

**LNAPL and
The Massachusetts Contingency Plan**

Part II

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TABLE OF CONTENTS

1.0	INTRODUCTION	1
1.1	Background	1
1.2	Purpose of Part II	2
1.3	Review of MCP Requirements	2
1.4	Applicability to DNAPL	3
2.0	REGULATORY CHANGE RECOMMENDATIONS	4
3.0	DEFINITIONS	6
4.0	LNAPL CHARACTERIZATION FRAMEWORK	8
5.0	LNAPL CHARACTERIZATION CONSIDERATIONS	12
5.1	Introduction	12
5.2	Delineating LNAPL Distribution	12
5.3	Mobility Parameters	17
5.4	Quantifying In-Situ LNAPL Mass or Volume	21
6.0	LNAPL MOBILITY EVALUATION	23
6.1	The Meaning of Mobility	23
6.2	LNAPL Mobility Evaluation Approaches	24
7.0	RISK CHARACTERIZATION CONSIDERATIONS	30
7.1	Risk Characterization Methods	30
7.2	Vapor-Phase Migration	31
7.3	Exposure Pathways	31
7.4	Dissolved Groundwater Migration Pathway	32
7.5	Effect of LNAPL on Risk Characterization Assumptions	33
7.6	Characterizing Risks to Safety, Public Welfare, and the Environment	33
7.7	Managing Exposures via the Implementation of an Activity and Use Limitation ..	34
8.0	SUMMARY AND CONCLUSIONS	35
8.1	Regulatory Change	35
8.2	LNAPL Characterization	36
8.3	Risk Characterization	37
9.0	REFERENCES	39
	ACKNOWLEDGEMENTS	41

APPENDIX – PUBLISHED VALUES FOR RESIDUAL SATURATION AND RESIDUAL CONCENTRATION

1.0 INTRODUCTION

In April 2005 the LSP Association (LSPA) Technical Practices Committee (TPC) issued a White Paper entitled “LNAPL and the Massachusetts Contingency Plan - Part I” (Part I) (LSPA, 2005 Part I). In Part I, it was documented that the conceptual model used to describe the nature, extent, migration and risks associated with light non-aqueous phase liquids (LNAPL) has been shown to be scientifically invalid. This paper (Part II) presents LSPA’s recommended changes to regulations, practice standards and risk assessment procedures as they relate to LNAPL.

1.1 Background

In Part I, conceptual models used to evaluate the presence and behavior of Light Non-aqueous Phase Liquid (LNAPL) in the environment were reviewed. It was concluded that the model proposed by the American Petroleum Industry (API) at <http://groundwater.api.org/lnaplguide> provided the most current thinking on LNAPL behavior. Based on these theories, it was concluded that the model upon which the Massachusetts Contingency Plan (MCP) has based its current LNAPL standards is not an accurate or reliable conceptual model for the existence of LNAPL or to predict LNAPL behavior in the environment. While the presence of LNAPL in a monitoring well may indicate the presence of LNAPL in the environment, the absence of LNAPL from a monitoring well does not indicate the absence of LNAPL in the environment. In the API multiphase flow model, LNAPL contamination is characterized using either a soil concentration or a percent pore saturation basis. In either case, LNAPL is treated as a soil contaminant, as opposed to being considered a “separate” phase contaminant.

LNAPL thickness as measured in monitoring wells is also not a meaningful indicator of the risks to harm required to be addressed by the MCP. Part I concluded that the conceptual model used to evaluate and predict movement and risks associated with LNAPL by the MCP should be reviewed and updated based on the current state of science and technologies used for characterizing the conditions of multiphase fluid flow in porous soil media.

It was recommended that a systematic evaluation be undertaken of the manner in which LNAPL releases are addressed under the MCP. Part I concluded that this evaluation should consider the following:

- LNAPL Site Characterization Requirements
- Data Needs
- Traditional and Emerging Site Characterization Methods
- Applicable and Alternative Analytical Methods
- Data Assessment Methods
- Special Risk Evaluation Requirements
- Recommended Regulatory and Policy Updates/Changes

1.2 Purpose of Part II

“LNAPL and the Massachusetts Contingency Plan, Part II” identifies areas for improvement for evaluating LNAPL sites under the MCP and presents recommendations for:

- Regulatory Change;
- Practice Standard Change; and,
- Risk Characterization.

It further reviews existing requirements of the MCP and identifies alternative methodologies to improve data collected for release characterization, risk characterization and MCP compliance purposes. Recommendations for changing/refocusing technical practice standards and clarifications for practice improvements for risk characterization at LNAPL sites are provided. Alternative evaluation approaches to the LNAPL UCL in the MCP are discussed and recommendations for regulatory changes are provided, including modification of the current product thickness-based notification criteria and options to the elimination of the LNAPL UCL.

1.3 Review of MCP Requirements

LNAPL can migrate significant distances if the release source is not eliminated or if preferred migration pathways are encountered. Migrating LNAPL has the potential to impact soil, groundwater, sediment, surface water bodies and water supply wells, and it can appear in underground utilities that intercept the release. LNAPL can also act as a source for vapor migration to ambient or indoor air and pose an odor nuisance. It can be a source of dermal and inhalation risk and a possible explosion hazard if encountered unexpectedly during excavation activities.

The MCP currently requires the assessment and evaluation of risks associated with these various pathways and contaminated media. The MCP contains performance standards for site characterization, including determining the nature and extent of contamination, and routes of exposure. Temporal data is needed to evaluate groundwater contamination migration potential. Risk characterization requirements and guidance documents provide characterization methods and approaches for evaluating the regulatory impacts of identified contaminated soil gas, soil, groundwater, sediment and surface water. The MCP provides concentration-based Upper Concentration Limits (UCLs) to assess public welfare risk for petroleum contamination fractions and compounds of concerns in soil and groundwater. Criteria are also provided to define environmental risks in the form of an environmental Area of Readily Apparent Harm (ARAH). This paper presents suggestions for refinements in the manner by which some of these potential risks are addressed at LNAPL sites.

This paper takes the position that there are sufficient provisions currently present in the MCP to determine remediation requirements for LNAPL releases without compliance with a thickness-based UCL. Most of the provisions exist within the current MCP requirements used to characterize risk. However, an important, and often under-addressed, criteria for evaluating the impacts of LNAPL releases exists within the supplemental requirements that apply to obtaining all permanent solution Response Action Outcome Opinions contained in

310 CMR 40.1003(5). This is the obligation to demonstrate that the release is not a continuing source of contamination as a consequence of intermedia transfer.

Assuming the evaluation of preferred LNAPL migration pathways and soil, vapor and groundwater related risks are addressed within the current structure of the MCP, temporal data and the comparison of site data to soil and groundwater UCLs provides most of the assessment methodology needed to evaluate response action requirements for LNAPL releases. For a permanent solution, the last demonstration in 310 CMR 40.1003(5) requires that it be shown that the LNAPL is not a source of new or increased contamination in soil gas, groundwater, sediment, surface water and soil. Evaluation of possible new contamination of soil has often been overlooked. While it could be said that the layer thickness-based UCL for LNAPL served, in part, as a check or bound for this continuing source evaluation, work by API has shown that alternate, scientifically based methods are available to make this evaluation. The most applicable to this provision of the MCP is the evaluation of LNAPL mobility in soil that can now be evaluated through site characterization and analytical and field-testing protocols. Thus, the LNAPL thickness-based UCL is superfluous. This paper proposes that a mobility evaluation approach replace the current, arbitrarily selected LNAPL UCL, while still retaining the existing soil concentration-based approach to UCLs.

1.4 Applicability to DNAPL

This paper specifically addresses recommended regulatory changes and alternate practice standards for the evaluation of LNAPL releases into the environment. The TPC discussed including DNAPL in this paper, but concluded that since the API science has been developed for LNAPLs, there could be significant technical differences between LNAPL and DNAPL characteristics, mobility forces, assessment procedures and risk evaluation methods, and therefore only LNAPL should be addressed. Nevertheless, the TPC recognizes that many of the technical concepts that apply to LNAPL (e.g., multiphase flow theory), will also apply to DNAPL. Therefore the TPC recommends that current regulatory requirements affecting DNAPL sites, in particular a DNAPL thickness UCL, be evaluated to assess whether better scientifically valid procedures can be used.

2.0 REGULATORY CHANGE RECOMMENDATIONS

LSPA recommends changes to the Massachusetts Contingency Plan that incorporate the current understanding of LNAPL behavior in the environment as summarized in Part I. The following specific changes to the MCP are recommended:

1. Eliminate the LNAPL Thickness-Based Upper Concentration Limit (UCL) – In Part I, the scientific invalidity of the “tank and pancake model” was demonstrated, and the need for updated regulations based on scientifically defensible theories was recommended. Consequently, the LSPA recommends eliminating the existing LNAPL thickness-based UCL. A principal recommendation of Part I was to characterize LNAPL in the environment as a contaminant in soil. Therefore, the existing concentration-based UCLs for soil are sufficient for the evaluation of risk of harm to public welfare.
2. Streamline Notification Regulations for LNAPL – The presence of a measurable amount of LNAPL in a monitoring well is a reasonable and conservative indicator of the possible need to further characterize a release of LNAPL to the environment. It also provides an easily measurable notification criterion. However, concluding that there is a distinction between a thickness of 1/8-inch and 1/2-inch in a well or the environment that justifies different notification criteria is not currently supported. Therefore, the LSPA recommends that the MCP should contain only one notification criteria based on a measured thickness of LNAPL in the environment. The recommended criterion is the minimum measurable amount (typically 0.01 feet [1/8 inch] or greater) and the notification time frame is recommended to be within 72 hours of obtaining knowledge.
3. Redefine Nonaqueous Phase Liquid and NAPL – The current definition of NAPL in the MCP is as follows:

Nonaqueous Phase Liquid and NAPL each means oil and/or hazardous material that is present in the environment as a continuous separate phase as measured in a groundwater monitoring well or otherwise observed in the environment. (310 CMR 40.0006)

LSPA recommends changing the definition of NAPL to reflect the fact that NAPL may be discontinuous within a soil pore space, and may be present in soil but not detectable in a groundwater monitoring well. This understanding of how NAPL is defined will allow characterization of NAPL solely as a contaminant in soil consistent with recommendations in Part I. LSPA recommends the following definition of NAPL:

Nonaqueous Phase Liquid and NAPL each means oil and/or hazardous material, or a mixture thereof, that is present in the environment as a separate non-gaseous phase liquid and that is relatively immiscible with water.

4. Define “Secondary LNAPL Source” – Add a definition to 310 CMR 40.0006 for “Secondary LNAPL Source” to reflect the ability of residual LNAPL to act as an ongoing source for intermedia transfer of LNAPL constituents to groundwater and soil vapor, or to create a sheen on surface water. The purpose of the proposed definition is to differentiate *in-situ* residual sources from the recognized definitions in the MCP for Known Source, Point Source and Unknown Source, all of which generally refer to original sources of release, typically from tanks, vessels, conduits, tunnels, etc. The following definition is recommended:

Secondary LNAPL Source means LNAPL that exists in soil pore spaces or rock fractures, and that is acting or has the potential to act as an ongoing source for intermedia transfer of contaminants to soil, rock, groundwater, surface water or soil vapor at increasing concentrations.

5. Eliminate references to LNAPL thickness from the definition for “Hot Spot” listed in 310 CMR 40.0006. LSPA recommends that LNAPL hot spots be defined based on soil concentration data only.

3.0 DEFINITIONS

The current definition for Nonaqueous Phase Liquid (NAPL) as identified in the MCP (310 CMR 40.0006) is:

“Nonaqueous Phase Liquid and NAPL each means oil and/or hazardous material that is present in the environment as a continuous separate phase as measured in a groundwater monitoring well or otherwise observed in the environment.”

