REPORT ON

GUIDANCE ON ASSESSMENT OF LIGHT NON-AQUEOUS PHASE LIQUID MOBILITY FOR SITE CLASSIFICATION PURPOSES IN BRITISH COLUMBIA

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1.0 INTRODUCTION

This document, prepared by Golder Associates for the BC Ministry of Environment (MoE), presents a framework and methodology for the assessment of the mobility of lighter-than-water non-aqueous phase liquids (LNAPLs) in support of contaminated sites regulation and management in British Columbia.

The regulatory context of this document is to provide a scientific basis for defining when LNAPL is considered to be potentially mobile as part of the draft BC MoE Protocol 12, entitled: "*Classifying Site Risk Levels*" (BC MoE, 2008a). Under draft Protocol 12, sites are classified as "high risk" or "low to moderate" risk. Sites classified as high risk under Protocol 12 are *not* eligible for regulatory review by approved professionals, as described under Protocol 6, entitled: "*Eligibility of Applications for Review by Approved Professionals*" (BC MoE, 2008b). BC MoE desires that one of the criteria for determination of high risk versus low to moderate risk be based on LNAPL mobility.

LNAPLs are frequently encountered at impacted sites and include common petrochemical products such as gasoline, diesel and lubricating oils. When released to the 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 LNAPL" or "free LNAPL"). 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.

This guidance examines the potential for LNAPL mobility at contaminated sites based on the thickness of LNAPL that may be measured in monitoring wells at a site. Modeling is used to derive approximate thickness thresholds for LNAPL mobility for a range of subsurface conditions. These thresholds may then be used administratively to define high risk versus low to moderate risk sites.

The guidance follows a multiple lines-of-evidence approach for assessment of potentially mobile LNAPL. The primary lines of evidence are site monitoring ("observational") data and model-predicted thresholds for potential mobility based on the measured LNAPL thickness in wells. While a number of factors were considered as part of the development of LNAPL thickness thresholds, a relatively simple approach based on soil type was adopted. The secondary lines-of-evidence may include laboratory testing of LNAPL properties, LNAPL recovery testing, indirect monitoring techniques or tools, and analysis of other factors such the age and weathering of a LNAPL release.

Following this introduction, this guidance consists of five sections, as follows:

- **Section 2: LNAPL basics and definitions:** Key concepts for LNAPL distribution and mobility are described.
- **Section 3: LNAPL conceptual model**: The multi-phase conceptual model for LNAPL and theoretical basis for estimation of LNAPL mobility is presented. The equations for mobility are provided in Appendix I.
- **Section 4: LNAPL mobility modeling:** The models used for estimating potential LNAPL velocity in the core of the plume and potential for LNAPL migration into pristine soils are described.
- **Section 5: LNAPL mobility assessment framework**: The framework for assessing LNAPL mobility begins with conceptual site model development and definition of precluding conditions, an important step in the assessment process. Next, the framework describes LNAPL site characterization and how to evaluate potential LNAPL mobility based on observational data on LNAPL thicknesses in wells.
- **Section 6: Summary and recommendations.** The document provides a summary of the approach for evaluation of LNAPL mobility and recommendations for additional work that could help refine the methods described.

This document does not address LNAPL recovery, except to reference several documents that provide information on this issue. This guidance is not intended for sites with dense non-aqueous phase liquid (DNAPL).

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 that 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 potentially present at refineries and petroleum distribution facilities include feedstocks, intermediation process streams, and final products (American Petroleum Institute (API), 2002).

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 soil zone until its mass is immobilized within soil pores as a result of capillary forces. The water and the LNAPL have different densities and therefore different pressures in the pore spaces. The difference in the pressure of the two liquids is the capillary pressure. 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 and limit the depth to which LNAPL can migrate within the saturated zone. 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 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 subsequently discussed in this guidance. 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.

For finite releases of LNAPL, the pressure head of LNAPL at the source of the spill will decrease as the LNAPL spreads laterally. The LNAPL will more readily move through larger pores than smaller pores since capillary pressures within larger pores are lower.

Eventually, lateral migration of LNAPL will cease when the driving force represented by the displacement head is balanced by the capillary pressure equal to that needed to penetrate the largest pore size. For this condition, LNAPL at the plume edge will be immobile. The time needed for LNAPL releases to reach a stable endpoint will depend primarily on the size of the release and the LNAPL viscosity. A smaller release of lower viscosity LNAPL (*e.g.*, gasoline) may take weeks to months to reach hydrostatic equilibrium, whereas a larger release of higher viscosity LNAPL (*e.g.*, bunker oil) may take many years to reach equilibrium.

LNAPL may occur as either *residual-phase LNAPL* or as *free-phase LNAPL (also referred to as residual LNAPL and free LNAPL)* within the subsurface environment. LNAPL that is retained by soil capillary forces and that is trapped within pore spaces is termed residual LNAPL. At or below residual saturation, LNAPL is not mobile unless the chemical or physical properties are altered. Free 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 LNAPL volume may move vertically or laterally within soil in response to gravity or, less commonly, viscous forces, although as described above, lateral migration of LNAPL will be constrained by capillary forces at the leading edge of the LNAPL plume.

The above conceptual model is applicable to porous media, but not to fractured media, since LNAPL behaves differently within fractured rock. Site conditions that influence the distribution and migration of LNAPL are the geometry of the fracture network, rock matrix properties, the properties of the LNAPL and hydraulic forces. Relatively small volumes of LNAPL and vertical or near-vertical fractures can result in significant pressure heads and deeper vertical penetration of the saturated zone relative to that observed for porous media. A rising and falling water table may result in movement of LNAPL that may not be in the direction of the regional hydraulic gradient but, instead, is controlled by the fracture network geometry.

There may be processes at a site that, over longer periods of time (often decades), will tend to reduce the potential for lateral mobility and expansion of a LNAPL plume. For example, whenever there is a fluctuating water table, a smear zone of residual LNAPL is formed thus removing mass from the zone of interconnected pores containing LNAPL that could represent mobile LNAPL. The dissolution of compounds from the LNAPL and volatilization will over time deplete the LNAPL, reducing saturation and potential mobility. There is also the potential for solubilization to change the interfacial tension between the LNAPL and water, thus changing the interfacial tension properties.

An excellent glossary of technical terms for characterizing immiscible fluids in geologic media is provided in ASTM (2006) (Appendix X6).

EXHIBIT 1: Surface Tension, Wettability and Capillarity Concepts

For immiscible liquids such as LNAPLs, the molecular forces at interfaces between fluids are of critical importance. Since forces are unbalanced, there is a tendency for molecules to move away from the surface and the surface to curve. The tension that arises between two phases when a fluid is in contact with its own vapour is called *surface tension*, while when a liquid is in contact with a different fluid, be it gas or liquid, the resulting tension is called *interfacial tension*.

Wettability between different phases is characterised by the contact angle, θ_c, at the interface between the solid phase and fluids. The phase with the smaller contact angle preferentially covers the surface, and is called the wetting phase. Different conditions of wettability are shown in Figure 1. The typical wettability sequence observed for LNAPL within soils is water, followed by NAPL and then air, with water being the most wetting and air the least wetting phase.

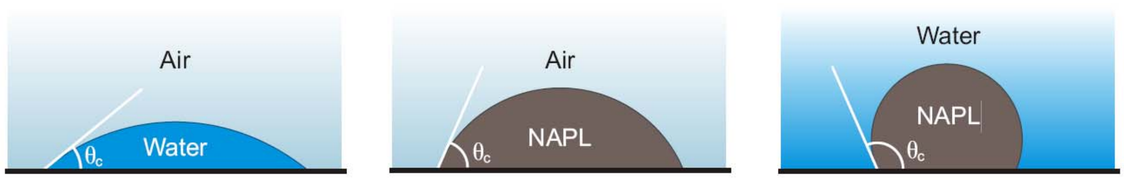


FIGURE 1. Wettability and Contact Angle

The pressure difference between two fluid phases is called the *capillary pressure*, which depends on the interfacial energy or tension (σ), contact angle (θ_c), and mean radius of curvature (r), approximated by the radius of the pores. For the LNAPL-water interface, the capillary pressure (P_{cow}) that must be overcome for a non-wetting NAPL to enter water-saturated media is called the *displacement entry pressure* (Mercer and Cohen, 1990) and may be calculated using the Young-Laplace equation, as follows (API, 2007):

$$P_{cow} = P_o - P_w = 2\, \sigma_{ow} \cos \theta_c / r$$

where P_o is the non-wetting (LNAPL) phase and P_w is the wetting (water) phase. The subscript o is used to denote oil (*i.e.*, LNAPL). If atmospheric pressure is taken as the reference level, then the capillary pressure head required to balance the upward buoyant force of LNAPL may be calculated, as follows:

$$h_{cow} = P_{cow} / (\rho_w - \rho_o)\, g$$

where ρ_w and ρ_o are the density of water and LNAPL, and g is the gravitational constant. The capillary pressure decreases as the radius of the pores increases and/or as the interfacial tension decreases. The interfacial tension is primarily a function of the fluid, temperature and the presence of surface-active agents (*e.g.*, surfactants in LNAPL lower the interfacial tension). These theoretical concepts have significant practical implications for LNAPL mobility, as subsequent described in this guidance.

3.0 LNAPL CONCEPTUAL MODEL

3.1 Early 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.

3.1.1 Multi-phase Conceptualization and Capillary Pressure – Saturation Curves

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 and, in some cases, at significant depths below the water table (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 (Aqui-Ver, Inc., 2004).

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.

An example of a capillary pressure – saturation curve is shown in Figure 2a. These curves may be experimentally derived through measurements using a Tempe cell or centrifuge test. If the experiment begins with a fully saturated condition and a non-wetting fluid (LNAPL) is introduced under increasing capillary pressure (representative of conditions near the water table), the wetting fluid (water) will undergo *drainage*, theoretically reaching an end-point value where no further reduction in wetting phase saturation is measured (S_{wr}). In turn, if the capillary pressure is lowered, then the resulting saturation versus capillary pressure values follow the *imbibition* curve. At zero capillary pressure, soil will not be fully saturated, but will contain residual LNAPL. This end-point is called the non-wetting phase residual saturation (S_{nwr}). The relationship between fluid saturation and capillary pressure is hysteretic in that the saturation at any particular capillary pressure is less during the wetting process than during drainage. This hysteresis is related to pore geometry, topology and surface characteristics, and differences in wettability between saturation and desaturation. An infinite number of scanning curves or scanning lines exist between the limiting drainage and imbibition curves shown in Figure 2a.

For practical application, the above capillary pressure – saturation relationships must be interpreted in the context of typical field conditions. Since the capillary pressure imposed by the LNAPL release is typically relatively small, the initial drainage conceptually will only proceed to point A shown on Figure 2b. When imbibition occurs, the LNAPL residual saturation will be smaller than that predicted using the limiting curves in Figure 2a. The key points are: (i) the initial LNAPL saturation is dependent on capillary pressure, and (ii) the residual saturation is dependent on initial LNAPL saturation or maximum capillary pressure achieved. The initial and residual saturation are important parameters for estimation of LNAPL volume and mobility as subsequently described in this guidance. The residual saturation may be estimated from empirical relationships (*i.e.*, that use the initial LNAPL saturation) or measured from laboratory tests.

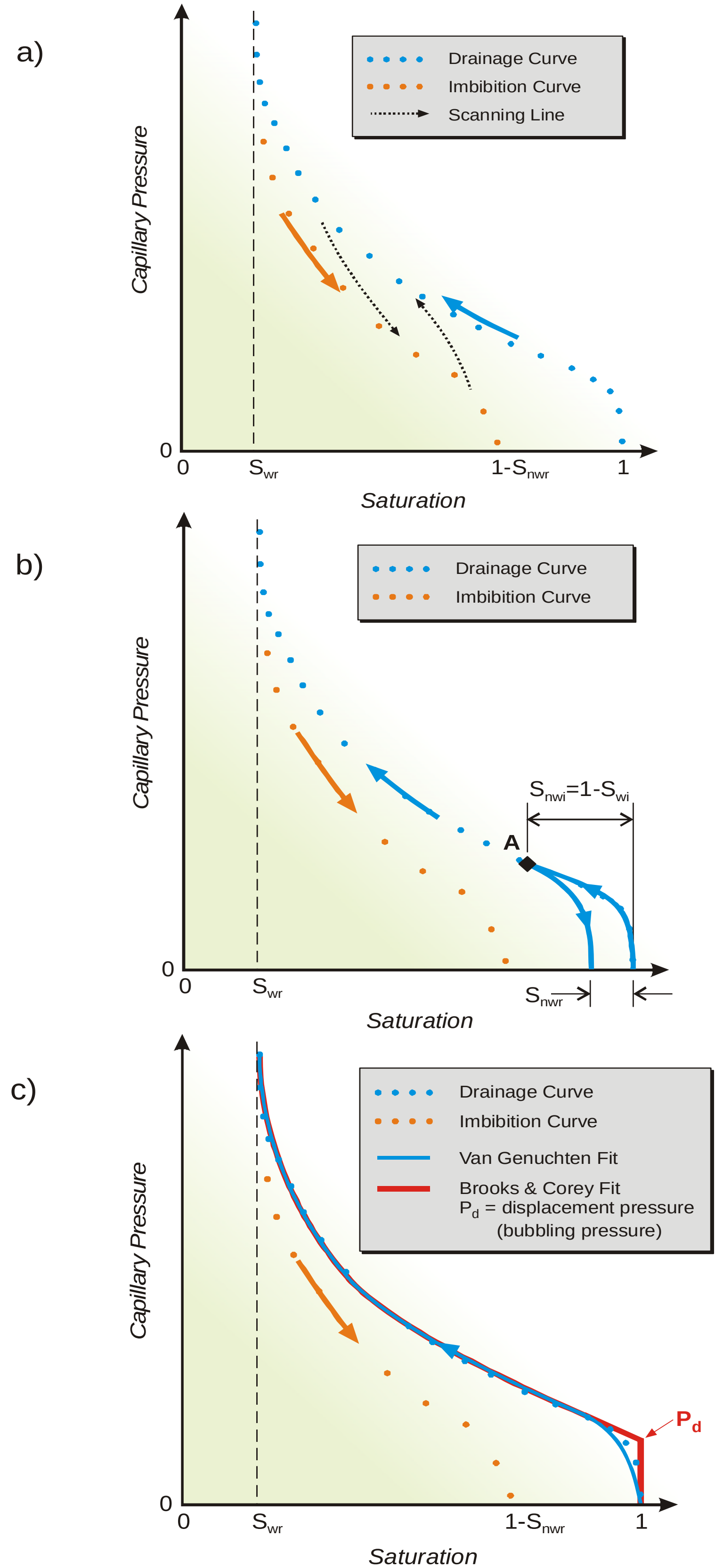


FIGURE 2a,b,c. Capillary Pressure - Saturation Curves (S_{wr} = wetting phase (*i.e.*, water) residual saturation, S_{nwr} = non-wetting phase (*i.e.*, LNAPL) residual saturation, S_w = wetting phase saturation, S_{nw} = non-wetting phase saturation).

