methods to estimate the ability of an LNAPL plume to penetrate soil pores at the LNAPL plume front; and,
- (v) Laboratory Tests: LNAPL mobility is indirectly evaluated using laboratory tests.

The emerging trend is to use a combination of these approaches to evaluate LNAPL mobility based on multiple lines-of-evidence (*i.e.*, a tool box approach) with the primary emphasis on observational data at wells and field tests to evaluate LNAPL presence and mobility. Field-based tools that can be used to assess LNAPL include analysis of soil cores, direct push cone penetrometer methods combined with laser-induced fluorescence sensor, product bail-down tests, and short-term pilot tests of LNAPL recovery.

Site characterization programs for LNAPL sites should take into account the unique challenges associated with LNAPL characterization and importance of taking spatial and temporal variability into account.

Each of the above five approaches is described below.

## 8.2 Method 1 - Observational Approach

Repeated observations of the presence or absence of LNAPL, and the thickness of LNAPL in wells where present, can be used to infer potential LNAPL mobility. This method is considered the most direct indication of LNAPL mobility. The monitoring well network should include appropriately located sentinel wells in the down-gradient direction of the NAPL plume. Wells should be adequately developed and temporal monitoring data from wells should be obtained over a sufficient length of time to determine trends, and should include monitoring conducted at times corresponding to the range of seasonal high and low water tables. In general, this would require monitoring over at least one year, and likely longer. For tidally influenced zones, a different approach consisting of more frequent monitoring would likely be warranted. The dissolved plume stability can also be used to infer LNAPL stability, since a stable or shrinking dissolved plume provides a strong line-of-evidence for LNAPL being largely stable (G.D. Beckett; as quoted in API, 2003).

## 8.3 Method 2 - LNAPL Recovery Analysis

The analysis of LNAPL recovery data can not be directly used to evaluate LNAPL plume stability since the rate and total volume of LNAPL recovered from the central area of a LNAPL plume may have no bearing on the stability of the LNAPL plume as a whole. However, declining LNAPL thicknesses in wells and reduced rates of LNAPL recovery would normally represent a reduced risk potential for LNAPL migration, although this may depend on recovery system parameters (*e.g.*, well spacing, LNAPL removal method).

Sale (2003) presents a method for decline-curve analysis based on the assumption of first-order decay, where the LNAPL extraction rate is plotted versus the cumulative production. If the data asymptotically approach a straight line, the line can be extrapolated to predict the maximum free product recoverable.

Recovery analysis, as described above, assumes that the removal of product has occurred over an extended period of time. A bail-down test (*i.e.*, single or limited number of tests) may also provide some qualitative information, for example, if LNAPL recharge into a well is very slow, this may indicate limited LNAPL mobility. The limitations of bail-down tests should be recognized; these include spatial and temporal variability in conditions affecting LNAPL recharge into a well.

## 8.4 Method 3 - Theoretical Estimates of LNAPL Mobility

Theoretical methods can be used to estimate the potential macro-scale movement of a LNAPL plume. Since the theoretical methods for estimation of potential LNAPL

mobility are relatively complex, automated software tools are typically utilized to evaluate LNAPL mobility. The theoretical basis for these tools is provided below; a brief summary of available automated tools follows in Section 8.4.4.

The theoretical estimates of mobility described in this section are based on an idealized conceptual model that assumes vertical equilibrium. Non-equilibrium conditions and hysteresis complicate estimation of LNAPL volume and mobility since the degree of oil or water saturation depends on the history of wetting and drainage. In addition, theoretical estimates of inherent mobility and macro-scale velocity do not take into account conditions at the periphery of the LNAPL plume, where capillary forces tend to immobilize LNAPL from further migration (after an initial period of migration). It is important to recognize that, over time, weathering and smearing of LNAPL, due to water table fluctuations, will reduce LNAPL mobility.

The key parameters required to evaluate potential LNAPL mobility (see equations 2 and 5) are:

- 1. Intrinsic permeability (Section 8.4.1);
- 2. Relative permeability and LNAPL physical properties (Section 8.4.2); and,
- 3. LNAPL gradient (Section 8.4.3).
- 8.4.1 Intrinsic Permeability

The intrinsic permeability of a medium can be calculated from the saturated hydraulic conductivity of the medium (obtained from slug test or pumping test data) or estimated using a water retention model (*e.g.*, Van Genuchten model, see below). The relationship between hydraulic conductivity ( $K_{w,}$  cm/s) and intrinsic permeability ( $k_i$ , cm<sup>2</sup>) is as follows:

$$K_{w} = \rho_{w} * k_{i} * g / \mu_{w}$$
(6)

where,

 $\rho_w$  = density of water (g/cm<sup>3</sup>),

 $\mu_w$  = dynamic viscosity of water (g/cm-sec).