The LSPA recommends the definition for Nonaqueous Phase Liquid (NAPL) be changed to:

“Nonaqueous Phase Liquid and NAPL each means oil and/or hazardous material, or a mixture thereof, that is present in the environment as a separate non-gaseous phase liquid, and that is relatively immiscible with water.”

This recommended definition is the definition used throughout this paper. Definitions of other terms used in this paper and not otherwise defined in the MCP (310 CMR 40.0006) include:

Dense Nonaqueous Phase Liquid and DNAPL – NAPL with a specific gravity greater than the specific gravity of water.

Intrinsic Permeability – A measure of the relative ease with which a permeable medium can transmit a fluid (liquid or gas). Intrinsic permeability is a property only of the medium and is independent of the nature of the fluid.

Light Nonaqueous Phase Liquid and LNAPL – NAPL with a specific gravity less than the specific gravity of water.

LNAPL Mobility (M_o) – Potential for LNAPL to move through soil based on local area effective conductivity and gradients with respect to the LNAPL. LNAPL mobility can occur when the pressure in the NAPL is great enough to displace water at the limits of the NAPL Plume.

LNAPL Plume Stability – General term for conditions where, for practical purposes, the LNAPL-impacted zone is not expanding laterally or vertically.

LNAPL Recoverability – The ability to extract some portion of LNAPL from the soil pore space using gravitational recovery methods.

LNAPL Residual Concentration – Concentration-based equivalent to LNAPL Residual Saturation (often expressed as milligrams (mg) of LNAPL per kilogram (kg) of soil).

LNAPL Residual Saturation – a percentage of pore space occupied by LNAPL below which LNAPL will not migrate due to convection or gravity.

LNAPL Specific Volume – Volume of LNAPL per unit area at a specific location.

LNAPL Total Volume – Volume of LNAPL present in the LNAPL-impacted area.

PM₁₀: Particulate matter that is equal to or less than 10 microns in diameter (DEP, 2002e).

Pore Saturation – Portion of the pore space occupied by a given fluid.

Porosity – Volume of the matrix void space divided by the total matrix volume.

Potential LNAPL Mobility – A condition where LNAPL saturation exceeds LNAPL residual saturation.

Primary LNAPL Source – Vessel (e.g., a leaking storage tank) or activity (e.g., spills) that first introduced the LNAPL into the environment.

Recoverability – General term for the degree to which a volume of LNAPL is hydraulically recoverable as compared to the LNAPL Total Volume, expressed as a percentage of the total LNAPL volume.

Relative LNAPL Permeability – A parameter that expresses the ability of one fluid to flow in soil pore space in the presence of other pore fluids. Relative LNAPL permeability is defined as the ratio of the permeability of LNAPL at a given saturation to the LNAPL permeability at 100 percent saturation. If LNAPL completely saturates the pore space, the relative LNAPL permeability is equal to 1.0. If no mobile LNAPL is present, the relative LNAPL permeability is zero.

Secondary LNAPL Source – LNAPL that exists in soil pore spaces or rock fractures, and that is acting or has the potential to act as an ongoing source for intermedia transfer of contaminants to soil, rock, groundwater, surface water or soil vapor at increasing concentrations.

Soil Saturation Limit (C_{sat}) – Contaminant concentration in soil at which the absorptive limits of the soil, the solubility limits of the soil pore water, and the saturation of the soil pore air have been reached. Above this concentration, the contaminant will be present in a non-aqueous phase.

Weighted Dermal Adherence Factor (WDAF): Skin-soil adherence factor that describes the amount of soil that adheres to the skin per unit of skin surface area (DEP, 2002c).

4.0 LNAPL CHARACTERIZATION FRAMEWORK

This section describes a framework for characterizing the nature and extent of LNAPL contamination that is consistent with the Part I recommendation to characterize LNAPL as a soil contaminant.

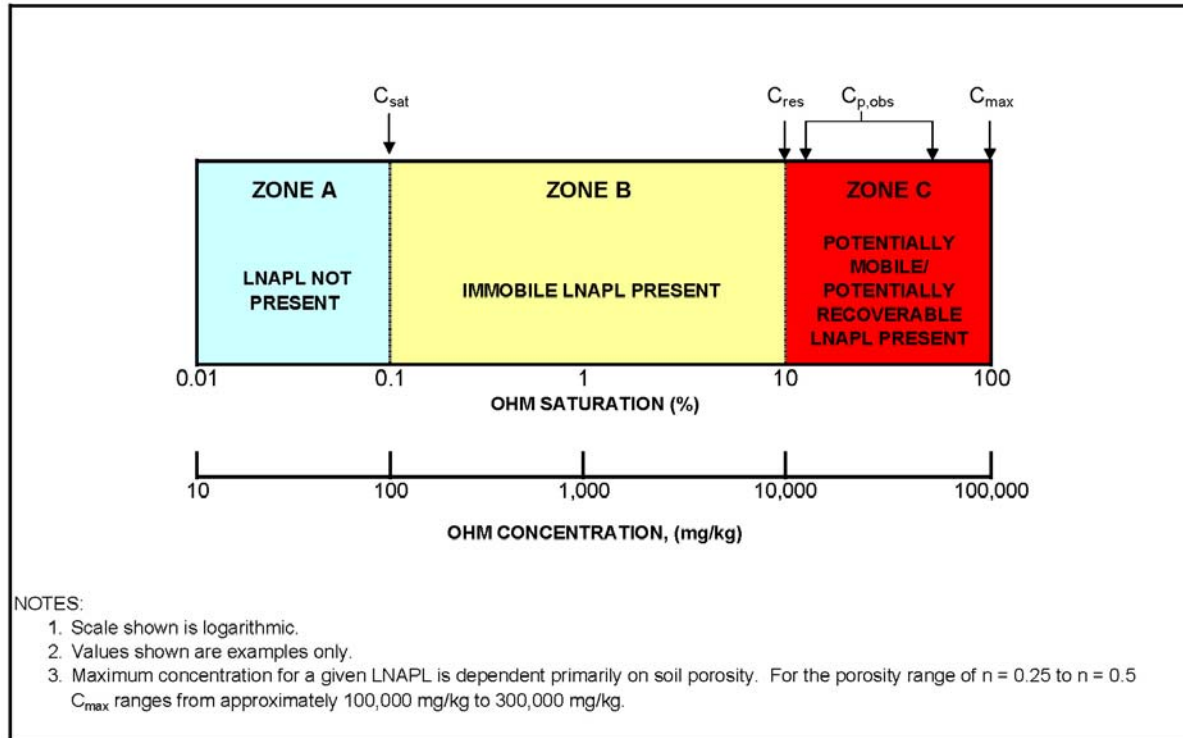
The quantity of LNAPL in a soil matrix is typically characterized on either a concentration basis (weight of LNAPL/weight of soil), or a saturation basis (percentage of pore space occupied by LNAPL). Concentration data may be expressed as either wet weight or dry weight. The convention in the MCP is to use dry weight. The choice of a characterization method is based on the intended use of the data. Most LNAPL data currently generated by LSPs is concentration based using the Extractable Petroleum Hydrocarbons (EPH) and Volatile Petroleum Hydrocarbons (VPH) testing procedures developed by the Massachusetts Department of Environmental Protection (MassDEP). Nationally, many practitioners prefer to use LNAPL saturation, especially when using data as inputs to commonly used computer models.

Regardless of the method used to express the quantity of LNAPL in soil, it is important that LSPs have a consistent method for incorporating the data into a meaningful conceptual site model. For this reason, this section describes a framework referred to as the “LNAPL Continuum” for understanding LNAPL characterization data. The LNAPL Continuum is simply the range of possible LNAPL concentrations or saturations, shown on a linear scale, divided into three zones that are separated by measurable or easily estimated values. The three zones of the LNAPL Continuum are described below:

- Zone A – LNAPL Not Present – In Zone A LNAPL constituents may be present in pore water in the dissolved phase, in pore air in equilibrium with the dissolved phase fraction, and sorbed to organic carbon in soil. Zone A is defined as soil containing LNAPL constituent concentrations (or equivalent saturations) less than the soil saturation limit (C_{sat}) (Brost et al., 2000).
- Zone B – Non-mobile LNAPL Present – Zone B is defined by soil concentrations (or equivalent saturations) greater than C_{sat} , but less than C_{res} , the residual soil concentration (or equivalent saturation). In Zone B of the LNAPL Continuum LNAPL is present in soil but is effectively immobile and non-recoverable under gravitational forces.
- Zone C – Potentially Mobile/Potentially Recoverable LNAPL Present – Zone C is defined as soil concentrations (or equivalent saturations) greater than C_{res} . The word “potential” is used to describe both the mobility and recoverability of LNAPL in Zone C because simply exceeding C_{res} does not necessarily mean that LNAPL is actually migrating, nor does it mean that the LNAPL will be recoverable in any significant quantity. The value of C_{res} can also be considered the lower limit of LNAPL recoverability. Therefore, if LNAPL concentrations in the field only slightly exceed C_{res} , the quantity of LNAPL likely to be recovered will be minimal. LNAPL in Zone C has a relative permeability to flow greater than zero.

The LNAPL Continuum is graphically depicted in Figure 1 below:

Figure 1 – The LNAPL Continuum



As described above, the separation points between zones of the LNAPL continuum are the soil saturation limit (C_{sat}) and residual NAPL (C_{res}). The soil saturation limit (C_{sat}) is a parameter that can be calculated for any NAPL, and is most sensitive to aqueous solubility. According to Brost et al. (Brost et al.,2000), “For a pure chemical, NAPL will not be present at concentrations below the soil saturation limit.” Also from Brost et al. “For mixtures of miscible chemicals that are fractionally soluble in water, including petroleum, the concentration at which NAPL will be present is a function of the mixture composition.”

From the definition of C_{sat} above, it is clear that C_{sat} can be used to define the lowest concentration at which LNAPL would be present at release sites. Understanding the meaning of C_{sat} is also important for LSPs because LNAPL existing at concentrations greater than C_{sat} may act as a continuing source for dissolved phase and vapor phase migration of contaminants for an indefinite period of time.

Table 1 below shows values of C_{sat} presented by Brost et al. for common LNAPLs.

Table 1 – Values of C_{sat} for Common LNAPLs

LNAPL TYPE	AQUEOUS SOLUBILITY (mg/L)	C _{sat} (mg/kg)
Benzene	1,750	444
Gasoline	164	106
Diesel Fuel	3.9	18
Mineral Oil	0.36	3

Source: Brost et al, 2000.

Note that for the example illustrated above, a soil water content of 0.12 cm³-water/cm³-soil and a mass fraction of organic carbon (f_{oc}) of 0.05 g-oc/g-soil were assumed. This example primarily illustrates the dependency of C_{sat} on aqueous solubility.

Residual concentration, C_{res}, is defined by Brost et al. as “a soil concentration below which NAPL, if present, will not migrate due to convection or gravity.”

The following passage, also from Brost et al. aptly describes the significance of C_{res}:

Below the residual NAPL concentration in soil, C_{res,soil} capillary retention forces are greater than the gravitational forces which tend to mobilize the NAPL. These capillary forces (in this context, including surface tension effects, van der Waals, and Coulombic forces), particularly at low residual non-aqueous phase levels, may exceed the gravitational force by several orders of magnitude. The residual NAPL concentration in soil, C_{res,soil} may depend on NAPL properties including liquid density, surface tension, and viscosity. It also may depend on soil properties including porosity, organic carbon fraction, moisture content, relative permeability, moisture wetting history, and soil heterogeneity.