3.2 Multiphase Model Application

The purpose here is to provide a conceptual overview of the application of the multiphase model, which is the basis for LNAPL mobility calculations subsequently described in this manual. Additional details on theory are described in Appendix I.

The multiphase model, in conjunction with the measured LNAPL thickness in wells, may be used as a basis to estimate the LNAPL saturation, the volume of LNAPL in soil, and potential LNAPL mobility. The multiphase model for estimating LNAPL volume and mobility assumes vertical static equilibrium (*i.e.,* gravity forces are balanced by capillary forces).

At the heart of the multiphase model are capillary pressure–saturation curves that are derived for a LNAPL based on soil and fluid properties, which may be used to estimate the vertical LNAPL saturation profile and the relative permeability of the LNAPL, a key parameter needed for a mobility assessment. Typically, an algebraic expression such as the van Genuchten (1980) (vG) equation or Brooks-Corey (Brooks and Corey, 1966; Corey, 1994) (B-C) equation is used to represent the capillary pressure-saturation curve. These algebraic expressions may be fit to the capillary pressure-saturation data, as conceptually shown in Figure 2c, or estimated using other techniques (SABCS, 2006). A key difference between the Brooks-Corey and van Genuchten model equations is that the Brooks-Corey model has a defined displacement head, which must be exceeded before mobility is predicted. In contrast, for any positive LNAPL head, the van Genuchten model predicts that part of the porous medium will have a LNAPL saturation exceeding the LNAPL residual saturation and thus there is the potential for LNAPL mobility. As subsequently indicated in this guidance, the Brooks-Corey model is used to predict LNAPL movement into pristine soils.

An idealized conceptual relationship between free-product thicknesses in the well and the LNAPL saturation in soil is shown in Figure 3. In general, for a given observed product thickness in a monitoring well, the potentially mobile LNAPL volume is greater within a coarse-grained medium such as sand, than a fine-grained medium such as silt. Under conditions encountered at many sites, the thickness of potentially mobile LNAPL within the aquifer may be approximated by the LNAPL thickness in the well. However, since the LNAPL saturation is typically much less than unity, the LNAPL volume is not equivalent to the LNAPL thickness in the well. This “volume exaggeration”, suggested by the thickness of LNAPL in a well, is greater in fine-grained media than in coarse-grained media.

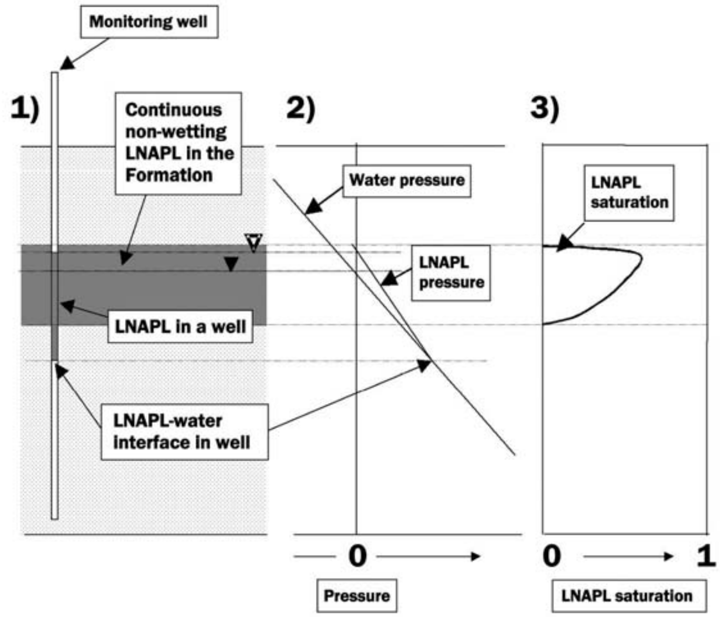


FIGURE 3: Idealized Conceptualization of LNAPL in a well and adjacent formation (from API, 2003).

3.2.1 Multiphase Model Assumptions and Limitations

The multiphase model for estimating LNAPL volume and mobility assumes vertical static equilibrium (*i.e.*, 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. The accuracy of the model is potentially reduced with larger water table fluctuations and as the geologic heterogeneity increases. Vertical hydraulic gradients can also reduce the accuracy of predictions using the multiphase model.

Information provided by LNAPL Measurements in Wells

1. The thickness of potentially mobile LNAPL within a aquifer may be approximated by the LNAPL thickness in the well.

2. The LNAPL volume is not proportional to the LNAPL thickness in the well. The "volume exaggeration" suggested by the thickness of LNAPL in a well is greater in fine-grained media than in coarse-grained media.

3. For an unconfined aquifer system, a decline in the water table typically results in an increase in LNAPL thickness in a well.

4. For a confined system, the LNAPL thickness may increase in proportion (when density differences are taken into account) to the rise in the potentiometric surface.

5. Other LNAPL thickness responses may be observed for perched, fractured, or complex layered systems.

Water table fluctuations are important to consider when using the multiphase model since a falling water table for an unconfined system typically results in greater observed thickness of LNAPL in wells, and an increased volume of potentially mobile product (Figure 4). As the water table falls, LNAPL 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). This is because LNAPL more readily drains from the coarse soil when transitioning from a two-phase LNAPL-water to three-phase LNAPL-water-air system. Water table fluctuations complicate the estimation of LNAPL saturation and total 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).

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 5. Additional information on LNAPL distribution in secondary porosity features such as fractures and root casts is provided in Adamski *et al.* (2005).

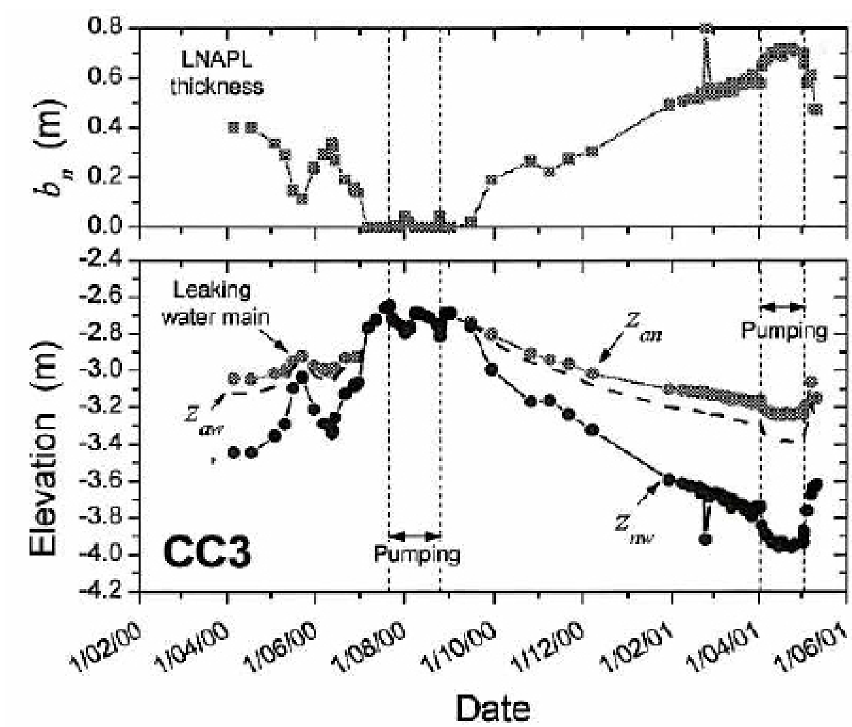


FIGURE 4: Relationship between Water Table Elevation and LNAPL Thickness showing Increasing LNAPL Thickness (difference between Z_{an} and Z_{nw}) as the Water Table Decreases (CSIRO LNAPL in the Subsurface Short Course, Dr. Colin Johnston, 2005)

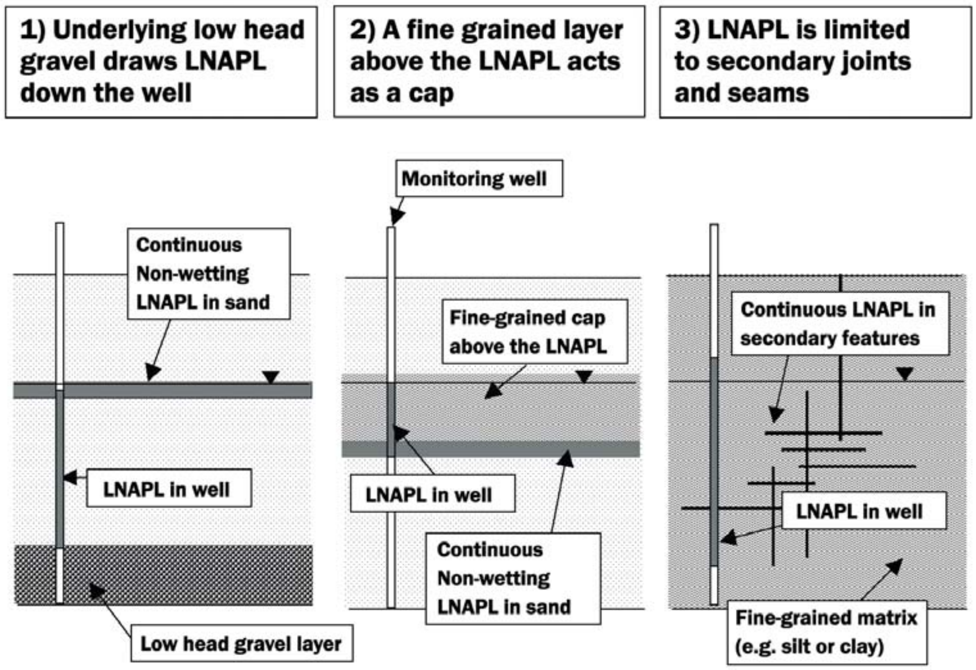


FIGURE 5: Conditions Affecting Thickness of LNAPL in Wells (from API, 2003).

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.

4.0 LNAPL MOBILITY MODELING

4.1 Introduction

The purpose of this chapter is to describe the modeling and scientific rationale for the LNAPL well thickness thresholds proposed as part of the LNAPL mobility assessment framework described in Chapter 5.

The objective of the modeling was to develop thresholds for mobility based on the measured LNAPL thickness in wells combined with readily obtainable site data (*e.g.*, soil type). The objective was not to develop a framework for site-specific modeling of LNAPL mobility, although the approach described below may be useful for this purpose.

Two models were used to evaluate LNAPL mobility based on LNAPL thickness measurements in monitoring wells and multiphase modeling concepts. The first model is Darcy's Law, used to estimate the lateral LNAPL velocity (*LNAPL mobility model*), while the second model utilizes capillary concepts to estimate the thickness of LNAPL needed to displace water within pristine soil at the fringe of the LNAPL plume (*displacement entry pressure model*). The first model applies to the core of the plume, but is nevertheless considered a *potential mobility* since the overall movement or expansion of a finite LNAPL plume (*i.e.*, where the release has stopped) is constrained by the capillary forces at the leading edge of the LNAPL plume. The second model applies to the fringes of the LNAPL plume.

The multiphase concepts underlying the mobility model were also used to estimate the LNAPL mass based on the measured LNAPL thickness in wells. While not directly indicating mobility, estimates of mass provide insight on the significance of possible impacts if LNAPL were to be mobile.

The details of the modeling are provided in Appendices I and II.

4.2 LNAPL Mobility and Mass Model

4.2.1 Model Description

The potential lateral LNAPL mobility was estimated using Darcy's Law, which is a function of the LNAPL relative permeability, intrinsic permeability of soil, LNAPL viscosity and lateral LNAPL gradient. The API Interactive LNAPL Guide computer model (Version 2.0.3, July 2004) was used to estimate the potential LNAPL mobility (henceforth referred to as "API computer model"). Using multiphase concepts and capillary pressure – saturation relationships described previously, the LNAPL velocity for different soil types was estimated using this model.

The starting point for the estimation of relative permeability is to define the van Genuchten capillary parameters for a water-air system (*i.e.*, water retention curve). Scaling parameters based on LNAPL properties (LNAPL/water interfacial tension, LNAPL/air interfacial tension) are applied to the water retention curve to obtain the capillary pressure–saturation relationship for a LNAPL-water system. The vertical LNAPL saturation profile is estimated from the van Genuchten capillary pressure-saturation model using the LNAPL thickness in the well and assuming vertical hydrostatic equilibrium.