## 8.4.2 Relative Permeability

The relative permeability is typically calculated or estimated in one of two ways:

- 1. *Theoretical estimates from LNAPL thickness in wells*: Using capillary pressuresaturation relationships, along with soil and fluid properties, the LNAPL saturation profile and relative permeability are estimated.
- 2. *Field LNAPL bail down tests*: A field bail down test can used to estimate field transmissivity and average LNAPL conductivity.

Two other less common methods that can be used to estimate relative permeability are: (i) laboratory measurements on soil cores from discrete locations that provide information on measured LNAPL saturation, which can be used to derive Van Genuchten or Brooks-Corey capillary parameters through statistical curve-fitting to the saturation profile, and (ii) laboratory measurements to obtain the specific permeability of soil to LNAPL.

## Theoretical Methods from LNAPL Thickness in Wells

The most common, currently employed methodology to estimate relatively permeability is based on theoretical estimates that assume vertical hydrostatic equilibrium to derive capillary pressure-saturation relationships. The method involves the following five steps:

- 1. Measurement of LNAPL thickness in wells;
- Estimation or measurement of LNAPL properties (interfacial tension, density, viscosity). It is recommended that these parameters be measured by a laboratory. Alternatively, a comprehensive compilation of values for various types of product is provided in API, 2005 and Charbeneau (2003);
- 3. Estimation of capillary parameters for a water retention model (air-water capillary pressure saturation curve), which typically is either the Brooks and Corey model or the Van Genuchten model (see discussion in Exhibit 1 and example water retention curve in Figure 4);



FIGURE 4: Water Retention Curve for Sandy Loam

- 4. Application of scaling parameters (oil/water interfacial tension, oil/air interfacial tension) to obtain the capillary pressure–saturation relationship for LNAPL, and estimation of the LNAPL saturation profile using the multiphase model;
- 5. Estimation of LNAPL relative permeability profile through integration of the Burdine (1953) equations with the Brooks and Corey (1964) water retention model, or the equations of Mualem (1976) with van Genuchten's water retention model. According to (API, 2005), using the same set of fluid saturation values, the equations of Mualem generally predict larger values for LNAPL relative permeability and some practitioners advocate using the Burdine equations for sands and the Mualem equations for silty materials. The effective (average) relative permeability is obtained by integrating the effective permeability profile. As an alternative to the above, a simple empirical relationship between the average effective permeability and average effective saturation ( $\overline{k_{ro}} = \overline{S_o}^2$ ) proposed by Charbeneau (2003) can be used, where  $\overline{k_{ro}}$  is the effective permeability and  $\overline{S_o}$  is the effective free-phase LNAPL saturation (LNAPL saturation minus residual saturation).

Estimation of the free-phase volume, while not directly needed to obtain the relative permeability, is useful for evaluation of LNAPL recovery alternatives and assessing the significance of LNAPL measurements in wells. The free-phase volume is obtained through subtraction of the residual saturation from the saturation values. An estimate of residual saturation is required for both the unsaturated and saturated zones. Residual saturations are generally less than 10 percent for the unsaturated zone and between 10 to 30 percent for the saturated zone (Aqui-Ver, Inc., 2003). Literature values of residual saturation are available in Brost and DeVaull (2000), Charbeneau (2003) (quoting Mercer and Cohen, 1990) and (API, 2005).<sup>5</sup>

## Field LNAPL Bail Down Tests

The estimation of transmissivity from a bail down test is based on the Bouwer-Rice solution for slug-tests modified to account for unique aspects relating to LNAPL migration into wells and filter pack effects (Sale (2003)). The transmissivity is used to estimate the average LNAPL conductivity, which in turn, is used to estimate the effective relative permeability and mobility.