Two additional markers along the LNAPL continuum worthy of mention are the maximum theoretical concentration (C_{max}), and observed peak concentration in the field (C_{p,obs}). Maximum concentration, C_{max} is simply the soil concentration equivalent to 100% pore saturation. Maximum theoretical concentration of the LNAPL in soil (C_{max}) can be calculated for a given soil type and LNAPL type using the following equation:

$$C_{\max} = \frac{(n G_L)}{(1-n) G_S} \cdot 1E6 \quad (1)$$

Where:

C_{max} = Maximum theoretical concentration of LNAPL in soil at 100% pore saturation (mg/kg)

n = Porosity (dimensionless)

G_L = Specific gravity of LNAPL (dimensionless)

G_S = Specific gravity of solids (dimensionless)

For sands and silty sands porosity typically varies from approximately $n = 0.25$ to $n = 0.50$ (Freeze and Cherry, 1979). The specific gravities of common LNAPLs (γ_L) such as gasoline and fuel oil typically range from about 0.8 to 0.9, and the specific gravity of soil (γ_S) of 2.7 is commonly assumed. Using these values, C_{max} ranges from approximately 100,000 mg/kg to 300,000 mg/kg. From this example it is demonstrated that the maximum theoretical concentration of LNAPL in soil is highly sensitive to porosity.

While 100% LNAPL saturation is theoretically possible, it has been observed that in the field the observed peak saturations are typically between 10% and 50% (Adamski, et al. 2003). LNAPL that exists in the narrow range of the LNAPL Continuum between C_{res} and $C_{p,obs}$ represents the potentially recoverable fraction of LNAPL using gravitational recovery methods.

5.0 LNAPL CHARACTERIZATION CONSIDERATIONS

5.1 Introduction

In Part 1 it was established that the “Tank and Pancake” model does not accurately predict the spatial distribution or temporal behavior of LNAPL in the environment. Since the Tank and Pancake model has been the dominant LNAPL conceptual model for several years, many practice procedures have evolved to gather data based on this model.

A conceptual model referred to as the “multi-phase flow model” was introduced in Part 1. This model is considered to more accurately describe the distribution and mobility of LNAPL in the environment. The purpose of this section is to present site characterization procedures that can be used to obtain the data needed to evaluate LNAPL conditions, characterize risk and evaluate intermedia contaminant transfer. These procedures are founded on the conclusion of Part I that LNAPL should be treated as a soil contaminant, rather than as a “separate-phase” liquid contaminant. The goals of these data collection procedures are to develop a data set for:

- Delineating the three-dimensional distribution of LNAPL at MCP disposal sites;
- Performing LNAPL mobility assessments; and,
- Calculating LNAPL release volume/mass estimates.

5.2 Delineating LNAPL Distribution

This section describes techniques for characterizing the three-dimensional distribution of LNAPL at disposal sites. It is recognized that each disposal site is unique, and that these unique characteristics must be considered when designing a field program. Nevertheless, certain features of LNAPL releases are predictable, and should be understood when designing field assessment programs. These features are:

- LNAPL does not “float” on the groundwater table in a continuous and discrete layer, but rather is found in a zone of variable saturation/concentration in soil extending both above and below the average water table level. The thickness of this LNAPL-impacted soil horizon can greatly exceed the thickness of LNAPL measured in groundwater monitoring wells.
- In most cases, LNAPL will not completely saturate the soil pore space where both LNAPL and water are present. Generally, the denser fluid (i.e. water) in a porous medium will coat the soil particles; this denser fluid is referred to as the “wetting” fluid. LNAPL is generally the “non-wetting” fluid below the water table, and will only fill the intermediate and larger pore spaces. Water will occupy the smaller interstitial pore spaces, and usually accounts for a greater percentage of the filled pore space than does LNAPL. As described in Section 4.0, peak LNAPL saturation is generally measured between 10 to 50 percent pore saturation.

- The highest concentration of LNAPL-impacted soil in a vertical profile is usually found near the average water table. However, LNAPL-impacted soil will usually be found both above and below the peak impacted zone, and may extend several feet below the average water table elevation. The classical vertical distribution of LNAPL contamination in a uniform soil is typically triangular in shape increasing to a high concentration and then decreasing with depth. However, LNAPL saturation profiles can vary widely with changing soil properties across the LNAPL impact zone.

LNAPL site characterization should therefore include installing a sufficient number of soil borings to define the lateral extent of contamination, and collecting and testing a sufficient number of locations within the impact zone to understand the vertical LNAPL distribution and saturation conditions. The number of assessment locations will vary on a site-by-site basis depending on the LNAPL and the magnitude of the release. Iterative assessments are frequently required to adequately define the extent of contamination and preferential migration pathways of the LNAPL.

5.2.1 Soil Sampling

The key to successful vertical delineation of the LNAPL saturation profile is collecting and analyzing a representative number of soil samples from the LNAPL-impacted vertical profile. Samples can be collected using many methods, including direct-push, split-spoon samplers, fixed-piston tube samples, etc. A complete discussion of sampling techniques is beyond the scope of this paper, but it should be recognized that the types of soil expected to be found at a site should be considered when designing a field sampling program. Samples within the impacted zone generally need to be collected sequentially and more frequently than the standard 5-foot intervals. At many sites it may be possible to collect soil samples using a direct push drilling rig such as a Geoprobe™. However, direct push methods may be unsuccessful at sites containing large quantities of fill, debris, gravel, cobbles and boulders. Use of 3-inch diameter split-spoon samplers, Shelby tubes and other undisturbed samplers is helpful on some sites. Continuous sampling over the critical depth interval is often required.

After soil samples are collected, samples need to be selected for laboratory analysis. While this may seem trivial, careful selection and preparation of samples is necessary. For example, if direct-push methods are used, cores that exceed 4 feet in length may be in-hand. Since the LNAPL-impacted zone may be less than ten feet thick, the question becomes how many sub-samples to submit to get adequate vertical resolution.

When split-spoon soil samples are collected, the sample length is usually 2 feet or less. Collecting a single composite sample from each spoon is usually adequate to provide good vertical resolution. However, it may be desirable to subdivide the sample if strata changes or zones with more LNAPL impact are observed within a split-spoon sample. In situations where site soils are highly stratified, and where the

strata are laterally continuous, it will be necessary to carefully evaluate the LNAPL impacted zone to identify individual strata that may account for the bulk of LNAPL mobility.

5.2.2 Evaluating LNAPL Soil Saturation and Concentration

The selection of appropriate analytical testing methods must take into account the intended use of the data. In Massachusetts, the Extractable Petroleum Hydrocarbon (EPH) and Volatile Petroleum Hydrocarbon (VPH) tests are the most commonly used methods for characterizing soils from petroleum LNAPL sites. These methods were developed as health risk-based alternatives to Total Petroleum Hydrocarbon (TPH) tests, and are therefore well suited to petroleum-based LNAPL risk characterization. However, when the LNAPL is non-petroleum, or when data uses beyond risk characterization are important, other analytical methods may be selected, in order to quantify all fractions (volatile, non-volatile and heavy) of the hydrocarbon present.

Practitioners nationwide characterize LNAPL by a variety of established methods, using differing standards and extraction procedures, to quantify the volume of LNAPL by percentage of pore space containing LNAPL and weight of LNAPL per weight of soil (concentration basis). Appropriately collected data from these analyses may be used to evaluate LNAPL mobility and potential recoverability.

While not routinely employed, freezing core samples (using dry ice or liquid nitrogen) immediately after sampling is becoming a more common procedure for large or sensitive LNAPL-impacted sites. The purpose of soil freezing is to minimize redistribution of LNAPL within the soil sample, and to preserve the soil structure. Frozen samples are typically cut vertically upon receipt at the laboratory and photographed under white light and ultraviolet (UV) light. White light photography is used to evaluate grain shape, porosity, soil structure and preferential drainage pathways. UV photography allows the practitioner to identify LNAPL that fluoresces under ultraviolet light, and to identify LNAPL/moisture/air distribution relationships within the soil structure. This information can then be used to select sub-samples for applicable laboratory procedures.

5.2.3 Field Soil Screening Techniques

Traditional screening techniques, such as headspace screening using photo-ionization detectors, are not well suited for accurate LNAPL quantification, and are recommended only as an indicator of the presence of LNAPL or dissolved phase hydrocarbons in soil. Many other field soil screening methods are available to quantify LNAPL in soil samples. LSPA (2005) summarized an evaluation program conducted by EPA as part of its Superfund Innovative Technology Evaluation (SITE) program where seven field TPH screening devices were compared.

TPH detection technologies evaluated by EPA included ultraviolet fluorescence (UVF), synchronous fluorescence, emulsion turbidimetry, infrared analysis, modified

Friedel-Crafts alkylation reaction and colorimetry, and immunoassay-colorimetry. Complete results of the EPA evaluation are available at <http://www.epa.gov/nerlesd1/cmb/site/pdf/papers/sb103.pdf>.

Of the seven technologies evaluated, EPA concluded that those employing UVF and modified Friedel-Crafts alkylation reaction and colorimetry could be considered reliable. EPA recommended exercising caution when using the other technologies.

5.2.4 In-situ Vertical Profiling

For large and/or complicated sites, a number of in-situ techniques have been developed to provide rapid, high-resolution vertical profiles for LNAPL sites. These techniques generally employ direct push or vibratory push techniques to advance a probe through the LNAPL contaminated zone. The probes are fitted with various sensors or solid phase extraction devices to detect and quantify LNAPL saturation/concentration. Soil conditions strongly influence the applicability of these methods on Massachusetts sites. Each technique offers the advantage of speed and resolution, but calibration of the data to known saturations/concentrations must be performed to provide quantitative data.

It is beyond the scope of this paper to provide a thorough review of all available *in-situ* profiling techniques. Some commonly used methods are described briefly below. Many of these techniques may have limited applicability in Massachusetts due to the predominance of glacial till, shallow bedrock, and fills containing large obstructions.

Laser Induced Fluorescence (LIF)

Laser-induced Fluorescence (LIF) refers to a fluorescence-based technology adapted for in-situ vertical characterization of LNAPL source areas. Available LIF systems include the Ultraviolet Optical Screening Tool (UVOST™), and the Rapid Optical Screening Tool (ROST™) systems. The UVOST™ system is available commercially from Dakota Technologies, Inc., and the ROST™ system is available through Fugro, Inc.

Both systems work in a similar manner, and use a laser to provide excitation energy to polyaromatic hydrocarbons in LNAPL in the subsurface. The laser energy excites the aromatic hydrocarbons, causing them to emit fluorescence. The emitted fluorescence is detected by a down-hole sensor, and the signal is transmitted to receiving and recording equipment at the ground surface.

Benefits of LIF include the ability to generate real-time, highly detailed vertical profiles. By varying the laser wavelength it is possible to measure the fluorescence of different portions of the carbon spectrum, and thus provide a simplified “hydrocarbon fingerprint.”

Although LIF provides a high resolution LNAPL profile, the data generated is qualitative or used semi-quantitatively for LNAPL concentrations in soil down to 100 mg/kg. To develop meaningful quantitative data, the LIF data must be calibrated to known LNAPL concentrations.

Membrane Interface Probe System (MIPS)

The Membrane Interface Probe System (MIPS) is a cone penetrometer-based probe used to screen for the presence of high concentrations of dissolved volatile organic compounds (VOCs) in groundwater. MIPS uses a heated, semi-permeable membrane in the tip of the cone penetrometer. VOCs diffuse through the MIPS membrane into a carrier gas that circulates through tubing in the CPT tip. The carrier gas is carried to instruments at the ground surface for detection and analysis.

Since MIPS is primarily intended to quantify dissolved phase VOCs, its application for NAPL sites is limited primarily to identifying the vertical limits of the NAPL saturated zone and not quantifying the soil concentration.