The vertical LNAPL saturation profile is used to estimate the vertical LNAPL relative permeability profile through integration of the Mualem (1976) equation with van Genuchten's fluid retention model. The effective (average) relative permeability is obtained by integrating the effective permeability profile. The intrinsic permeability of the soil may also be estimated from the van Genuchten model.

The API computer model, through integration of the vertical LNAPL saturation profile, also provides an estimate of the LNAPL mass, which is a representative mass for a static water table condition. The mass is calculated by multiplying the estimated mass per unit area by the width and length of the LNAPL zone, which are user-defined inputs. The LNAPL mass predicted by the model is a conservative estimate of the ***potentially mobile LNAPL***, since the residual LNAPL saturation must be subtracted from the LNAPL saturation to obtain the potentially mobile fraction. To provide a conservative estimate, the LNAPL mass used for this assessment included the mass that would be left as residual.

For an unconfined aquifer, greater LNAPL thicknesses will be measured when the water table is low; therefore, the LNAPL mass model results should be interpreted for LNAPL measurements obtained for low water table conditions.

4.2.2 Model Scenarios and Input Parameters

The API computer model was utilized to predict the potential LNAPL mobility (velocity) and mass for a number of different scenarios based on the measured LNAPL thickness in the well, soil type, fuel type and LNAPL gradient. The van Genuchten capillary parameters, a key soil property, are described in the section below. Two different fuels, gasoline and diesel were evaluated. While products heavier and more viscous than diesel may be less mobile, the intent was to develop thresholds that would be representative of more mobile petroleum products. The interfacial tension, density and viscosity values for gasoline and diesel were mostly default values, although some adjustments were made (Appendix II). The LNAPL well thickness was varied from 0.03 m to 1 m, while the LNAPL gradient was varied between 0.001 m/m and 0.01 m/m. The assumed width and length of the LNAPL zone was 30 m by 30 m, which is considered representative of a moderate sized plume. The LNAPL area was used to estimate the LNAPL mass, but does not affect the mobility calculations.

4.2.3 Van Genuchten Capillary Parameters

Mobility estimates are highly sensitive to the van Genuchten capillary parameters, and therefore the capillary parameters are a key input to the API computer model. The API model provides default van Genuchten parameters for nine soil textures based on qualitative sedimentologic descriptions of grain size distribution and the Folk soil classification system (Aqui-Ver, Inc., 2004). The default van Genuchten parameters for these soil textures are highly approximate estimates that are based on test data compiled in the API soil property database (API, 2006), henceforth referred to as “API database”.

The API database presents the results of testing conducted on 519 soil samples obtained from multiple sites and includes the results of water retention tests (from centrifuge or Tempe cell tests), grain size distributions and other physical property data. The database also provides the estimated van Genuchten and Brooks-Corey model parameters for each individual soil sample, obtained by fitting these models to the test data. The API database represents test data from soil samples obtained near the water table, where soil tends to be more consolidated and of greater density, compared to several other common databases and published capillary parameters (*e.g.*, Carsel and Parrish, 1988; Schaap and Leij, 1998) that were developed primarily from testing of shallow soils used for agricultural purposes. For this reason, the API database is considered to be more representative of soil properties that may influence LNAPL mobility.

Since the objective of this guidance was to develop a generic approach, the use of default van Genuchten capillary parameters, although highly approximate, was considered appropriate. When following a site-specific approach, the use of parameters estimated from retention tests on representative soil samples from the site will typically be a more accurate and defensible approach for assessment of LNAPL mobility (although it is acknowledged that such testing is relatively complex and expensive). A less accurate approach, but generally superior to the use of default values based on generic soil texture classifications (*e.g.*, the defaults in API model), is the estimation of van Genuchten parameters from a grain size distribution, or comparison of the grain size distribution for site soil to distributions provided in the API database for different soil samples, and adoption of parameters for the soil sample with the closest grain size match to the site soil (Appendix I).

4.2.4 LNAPL Mobility and Mass Model Results

The model-predicted LNAPL velocity results for gasoline and diesel using the default API van Genuchten model parameters, for a LNAPL gradient of 0.001, are shown in Figures 6 and 7. The LNAPL velocity is highly sensitive to the soil type, but less sensitive to the type of fuel, as shown. The LNAPL velocity is proportional to the gradient.

To illustrate the model sensitivity to the van Genuchten parameters, the potential LNAPL velocity was also calculated for measured parameters for individual test results reported in the API database (Figure 8). There is approximately two to three orders-of-magnitude variability in predicted velocities for the three soil types evaluated (coarse sand, medium sand, fine sand)[1]. The velocities calculated using the default van Genuchten parameters provided in the API Interactive LNAPL Guide are toward the high end of the range calculated using the individual test results from the database.

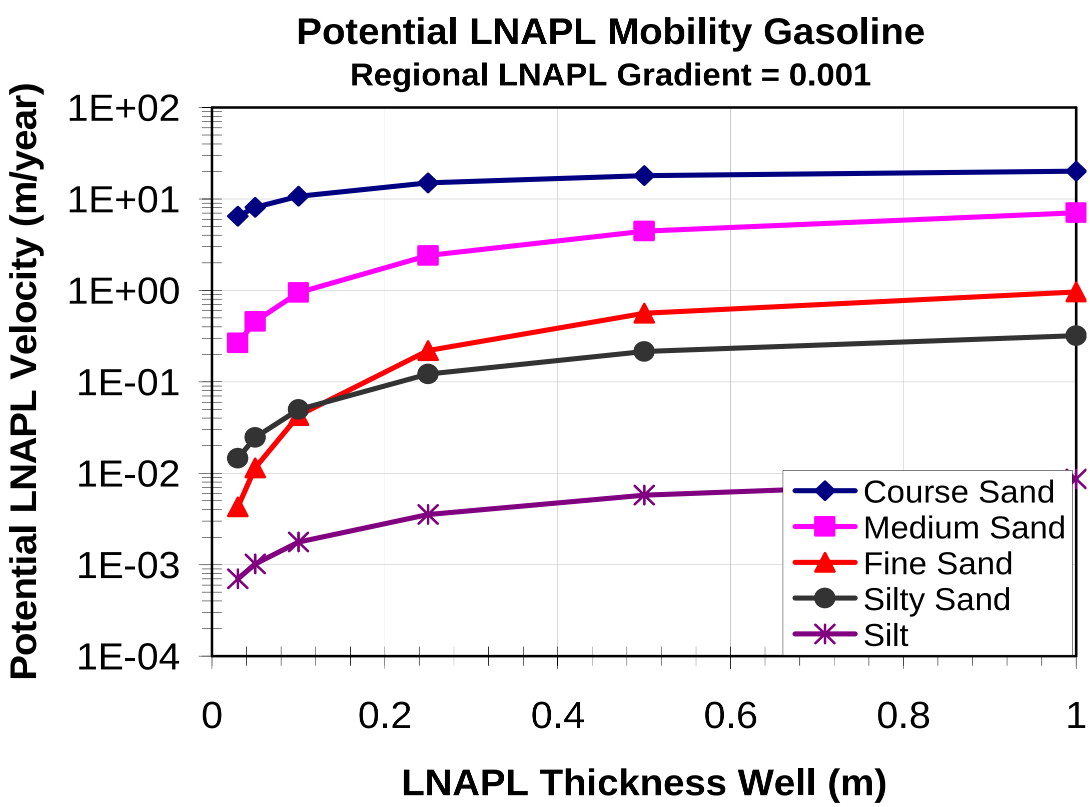


FIGURE 6: Predicted Potential LNAPL Mobility of Gasoline using API Interactive LNAPL Guide computer model (Version 2.0.3, July 2004)

[1] In the API soil property database, the soil texture classifications for predominantly coarse grained soils under the Folk classification method are: "Silty Sand", "Sand", "Slightly Gravelly Sand, and "Gravelly Sand". The API Interactive computer model default soil textures for coarse-grained soils are "Silty Sand", "Fine Sand", "Medium Sand", "Coarse Sand" and "Gravel". The details of the classification scheme and linkage between the two tools are not provided.

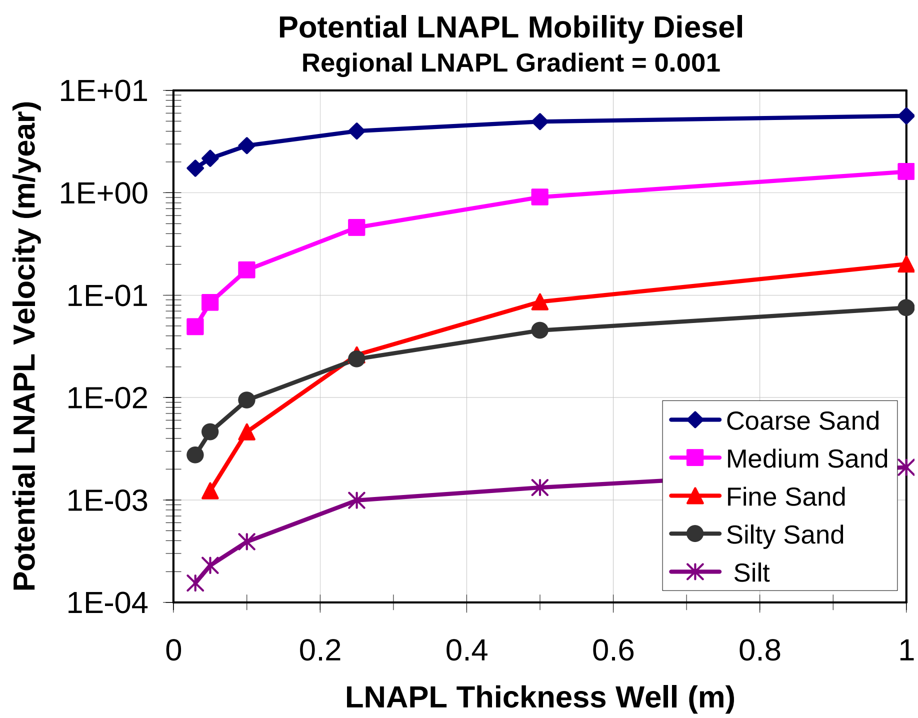


FIGURE 7: Predicted Potential LNAPL Mobility of Diesel using API Interactive LNAPL Guide computer model (Version 2.0.3, July 2004)

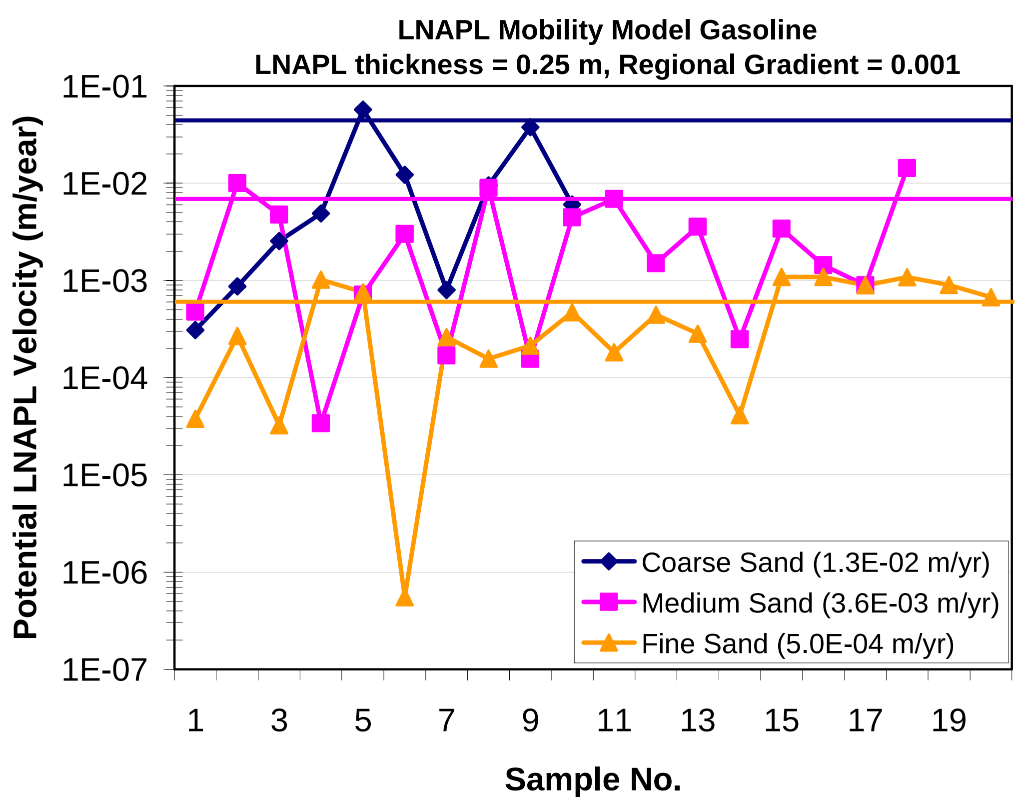


FIGURE 8: Predicted Gasoline LNAPL Mobility using API Parameter Database Values and API Interactive LNAPL Guide Model (solid lines are velocities calculated using default values in the API Interactive Guide)

The model-predicted LNAPL mass is shown in Figure 9. This mass is the total LNAPL mass (including the mass that would be left as residual but excluding smeared LNAPL from water table fluctuations) and therefore over-predicts the potentially mobile LNAPL mass. The LNAPL mass is highly sensitive to the LNAPL thickness for small thicknesses, but there is little difference between predictions for different soil types, excluding coarse sand.