There are limitations associated with field bail down tests due to non-representative conditions arising from water table fluctuations and geologic heterogeneity. A complicating factor for test interpretation is that the oil transmissivity is a non-unique parameter that does not provide information on the LNAPL and conductivity distribution at the local-scale (see, for example, the LNAPL saturation plot in Figure 1). It is important to recognize that there can be cases where identical transmissivities are measured, but where the conductivity distribution, and therefore LNAPL velocity, are very different. These issues are described in detail in API, 2005.

## 8.4.3 LNAPL Gradient

The LNAPL gradient is defined as the change in the elevation of the air-oil interface ("oil table") with distance. The LNAPL gradient can be derived as follows: 1) by assuming the LNAPL observed in wells is in hydrostatic equilibrium with the aquifer, and deriving a gradient after applying a density correction based on the LNAPL thickness; 2) measuring the elevation of the surface of the LNAPL in wells and contouring the data; or 3) through numerical or other modeling estimates. In general, where LNAPL plumes have equilibrated over time, the LNAPL gradient will approximate the water-table gradient.

<sup>&</sup>lt;sup>5</sup> The API, 2005 Interactive LNAPL Guide documentation presents typical ranges of residual saturation for US SCS soil texture types; however, a different soil classification is used in the automated tools. The source of the residual saturation values is not clear. Work is on-going in this area; a simple method for

If the LNAPL is in vertical hydrostatic equilibrium with the geologic system (an important assumption that is not always met), then the LNAPL gradient would simply be a modified groundwater gradient that accounts for the buoyancy component in the LNAPL. Thus, the corrected phreatic surface would occur above the static groundwater elevation by a factor of  $(1-\rho_o)b_o$ , where  $\rho_o$  is the LNAPL density and  $b_o$  is the LNAPL thickness in a well at hydrostatic equilibrium.

## 8.4.4 Automated Tools for Evaluation of Potential LNAPL Mobility

Automated tools developed by Charbeneau (2003), "<u>API Models for Design of Free-</u><u>Product Recovery Systems for Petroleum Hydrocarbon Liquids</u>" and by Aqui-Ver, Inc. (2004), "<u>API Interactive LNAPL Guide</u>", provide in-depth information on LNAPL assessment and management, and can be used to estimate parameters relevant to evaluation of LNAPL mobility, including LNAPL saturation, free-phase LNAPL volume, effective permeability, conductivity and mobility. The Charbeneau (2003) model does not calculate the inherent mobility of LNAPL or the plume-scale velocity, whereas the Aqui-Ver, Inc. model does. The Charbeneau (2003) tool includes both the Brooks-Corey and Van Genuchten soil characteristic models. The Aqui-Ver, Inc. (2004) tool includes only the Van Genuchten model. It appears that both models use the simple empirical model described above to estimate the effective relative permeability ( $\overline{k_{ro}} = \overline{S_o}^2$ ).

### 8.4.5 Implications of Mobility Estimates and *de Minimus* Values

An important consideration in defining LNAPL mobility is the interpretation of the estimated velocity of a LNAPL plume at the macro-scale. For instance, in ASTM (2005), an example is given where an LNAPL "velocity potential"<sup>6</sup> of less than  $1 \times 10^{-6}$  cm/sec (310 mm/year) is inferred as indicating LNAPL mobility below *de minimus* levels. The rationale for this velocity potential is from analogy to the allowable permeability of Class I landfill liner in the U.S. Local site conditions should also be considered when defining a *de minimus* velocity.

It is suggested that the estimated macro-scale velocity be evaluated in the context of site-specific conditions, as discussed in Section 6.0. It is also noted that using the automated tools described above, if the LNAPL well thickness is below a certain thickness (very roughly 0.1 m to 0.3 m, depending on the soil type and product type), no mobility is predicted since the relative permeability over the entire profile is negligibly small.

residual saturation recently proposed is 30 percent of the maximum LNAPL saturation (personal communication, Vic Kremesec, BP Amoco, June 2005).

<sup>&</sup>lt;sup>6</sup> The ASTM "velocity potential" is equivalent to the "macro-scale LNAPL velocity" defined in this report. The basis for the  $1 \times 10^{-6}$  cm/sec criteria for velocity potential is based on a similar conductivity criteria that has been applied to landfill liners (G.D. Beckett, personal communication, June 20, 2005).