5.2.3 Groundwater Monitoring Wells

While the emphasis of this section is on the collection of representative soil samples, the use of groundwater monitoring wells for LNAPL site characterization is also of importance. Groundwater monitoring wells located within LNAPL-impacted soil zones are frequently used primarily to measure in-well LNAPL thickness. As discussed in Part 1, this practice is discouraged as a principal technique for delineating LNAPL spatial distribution in soil. Nevertheless, groundwater monitoring wells still serve a useful function for LNAPL investigations. In particular, the following uses are identified for LNAPL investigations:

- Collecting groundwater samples for dissolved phase characterization;
- Measuring piezometric elevation;
- Collecting LNAPL samples to measure physical properties (such as viscosity, density, interfacial tension) and to measure chemical properties (LNAPL fingerprinting or more advanced forensic testing);
- Measuring for the absence or presence of LNAPL or sheen on groundwater;
- Performing borehole hydraulic conductivity (permeability) tests; and
- Performing “bail-down” tests to evaluate potential product recovery rates.

Groundwater monitoring wells may also be used to perform pilot scale LNAPL recovery tests, or may be incorporated into full-scale recovery systems (e.g., multi-phase extraction systems). They may not be ideal for use as recovery wells if the monitoring well screen is not centered on the LNAPL-impacted soil zone.

When a significant LNAPL thickness is present in a groundwater monitoring well, it is customary to calculate a “corrected” piezometric elevation based on the elevation

of the air/LNAPL interface, the thickness of LNAPL, and the density of the LNAPL in the well.

5.3 Mobility Parameters

As described in Section 6.0, the mobility of LNAPL in soil can be calculated with knowledge of LNAPL viscosity, relative LNAPL permeability and intrinsic soil permeability. Knowing the intrinsic soil permeability allows the calculation of the conductivity of the soil matrix with respect to different pore fluids of known dynamic viscosity and density.

Dynamic Viscosity

Dynamic viscosity (μ) is a measure of a fluid's resistance to shear force, and is typically measured in a laboratory using available test procedures (e.g., ASTM D445-06 *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)*). Dynamic viscosity is frequently expressed in units of centipoises.

Viscosity is highly dependent on temperature. Therefore, laboratory measurement of viscosity should be performed at the in-situ groundwater temperature, or over the range of known site groundwater temperatures. Generally speaking, over small temperature ranges the logarithm of viscosity will be inversely proportional to temperature.

Density

LNAPL by definition is less dense than water. The density of petroleum LNAPL is generally found in the range of about 0.7 to 1.0 g/cc. LNAPL's density is much less temperature dependent than its viscosity, and can generally be considered a constant over the normal range of groundwater temperature fluctuation. Density can be measured in accordance with ASTM D1481.

Relative LNAPL Permeability

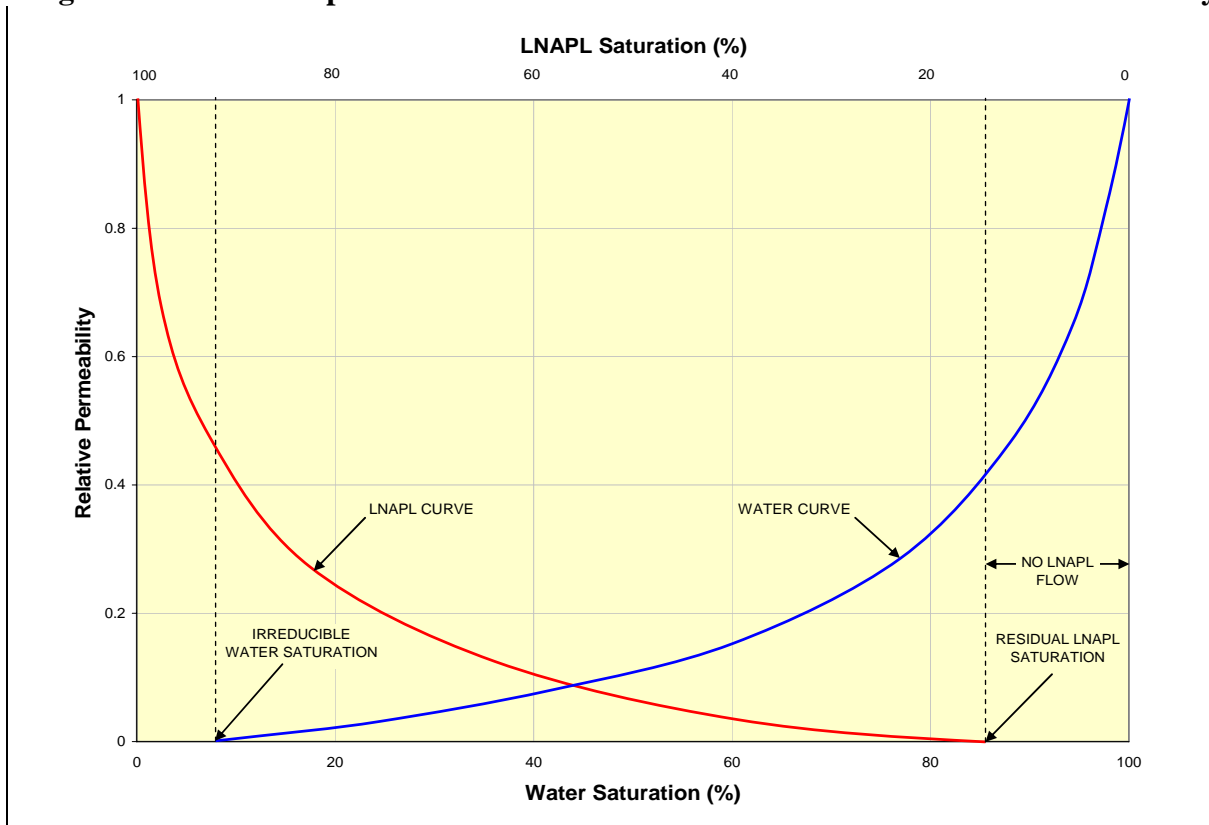
When immiscible fluids are present in soil pore spaces, they generally flow independently of one another. Relative permeability is defined as the ratio of the effective permeability for a particular fluid at a given saturation to the saturated permeability for that fluid. Effective permeability is the permeability at a saturation less than 100 percent. Relative permeability can also be used to quantitatively represent the ability of one fluid to flow in the presence of another. In most LNAPL situations, the two fluids are the LNAPL and water.

Relative LNAPL permeability (k_{ro}) is used to quantitatively describe the reduced permeability of soil to LNAPL resulting from LNAPL occupying only a portion of the total pore space. Note that while the term "Relative Oil Permeability" is more commonly found in the literature, the term "Relative LNAPL Permeability" is used in this paper to provide consistent terminology.

As the LNAPL concentration in soil increases as a non-wetting fluid in the presence of groundwater, a minimum level of LNAPL saturation must be achieved before LNAPL can

flow. At a level of saturation known as the residual saturation, the relative permeability of the LNAPL, k_{ro} is equal to 0.0. To quantify LNAPL mobility at LNAPL saturations greater than residual saturation, the relative LNAPL permeability-saturation curve can be developed. Figure 2 illustrates the general relationship between relative LNAPL permeability and LNAPL.

Figure 2 - Relationship Between LNAPL Saturation and Relative LNAPL Permeability



Developing the relative permeability relationships between fluid saturations (e.g., water and LNAPL) in soil can be performed in the laboratory using capillary pressure testing (ASTM Method D425 centrifugal method) or unsteady state relative permeability tests (ASTM D6836-02). These types of tests are used to simulate the flow of LNAPL in the field under various pressure, flow and saturation conditions. The centrifugal method of capillary testing can also be used to provide an estimate of the residual oil saturation in soil.

More advanced techniques for assessing the relationship of LNAPL movement to groundwater flow utilize the unsteady state relative permeability test to simulate field conditions. The test can demonstrate how an LNAPL saturated sample would drain under constant groundwater flow conditions. The simulation of the seepage velocity of groundwater in the field will show how the relative permeability and LNAPL volume in the sample will change with pressure, drainage of LNAPL, and pore volume.

Both testing procedures described above characterize the mobility, fate and transport conditions of LNAPL. Testing of this type must carefully consider sample collection, selection and handling procedures as “undisturbed” representative samples are required.

Intrinsic Permeability

Intrinsic permeability (k_i) is a parameter used to express the resistance to flow of fluids in a porous matrix independent of the fluid type. Theoretically, intrinsic permeability can be used to calculate the hydraulic conductivity of any single fluid in a soil using the first of the following relationships:

$$K = (k_i \rho g) / \mu \quad \text{or} \quad k_i = (K\mu) / \rho g \quad (2)$$

Where:

K = Hydraulic conductivity at 100% pore saturation [L/T]

k_i = intrinsic permeability [L^2]

ρ = fluid density [M/L^3]

g = gravitational constant [L/T^2]

μ = dynamic viscosity [M/LT]

Both intrinsic permeability and hydraulic conductivity can be measured using field or laboratory techniques. It is beyond the scope of this paper to provide a thorough review of these techniques. Nevertheless, it should be noted that field measurements are generally considered more indicative of actual formation conditions than laboratory measurements.

Baildown Tests

The use of baildown tests for LNAPL mobility evaluation is documented by API (API, 2004). The definition and units for LNAPL mobility based on slug tests are different than the recommended definition for mobility presented in Section 2.0. The API baildown test results are analyzed using procedures similar to those for analyzing borehole permeability “slug” tests. Test results are expressed as LNAPL transmissivity values. These transmissivity results are used to calculate LNAPL inherent mobility.

Residual Concentration/Saturation

Residual soil concentration (C_{res}) or residual soil saturation (S_{res}) can be measured directly for a soil sample in the laboratory. These measurements can be used to estimate LNAPL recoverability and for evaluating LNAPL mobility.

Methods for measuring LNAPL saturation conditions in soil in the laboratory utilize Dean Stark (API RP40) and other procedures such as Soxhlet extraction to extract and quantify the LNAPL on a pore saturation basis.

In the laboratory, residual saturation levels can vary significantly between soil types with varying levels of gradation, composition, texture and other physio-chemical properties, in combination with the LNAPL itself. Capillary pressure testing (centrifugal method) has been used to define a high boundary value for a residual saturation level of LNAPL in soil using ASTM Method D425. This method evaluates the residual saturation and potential mobility of a sample utilizing a single point of applied pressure of 1000 G's on a soil for 1 hour to simulate long-term drainage effects (change in soil LNAPL saturation). Applications of this method have been used to define highly conservative levels of residual LNAPL saturation in impacted soil. The method has further value in the simple evaluation of the change in saturation in the sample under extreme conditions to determine: 1) what volume of LNAPL might be recovered from the soil under rigorous pressure conditions, and 2) whether or not LNAPL will drain from the sample. The method has some variance, typically less than one percent of the change in LNAPL, attributed to matrix compression.

Establishing a residual level of saturation in soil can be more practically developed from the moisture saturation relationship between fluids in soil, at increasing levels of capillary pressure above zero. Capillary pressure curves that develop the drainage/imbibition (displacement of the non-wetting phase) relationship between LNAPL, water, and air will typically stabilize at significantly lower testing pressures than the centrifugal method. These curves, where they approach saturation equilibrium, can be used to define LNAPL residual saturation/concentration under unsteady state flow testing (ASTM D6836-02).

The ability of LNAPL to flow in the presence of air/groundwater can be assessed to evaluate the residual level of saturation in the soil. Both methods (ASTM D425 and ASTM D6836) advance the LSP's understanding of the residual limits for cleanup in soil and the level and degree to which LNAPL recovery is possible as a performance-based cleanup standard.

These methods for evaluating residual saturation are typically developed for two-phase fluid conditions (commonly LNAPL/Air or LNAPL/water). Since partially saturated soil requires a significantly more complex analysis of LNAPL behavior, further discussion is not within the scope of this paper. In addition, a residual saturation field method applied to coal tars has been developed by the Electric Power Research Institute (EPRI). This tool, referred to as the Res-SAT field tool, provides a field method to quantify residual levels of NAPL in soil from reconstituted or undisturbed samples recovered on-site. The tool is calibrated to field conditions from development of the saturation and capillary pressure relationships of the NAPL in the soil.