Starting with the estimated LNAPL mass, a simple calculation method may be used to estimate a possible down-gradient distance for LNAPL migration, assuming that all LNAPL within a defined source area moves laterally into pristine soils. This is a conservative assumption since only a portion of the LNAPL is potentially mobile. The down-gradient distance is estimated assuming that the capacity of soil to retain LNAPL is defined by the residual saturation and a wedge-shaped migration zone (a wedge shape is chosen since it is expected that LNAPL will pinch out in an approximate wedge shape). An example calculation is shown in Figure 10 for the predicted LNAPL mass for medium sand and a LNAPL thickness of 0.25 m, where the predicted down-gradient LNAPL migration distance is 5.3 m. This calculation illustrates that the distance for potential further down-gradient migration may be small when the LNAPL thicknesses and masses are relatively small.

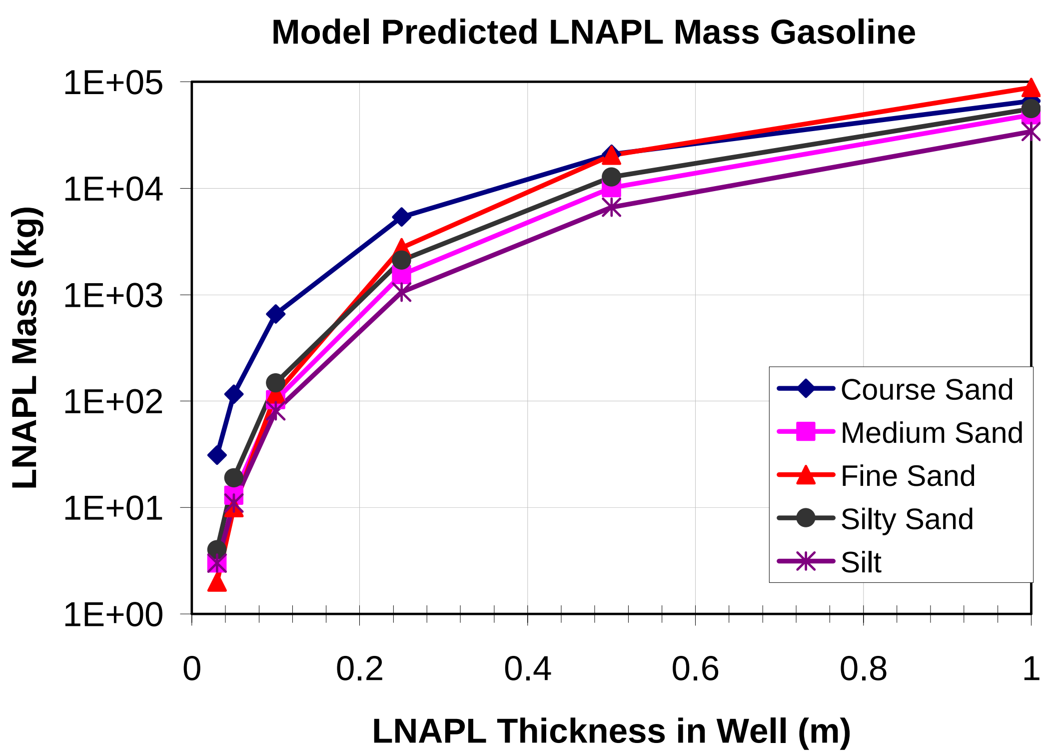
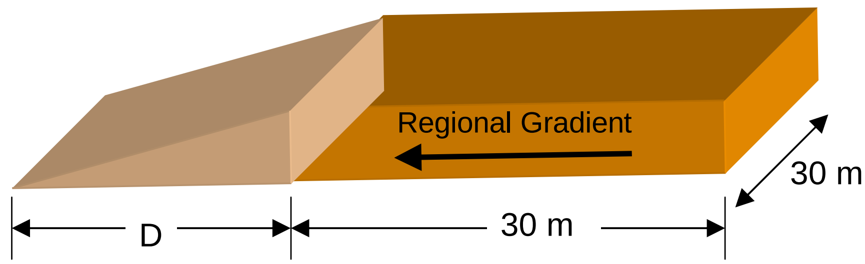


FIGURE 9: Model Predicted LNAPL Mass for Gasoline using API Interactive Guide and Default Values)

Assume all LNAPL within 30 m by 30 m area is mobile, how much further could it go (assuming capacity for soil to retain LNAPL is defined by residual saturation)?



Medium Sand
LNAPL Mass = 1,550 kg
LNAPL Volume = 1131 litres
Residual LNAPL Saturation = 0.15
Total Porosity = 0.38
Distance (D) = 5.3 m

FIGURE 10: Calculation of Potential LNAPL Migration Distance Beyond Source Area

4.3 LNAPL Displacement Entry Pressure Model

4.3.1 Model Description

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 saturated soil pores if the capillary displacement pore entry pressure is exceeded. For soil pores filled with air, a much lower displacement pore entry pressure must be overcome for LNAPL to invade soil pores; however, near the water table, soil pores will be filled or mostly filled with water. As previously discussed, the Brooks-Corey capillary model has a well-defined displacement head, which must be exceeded before mobility is predicted. In contrast, for the van Genuchten model, for any positive LNAPL head, the model predicts that part of the porous medium will have a LNAPL saturation exceeding the LNAPL residual saturation, and therefore has the potential for LNAPL mobility.

The Brooks-Corey model air-water displacement head (“bubbling pressure”) may, through the application of appropriate scaling parameters, be converted to a LNAPL displacement head. If the thickness of LNAPL in the well is greater than the LNAPL displacement head, the free-phase LNAPL is potentially mobile (Lefebvre and Boutin, 2000; API, 2007). 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.

The Brooks-Corey model displacement pressure, while a reasonable conceptual construct for potential mobility, is a finite approximation in that, by virtue of its definition as a sharp point on the retention curve (*i.e.*, in contrast to the van Genuchten model), will tend to over-estimate the actual displacement head needed for mobility. While potentially a non-conservative model for mobility, it is nevertheless considered a useful assessment tool when interpreted in the context of other model results.

The Brooks-Corey model calculations were performed for different soil types using a spreadsheet developed by Golder Associates.

4.3.2 Model Scenarios and Input Parameters

The Brooks-Corey model was used to estimate the LNAPL displacement head for different soil types (same as those described above) for gasoline and diesel. There are no default Brooks-Corey air-water displacement heads provided in the API computer model or database, so this parameter was estimated using two different approaches:

1. The Lenhard equation (Charbeneau, 1999) was used to estimate the Brooks-Corey air-water displacement head from the van Genuchten capillary parameters, which were the defaults provided in the API model.

2. The measured Brooks-Corey air-water displacement heads provided in the API database for individual sample test results were used directly. This method provides insight on the variability in displacement head predictions.

The interfacial tension, density and viscosity values that were used for gasoline and diesel were mostly default values, although some adjustments were made (Appendix II).

4.3.3 LNAPL Displacement Entry Pressure (Head) Model Results

Using the first method, the estimated LNAPL displacement head for gasoline and diesel for different soil types obtained from the van Genuchten default parameters are presented in Figure 11. For gasoline, the LNAPL displacement heads range from 9.5 cm for coarse sand to 32 cm for silt. The LNAPL displacement head for medium sand is greater than that for fine sand or silty sand. There is no obvious reason for this unexpected result, but this highlights the uncertainty in soil property input parameters.

Using the second method, the estimated LNAPL displacement heads for gasoline are shown for individual test results for three different soil types in Figure 12. There is significant variability in the results, but the average LNAPL displacements heads increase with decreasing grain size, as expected.

The complete API database for all soil types tested was also evaluated where the estimated LNAPL displacement heads (calculated for each individual test result) are plotted as a function of the median grain size and the D10 (*i.e.,* the grain size where 10% of the grains are finer than this value) (Figure 13). As illustrated, there is an apparent weak correlation between the LNAPL displacement head and grain size.

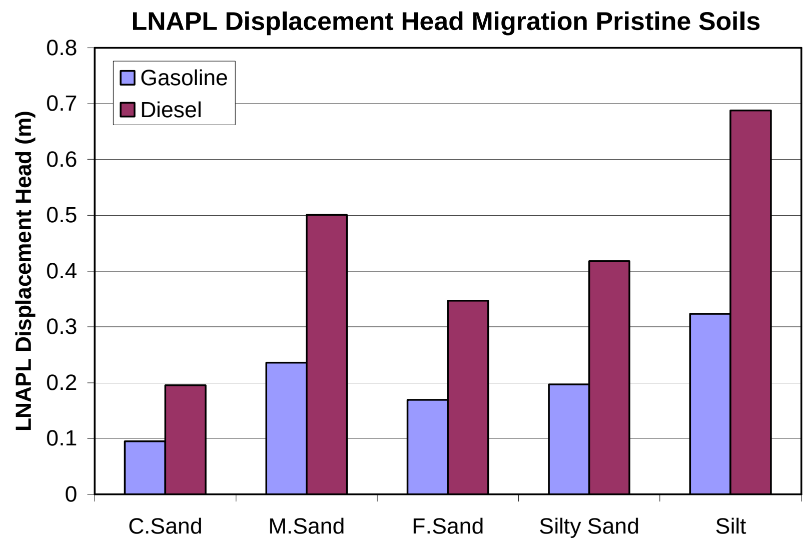


FIGURE 11: Predicted LNAPL Displacement for Migration into Pristine Soils. Brooks-Corey Air-Displacement Head Predicted from Default Van Genuchten Alpha from API Interactive Guide (Version 2.0.3) and Lenhard Equation.

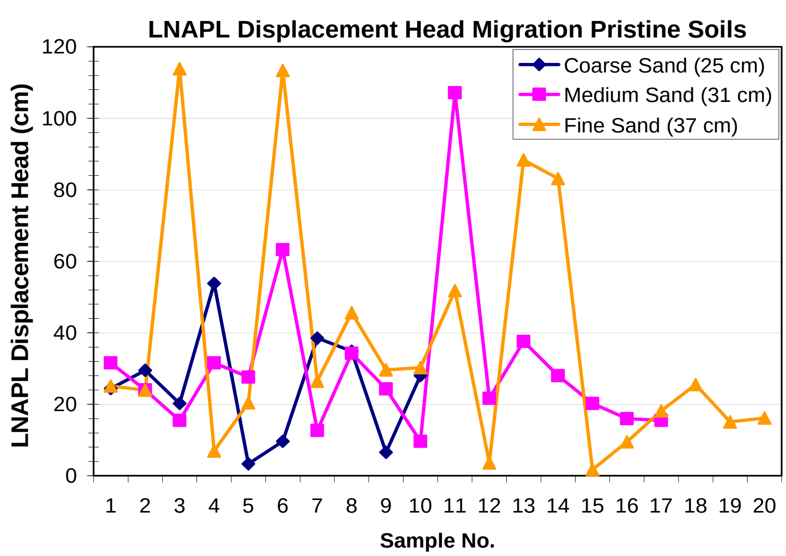
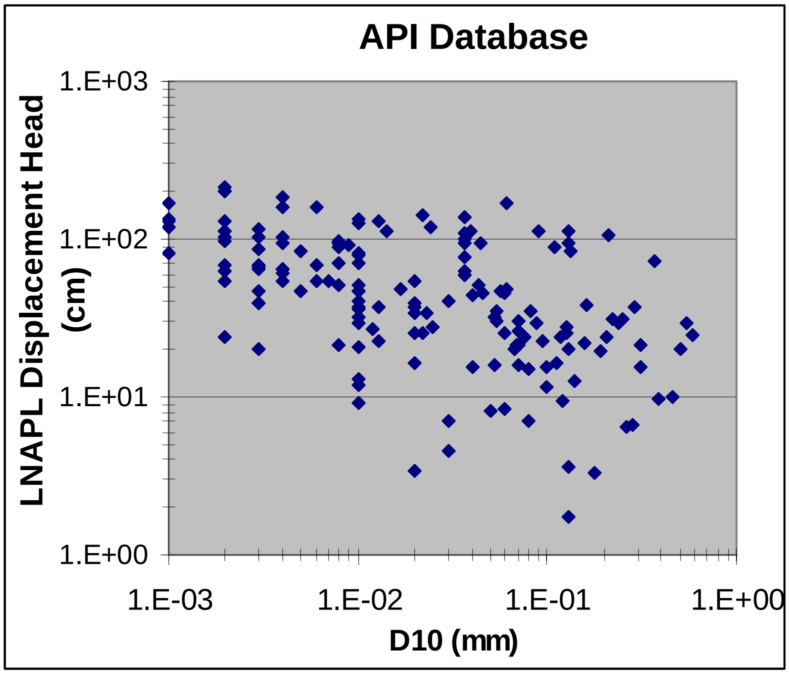


FIGURE 12: **Predicted Gasoline LNAPL Displacement for Migration into Pristine Soils. Measured Brooks-Corey Air-Displacement Heads in API Database.**
"Coarse Sand" = > 20% coarse sand, < 20% gravel, < 10% fines;
"Medium Sand" = > 50% medium sand, < 10% fines;
"Fine Sand" = >50% fine sand, < 10% fines. Average values in parentheses.