## 8.5 Method 4 - Theoretical Estimate of Local-Scale LNAPL Movement at Plume Front

A LNAPL plume present near the water table (*i.e.*, where LNAPL is the non-wetting fluid with respect to water) will only migrate laterally into soil pores if the capillary displacement pore entry pressure is exceeded. The multiphase model, as described in Section 8.3, can be used to estimate the displacement head, assuming the Brooks-Corey soil characteristic model. Based on this method, if the thickness of LNAPL in the well is greater than the displacement head, free-phase LNAPL is potentially mobile (Lefebvre and Boutin, 2000). If there are wells near the periphery of the plume where the thickness of LNAPL in the well is less than the displacement head, then the free-phase LNAPL, while mobile in so far as it is able to migrate into the well, may no longer be moving laterally beyond these wells.

This method is based on the Brooks-Corey water retention model, which assumes that a minimum capillary pressure must be applied before the interface between the wetting and non-wetting fluids is displaced from the largest pore spaces (Brooks and Corey bubbling pressure, or air/water displacement head). The displacement head ( $\Delta\Psi$ ) is estimated based on theory developed by Parker and Lenhard (1989) and Charbenaeu and Chiang (1995), as follows:

$$\Delta \Psi = \Psi_{bow} - \Psi_{boa}$$

$$\Psi_{boa} = \frac{\Psi_{baw} \sigma_{ao}}{\rho_o \sigma_{aw}} \tag{8}$$

$$\Psi_{bow} = \frac{\Psi_{baw} \sigma_{ow}}{(1 - \rho_o) \sigma_{aw}}$$
<sup>(9)</sup>

where,

 $\Psi_{\text{boa}}$  = LNAPL/air displacement head (m),

 $\Psi_{\text{bow}} = \text{LNAPL/water displacement pressure head (m)},$ 

- $\Psi_{baw}$  = air-water displacement head (bubbling pressure) (m),
- $\sigma_{aw} = air/water surface tension (dyne/cm),$
- $\sigma_{ao} = air/LNAPL$  surface tension (dyne/cm),
- $\sigma_{ow}$  = water/LNAPL surface tension (dyne/cm),
- $\rho_{ro}$  = density of oil relative to water (dimensionless).

There are no readily available automated tools for the displacement head calculation; however, it is relatively simple to perform. The Brooks-Corey bubbling pressure ( $\Psi_{baw}$ ) can be obtained from Charbenaeu (2003) for different soil types, while surface tension values can be measured or estimated, as described in Section 8.3. The displacement head should be compared to the maximum LNAPL thickness observed in wells. An example calculation for estimation of the displacement head for gasoline is provided in Table 1.

TABLE 1: Example Calculations for Estimation of Displacement I	Head (Gasoline)
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Soil Type	Air-Water Displacement Head (m)	Oil-Air Surface Tension (dyne/cm)	Oil-Water Interfacial Tension (dyne/cm)	Air-Water Surface Tension (dyne/cm)	Relative Density	Displacement Head (m)
Sand	0.069	21	50	72	0.73	0.15
Sandy Loam	0.13	21	50	72	0.73	0.28

Note: The Air displacement head (bubbling pressure is from Carsel and Parish as reported in Charbeneau (1999)

A potential limitation of this method is that there can be significant variability in airwater bubbling pressure, depending on the soil grain size. A conservative air-water bubbling pressure that reflects the possible range of soil grain size gradation should be chosen and sensitivity analysis using a range of pressures corresponding to soil types present should be conducted. In addition, the Brooks-Corey model tends to over predict the entry pressure, since LNAPL can and does enter pores at lower entry pressures.

For the above reasons, this method can only be used to provide an approximate semiquantitative indication of potential LNAPL mobility, when used with other primary linesof-evidence (observations, age of release), as recommended in Section 9. This method may also be used to provide insight on the approximate relative thickness of LNAPL indicating potential mobility, for different soil types.

## 8.6 Method 5 - Laboratory Tests

Laboratory tests can be used to evaluate LNAPL mobility. For example, one test involves a centrifuge test where a centrifugal force of 1,000 times gravity is used to evaluate product mobility (ASTM D425M). This test is considered an index-type test that could be useful in providing a relative indication of mobility. Laboratory centrifuge tests are not widely used to evaluate LNAPL mobility.