Residual Concentration/Saturation-Literature Values

Various values for residual LNAPL concentration in soil have appeared in the literature or have been developed by various state and county regulators. Tables from these sources have been extracted and placed in the Appendix to this paper. It appears that some of these values have been derived from post-remediation field measurements as well as from laboratory testing. Little information is available as to the specific methodologies used to derive each of the values provided.

5.4 Quantifying In-Situ LNAPL Mass or Volume

It is often desirable to understand the mass or volume of LNAPL that is present *in-situ* at disposal sites. This is useful for:

- comparing *in-situ* mass or volume to a known or assumed release quantity;
- estimating the quantity of LNAPL that might be generated during an LNAPL recovery program;
- calculating the amount of remedial additive that might be needed to reduce LNAPL concentrations to desired regulatory endpoints; and
- evaluating the feasibility of reaching MCP endpoints.

If quantification of the *in-situ* mass or volume of LNAPL is required, either a concentration or pore saturation basis may be used. Either method is highly sensitive to the reliability of the concentration/saturation data used to calculate mass or volume. Therefore, it is important to understand the limitations and sensitivities of available analytical testing procedures, and to select the most appropriate testing procedures appropriate for the contaminants of concern (COCs) at the site.

In selecting the appropriate analytical method for site contaminants of concern, the LSP should consider whether target compound data is needed, or whether a simple total petroleum hydrocarbon test is more appropriate. In selecting TPH procedures such as diesel range organics (DRO), gasoline range organics (GRO), EPH, or VPH, the LSP needs to understand the relative contribution of carbon fraction ranges to the COCs at the site. This is critical since most petroleum products contain a wide range of carbon compounds and testing for just a limited portion of the carbon spectrum may result in under-quantification of LNAPL mass or volume.

Once the appropriate analytical procedure is selected, the practitioner should evaluate the impact of the analytical quantification limitations on the calculated mass or volume. Assuming that reliable analytical data is available, estimating *in-situ* mass or volume is a relatively straight forward process provided adequate spatial characterization data has been developed. To simplify the calculation, API defines the parameter “Specific Volume (*V*)” representing the volume of LNAPL existing *in-situ* beneath a unit area of ground surface. Thus *V* has units of L³/L² (typically converted and expressed as gallons per square foot). A comparable parameter can be defined for mass-based calculations, i.e. “Specific Mass (*M*)” having units of M/L² (e.g., lbs/sq. ft.).

With adequate vertical profile data the value of *V* or *M* can be calculated at each soil boring. These values are calculated by performing a numerical integration of the vertical profile data using the unit ground surface area as an integration parameter. As an example, the specific mass (*m_i*) in a single soil sample from a soil boring can be estimated using the equation below:

$$m_i = C_i * l_i * \gamma * E-6 \quad (3)$$

Where for interval *i*:

m_i = specific mass in the soil sample (lbs/ft²);
 C_i = TPH concentration in the soil sample (mg/kg);
 l_i = length of the representative sample interval (ft); and,
 γ = unit weight of soil (lbs/ft³).

Total specific mass for the soil boring is then calculated as follows:

$$M = \sum m_i \quad (4)$$

M or V can be calculated using LNAPL saturation data obtained from soil tests, or LNAPL concentration data.

Total in-situ volume or mass can then be calculated by multiplying M or V times the applicable lateral area of equivalent impact. This is usually done by determining the value of M or V for each soil boring location, developing contours of M or V , and determining the area between contour lines and multiplying these areas by the applicable value of M or V .

6.0 LNAPL MOBILITY EVALUATION

This section summarizes available approaches to evaluate LNAPL mobility, a key parameter in evaluating the potential for future LNAPL migration.

All of these approaches assume that the original release source(s) has been eliminated or otherwise controlled, and that preferential pathways (man-made and natural) are not present. It is the LSP's obligation to identify these pathways and address them appropriately. In addition, the LSPA recognizes that in certain instances the risk posed to human health and the environment from an intermedia LNAPL source will require containment or removal actions regardless of the potential mobility of the residual NAPL. In these instances, it would not be necessary to also evaluate mobility.

6.1 The Meaning of Mobility

Before discussing mobility evaluation procedures, it is important to define what mobility means. Various expressions for mobility are available in the literature. For example, Sale (2001) presents the following equation for mobility:

$$M_o = k_i k_{ro} / \mu_o \quad (5)$$

Where:

M_o is LNAPL mobility [L^3T/M];
 k_i is soil intrinsic permeability [L^2];
 k_{ro} is the relative LNAPL permeability (dimensionless); and,
 μ_o is LNAPL dynamic viscosity [M/LT].

As used here, M_o is used to calculate the volumetric flux of NAPL in a porous media using a variation of Darcy's Law, as shown below:

$$q_o = - k_i k_{ro} / \mu_o [\rho g (dP_o/dx) + \rho g (dz/dx)] \quad (6)$$

In this equation, the volumetric flux q_o is the product of mobility, M_o , and the NAPL gradient. In this regard, M_o is similar to hydraulic conductivity in Darcy's law; that is, M_o expresses the relative ability of NAPL in a porous medium to flow, independent of the NAPL gradient.

This expression of M_o implies LNAPL migration for any non-zero value of M_o (i.e., for LNAPL above residual saturation). However, potentially mobile LNAPL does not necessarily imply actual LNAPL migration. According to API (API 2004)

.....Darcy's Law cannot describe all of the factors controlling LNAPL mobility and applied alone can produce misleading results suggesting LNAPL velocity potential where the plume is in fact stable. Irrespective of those issues, the various approaches

for evaluating LNAPL mobility fundamentally hinge on how the oil conductivity and gradient terms are derived.

An alternative term to describe mobility is presented by Parker et al. (Parker et al. 1996). This term is referred to as “Inherent Mobility,” and is expressed as the ratio of free oil transmissivity to specific oil volume at a given location:

$$M_i = T_o/V_o \quad (7)$$

Where M_i = Average LNAPL “Inherent Mobility” (ft/day)
 T_o = Oil transmissivity, integrated along the oil saturation profile, ft²/day; and
 V_o = Specific oil volume per unit area, ft³/ft²

These two alternative definitions of mobility are not the same. Mobility, as defined in equation 5 is an expression of LNAPL mobility that can be calculated at any point within the NAPL-impacted zone. The expression for inherent mobility presents an average value for the portion of the LNAPL-impacted zone where potentially mobile LNAPL is found.

6.2 LNAPL Mobility Evaluation Approaches

This section presents four LNAPL mobility evaluation approaches that LSPA recommends be considered for use at MCP sites. Each method varies in both the complexity of the approach, and in the site-specific data collection efforts.

6.2.1 Approach 1 – Weight of Evidence Approach

A weight of evidence approach may be appropriate where the nature and extent of contamination is well understood, and where potential risks to human and environmental receptors are likely to be low. The weight of evidence approach consists of evaluating the database of site information in its entirety, and forming an opinion regarding the potential for significant LNAPL migration based on the site understanding. The following factors should be included in forming a weight of evidence opinion:

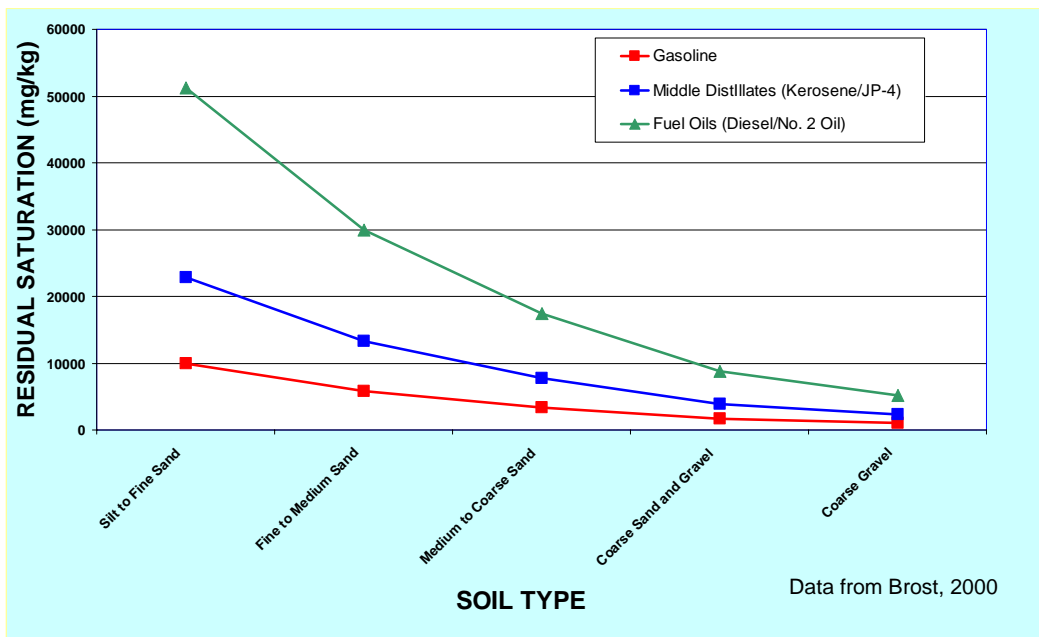
LNAPL Type – Knowledge of LNAPL type may allow reasonable prediction of LNAPL viscosity. Since mobility is inversely proportion to viscosity, reliable information about the type of product released could be valuable in predicting the potential for mobility (e.g., more viscous LNAPLs, such as No. 4 and No. 6 oil, will be less mobile than gasoline in similar soils and at similar saturations).

LNAPL Release Date – Knowledge of the date of release or, more accurately, the date when the release was terminated can be an important factor in addressing the potential for migration. It is commonly recognized that most LNAPL releases reach a condition of stability within a matter of years after termination of the release. Therefore clear documentation of the date of release termination may support a weight of evidence migration evaluation.

LNAPL Release Volume – When release volumes are small, the potential for significant migration is reduced, even when soil permeability is high and viscosity is low. The primary reason for this limitation on mobility is the inherent ability of soil to retain LNAPL at residual saturation. Thus, small releases have a limited ability to spread significant distances.

Soil Type – LNAPL migration potential is strongly impacted by soil properties. In particular, LNAPL mobility varies proportionally to soil intrinsic permeability, and intrinsic permeability has a range of several orders of magnitude. Thus, small LNAPL releases to low permeability soils, such as marine clay, will have little potential to migrate beyond the immediate release area.

Soil type also impacts residual saturation. For a given LNAPL type, residual saturation is inversely proportional to soil permeability. Therefore, lower permeability soils can retain proportionally higher quantities of LNAPL, and thus reduce the potential for mobility of LNAPL. A graphical depiction of the influence of LNAPL and soil type on residual saturation is presented below.



Site Environmental Setting – The environmental setting of the site can significantly affect the potential for risk from a residual LNAPL source. If there is an absence of environmental or human receptors or the distance to sensitive receptors is large, it may be reasonable to conclude that LNAPL mobility is not a significant concern, provided there is no longer an ongoing release to the environment. Presence of natural or artificial barriers to migration in the form of geologic or man-made features could also be considered.

Plume Stability –

Stable or shrinking plumes of dissolved LNAPL components in the groundwater and repeated stable measurements of LNAPL in soil at the limits of LNAPL present in soil can serve as indicators of LNAPL stability. The monitoring well network and soil data needed includes soil samples and wells to provide data at the down-gradient limit of the plume.

Sufficient data should be collected to demonstrate seasonal trends, and seasonal high and low ranges in the water table. Groundwater data would need to be collected, at appropriate intervals, over a minimum two-year period. A minimum of three sets of soil data, obtained in the preferred direction of LNAPL movement over a similar period of time would be needed if soil data alone were used as the basis to support lack of mobility.