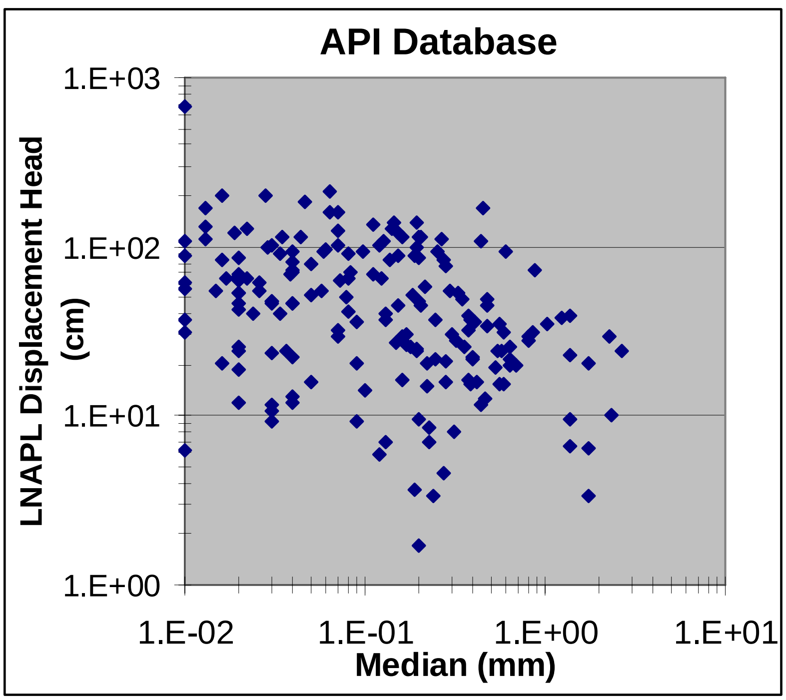


FIGURE 13: Predicted Gasoline LNAPL Displacement for Migration into Pristine Soils Relative to D10 and Median Grain Size. Measured Brooks-Corey Air-Displacement Heads in API Database.

4.4 Interpretation and Implications of Combined Model Results

This section summarizes the results of the three modeling studies.

4.4.1 LNAPL Mobility Model

The **LNAPL mobility model** predicts the potential velocity in the core of the plume, which may not be indicative of the overall stability of the LNAPL plume. A large range of potential velocities are estimated depending on the soil type. To interpret the significance of the model results, it is helpful to define a potential velocity of concern. For instance, in ASTM (2006), an example is given where a LNAPL "velocity potential"[2] of less than $1x10^{-6}$ cm/sec (~0.3 m/year) is inferred to indicate that LNAPL mobility is below *de minimus* levels. Although arbitrary, the same definition is adopted here, with the following observations for the mobility of gasoline and a regional LNAPL gradient of 0.001:

- For **coarse sand**, the potential LNAPL velocity for all cases evaluated exceeds 0.3 m/year;
- For **medium sand**, the LNAPL thickness corresponding to a 0.3 m/year threshold velocity is approximately 0.04 m;
- For **fine sand**, the LNAPL thickness corresponding to a 0.3 m/year threshold velocity is approximately 0.33 m;
- For **silty sand**, the LNAPL thickness corresponding to a 0.3 m/year threshold velocity is approximately 0.91 m; and,
- For **silt**, the potential LNAPL velocity for all cases evaluated is less than 0.3 m/year.

Higher LNAPL mobility and smaller thresholds are predicted for larger gradients. Less mobility is predicted for diesel than gasoline.

4.4.2 LNAPL Mass Model

The **LNAPL mass model** was used to predict the LNAPL (gasoline) mass based on the measured LNAPL thickness in the well and a 30 m by 30 m source area. For interpretation of the model results, a LNAPL mass of 100 kilograms is chosen as an arbitrary threshold, but one that is considered to represent a relatively small mass. For coarse sand, the LNAPL well thickness that corresponds to the above mass threshold is approximately 0.05 m. For other soil types, the LNAPL mass is less than 100 kilograms for thicknesses less than approximately 0.1 m.

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[2] The rationale for this velocity potential is provided by the from analogy to the allowable permeability of a Class I landfill liner in the U.S. (G.D. Beckett, personal communication, June 20, 2005). Local site conditions should also be considered when defining a *de minimus* velocity.

4.4.3 LNAPL Displacement Entry Pressure Model

The **LNAPL displacement entry pressure** model predicts the thickness of LNAPL in a well needed to cause LNAPL to displace water-saturated soil pores. There is significant variability in the model results, ranging from a few centimetres to over a metre; however, the predicted displacement heads generally increase with decreasing grain size, as expected. For example, the model-predicted threshold LNAPL gasoline thickness to displace water-saturated pores is 0.1 m for sand and 0.32 m for silt, using default model parameters.

4.4.4 Recommended Thresholds for Defining Potentially Mobile LNAPL

There is significant variability and uncertainty in model results. Nevertheless, for the purposes of this guidance, which is to define potentially mobile LNAPL for classifying site risk levels, the modeling results may be used to define approximate thresholds for LNAPL thicknesses in wells. The main factor controlling LNAPL mobility is soil type, with only relatively small differences in mobility predicted for gasoline and diesel. For this reason, a simple ***preliminary*** matrix for LNAPL thickness is proposed based on gasoline mobility and soil type only, as described below:

- Coarse Sand or Gravel (> 20% C. Sand, < 3% fines) – 0.03 m;
- Coarse Sand or Gravel (> 20% C. Sand, 3-10% fines) – 0.05 m;
- Medium Sand (predominant fraction M.Sand, < 10% fines) – 0.1 m;
- Fine Sand (predominant fraction F.Sand, < 10% fines) – 0.2 m; and,
- Silty Sand (predominant fraction Sand, > 10% fines) – 0.3 m;

Soils with grain sizes finer than silty sand were not evaluated in detail for this guidance since there is less basis for defining thickness thresholds for finer-grained soils. A preliminary threshold of 0.3 m is recommended for soils finer than silty sand.

The rationale for grain size fractions given above is based on analysis of the API soil property database.

5.0 LNAPL MOBILITY ASSESSMENT FRAMEWORK

The evaluation of potential LNAPL mobility for this guidance involves the following steps:

- Develop a conceptual site model;
- Identify whether there are precluding conditions;
- Obtain LNAPL site assessment data; and,
- Conduct a multiple lines of evidence evaluation of potential LNAPL mobility.

The primary lines of evidence are site monitoring (“observational”) data and comparison of measured LNAPL thicknesses in wells to model-predicted thickness thresholds for potential mobility. The secondary lines-of-evidence may include product laboratory testing, product recovery testing, indirect monitoring techniques or tools, or analysis of other factors such as age and weathering of a LNAPL release.

“LNAPL” means light non-aqueous phase liquids having a specific gravity less than 1.0. LNAPL is considered present when:

a) Free liquid is found in soil; and,

b) Free liquid is found in monitoring wells at an apparent thickness of greater than 2 mm.

“mobile LNAPL” means LNAPL that is moving through geologic media under prevailing site conditions (*e.g.,* hydraulic gradients, geologic conditions). LNAPL is considered mobile when:

a) Temporal sampling indicates increasing thicknesses of LNAPL in monitoring wells;

b) Temporal sampling indicates advancement of LNAPL across a monitoring well network; or,

c) LNAPL is measured in monitoring wells at thicknesses exceeding values indicated in Section 5.5.

While the purpose of this guidance is a determination of LNAPL mobility for site classification purposes, it is important that an evaluation of free-phase LNAPL mobility consider the broader issues and potential risks associated with free-phase and residual-phase LNAPL at contaminated sites. Where warranted, LNAPL management (recovery, treatment or control) should be implemented to mitigate unacceptable risks to human health and/or the environment.

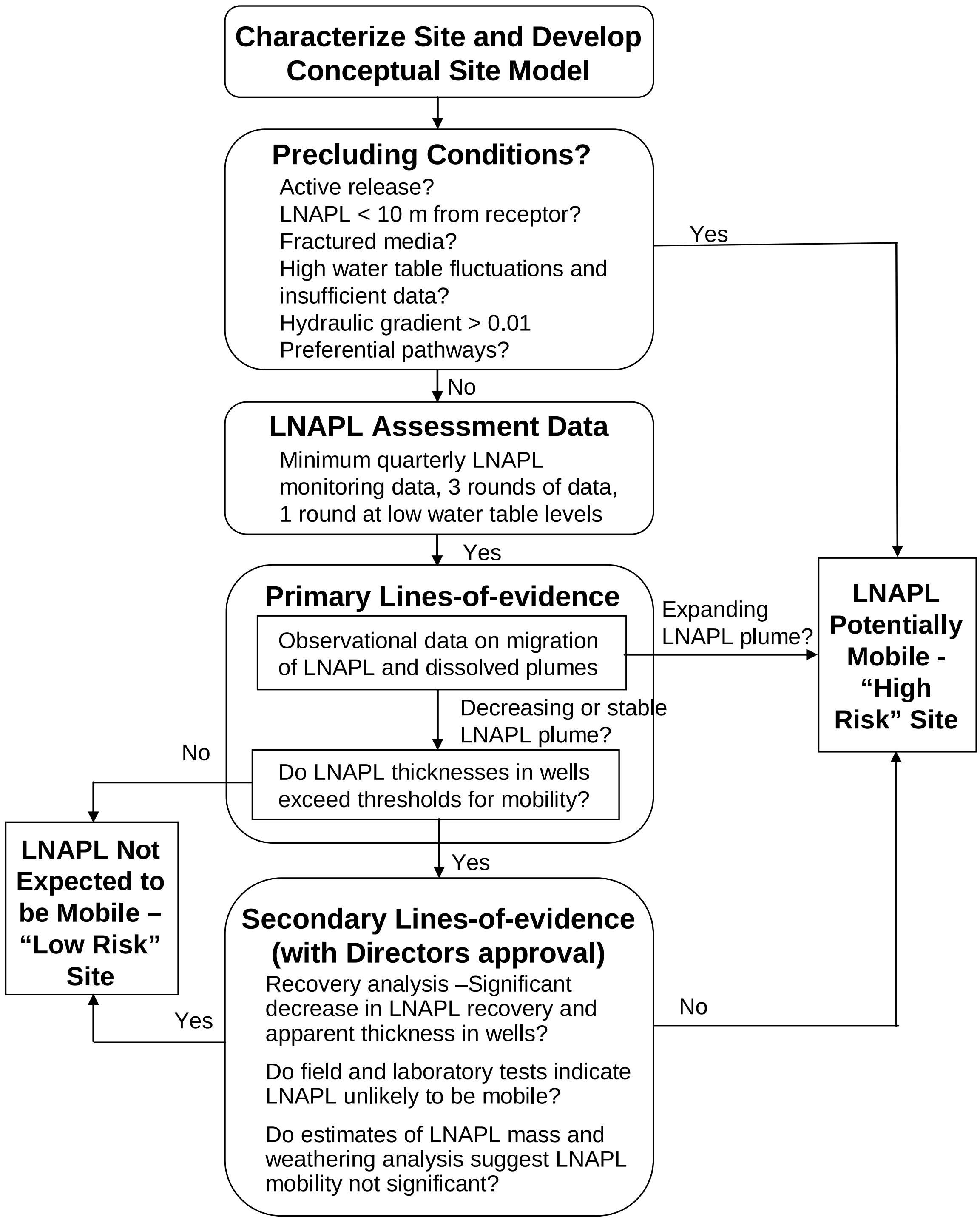

FIGURE 14: LNAPL Mobility Assessment Flowchart

5.1 Conceptual Site Model

The essential starting point for any assessment of LNAPL mobility is a sound conceptual site model that is developed on the basis of a sufficiently detailed field investigation. The conceptual site model should integrate historical, physical, chemical and biological information for the site to provide the needed context for evaluation of LNAPL mobility. An essential starting point in the development of the conceptual model is the identification of potential LNAPL source zones, including their location, volume (to the extent this is known), composition and history of the release. The type of LNAPL, the properties of the unconsolidated soil deposits or underlying bedrock, if present, including particle gradation, layering, fractures, and secondary porosity features (*e.g.*, root holes, cracks), and hydrogeologic conditions will all have a significant influence on the LNAPL distribution and mobility. The physical setting, including possible nearby surface water bodies is also important. Potential anthropogenic preferential pathways such as utility corridors or other below-ground structures that could influence LNAPL migration should also be considered.

There are a number of different tools or methods that may be used for characterization of the LNAPL source zone. Simple tools include direct visual observations of sheens or dyed LNAPL (*e.g.,* using dye shake tests on soil samples), and indirect approaches to define LNAPL zones using jar or bag headspace vapour tests on multiple soil samples. More advanced tools include the use of cone penetrometers equipped with an infrared or laser induced fluorescence sensor, which can provide detailed information on soil properties and potential LNAPL zones, and a membrane interface probe, which can provide similar detailed data on chemical distributions. Additional information on these technologies is provided in Golder (2008).

Additional information may be used to build the conceptual model including, for example, the results of a petrophysical analysis of soil properties (*e.g.,* soil porosity, bulk density, grain size distribution, permeability and conductivity), and LNAPL properties (*e.g.,* viscosity, density and interfacial tension with water and air).

5.2 Precluding Site Conditions

If precluding conditions are present at a site, then LNAPL is considered potentially mobile and the site is considered to be a high risk site. This guidance is not applicable where precluding conditions are present.

The presence of LNAPL within the exposure zone, defined as the zone where receptors may come into contact with LNAPL, is a precluding condition. Examples of exposure zones with LNAPL include areas where visible product is observed to be seeping on ground surface, and areas where product is observed to be migrating into a water body. Mobile LNAPL is confirmed at such sites, and therefore they are designated as high risk sites.