### **Exhibit 1. Determination of Water Retention Model Capillary Parameters**

Determination of the capillary parameters for the water retention (soil characteristic) curve is an important component of theoretical methods used to evaluate LNAPL mobility. Functions by Brooks and Corey (1964) and van Genuchten (1980) historically have been the most widely adopted to describe water retention curves. In these functions, water content is sometimes alternatively expressed in terms of effective saturation,  $S_e = (\theta - \theta_r)/(\theta_s - \theta_r)$ , where  $\theta_s$  and  $\theta_r$  indicate saturated and residual values of  $\theta$ . One view of residual water content is that it represents the water content where unsaturated hydraulic conductivity goes to zero (Mualem, 1976). The Brooks and Corey (1964) function is:

$$S_{\rm e} = (\psi/\psi_{\rm c})^{-\lambda} \quad \psi < \psi_{\rm c}$$
  

$$S_{\rm e} = 1 \quad \psi > \psi_{\rm c} \qquad [i]$$

Where  $\psi_c$  and  $\lambda$  are fitting parameters. The van Genuchten (1980) function, with an inflection point, is:

$$S_{\rm e} = [1 + (\psi/\psi_1)^{\alpha}]^{-\beta}$$
 [ii]

where  $\Psi_1$ ,  $\alpha$ , and  $\beta$  are fitting parameters.

These functions, Eq. [i] and [ii], have been widely used as the basis for calculating relative permeability  $(k_r)$ . The Burdine model is most often associated with the Brooks and Corey capillary pressure model, with the relative permeability estimated as follows:

$$k_{ro} = \left(\frac{S_o - S_{or}}{1 - S_{or}}\right)^2 \left[ \left(\frac{S_w + S_o - S_{wr}}{1 - S_{wr}}\right)^{\frac{\lambda + 2}{\lambda}} - \left(\frac{S_w - S_{wr}}{1 - S_{wr}}\right)^{\frac{\lambda + 2}{\lambda}} \right]$$

The  $S_o$  and  $S_w$  are the effective saturations for oil and water based on estimated value, while the  $S_{wr}$  and  $S_{or}$  are the effective saturations at their residual value. The Mualem (1976) model for relative permeability is commonly associated with the Van Genuchten model.

$$k_{ro} = \left(\frac{S_{o}}{1 - S_{m}}\right)^{1/2} \left\{ \left[1 - \left(\frac{S_{w} - S_{m}}{1 - S_{m}}\right)^{1/M}\right]^{M} - \left[1 - \left(\frac{S_{w} + S_{o} - S_{m}}{1 - S_{m}}\right)^{1/M}\right]^{M}\right\}^{2}$$

There are several methods that can be used to obtain the capillary parameters for the water retention curve:

- 1. Fitting of capillary parameters to measured water retention curve from site-specific tests of soil cores.
- 2. Look-up of capillary parameters for defined soil types or textures.
- 3. Fitting capillary parameters to measured grain size distributions from site-specific tests of soil samples.

## Fitting Using Measured Water Retention Tests

Water retention tests can be conducted using porous diaphragm or centrifuge methods. Pressure plate extractors commonly referred to as "Tempe" cells are used for applications where lower suctions are to be applied (<100 kPA or 10 m of water), whereas more robust pressure cells are used for higher matric suctions (Wang and Benson, 2004). If possible, a relatively undisturbed soil sample should be obtained for testing (e.g., a Shelby tube sample or similar type of core sample). Alternatively, disturbed soil samples can be re-compacted to their approximate in situ density, if disturbed. The capillary-moisture data can be analyzed to determine the van Genuchten or Brooks-Corey parameters and the residual water content using a statistical best-fit curve of a plot of these data (Sale, (2003); van Genuchten et al., (1991)). The RETC computer code (van Genuchten et al., 1991) can be used to analyze both the soil water retention and hydraulic conductivity functions of an unsaturated soil. This software is available on a CD with documentation free of charge from the U.S. Salinity Laboratory, USDA, Agricultural Research Service, Riverside, California 92501 (http://www.ussl.ars.usda.gov/models/hydrus2d.htm). The documentation is readable and the software is user friendly. Fredlund and Xing (1994) provide another method for fitting of experimental water retention data, which is based on a non-linear least squares procedure, and on the assumption that the shape of the soil-water characteristics curve is dependent on the pore-size distribution of the soil.

## Look-Up of Capillary Parameters for Defined Soil Types or Textures

There are several databases providing fitted capillary parameters for different soil types or textures. One of the largest databases is that compiled by Carsel and Parish (1988), which is based on the US SCS soil texture classification system (12 soils) and testing of agricultural soils. Aqui-Ver, Inc. (2004) include the "API database" of capillary parameters based for 78 samples of more consolidated earth materials collected near the water table and classified by grain-size analyses and the Folk Classification System. The API database is expected to be more representative of subsurface earth materials near the water table.