Product Thickness Measurements – While LSPA does not endorse using LNAPL thickness measurements as the sole criterion for LNAPL assessment, the presence or absence of LNAPL in groundwater monitoring wells could be considered in evaluating the potential for LNAPL mobility. For example, the persistent presence of LNAPL in groundwater monitoring wells could be taken as an indication of potentially mobile LNAPL. Conversely, long-term monitoring records that show only the intermittent presence of LNAPL are more than likely indicative of low mobility LNAPL in a stable plume. If LNAPL thickness measurements are to be used as a indicator of the lack of mobility, the literature indicates that product thickness records should cover a period of two years or more after removal of the original LNAPL release source. Incorporating specific monitoring well geometry and an average spatial and temporal de minimus LNAPL thickness target into this approach may also be useful. For example, a temporal and spatial average LNAPL thickness of one inch, as measured in maximum 2-inch diameter wells over a two-year period, could be used.

6.2.2 Approach 2 – Comparison to Residual Saturation or Residual Concentration

A simple method for evaluating LNAPL mobility is to compare appropriately characterized site LNAPL saturations/concentrations to the residual saturation/concentration. In this approach, LNAPL at a saturation/concentration less than the residual concentration/saturation is presumed to be immobile. The residual values could be compared to the maximum or the average saturation/concentration depending upon the desired degree of conservatism. The use of maximum values is likely to have limited applicability at many sites since the maximum LNAPL saturation will typically be higher than the residual saturation if remediation has not been undertaken. Nevertheless, in situations where remedial measures have been taken, but it has not been possible to reduce LNAPL concentrations to background, a comparison of site conditions to residual saturation may be used to adequately demonstrate lack of LNAPL mobility.

Approach 2 can be implemented by testing soil samples from the site for both field saturation (i.e., *in-situ* saturation) and residual saturation. Alternatively, published values of residual saturation may be used as an initial screening tool. However, published values for residual saturation/concentration should be used with caution due to the sensitivity of residual saturation to soil type, LNAPL viscosity and the manner by which the value is determined. In situations where concentrations have been sufficiently reduced through remediation such that site saturations/concentrations are lower than reasonably conservative values of residual saturation/concentration, published values of residual saturation/concentration can be appropriate. A specific case where this approach could be used is when excavation has been successful in removing high LNAPL concentrations near the average water table elevation, but the removal of LNAPL-impacted soil several feet below the water table is not feasible. In these cases, some LNAPL contaminated soil may remain at depth, but at concentrations well below peak saturation/concentration. This approach would be used to demonstrate the immobility of this lower concentration secondary source material.

This method also has utility for monitoring the success of LNAPL recovery programs. *In-situ* LNAPL soil concentrations should approach (asymptotically) residual saturation/concentration as LNAPL recovery proceeds. Practical experience has shown, however, that even well-designed LNAPL recovery systems do not typically reduce field LNAPL saturation/concentration to residual levels. LNAPL recovery rates typically decline during system operation and asymptotically approach a non-zero recovery rate. This approach can be used in these situations to evaluate the success of the recovery system. For a well-designed system, if *in-situ* concentrations have reached a relatively constant value, the system has likely been successful in reducing LNAPL to a condition of LNAPL immobility. Conversely, if hot spots appear to exist, the system layout may need modification.

6.2.3 Approach 3 – Site Specific LNAPL Mobility Evaluation

Site specific LNAPL mobility evaluations can be performed by calculating LNAPL mobility using equation 5:

$$M_o = k_i k_{ro} / \mu_o$$

Site specific mobility evaluations require an understanding of the distribution of k_i , k_{ro} , and μ_o throughout the LNAPL-impacted areas of the disposal site. In many cases only a single LNAPL is present, and μ can be determined by performing a single test for dynamic viscosity at the appropriate temperature. Similarly, permeability testing is a straightforward procedure. Borehole hydraulic conductivity tests are recommended to characterize hydraulic conductivity, and intrinsic permeability can then be calculated from the hydraulic conductivity test results (see Section 5.3).

Once k_i and μ_o are determined, the relative LNAPL permeability must be determined to calculate M_o . Methods for evaluating relative LNAPL permeability are discussed

in Section 5.0 of this paper. Alternatively, a value of 1.0 can be assumed. This assumption will result in a conservative estimate of mobility.

It is beyond the scope of this paper to address the appropriate number of locations (vertically and horizontally) needed to calculate a value for site-specific mobility. In most cases, however, the highest mobility within a vertical contaminant profile will correspond to the location of the peak LNAPL saturation/concentration. Thus, an appropriate strategy for characterizing site specific mobility at most sites will be to calculate the peak LNAPL mobility at each impacted soil boring.

The LSPA recommends that a “Practical Limit of Mobility,” or “PLM,” be established for the purpose of evaluating whether site-specific values of M_o are likely to represent an unacceptable LNAPL migration risk. If mobility throughout the site is lower than the PLM, then LNAPL can be presumed to be effectively immobile. The assumption of a PLM based on the mobility equivalent of water saturated soil having a hydraulic conductivity of 1×10^{-4} cm/sec may be appropriate. The PLM for water saturated soil can then be calculated using the following equation:

$$PLM = k_h / (\rho g) \quad (8)$$

Where:

PLM = Practical Limit of Mobility [L^3T/M]
 k_h = soil hydraulic conductivity [L/T]
 ρ = Fluid density [M/L^3]
 g = Gravitational constant [L/T^2]

In this case, the appropriate units for calculating PLM are based on the fluid properties of water, and the suggested soil hydraulic conductivity of 1×10^{-4} cm/sec. Thus the units of PLM will be cm^3sec/g , and M_o should be in these units for comparison.

The following values are recommended for calculating the PLM:

$$\begin{aligned} k_h &= 1 \times 10^{-4} \text{ cm/sec} \\ \rho &= 1.0 \text{ g/cm}^3 \\ g &= 32.2 \text{ ft/sec}^2 = 981 \text{ cm/sec}^2 \end{aligned}$$

The recommended PLM is therefore calculated to be approximately $1.0 \times 10^{-7} \text{ cm}^3\text{sec/g}$.

6.2.4 Approach 4 – Inherent Mobility Based on Baildown Testing

Baildown tests have been used to estimate LNAPL conductivity. In this test, only the LNAPL is removed from the well. The elevation of the LNAPL-air and LNAPL-water interface is monitored during the recovery portion of the test. Two methods are presented in the literature to analyze the results of the baildown test, ((Huntley, 2000) and (Lundy and Zimmermann, 1996)). These two methods have been shown to give different LNAPL conductivity results.

As described previously, a mobility evaluation procedure based on baildown test results is available. This procedure, presented by Parker (Parker, 1996), defined “Inherent Mobility” as the ratio of free oil transmissivity (determined from the baildown test) to specific oil volume (as defined in Section 5.4). Knowing Inherent Mobility may allow one to make conclusions on a value for LNAPL mobility.

RTDF (RTDF, 2005) presented a comparison of LNAPL conductivity values determined based on site-specific data, (primarily from laboratory tests), to results determined from baildown testing procedures. The comparison showed a poor correlation between the two methods.

7.0 RISK CHARACTERIZATION CONSIDERATIONS

In addition to the provisions and procedures described elsewhere, the presence of LNAPL must be evaluated in terms of risk to human health, public welfare, safety, and the environment under the MCP. This section reviews how current Risk Characterization procedures are used in the context of the MCP and how the presence of soils that may contain elevated levels of LNAPL contaminants can be incorporated into those procedures. Also, all other evaluations described in 310 CMR 40.0000, including Critical Exposure Pathways (CEP's) and Imminent Hazard (IH) evaluations, must be considered. CEP's and IH's were discussed in Section 2.2 of Part I. This section addresses standard exposure pathways; however, the results of the LNAPL mobility evaluation described in Sections 5.0 and 6.0 may reveal additional site-specific exposure pathways that must be considered.

As part of any risk characterization, applicable contaminant migration pathways, and their resultant exposures related to the presence of LNAPL, must be identified. Potential migration pathways of particular interest in a LNAPL scenario include vapor migration, LNAPL migration through subsurface utilities and other structures, and dissolved transport to groundwater resource areas. Exposure pathways include direct contact with soil/groundwater and possibly drained LNAPL, inhalation of vapor and particulate matter, and ingestion of particulate matter. Particular attention needs to be paid to the current and future utility worker exposure scenario. The utility worker exposure should include a comparison of known existing and proposed future utility location and depth information with the extent of LNAPL and an evaluation of exposure risks. The LSP is also obligated to demonstrate that the original source of the release has been removed or otherwise controlled, and that any continuing source(s) (i.e., residual LNAPL) in the environment are controlled and the LNAPL is not mobile.

Assuming it is demonstrated that the LNAPL is not mobile, migration and exposure pathways must be evaluated to determine whether they represent current and reasonably foreseeable exposures to site Contaminants of Concern (COCs). The relative importance of these pathways will depend significantly on the nature of the LNAPL that is present. Gasoline, for example, generally contains a volatile fraction that could be a source of vapor-phase migration. The same is true for many other industrial hydrocarbons (e.g., cyclohexane, n-heptane). Gasoline constituents and lower molecular weight hydrocarbons also tend to be more soluble than those in higher molecular weight substances, which may cause the dissolved groundwater transport pathway to be an important consideration. Conversely, some constituents in higher molecular weight substances/mixtures (e.g., polynuclear aromatic hydrocarbons – PAH's in petroleum products) are less mobile, but can pose risk from the direct contact/ingestion pathway.

7.1 Risk Characterization Methods

Risks to receptors may be evaluated in LNAPL scenarios using either Method 1 (typically using S-3 Soil Standards and an Activity and Use Limitation (AUL)) or Method 3. The Method 2 approach to screening for potential impacts to indoor air is typically the procedure

that is employed in conjunction with Method 1. However, the Method 2 approach of modifying leaching-based standards may not be sufficient to address the migration of dissolved-phase hydrocarbons in an LNAPL scenario. Steps to address leaching in an LNAPL scenario are described elsewhere in this document.

If the groundwater at the site is classified as GW-1, a condition of 'No Significant Risk' may not be attainable, and remediation may be necessary. The assumption here is that, at least at the interface of the soil containing LNAPL and the groundwater, it will be very difficult to demonstrate compliance with Method 1 GW-1 and Drinking Water standards or Total Site Risk in a Method 3. While recent revisions to the MCP will allow some petroleum releases in GW-1 areas to be brought to closure, a conclusion of 'No Significant Risk' in most GW-1 settings will be difficult to demonstrate.

7.2 Vapor-Phase Migration

When LNAPL is present, the use of soil gas data is recommended for the evaluation of potential impacts to indoor air, likely to be of greatest significance when gasoline or other lighter-end petroleum products are present. The United States Environmental Protection Agency (USEPA) has developed dissolved-phase/soil gas and NAPL-based models for evaluation of vapor-phase migration into indoor air. These models are based on the Johnson & Ettinger model (Johnson and Ettinger, 1991) and are available on the Internet at: http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm. The MassDEP has used the Johnson & Ettinger model in the derivation of Method 1 GW-2 clean-up Standards and in guidance for screening potential impacts to indoor air; hence this model is recognized by MassDEP.

The use of soil and/or groundwater concentrations for evaluating potential impacts to indoor air when LNAPL is present is not recommended (see Section 4.7.3 of DEP, 2002a). In collecting site-specific data to evaluate potential impacts to indoor air, the use of soil gas sampling is more directly applicable in LNAPL situations. When using site-specific soil gas data in a LNAPL scenario, the use of the non-NAPL Johnson & Ettinger model is more appropriate (USEPA, 2000; USEPA, 2004). This is because the LNAPL model estimates the partitioning of vapor from soil to soil gas. Direct measurement of soil gas concentrations obviate the need for such calculations, and the non-NAPL models (SG-SCREEN and SG-ADV) are appropriate for LNAPL scenarios in which soil gas data have been collected. Soil gas sampling procedures can be found in the following sources: (USEPA, 2000, DEP, 2002a, and DEP, 2002b).