The presence of LNAPL within monitoring wells, defined as free liquids with a thickness greater than 2 mm, when combined with any of the following site characteristics, is considered a precluding condition for determining the presence of mobile LNAPL:

- There is still an active or on-going LNAPL release;
- LNAPL is present in monitoring wells located within 10 m of a potential receptor or exposure zone (*e.g.*, LNAPL is located within 10 m of the high water mark of a water body);
- LNAPL is present within fractured media (*e.g.,* fractured bedrock or fractured clay);
- Water table fluctuations (greater than 1 m) are present, unless there are seasonal data on LNAPL presence in monitoring wells during low water table periods;
- Hydraulic gradients are high (greater than 0.01); and,
- Anthropogenic preferential pathways (*e.g.*, utility corridors) are present that have or may intersect LNAPL zones.

5.3 Obtain LNAPL Site Assessment Data

A detailed site investigation is required to develop a conceptual site model that describes the distribution and potential mobility of LNAPL. General guidance on site investigation is provided in Golder (2008) and Health Canada (2008). Specific issues and data needs for an assessment of LNAPL mobility under this protocol are described below.

5.3.1 Monitoring Well Network Design

The monitoring well network needed to evaluate LNAPL presence and potential mobility is site specific, and will depend on the extent to which other investigation technologies, such as laser-induced fluorescence, are used. Monitoring wells should be located to both characterize the core of the LNAPL plume (usually near the source of LNAPL release) where the thicknesses of LNAPL in wells are typically greatest, and to delineate the lateral LNAPL extent along the periphery of the LNAPL zone. The spacing required to delineate the LNAPL extent is site specific, but is expected to be approximately 5 m to 10 m at most sites.

The monitoring well network should include appropriately located sentinel wells in the down-gradient groundwater flow direction of the LNAPL plume. These wells should be placed to monitor the possible expansion of the LNAPL plume and dissolved hydrocarbon concentrations in groundwater, since an expanding dissolved plume is an indirect indicator of possible expansion of the LNAPL plume.

In addition to LNAPL, the monitoring network should be designed to monitor the associated dissolved plume. Many factors should be considered to address the dissolved plume, including the groundwater velocity, temporal changes in groundwater flow direction, and distance from the LNAPL zone to possible receptors. An important concept that may be incorporated into network design is the use of closely-spaced wells placed in a transect along the approximate centerline (longitudinal axis) of the dissolved plume to monitor transient changes in the plume length and plume stability.

The monitoring well screens for detection of LNAPL should be sufficiently long to straddle the water table during seasonal (and tidal, if applicable) changes in water table elevation. Where seasonal or tidal water table fluctuations are high (more than 2 m or 3 m), then as a practical consequence, multiple wells with screens completed over different depth intervals will typically be required. When there are complex geologic formations (*e.g.*, as shown in Figure 5), the monitoring well screen should be carefully placed to avoid biased results, where possible. Well screen openings should be designed considering particle gradations of the native soil and the filter pack. Additional guidance on monitoring well construction is provided in Golder (2008).

5.3.2 Monitoring Well Development

Upon completion of the well, it should be developed, preferably using surge blocks (unless in fine-grained deposits), with bailing or pumping of water from the well. The use of high intensity methods and removal of larger quantities of groundwater over longer periods may be required if fluids were introduced to the formation when drilling, when the drilling method results in smearing of fine-grained soils along the borehole wall, or where drilling mud is used that may coat the borehole wall. This is important since the presence of fine-grained soils or mud may limit the migration of LNAPL into a well. At least twice the volume of any water added during drilling should be removed; temperature, pH and electrical conductivity should be monitored during this process to confirm that adequate fluids have been removed. If present, odours and LNAPL liquids or sheens in the development water should be recorded.

5.3.3 LNAPL Monitoring Method

The thickness of LNAPL in monitoring wells should be measured preferably using an infrared beam and detector or optical sensor (*i.e.*, interface probe) with a measurement accuracy of 1 mm. Coated measuring tapes and clear bailers may also be used to provide an indication of LNAPL presence and semi-quantitative estimates of the LNAPL thickness.

5.3.4 Monitoring Frequency for LNAPL Evaluation

Temporal monitoring data are needed to evaluate potential LNAPL mobility for several reasons. Depending on site conditions, there may be slow migration or expansion of the LNAPL plume, although the potential for lateral LNAPL mobility decreases with increased age of the LNAPL plume since all finite LNAPL plumes tend to stop migrating within relatively short time frames. Lateral LNAPL mobility may be induced when there are fluctuations in water table elevation or an increase in the hydraulic gradient. Water table fluctuations will also result in vertical movement of LNAPL and varying thicknesses of LNAPL in monitoring wells. Typically, the greatest LNAPL thicknesses are observed during low water table conditions.

For the above reasons, sufficient observational data should be collected to determine seasonal (or other temporal) trends and should include monitoring conducted at times corresponding to the range of seasonal high and low water tables. The minimum data required for making a determination that LNAPL is not potentially mobile at a site are a) quarterly data obtained over six months (*i.e.*, at least three monitoring rounds), with one set of data obtained during the low water table period, and b) data needed to evaluate precluding conditions listed in Section 5.2. Where feasible, consideration should be given to obtaining data collected over durations longer than a year and at a greater frequency (*e.g.*, monthly). For tidally influenced zones, more frequent monitoring is necessary.

Monitoring data for the dissolved plume can be an important indirect indicator of LNAPL plume stability. The temporal trends for dissolved plume monitoring should be analyzed using appropriate statistical methods, including techniques such as Mann-Kendall trend analysis (Aziz *et al.*, 2003).

5.3.5 Climate Data

Climatic data such as precipitation and temperature should be obtained to assist in the interpretation of likely seasonal trends in water table elevations. In milder wet areas of British Columbia, water table elevations are typically highest during the winter months. In colder interior areas, water table elevations may be at their lowest levels in winter and may quickly rise in the spring during snow melt. Water table elevations near rivers may also be influenced by the river stage or water level in the river. Supporting data on water table levels and climatic data should be provided when making determinations on LNAPL mobility.

5.4 Primary Lines of Evidence

5.4.1 Monitoring (Observational) Data

The definition of mobile LNAPL is consistent with BC MoE Protocol 12 and is considered present when temporal sampling indicates either of the following:

a) increasing thickness of LNAPL in monitoring wells, and/or,

b) advancement of LNAPL across a monitoring well network, indicating that the LNAPL zone is expanding.

The above indicators of mobile LNAPL take precedence over the LNAPL thickness measurements described below.

The dissolved plume stability can also be used to infer LNAPL stability, since a stable or shrinking dissolved plume provides a line-of-evidence that the LNAPL is likely stable. However, an expanding dissolved plume is not necessarily evidence for mobile LNAPL since, depending on the biogeochemical conditions at the site, the dissolved plume may continue to expand for some period of time in the absence of LNAPL expansion.

At some sites with longer-term temporal data, there may be early data that indicates LNAPL mobility followed by more recent data indicating no further mobility. While appropriate actions should be taken early on to mitigate LNAPL mobility, if such data exists, the determination of mobility may be made on the most recent two years of quarterly data.

5.5 Theoretical Estimates of LNAPL Mobility from LNAPL Thickness in Wells

Predictive models were used to relate the measured LNAPL thickness in wells to the potential LNAPL velocity in the core of the plume and the potential for LNAPL to exceed displacement entry pressure and enter water-wet pores at the periphery of the LNAPL plume. Using multiphase modeling concepts, the mass of LNAPL was also predicted based on LNAPL thickness in wells. Based on the modeling results, approximate thickness thresholds for LNAPL were developed in the context of this guidance, which is to develop thicknesses for potential mobility for administrative purposes to define high versus low to moderate risk sites.

If the maximum LNAPL thickness based on a minimum of one year of quarterly data exceeds the ***preliminary*** thresholds below, the LNAPL is considered to be potentially mobile for the purposes of this guidance.

- Coarse Sand or Gravel (> 20% C. Sand, < 3% fines) – 0.03 m;

- Coarse Sand or Gravel (> 20% C. Sand, 3-10% fines) – 0.05 m;

- Medium Sand (predominant fraction M.Sand, < 10% fines) – 0.1 m;

- Fine Sand (predominant fraction F.Sand, < 10% fines) – 0.2 m; and,

- Silty Sand (predominant fraction Sand, > 10% fines) – 0.3 m

Soils with grain sizes finer than silty sand were not evaluated in detail for this guidance and there is less basis for defining thickness thresholds. A preliminary threshold of 0.3 m is recommended for soils finer than silty sand.

If there are longer-term temporal data, then the determination of mobility may be made on the most recent two years of data. Grain size distribution tests from soil obtained near to the water table should be conducted to enable appropriate classification of site soils in accordance with the Unified Soil Classification System (USCS). For purposes of this guidance, the key classifications are:

- Gravel: > No. 4 Sieve
- Coarse Sand: No. 4 (4.75 mm) to No. 10 Sieve (2 mm)
- Medium Sand: No. 10 (2 mm) to No. 40 Sieve (0.425 mm)
- Fine Sand: No. 40 (0.425 mm) to No. 200 Sieve (0.075 mm)
- Fines: < No. 200 Sieve (0.075 mm)

5.6 Secondary Lines of Evidence

Secondary lines of evidence include observations indicating declining LNAPL recovery for remediation systems, field LNAPL bail tests, field characterization methods, and laboratory tests. An evaluation of secondary lines of evidence would not normally be directly used for determinations made under this guidance, but could be useful for a broader assessment of LNAPL mobility. When there is compelling evidence that LNAPL is not mobile (for example, based on slow recovery during bail-down tests), such evidence may supersede the thickness thresholds defined above, although such a determination must be approved by the BC MoE Director.

5.6.1 LNAPL Recovery and Bail-Down Tests

LNAPL recovery data may be used qualitatively to evaluate LNAPL plume stability. A decrease in the equilibrium LNAPL thickness in wells (measured under appropriate water table conditions) and a decrease in LNAPL recovery rate would normally represent a reduced risk from potential LNAPL migration. The LNAPL removal program should take place over a sufficient time period to evaluate seasonal trends. In most cases, this would require operation of the LNAPL extraction system over at least one year, and likely longer. While a bail-down test may provide some useful information with respect to LNAPL recovery, limitations with a single or limited number of bail-down tests should be recognized.

5.6.2 Field Bail-Down Tests

Although LNAPL bail-down methods and data assessment procedures are relatively new, methods for estimation of LNAPL transmissivity have been derived from traditional slug test methods for groundwater. The estimation is based on the Bouwer-Rice or Cooper *et al.* solution for slug-tests modified to account for unique aspects relating to LNAPL migration into wells, a density correction for LNAPL as it is lighter than water, and filter pack effects (Sale, 2001).

One of the most comprehensive descriptions of LNAPL bail-down methods and data analysis procedures is provided in Aqui-Ver (2004), where two papers are presented:

1. “Lundy and Zimmerman” approach, where changes in LNAPL thickness in a well from which a slug of LNAPL is withdrawn are analyzed based on modified Bouwer-Rice slug test procedure (Lundy and Zimmerman, 1996). This method is best where the water table is not significantly depressed by the removal of the LNAPL slug since it assumes only LNAPL enters the well.

2. “Beckett and Lyverse” approaches, based on Huntley (2000), where air-LNAPL and LNAPL-water interfaces are measured through time, with data analyzed using a modified Bouwer-Rice solution (appropriate when the corrected potentiometric surface stays approximately constant over time) and a modified Cooper-Jacob solution (computationally more complex, but more accurate where the potentiometric surface does not stay constant over time).

The Lundy-Zimmerman method assumes that no water enters the well after the LNAPL slug is removed. The method provides a lower-bound estimate of the LNAPL conductivity. In contrast, the Huntley method assumes that the water enters the well instantaneously as the slug is removed, and provides an upper-bound estimate of the oil conductivity.

The average LNAPL conductivity may be estimated from the LNAPL transmissivity based on the initial LNAPL thickness in a well (Appendix I, Equation 3). The LNAPL conductivity, together with an estimate of LNAPL gradient, the average LNAPL saturation and total porosity may be used to estimate the LNAPL velocity, which may be compared to a *de minimus* velocity (Section 4.4.1). Estimation of the LNAPL saturation following a measurement approach would require analysis of multiple closely-spaced samples, but may also be estimated using the multiphase model.

LNAPL bail-down tests are measurements of potential mobility based on conditions at the time of the tests and only reflect the local area affected by the tests. There are several potential limitations associated with field bail-down tests including non-representative conditions arising from water table fluctuations and geologic heterogeneity. The interpretation of a LNAPL bail-down test is less straightforward than groundwater due to complicating factors associated with potential filter pack effects (the well must be thoroughly developed), density corrections and multiphase flow into the well. A complicating factor for test interpretation is that the LNAPL transmissivity is a non-unique parameter that does not provide information on the LNAPL and conductivity distribution at the local-scale. There can be cases where identical transmissivities are measured, but where the conductivity distribution, and therefore LNAPL velocity, are very different.

5.6.3 Field and Laboratory Tests

There are a number of emerging methods that may be considered as part of a broader assessment including field methods, such as ultraviolet induced fluorescence and laser induced fluorescence, membrane interface probes, and specialized laboratory tests, such as Tempe cell or centrifuge testing, which may be used to obtain capillary parameters as well as estimates of the potentially mobile and residual LNAPL saturations. For example, one laboratory 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 and residual saturation. Fluorescence testing may be correlated with LNAPL saturation (Dean-Stark) tests to obtain detailed LNAPL vertical profiles, which be used to validate model predictions of LNAPL saturation previously described in this guidance.

6.0 CONCLUSIONS AND RECOMMENDATIONS

A framework for the assessment of LNAPL mobility based primarily on measurement (observational) data and model predictions is provided in this guidance. The ***preliminary*** framework is that potentially mobile LNAPL is considered present when it is detected in the exposure zone or when temporal sampling at monitoring wells indicates either of the following:

1. increasing thickness of LNAPL in monitoring wells;
2. advancement of LNAPL across a monitoring well network, indicating the LNAPL zone is expanding.