## Fitting Using Measuring Grain Size Distribution

Although not recommended, grain size distribution can also be used as a basis for estimating soil hydraulic properties. The AP model by Arya and Paris (1981) represents a significant early study to predict water retention curves using the grain size distribution. Their physico-empirical approach is based mainly on the similarity between shapes of the cumulative grain size distribution and water retention curves. The AP model was later refined by Arya et al. (1999a) and included a model to compute the hydraulic conductivity function directly from the grain size distribution (Arya et al., (1999b)). A potential disadvantage of this method is that Arya et al. (1999a) suggest that at least twenty fractions are necessary to reasonably calculate the hydraulic properties. There are also other constraining assumptions based on particle shape and distribution.

## 9.0 SUMMARY OF RECOMMENDED APPROACH FOR EVALUATION OF LNAPL MOBILITY

An evaluation of free-phase LNAPL mobility should be conducted within a framework that considers the broader issues and potential risks associated with free-phase and residual-phase LNAPL at contaminated sites. As warranted, LNAPL management (recovery, treatment or control) should be implemented to mitigate unacceptable risk to human health or the environment. A sound conceptual site model for LNAPL distribution and potential mobility should be developed based on a sufficiently detailed field investigation. Since theoretical estimates are an important component of an evaluation of LNAPL mobility, practitioners should have a good understanding of multiphase LNAPL concepts and predictive models, including limitations and uncertainty associated with such models. There is much recent guidance and information on LNAPL mobility, including automated tools for the evaluation of LNAPL mobility (API, 2005).

The recommended approach for evaluation of free-phase LNAPL mobility involves the use of multiple lines-of-evidence to evaluate LNAPL stability, including observations of LNAPL and dissolved plume stability, analysis of recovery data (bail-down tests, pilot or full-scale LNAPL recovery data), theoretical estimates of mobility and pore-scale movement of LNAPL at the plume front, and laboratory data, where available (Figure 5). In general, the most reliable and direct indicator of LNAPL plume stability is observational data from wells providing information on both LNAPL and solute plumes, therefore, the primary line-of-evidence recommended for evaluation of LNAPL mobility is observational data. The time since the LNAPL release ceased is also important since the potential for LNAPL mobility decreases with increased age of the LNAPL plume since all finite LNAPL plumes must stop within relatively short time frames, which is a requirement of the applied physics. The analysis of recovery data, theoretical estimates of mobility and pore-scale movement, and laboratory tests are considered secondary lines-of-evidence.

The lines-of-evidence approach is designed to *help facilitate appropriate decisionmaking on a site specific basis*. With respect to theoretical methods, it is not considered appropriate to use these tools as a stand-alone method to determine whether LNAPL is potentially mobile or not mobile, since theoretical methods are relatively complex, still at relatively early stages of development and application to LNAPL mobility, and due to the difficulty in measuring the parameters needed for theoretical models and typically significant spatial variation in these parameters.





## 9.1 Primary Line-of-Evidence – Observational Data

The primary line-of-evidence for evaluation of free-phase LNAPL plume stability and mobility is observational data. If the observational data indicates that the LNAPL and dissolved plumes are stable or shrinking, the potential for LNAPL mobility is low. The key factors that should be considered for the observational approach are:

1. The monitoring well network should include appropriately located sentinel wells in the down-gradient direction of the plume.

- 2. Sufficient observational data should be collected to determine seasonal trends, and should include monitoring conducted at times corresponding to the range of seasonal high and low water tables. In general, this would require monitoring over at least one year, and likely longer.
- 3. Other complementary data such as observations and tests on soil cores and product bail-down tests should be used to test and support the conceptual site model developed on the basis of LNAPL measurements in wells.

It is important to consider how potential changes to site conditions could mobilize LNAPL in the future. For example, a declining water table could result in increased lateral mobility of free-phase LNAPL.

## 9.2 Secondary Lines-of-Evidence

The secondary lines-of-evidence, excluding laboratory tests, which are deemed of minor importance, are summarized below.