7.3 Exposure Pathways

Exposure pathways that may be applicable to LNAPL consist of the ingestion of and dermal contact with groundwater; the ingestion of, inhalation of and dermal contact with soil containing elevated levels of contamination resulting from LNAPL; and inhalation and ingestion of particulate matter (largely a utility worker/construction worker exposure scenario). These potential exposure pathways may need to be controlled by the implementation of an AUL or remedial action, as described in Section 7.7, if a Condition of No Significant Risk cannot be demonstrated.

An issue that arises here is that of the utility worker scenario. This scenario is typically modeled as an emergency situation assuming utility repair work that cannot be controlled by an AUL, although an AUL can be used to control future utility installation. The presence of LNAPL that may drain from the soil or cover infiltrated groundwater during subsurface utility repair may result in exposures that require additional modeling assumptions as discussed in Section 7.5.

The quantitative evaluation of certain potential exposure pathways for construction and utility workers may not be possible or necessary based on currently available exposure models, MassDEP guidance, and Site-specific conditions. The exposure pathways for construction workers for the inhalation of volatiles from soil and groundwater, and for direct contact with groundwater, are not currently considered in the MCP Method 1 Standards and the MassDEP's Method 3 Risk Assessment Shortforms for Construction Workers (DEP, 2007). The models that may be used to model EPCs for these exposure pathways in a Method 3 Risk Characterization have not been standardized and are not universally accepted by the risk assessment community.

In addition, MassDEP draft guidance indicates that direct contact with groundwater is generally experienced only occasionally by laborers repairing the pumps used to dewater excavated holes, an activity that would result in an acute exposure (DEP, 1996).¹ The MassDEP Guidance for Disposal Site Characterization specifies that the default exposure frequency for a utility worker is one day per year based on discussions with utility companies. This frequency represents a conservative estimate of the frequency of exposure to contaminated soil or vapors at depths that would be experienced by a utility worker, given the frequency of utility repairs, the time needed for repairs and the rotation of work crews (DEP, 1995).

Soil samples from LNAPL-impacted areas should be collected so as to allow the development of a horizontal and vertical profile of the LNAPL-impacted zone. For the calculation of Exposure Point Concentrations (EPCs), averaging results from within the same soil category in the LNAPL-impacted area should be sufficiently conservative. Since emergency utility work exposures cannot be controlled by an AUL, the collection of an LNAPL sample from the impacted area may be necessary to characterize risk from contact with LNAPL during the utility worker scenario.

7.4 Dissolved Groundwater Migration Pathway

As part of defining the nature and extent of contamination pursuant to 310 CMR 40.0002(1)(a)(3), information should be collected regarding the limits of the dissolved groundwater plume. This information, coupled with the current and reasonably foreseeable future uses of the groundwater, provides a basis for the evaluation of risk associated with this potential migration, and thus exposure (e.g., drinking water), pathway. Note that in cases where the groundwater is classified as GW-1, the presence of LNAPL will likely result in an

¹ MassDEP, 1996. *Draft Commercial/Industrial ShortForm Exposure Scenarios*.

exceedance of Drinking Water Standards in the area of LNAPL contamination as described in Section 7.1.

7.5 Effect of LNAPL on Risk Characterization Assumptions

For risk due to dermal contact with soil, weighted dermal adherence factors (WDAF) are determined per MassDEP's Technical Update (DEP, 2002c). WDAFs are used to calculate Average Daily Soil Dermal Contact Rates, and hence risk, for various age groups/receptors. Since soil that is saturated with petroleum or other LNAPL (or leaks free LNAPL) may adhere quite differently to skin than soil with lower residual contamination, the risk assessor and LSP should consider how the presence of LNAPL will affect the WDAFs that are used in a risk characterization. Although an LNAPL scenario is not discussed in MassDEP guidance, consideration could be given to the sediment "monolayer" model described in DEP, 2002c. The WDAF for sediment is 1.0 mg/cm². This is viewed by MassDEP as the critical level above which absorbed contaminant begins to decrease; however, it is not clear how this translates to a LNAPL scenario. The effect of a revised WDAF has a concomitant effect on the enhanced soil ingestion rate (ESIR), as it relates to the amount of soil that adheres to the skin of the hands and is subsequently ingested. MassDEP has presented 100 mg/day as a revised ESIR (DEP, 2002d). If LNAPL increases the WDAF, consideration must be given to what affect this increase will have on the ESIR used in the risk characterization. Additional guidance from MassDEP may be necessary to apply the LNAPL scenario to these risk characterization assumptions.

Similarly, the presence of LNAPL (and associated groundwater presence) will likely have a marked decrease on the amount of dust (e.g., PM₁₀, PM₃₀) that is assumed to be generated in the fugitive dust exposure scenario. Inhalation and ingestion of fugitive dust is an important pathway in the utility worker and construction worker scenario for certain COCs; however, the presence of high levels of LNAPL and/or water saturation may render the levels of airborne particulates insignificant. To capture potential exposure in areas just outside of the heavily LNAPL-impacted areas, it may be appropriate to evaluate risk from inhalation and/or ingestion of particulate matter using EPCs from soil above the water table and above the zone of LNAPL saturation in conjunction with the assumptions in MassDEP's Technical Update "Characterization of Risks Due to Inhalation of Particulates by Construction Workers (DEP, 2002e)."

In both the utility worker and heavy construction worker scenarios, the presence of LNAPL may result in airborne vapor concentrations that could lead to a vapor inhalation pathway (in addition to the particulate inhalation and ingestion pathway). Currently, the inhalation of ambient vapor is not included in MassDEP's "Characterization of Risks Due to Inhalation of Particulates by Construction Workers (DEP, 2002e)." Additional guidance assumption development, agreed upon by all parties, may be necessary to apply the LNAPL scenario to the vapor inhalation pathway, as well as to the selection of appropriate WDAFs and ESIRs for the dermal and ingestion pathways.

7.6 Characterizing Risks to Safety, Public Welfare, and the Environment

The presence of LNAPL requires assessment activities that are not commonly employed during routine disposal site characterization. For example, vapor migration may lead to

exceedences of Lower Explosive Limits (LEL), and these and other applicable pathways must be considered in the characterization of risk to Public Safety. With respect to Public Welfare, the elimination of the 0.5-inch Upper Concentration Limit (UCL) will require that more qualitative measures of Public Welfare (e.g., odors, nuisance conditions) be used to assess the risk to Public Welfare.

A potential implication of the presence of LNAPL with respect to Environmental Risk characterization is that of ‘Readily Apparent Harm,’ defined at 310 CMR 40.0995(3)(b)1.c: *“The following conditions shall represent “readily apparent harm:” ... Visible presence of oil, tar, or other non-aqueous phase hazardous material in soil within three feet of the ground surface over an area equal to or greater than two acres, or over an area equal to or greater than 1,000 square feet in sediment within one foot of the sediment surface.”*

In addition, the assessment of potential impacts to sediments and/or in the vicinity of a surface water body is described at 310 CMR 40.0995(3)(a) and 310 CMR 40.904(2).

7.7 Managing Exposures via the Implementation of an Activity and Use Limitation

In cases where current conditions, including exposures to present utility workers, cannot be demonstrated to provide a condition of ‘No Significant Risk’, an AUL cannot be implemented, and other strategies (e.g., excavation and decommissioning/relocation of utility) may have to be employed. However, the restriction of exposures to soil, groundwater, and/or LNAPL may be used for future conditions (e.g., prohibit the installation of new utilities in the LNAPL area) to demonstrate a condition of ‘No Significant Risk.’ Implementation of an AUL to control the direct contact exposure pathway to soil, groundwater and/or LNAPL assumes that, as a practical matter, the LNAPL is not migrating, groundwater and vapor plumes are stable, and the source of the LNAPL has been removed or controlled. The direct contact exposure that is controlled with an AUL needs to include exposures associated with any construction work in the area subject to the AUL (including exposures mitigated by personal protective equipment). Future scenarios, including, but not limited to, the construction of potential migration pathways (e.g., conduits) through LNAPL zones and the risks associated with potential impacts to indoor air of a future occupied structure, may be included in the AUL. As previously noted, exposure pathways that may be encountered during the utility worker scenario for existing utilities cannot be controlled by an AUL. However, an AUL can be used to prohibit the installation of new utilities.

8.0 SUMMARY AND CONCLUSIONS

In 2003, the LSPA Technical Practices Committee formed a subcommittee to address issues related to regulation, site assessment and risk characterization for LNAPL-impacted sites. LSPA published a White Paper in May 2005 entitled “LNAPL and the MCP – Part I”. The White Paper identified technical deficiencies in scientific theories used to characterize LNAPL sites. Specifically, a conceptual model widely used to describe the nature and extent of LNAPL contamination, known as the Tank and Pancake model, was shown to be scientifically invalid.

In the conclusion to Part I of this White Paper the LSPA recommended reviewing those regulatory provisions of the MCP that are based on the Tank and Pancake model. A particular concern identified in Part I is the current MCP Public Welfare Upper Concentration Limit (UCL) risk standard for LNAPL.

LSPA also recommended reviewing practice standards used for characterizing the nature, extent and migration potential of LNAPL. An alternative model, referred to as the “multiphase flow model,” was suggested to form the basis for recommended practice standard changes. This model recognizes that the magnitude and distribution of LNAPL in the subsurface environment is significantly different than the simplified conceptualized distribution predicted by the Tank and Pancake model. LSPA recognized that LNAPL should be characterized primarily as a soil contaminant.

For Part II of this White Paper, the LSPA has focused on developing recommendations for change in the areas of regulation, technical practice standards, and risk characterization. Recommendations in these areas are summarized in the following sections.

8.1 Regulatory Change

- The definition of LNAPL in the MCP should be changed as recommended in Section 2.0 to be consistent with the current understanding of multiphase flow theory.
- A definition for Secondary LNAPL Source should be included in the MCP to recognize the potential of residual LNAPL to act as potential ongoing source for intermedia transport of contaminants, and to differentiate secondary sources from primary sources such as tanks and pipelines.
- The MCP Public Welfare UCL for LNAPL of 0.5-inch in “any environmental medium” is not based on valid scientific theory and should be eliminated in favor of alternative standards that are related to risk, and based on valid scientific theories. Existing concentration based UCLs for LNAPL are sufficient in this regard.
- The MCP reporting condition for LNAPL should be simplified to a single reporting condition, since LNAPL thickness in a well has been demonstrated to be unreliable indicator of risk. Varying thickness has little impact on site risk due to NAPL presence. LSPA recommends that an LNAPL thickness of 0.01 feet (1/8 inch) or more be considered a 72-hour reporting condition

8.2 LNAPL Characterization

LPSA encourages all LSPs and interested parties to adopt practice standards that will result in data that is reliable for characterizing the nature, extent and migration potential of LNAPL at disposal sites, and will be sufficient for accurate characterization of current and future risk. Specific recommendations are as follows:

- LPSA recommends a shift away from measuring LNAPL thickness in groundwater monitoring wells, and towards LNAPL plume delineation based on characterizing the magnitude (concentration or percent saturation) of LNAPL in soil.
- Use of the “LNAPL Continuum” concept described in Section 4.0 of this paper is suggested as a means of characterizing the vertical and lateral extent of LNAPL in soil, and for providing a preliminary assessment of LNAPL migration potential.
- Field investigation program design should focus on thoroughly delineating both the vertical and lateral extent of LNAPL in soil. Fully developed vertical profiles of LNAPL concentration vs. depth are suggested.
- Use of the soil saturation limit (C_{sat}) is recommended as a means of delineating the lateral extent of LNAPL. Concentrations of contaminants of concern in soil that exceed C_{sat} should be presumed to contain LNAPL.
- Residual concentration (C_{res}), or residual saturation (S_{res}) should be used to differentiate between LNAPL that is immobile and LNAPL that is potentially mobile and potentially recoverable.
- While measuring LNAPL thickness in groundwater monitoring wells is discouraged as a primary means of LNAPL characterization, the groundwater monitoring well will continue to be an integral component of LNAPL site characterization. Groundwater monitoring wells are recommended for collecting groundwater samples for dissolved phase characterization, collecting LNAPL samples, borehole conductivity testing, groundwater elevation measurement, and LNAPL recoverability testing.
- Field screening techniques are encouraged to characterize LNAPL in soil. Both in-situ and ex-situ techniques are available. Laser induced fluorescence (LIF) and ultra violet fluorescence (UVF) appear to be well suited to LNAPL sites.
- Reliable calculations of *in-situ* LNAPL mass (or volume) can be performed if adequate spatial characterization of LNAPL concentrations is available. Vertical profile data can be integrated to determine Specific Mass or Specific Volume. Results are valuable for determining the magnitude of a given release, and can be used to estimate potentially recoverable quantities of LNAPL.
- Potential LNAPL mobility is a function of soil properties, LNAPL properties, and the LNAPL saturation/concentration. LNAPL mobility parameters should be determined during the site characterization process. At a minimum, these parameters should include LNAPL viscosity, LNAPL density, and soil intrinsic permeability.