Two multiphase modeling approaches were used to evaluate LNAPL mobility based on the observed LNAPL thickness in wells, which were the potential LNAPL velocity (core of LNAPL plume) estimated from Darcy's Law and the displacement entry pressure that must be exceeded for LNAPL to migrate into pristine soils (periphery of LNAPL plume). These models were used to identify preliminary thresholds for potential LNAPL mobility. The purpose of the thresholds are to identify high versus low to moderate risk sites under the BC regulatory regime. The thresholds are subject to significant uncertainty, in particular arising from capillary parameters input in the models. Further evaluation of models and data sources for estimation of capillary parameters is recommended.

7.0 CLOSURE

We trust that the information presented in this report meets your current requirements. Should you have any questions or comments, please do not hesitate to contact Golder Associates Ltd.

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APPENDIX I

DESCRIPTION OF LNAPL SATURATION AND RELATIVE PERMEABILITY MODEL EQUATIONS AND METHODS FOR ESTIMATING CAPILLARY PRESSURE-SATURATION PARAMETERS

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LIST OF FIGURES

1.0 INTRODUCTION

This appendix describes the theoretical equations for models used for evaluation of LNAPL mobility, which are equations for the vertical LNAPL saturation distribution and relative permeability functions based on a multi-phase model and hydrostatic equilibrium. The appendix also describes methods for estimation of capillary parameters needed for saturation and permeability models.

Two models were used to evaluate LNAPL mobility based on LNAPL thickness measurements in monitoring wells and multiphase modeling concepts:

1. Model 1 - Darcy's Law: Used to estimate the lateral LNAPL velocity (*potential LNAPL mobility*). This model applies to the *core of the plume*, but is nevertheless considered a *potential mobility* indicator since the overall movement or expansion of a finite LNAPL plume (*i.e.*, where the release has stopped) is constrained by the capillary forces at the leading edge of the LNAPL plume.

2. Model 2 - Displacement Entry Pressure Model: Utilizes capillary concepts to estimate the pressure head or thickness of LNAPL needed to displace water within pristine soil at the *fringe of the LNAPL plume*.

2.0 MODEL 1: POTENTIAL LNAPL MOBILITY ESTIMATED FROM DARCY'S LAW

2.1 Pore-Scale LNAPL Flow Rate

A pore-scale LNAPL flow rate may be estimated from Darcy's Law, which is a function of the LNAPL conductivity and LNAPL gradient, as follows:

$$q_o = K_o\, i_o\, V_0 = K_o\, i_o / (\phi\ S_o) \qquad [1]$$

where q_o is the specific velocity of LNAPL (m/s), K_o is the LNAPL conductivity (m/s) and i_o is the LNAPL table gradient (dimensionless) (o subscript is henceforth used to denote LNAPL). To obtain the average linear velocity of LNAPL (V_o, m/s), the specific discharge is divided by the LNAPL-filled porosity (ϕS_o), where ϕ is the total porosity (dimensionless) and S_o is the LNAPL saturation (dimensionless).

The LNAPL conductivity may be estimated using the following equations:

$$K_o = k\, k_{ro}\, \rho_o\, g / \mu_o = k_{ro}\, K_w\, \rho_o\, \mu_w / (\rho_w\, \mu_o) \qquad [2]$$

where k is the intrinsic permeability (m^2) of the porous medium, k_{ro} is the relative permeability of LNAPL (dimensionless), K_w is the saturated hydraulic conductivity (m/s), ρ_o is the LNAPL density (kg/m^3), ρ_w is the water density (kg/m^3), g is the gravitational force (m/s^2), μ_o is the LNAPL viscosity (kg/m-s), and μ_w is the water viscosity (kg/m-s).

2.2 Macro Scale LNAPL Flow Rate

The LNAPL velocity defined in equation 1 describes pore-scale movement at a specific point in the aquifer. Given that LNAPL saturations are not uniform (Figure I-1) and relative permeability varies with saturation, lateral flow in a LNAPL lens will not be uniform. Nevertheless, since a computationally efficient method for calculation of the pore-scale velocity is not available, a model based on an effective mobility of the entire LNAPL layer thickness, as represented by an effective or "average" LNAPL conductivity or a LNAPL transmissivity is adopted. As defined by Parker (1999), Darcy's Law for the LNAPL flow rate is reformulated on the basis of an inherent mobility term, which is the ratio of the LNAPL transmissivity to the specific LNAPL volume at a given location (equation 3). The inherent oil mobility is similar to the effective or average relative permeability concept described by API (2003). The inherent oil mobility is equivalent to the ratio of the average LNAPL conductivity to the effective LNAPL porosity, as shown below:

$$V_{macro\text{-}scale} = M_o * i_o \qquad M_o = \frac{T_o}{V_{os}} = \frac{b_o\,\overline{K_o}}{b_o\,\phi\overline{\overline{S_o}}} = \frac{\overline{K_o}}{\phi\overline{\overline{S_o}}} \qquad [3]$$

where $V_{macro\text{-}scale}$ is the average or effective LNAPL velocity over the vertical interval with potentially mobile LNAPL (m/s), M_o is the inherent oil mobility (m/day), T_o is the LNAPL transmissivity, integrated along the oil saturation profile (m^2/day), V_{os} is the specific LNAPL volume per unit area (m^3/m^2), b_o is the free-phase LNAPL thickness in the well at static equilibrium (m), $\overline{K_o}$ is the mean LNAPL conductivity, averaged along the LNAPL saturation profile below the air-LNAPL interface in the well (m/day) and $\overline{S_o}$ is the mean LNAPL saturation, averaged along the oil saturation profile (dimensionless).

2.3 LNAPL Saturation

Mathematically, the vertical LNAPL distribution is estimated using a multiphase model assuming static vertical equilibrium, the in-well LNAPL thickness, the water retention (soil characteristic) curve, and scaling parameters to extrapolate from an air-water to LNAPL-water-air system. 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, the water content is sometimes alternatively expressed in terms of effective saturation (dimensionless), $S_e = (\theta - \theta_r)/(\theta_s - \theta_r)$, where θ_s and θ_r indicate saturated and residual values of θ. One view of residual water content is that it represents the water content at which the unsaturated hydraulic conductivity becomes zero (Mualem, 1976). The Brooks and Corey (1964) power-law function takes the form:

$$S_e = \left(\frac{h_d}{h_c}\right)^{\lambda} \; ; h_c \geq h_d \qquad [4]$$

$$S_e = 1 \; ; h_c < h_d$$

where h_d is the displacement pressure head (cm), h_c is the capillary pressure head (cm) and λ is the Brooks - Corey (BC) pore size distribution parameter (dimensionless).

The van Genuchten (1980) function, with an inflection point, is:

$$S_w(h) = S_{wr} + (1 - S_{wr})\left[\frac{1}{1+(\alpha h)^N}\right]^M \qquad [5]$$

where S_w is the water saturation (dimensionless), S_{wr} is the water residual saturation (dimensionless), α is the van Genuchten alpha for an air-water system (1/cm), h is the matric suction (cm) and N and M are van Genuchten fitting parameters (dimensionless). The van Genuchten alpha is inversely related to the thickness of the capillary fringe. The M and N parameters are related as M = 1 – 1/N when used in conjunction with the Muelum approximation for relative permeability and M = 1 – 2/N when used in conjunction with the Burdine approximation. The Brooks and Corey (1964) displacement pressure head (Ψ_b) is related to α through the approximate relation $\alpha \sim 1/\Psi_b$. The parameter N is proportional to the pore-size distribution (λ) of Brooks and Corey, where roughly N = λ + 1. Scaling parameters are applied to go from an air-water to LNAPL-water system (LNAPL here is denoted as oil (o) in subscripts), as follows:

$$a_{ow} = \left(\frac{P_w - P_o}{P_w}\right)\left(\frac{\sigma_{aw}}{\sigma_{ow}}\right)\alpha = (1 - P_r)\left(\frac{\sigma_{aw}}{\sigma_{ow}}\right)\alpha \qquad [6]$$

$$a_{ao} = P_r\left(\frac{\sigma_{aw}}{\sigma_{ao}}\right)a \qquad [7]$$

Where ρ_w is the water density, ρ_o is the oil (LNAPL) density, σ_{aw} is the air-water surface tension, σ_{ow} is the oil (LNAPL)-water interfacial tension, σ_{aw} is the air-oil (LNAPL) surface tension, α_{ow} is the Van Genuchten alpha for the LNAPL-water system, and ρ_r is the LNAPL/water density ratio.

Using the theoretical development described in API (2003), the equations for vertical LNAPL saturation distribution are as follows:

$$S_w(z)=S_{wr}+(1-S_{wr}-S_{ors})\left[\frac{1}{1+(a_{ow}(z-z_{ow}))^N}\right]^M \qquad [8]$$

$$S_t(z)=S_{wr}+(1-S_{wr}-S_{orv})\left[\frac{1}{1+(a_{ao}(z-z_{ao}))^N}\right]^M \qquad [9]$$

$$S_o(z)=S_t(z)-S_w(z) \qquad [10]$$

where S_o is the LNAPL saturation, S_{ors} is the LNAPL residual saturation in the saturated zone, S_{orv} is the LNAPL residual saturation in the vadose zone, z is the elevation (cm), z_{ow} is the elevation of the LNAPL-water interface (cm) and z_{ao} is the elevation of the LNAPL-air interface (cm). The LNAPL saturation profile predicted from equations 8 to 10 is shown in Figure I-1.

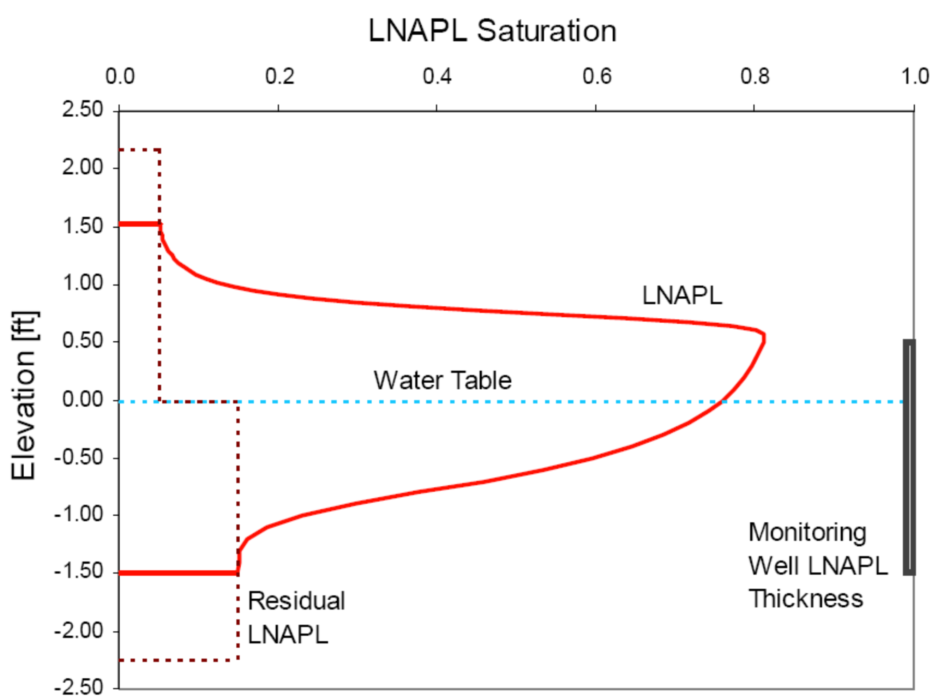

FIGURE I-1: LNAPL Saturation Distribution (from API, 2007)

The specific LNAPL volume, or volume of LNAPL per unit surface area, may be calculated using:

$$D_o(b_o) = \int^{z_{max}} n\, S_o(z)\, dz \qquad [11]$$

Above equation needs to be modified integral Zow to Zmax

The function Do(bo) may be approximated piecewise by a linear function of the form:

$$D_o = \beta\,(b_o - X) \qquad [12]$$

where D_o is the specific LNAPL volume (m^3/m^2), b_o is the thickness of LNAPL in the well (m), and B and X are fitting parameters.

2.4 Relative Permeability

A key parameter is the LNAPL relative permeability, which is a function of the LNAPL saturation. A conceptual relative permeability versus saturation relation is shown in Figure I-2. The relative permeability of the soil for LNAPL or water at 100% saturation is one. The relative permeability of LNAPL and water decreases rapidly as saturation declines from 100%. In the core of a LNAPL plume where saturations are highest, there will be the greatest potential for LNAPL mobility, whereas, at the fringes, the potential for LNAPL mobility will be less.

The relative permeability is calculated from theoretical models that derive relative permeability from fluid retention models, which are based on capillary pressure-saturation relationships. The LNAPL relative permeability profile is estimated 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 Aqui-Ver (2004), using the same set of fluid saturation values, the equations of Mualem generally predict larger values for LNAPL relative permeability. 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.