- 1. **LNAPL Recovery Data**: This data can be qualitatively used to evaluate LNAPL plume stability. A decrease in equilibrium LNAPL thickness in wells and decrease in LNAPL recovery rate would normally represent a reduced risk from potential LNAPL migration. The LNAPL removal program should take place over sufficient time to evaluate seasonal trends. In general, this would require operation of the LNAPL extraction system over at least one year, and likely longer. While a baildown test may provide some useful information, limitations with a single or limited number of bail-down tests should be recognized (Section 8.4.2).
- 2. Theoretical Estimates of LNAPL Mobility: Inherent mobility and macro-scale LNAPL velocity can be obtained using LNAPL measurements in wells and the multiphase model assuming vertical static equilibrium. Since it is not considered feasible for practitioners to reliably develop and utilize their own models on a routine basis, either Aqui-Ver, Inc. (2004), "<u>API Interactive LNAPL Guide</u>", or Charbeneau (2003) models, "<u>API Models for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids</u>" are recommended, although the Charbeneau model does not directly provide a mobility estimate. A macro-scale LNAPL plume velocity below *de minimus* levels, defined considering site-specific conditions (see discussion in Section 6.0), suggests that the LNAPL plume is likely stable. The suggested value in ASTM (2005) for plume velocity corresponding to a *de minimus* condition (approximately 300 mm/year) may be a reasonable starting point. The uncertainty associated with theoretical estimates should be recognized and a sensitivity analysis should be performed. The recommended methods and input parameters are provided in Table 2.

TABLE 2:	Recommended Methods and Data Sources for
Theoreti	cal Estimates of Potential LNAPL Mobility

Parameter	Method or Data Source
Relative Permeability	Theoretical analysis based on LNAPL thickness in well and capillary properties is currently recommended. Bail-down tests are not currently recommended, but may in the future become a viable approach as experience is gained with this test.
Water Retention Model	There is no clear preference over whether to use Van Genuchten (VG) or Brooks-Corey water retention model, although recent guidance gives precedence to use of the Van Genuchten model.
Capillary Parameters (Van Genuchten model)	Fitting of VG soil characteristic parameters to water retention test ( <i>e.g.</i> , RETC model), conducted on undisturbed soil core or re-compacted sample (preferred) or API Interactive LNAPL Guide Database values
Capillary Parameters (Brooks and Corey model)	Fitting of BC soil characteristic parameters to water retention test on undisturbed soil core or re-compacted sample (preferred) or default values from Charbeneau (2003)
LNAPL Physical Properties (density, viscosity, interfacial tensions)	Laboratory tests on LNAPL from site (preferred) or API Interactive LNAPL Guide Database

Note: method for residual saturation to be determined.

3. Theoretical Estimates of LNAPL Movement at Plume Front: The LNAPL thicknesses in wells is compared to the capillary displacement pore-entry pressure (for the Brooks-Corey model) to evaluate possible lateral LNAPL movement at the Use of this model involves consideration of some of the same plume front. theoretical constructs (e.g., water retention tests and use of scaling parameters to obtain capillary parameters) as the theoretical model used to estimate plume mobility, but is conceptually simpler. However, this method is approximate since it may somewhat overpredict the pore-entry pressure for initiating LNAPL migration into pores and because pore sizes in soil are highly variable. Due to these limitations, this method is semi-quantitative and should not be used as the sole secondary line-ofevidence to determine whether LNAPL is potentially mobile. A negative determination indicating LNAPL is not potentially mobile for this method must be supported by other secondary lines-of-evidence. This method may also be used to provide insight on the approximate relative thickness of LNAPL indicating potential mobility, for different soil types.

In conclusion, the primary line-of-evidence for evaluation of LNAPL mobility and stability is observational data. The secondary lines-of-evidence should also be collectively evaluated to further assess the potential for free-phase LNAPL mobility. If the primary and secondary factors indicate LNAPL is unlikely to be mobile, further recovery of LNAPL may not be warranted at a site, subject to other regulatory, liability, future use and non-risk-based considerations as described in Section 6.0. In addition, the use of SLRA-2 Soil and Groundwater Module would not be precluded.

If there are indications that LNAPL may be mobile, appropriate LNAPL management measures should be implemented. This could consist of monitoring (*e.g.*, additional wells, more frequent monitoring) or LNAPL control or recovery measures. The results of secondary line-of-evidence (*e.g.*, theoretical predictions) may also help prioritize further actions at a site.

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