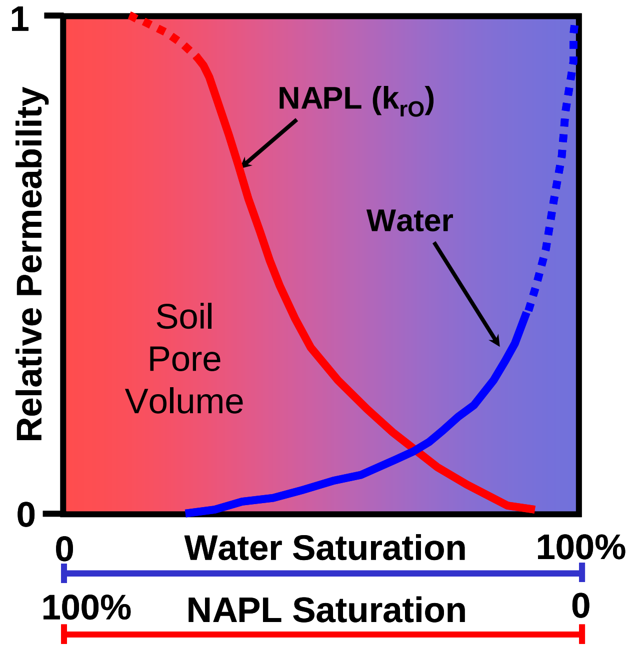

FIGURE I-2: Conceptual Relative Permeability versus Saturation Relation

The Burdine model is most often associated with the Brooks and Corey capillary pressure model, with the relative permeability estimated as follows:

$$k_{ro} = \left(\frac{S_o - S_{or}}{1 - S_{or}}\right)^2 \left[\left(\frac{S_w + S_o - S_{wr}}{1 - S_{wr}}\right)^{\frac{\lambda+2}{\lambda}} - \left(\frac{S_w - S_{wr}}{1 - S_{wr}}\right)^{\frac{\lambda+2}{\lambda}}\right] \qquad [13]$$

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.

$$K_{ro} = \left(\frac{S_o}{1 - S_m}\right)^{1/2} \left\{\left[1 - \left(\frac{S_w\ S_m}{1\ S_m}\right)^{1/M}\right]^M - \left[1 - \left(\frac{S_w + S_o - S_m}{1 - S_m}\right)^{1/M}\right]^M\right\}^2 \qquad [14]$$

2.5 LNAPL Gradient

The LNAPL gradient is defined as the change in the elevation of the air-LNAPL interface ("LNAPL table") with distance. The LNAPL gradient may 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.

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 (ρ_{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:

$$Z_{aw} = Z_{ow} + (\rho_{ro} Ho) \qquad [15]$$

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 ρ_o is the LNAPL density and b_o is the LNAPL thickness in a well at hydrostatic equilibrium.

3.0 LNAPL DISPLACEMENT ENTRY PRESSURE MODEL FOR MIGRATION IN PRISTINE SOILS

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 saturated soil pores if the capillary displacement pore entry pressure is exceeded. As previously discussed, the Brooks-Corey capillary model has a well-defined displacement head, which must be exceeded before mobility is predicted. In contrast, for the van Genuchten model, for any positive LNAPL head, the model predicts part of the porous medium will have a LNAPL saturation exceeding the LNAPL residual saturation, and therefore has the potential for LNAPL mobility.

The Brooks-Corey model air-water displacement head ("bubbling pressure") may, through the application of appropriate scaling parameters, be converted to a LNAPL displacement head. If the thickness of LNAPL in the well is greater than the LNAPL displacement head, the free-phase LNAPL is potentially mobile (Lefebvre and Boutin, 2000; API, 2007). 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 able to move laterally beyond these wells.

The displacement head ($\Delta\Psi$) is estimated based on theory developed by Parker and Lenhard (1989) and Charbeneau and Chiang (1995), as follows:

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

$$\Psi_{boa} = \frac{\Psi_{baw}\sigma_{ao}}{\rho_r \sigma_{aw}} \qquad [18]$$

$$\Psi_{bow} = \frac{\Psi_{baw}\sigma_{ow}}{(1-\rho_r)\sigma_{aw}}$$

where: Ψ_{boa} is the LNAPL-air displacement head (m) Ψ_{bow} is the LNAPL-water displacement head (m), and Ψ_{baw} is the air-water displacement head (bubbling pressure) (m).

The Brooks-Corey model displacement pressure is a reasonable conceptual construct for potential mobility. However, it is a finite approximation that, by virtue of its definition, will tend to over-estimate the actual displacement head needed for mobility. It is also important to recognize that it is a model for LNAPL displacement of saturated or nearly saturated soil pores. Above the capillary fringe, the water content decreases and LNAPL is much more readily able to enter air-filled pores. While potentially a non-conservative model for mobility, it is nevertheless considered a useful assessment tool when interpreted in the context of other model results using a multiple lines-of-evidence approach. This method may also be used to provide insight on the approximate relative thickness of LNAPL that would indicate potential mobility for different soil types.

The Brooks-Corey model was used to estimate the LNAPL displacement head for different soil types for gasoline and diesel. There are no default Brooks-Corey air-water displacement heads provided in the API computer model or database, so this parameter was estimated two different ways:

1. The Lenhard equation (Charbeneau, 1999) was used to estimate the Brooks-Corey air-water displacement head from the Van Genuchten capillary parameters, which were the API Interactive Guide defaults.

2. The measured Brooks-Corey air-water displacement heads provided in the API database for individual test results were directly used. This method provides insight on the variability in displacement head predictions.

For large capillary heads, the air-water displacement head may be estimated from the Van Genuchten alpha, since Ψ_{baw} is approximately equal to $1/\alpha$. However, API (1999) based on a model developed by Dr. Randall Charbeneau indicates that the Lenhard equation is a more accurate method of estimating the air-water displacement head for a broader range of water contents, as given below:

$$m = 1 - \frac{1}{n}$$

$$\lambda = \frac{m}{1-m}\left(1 - S_{we}^{1/m}\right) \qquad [19]$$

$$\overline{S}_x = 0.7 - 0.35e^{-n4}$$

$$\Psi_{baw} = \frac{\overline{S}_x}{\alpha}\left(\overline{S}_x{}^{1/m} - 1\right)^{1-m}$$

4.0 ESTIMATION OF CAPILLARY PARAMETERS

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

- Look-Up of capillary parameters for defined soil textures;
- Data mining;
- Empirical methods or pedotransfer functions (PTF);
- Fitting using measured grain size distribution; and,
- Fitting using measured water retention tests.

Regardless of the method used, it is critical that the Van Genuchten parameters clearly indicate whether the Van Genuchten - Mualem or Van Genuchten - Burdine approximation is used. Generally, if the curve fitting has been conducted for one method, that method should be used for the mobility assessment.

4.1 Look-Up of Capillary Parameters for Defined Soil Textures

Several researchers have published class (representative or average values) capillary parameters and other hydraulic parameters for different soil texture classifications based on statistical analysis of fitted data from water retention tests on relatively large number of samples (Rawls *et al.*, 1982; Carsel and Parish, 1988; Schaap and Leij, 1998). One of the largest databases is that compiled by Carsel and Parish (1988), which is based on the US SCS (US Department Agriculture (USDA)) soil texture classification system (12 soil textural types) and testing of agricultural soils. Schaap and Leij (1998) provide updated capillary parameters for a similar database of agricultural soil test data.

The API Interactive LNAPL Guide includes “default” values for soil properties (capillary parameters, porosity, and residual saturation) based on the soil classes for the Folk Classification System (Aqui-Ver, Inc., 2004). The defaults were obtained from the API database of soil properties, which include capillary parameters for 519 samples of more consolidated earth materials collected near the water table that tend to be more consolidated than agricultural soils. The API Interactive Guide uses the Folk Classification System for classifying soil. The API database is expected to be more representative of subsurface earth materials near the water table, than the agricultural databases described above. However, the defaults provided in the API Interactive LNAPL Guide are highly approximate, and further evaluation of capillary parameters using methods described below is recommended.

4.2 Data Mining

Data mining involves comparison of site data to a database that provides capillary and other soil property data. Typically, the measured grain size distribution is compared to grain size distributions in the database and the sample with the closest match is chosen for input parameters.

The API LNAPL database contains the following types of information:

- Estimated capillary parameters for the van Genuchten and Brooks-Corey capillary functions for individual samples, and the raw data from which they were derived. This information is available for nearly all samples in the database;

- Petrophysical data including density (bulk/grain), porosity, permeability, and conductivity;

- Water and hydrocarbon saturations, as available;

- Raw grain size distribution data (weight fraction vs. grain size);

- Grain size at various percentages of the cumulative sample weight (*i.e.*, the grain size at the 10th, 50th, and 90th percentiles);
- Grain size distribution statistics (mean, median, standard deviation); and,
- Fraction of the sample in various grain size classifications (% sand, % silt, *etc*.).

The SoilVision (v 4.34) software program includes capillary parameter and other unsaturated soil zone properties for over 6,000 soil samples. The SoilVision data is mostly from tests on agricultural soils. SoilVision v.4.34[1] is a commercially software available from www.**soilvision**.com/.

4.3 Empirical Methods or Pedotransfer Functions

Empirical methods, often called pedotransfer functions (PTFs), are methods where simple soil property data such as percentages of different soil types, bulk density or specific points from a water retention test are correlated to capillary parameters and other hydraulic parameters.

A common model incorporating empirical or neural network methods is the Rosetta model, developed by US Salinity laboratory, which may be used to estimate the following properties:

- Water retention parameters according to van Genuchten (1980);
- Saturated hydraulic conductivity; and,
- Unsaturated hydraulic conductivity parameters according to van Genuchten (1980) and Mualem (1976).

Rosetta offers five PTFs that allow prediction of the hydraulic properties with limited or more extended sets of input data. This hierarchical approach is of practical value because it permits optimal use of available input data. The models use the following hierarchical sequence of input data:

- Soil textural class;
- Sand, silt and clay percentages;
- Sand, silt and clay percentages and bulk density;
- Sand, silt and clay percentages, bulk density an a water retention point at 330 cm (33 kPa); and,
- Sand, silt and clay percentages, bulk density and water retention points at 330 cm and 15,000 cm (33 and 1500 kPa).

In addition to the hierarchical approach, the Rosetta model allows prediction of the unsaturated hydraulic conductivity parameters from fitted van Genuchten (1980) retention parameters (Schaap and Leij, 1999). This model is also used in the hierarchical approach such that it automatically uses the predicted retention parameters as input, instead of measured (fitted) retention parameters. All estimated hydraulic parameters are accompanied by uncertainty estimates that permit an assessment of the reliability of Rosetta's predictions. These uncertainty estimates were generated by combining the neural networks with the bootstrap method (see Schaap and Leij (1998) and Schaap *et al.* (1999) for more information). The Rosetta program is free software that may be downloaded from: http://www.ars.usda.gov/Services/docs.htm?docid=8953.

The SOILPARA program, commercially available software available from http://www.scientificsoftwaregroup.com/pages/product_info.php?products_id=81, allows estimation of the capillary parameters and other unsaturated zone parameters from pedotransfer functions and water retention data.

4.4 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, 2001; 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.

4.5 Fitting Using Measured Grain Size Distribution

Semi-physical methods recognize the shape similarity between the cumulative particle-size distribution and the water retention characteristic. Although these methods do not directly provide hydraulic properties such as the van Genuchten model parameters, they may be used to obtain a water retention curve, to which in turn the van Genuchten model parameters may be fit.

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.

Fredlund *et al.* (2000) present two new models to fit grain-size data and volume-mass data, based on the use of a unimodal and a bimodal mathematical function, which builds the curve by successively estimating a water retention curve for each particle-size group in the grain size distribution. The two new equations provide greater flexibility for fitting a wide variety of soils. The Fredlund *et al.* (2000) model is included in the software SoilVision v.4.34[1].

5.0 REFERENCES

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APPENDIX II

LNAPL MOBILITY MODELING STUDY INPUT PARAMETERS

This appendix presents the model input parameters for evaluation of LNAPL mobility using two models: (i) Darcy's Law used to estimate LNAPL velocity and (ii) displacement entry pressure model used to estimate thickness of LNAPL needed to displace water within pristine soil at the fringe of the LNAPL plume.

The input parameters for the first model are summarized in Table 1, which are soil dependent parameters, and Table 2, which are fixed parameters.

TABLE 1: Input Parameters for LNAPL Mobility Calculation

Parameter	Method or Data Source	Coarse Sand	Medium Sand	Fine Sand	Silty Sand	Silt
VG Alpha (1/m)	API Interactive LNAPL Guide default for different soil textures	3.87	1.51	2.8	1.81	1.1
VG N (dimensionless)	API Interactive LNAPL Guide default for different soil textures	1.62	2.04	2.61	2.02	1.85
Saturated Hydraulic Conductivity (m/day)	API Interactive LNAPL Guide default for different soil textures	11.6	7.3	1	0.292	0.01
Residual Saturation of Water (dimensionless)	API Interactive LNAPL Guide default for different soil textures	0.27	0.29	0.36	0.37	0.32
Total Porosity (dimensionless)	API Interactive LNAPL Guide default for different soil textures	0.33	0.38	0.41	0.46	0.43

TABLE 2: Input Parameters for LNAPL Mobility Calculation

Parameter	Method or Data Source	Value
Hydraulic Gradient (m/m)	Fixed value	0.001 m/m
LNAPL Thickness (m)	Range	Variable
LNAPL Length (m)	Assumed	30 m
LNAPL Width (m)	Assumed	30 m
Density (g/cm^3)	API Interactive LNAPL Guide default for gasoline and diesel	0.73 g/cm^3 (gasoline); 0.83 g/cm^3 (diesel)
Oil/Water Interfacial Tension (dynes/cm)	Representative estimate for weathered gasoline and diesel	24 dynes/cm
Oil/Air Interfacial Tension (dynes/cm)	API Interactive LNAPL Guide default	24 dynes/cm (gasoline); 25 dynes/cm (diesel)
Viscosity (dynes/cm)	API Interactive LNAPL Guide default	0.62 cp (gasoline); 2.7 cp (diesel)