Laboratory tests to estimate residual concentration/saturation are also available, as are tests to establish the relationship between LNAPL saturation and relative LNAPL permeability.

- For LNAPL sites that do not constitute a condition of significant risk under current site conditions, and as defined in the MCP, an LNAPL Mobility Evaluation should be performed to address the potential for future risk as a result of intermedia transfer of contaminants.
- The level of complexity of LNAPL mobility evaluations should be commensurate with the magnitude of the release, and the environmental setting of the MCP disposal site. LSPA presents in Section 6.0 of this report four LNAPL Mobility Evaluation methods.

8.3 Risk Characterization

This paper advocates that risk characterization for LNAPL-impacted sites be handled in much the same way that risk at any MCP site is currently handled. In lieu of the thickness-based UCL for LNAPL, LSPA recommends using existing soil concentration-based UCLs, and performing site-specific LNAPL mobility evaluations to address concerns about future risk from migrating LNAPL.

- In all cases it is the responsibility of the LSP to conduct sufficient assessment to demonstrate that there are no uncontrolled LNAPL releases or threats of release prior to considering site risk.
- The risk posed by LNAPL in the environment should be evaluated for current conditions using existing MCP risk assessment protocols, including identifying EPCs, migration pathways, receptors, exposure scenarios and dose/response parameters. To assess future risk, LNAPL mobility evaluation should be performed.
- Risk Characterization must evaluate all site conditions, including LNAPL, with respect to risk of harm to Human Health, Public Safety, Public Welfare, and the Environment. Risks to Public Safety (e.g., lower explosive limits) may have increased significance in LNAPL scenarios.
- Risk Characterization at LNAPL sites can be accomplished by Method 1 (typically to S-3 Standards with an AUL, possibly supplemented with a Method 2 approach to screen for potential impacts to indoor air, if applicable) or by Method 3.
- Where LNAPL is present, vapor migration to indoor air should be evaluated through the collection of soil gas data as opposed to soil or groundwater data. Level 2 and level 3 screening may also be needed pending screening results.
- The measurement of contaminants of concern across (vertically) the LNAPL-impacted zone is recommended for calculating exposure point concentrations for direct contact, ingestion, and construction worker inhalation/ingestion (particulate and vapor).

- Construction worker exposure to particulates (inhalation or ingestion) should be addressed in accordance with the assumptions in MassDEP’s Technical Update “Characterization of Risks Due to Inhalation of Particulates by Construction Workers (DEP, 2002e).”
- AULs at LNAPL sites should include provision for appropriate personal protective equipment for construction workers exposed to LNAPL. Potential construction worker exposures include dermal contact, ingestion and inhalation (both vapor and particulate).
- The presence of LNAPL will affect the weighted dermal adherence factors (WDAF’s) that are used in the Risk Characterization. WDAF’s are discussed in DEP guidance (DEP, 2002c); however, additional guidance from DEP regarding WDAF’s and LNAPL scenarios is warranted.
- The presence of LNAPL has an impact on WDAFs and a concomitant effect on Enhanced Soil Ingestion Rates (ESIR). ESIR’s are discussed in DEP guidance (DEP, 2002d); however, additional guidance from DEP regarding ESIR’s and LNAPL scenarios is warranted.

9.0 REFERENCES

Adamski, et al., 2003. *Residual Saturation. What Is It? How Is It Measured? Should We Use It*, 20th Conference: Petroleum Hydrocarbons and Organic Chemicals in Groundwater, Sponsored by the National Ground Water Association and the American Petroleum Institute.

Alaska, 2006. *Maximum Allowable Concentration, Residual Saturation and Free-Product Mobility*, Technical Background Document and Recommendations, Prepared for Alaska Statement of Cooperation Working Group, Geosphere, Inc-CH2MHILL, September 2006

API, 2000. *Non-aqueous Phase Liquid (NAPL) Mobility Limits in Soil*, API Soil and Groundwater Research Bulletin, Bulletin 9, June 2000

API, 2004. *API Interactive LNAPL Guide*, American Petroleum Institute, Environmental Systems and Technology and Aqui-Ver, Version 2.0, <http://groundwater.api.org/lnaplguide/>

Brost et al., 2000. *Non-Aqueous Phase Liquid (NAPL) Mobility Limits in Soil*, American Petroleum Institute, Soil and Groundwater Research Bulletin No. 9, June 2000.

DEP, 2002a. *Characterizing Risks Posed by Petroleum-Contaminated Sites: Implementation of the MassDEP VPH/EPH Approach*, Policy #WSC-02-411, Bureau of Waste Site Cleanup, October 31.

DEP, 2002b. *Indoor Air Sampling and Evaluation Guide*, WSC Policy #02-430, Office of Research and Standards, April.

DEP, 2002c. *Technical Update: Weighted Skin-Soil Adherence Factors*, Office of Research and Standards, April.

DEP, 2002d. *Technical Update: Calculation of an Enhanced Soil Ingestion Rate*, Office of Research and Standards, April.

DEP, 2002e. *Technical Update: Characterization of Risks Due to Inhalation of Particulates by Construction Workers*, Office of Research and Standards, April.

Freeze and Cherry, 1979. *Groundwater*, Freeze, R. A. and J. A. Cherry. Prentice Hall, Inc., 1979.

Huntley, 2000. *Analytic Determination of Hydrocarbon Transmissivity from Baildown Tests*, Huntley, D, Ground Water, 38(1): 46-52.

Johnson, P.C., and R.A. Ettinger, 1991. *Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors into Buildings*, Environ. Sci. Technol., 25(8).

Lundy and Zimmerman, 1996. *Assessing the Recoverability of LNAPL Plumes for Recovery System Conceptual Design*, Lundy, D.A., and L.M. Zimmerman, In: Proceedings of the 10th Annual National Outdoor Action Conference and Exposition, National Ground Water Association, Las Vegas, NV. May 13-15, 1996.

LSPA, 2005. *Field Analysis Kits for Total Petroleum Hydrocarbons*, LSPA News, October 2005

LSPA, 2005 Part I. *LNAPL and the Massachusetts Contingency Plan - Part I*, LSP Association Technical Practice Committee, April 2005

MassDEP, 2007. *Method 3 Risk Assessment for Chemicals in Soil – Construction Worker Shortform 2007 (sf07cw)*.

MassDEP, 1996. *Draft Commercial/Industrial Shortform Exposure Scenarios*.

MassDEP, 1995. *Guidance for Disposal Site Risk Characterization - In Support of the Massachusetts Contingency Plan*. Interim Final Policy WSC/ORS-95-141. BWSC and ORS.

Ohio, 2004. *Guidance for Assessing Petroleum Hydrocarbons in Soil*, Ohio EPA-DERR, No. DERR-00-DI-033, September 22, 2004

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

RTDF, 2005. *Understanding the Behavior of Light Non-Aqueous Phase Liquids (LNAPLs) in the Subsurface*. Remediation Technologies Development Forum

Sale, 2001. *Methods for determining inputs to environmental petroleum hydrocarbon mobility and recovery models*: American Petroleum Institute Publication No. 4711, 66p.

SAM, 2004. *Site Assessment and Mitigation Manual, Section 5*, Department of Environmental Health, County of San Diego, California, 2004

USEPA, 2000. *User's Guide for the NAPL-SCREEN and NAPL-ADV Models for Subsurface Vapor Intrusion into Buildings*, Office of Emergency and Remedial Response, Washington, D.C., prepared by Environmental Quality Management, Inc.

USEPA, 2004. *User's Guide for Evaluating Subsurface Vapor Intrusion into Buildings*, Office of Emergency and Remedial Response, Washington, D.C., prepared by Environmental Quality Management, Inc.

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APPENDIX

**PUBLISHED VALUES FOR RESIDUAL SATURATION AND RESIDUAL
CONCENTRATION**

Table 5-8 is from the Site Assessment and Mitigation Manual, County of San Diego, CA (SAM 2004)

TABLE 5-8 Petroleum Residual NAPL Saturation Based on Soil Type in Sedimentary Environments									
Soil Type ASTM- D2487	Approx. Particle Size (mm)	K_{ov} (cm/sec)	θ (dim)	S_{rw} (dim)	ρ_b (gm/cm ³)	TPH Concentration (mg/kg)			
						Gasoline / Naphtha (mg/kg)	Kerosene / JP-4 (mg/kg)	Diesel #2 (mg/kg)	Fuel Oil (mg/kg)
Gravel	76.2-4.75	100	0.30	0.001	2.00	560	780	1000	1400
Sandy Gravel	Based on % fines	5.0	0.36	0.005	1.86	1,500	2,100	2,800	3,800
M- Coarse Sand	4.75-0.425	1.0	0.37	0.007	1.83	2,300	3,200	4,400	5,900
Fine Sand	0.425- 0.074	0.5	0.38	0.009	1.81	2,900	4,000	5,400	7,300
Silty Sand	Based on % fines	0.05	0.41	0.018	1.76	5,600	7,800	10,000	14,000
Silt	0.074- 0.005	0.0005	0.48	0.10	1.65	19,000	27,000	36,000	49,000
Clay	<0.005	0.000005	0.56	0.39	1.56	44,000	61,000	82,000	110,000

1. The critical flow rate (q_c) used to calculate the above values was 1×10^{-7} cm/sec.
This table does not apply in fractured crystalline rock environments
2. The TPH concentration values were determined by using Equations 5-3 and 5-4.

Table 4 is from the Alaska Department of Environmental Conservation (Alaska 2006)

TABLE 4
Mercer & Cohen (1990) Vadose and Saturated Zone Residual Oil Concentrations

Vadose Zone Example Data From Mercer and Cohen Summary, 1990				
Soil Description/ Texture	Lower Measured Value of Residual Concentration (mg/kg)	Upper Measured Value of Residual Concentration (mg/kg)	Dil Type	Reference
coarse gravel	948	not reported	gasoline	Schwille, 1970
gravel, coarse sand	1,514	not reported	gasoline	Schwille, 1970
coarse sand, medium sand	2,838	not reported	gasoline	Schwille, 1970
medium sand, fine sand	4,730	not reported	gasoline	Schwille, 1970
fine sand, silt	7,568	not reported	gasoline	Schwille, 1970
coarse gravel	2,162	not reported	middle distillates/diesel	Schwille, 1970
gravel, coarse sand	3,459	not reported	middle distillates/diesel	Schwille, 1970
coarse sand, medium sand	6,486	not reported	middle distillates/diesel	Schwille, 1970
medium sand, fine sand	10,811	not reported	middle distillates/diesel	Schwille, 1970
fine sand, silt	17,287	not reported	middle distillates/diesel	Schwille, 1970
coarse gravel	4,895	not reported	fuel oil	Schwille, 1970
gravel, coarse sand	7,784	not reported	fuel oil	Schwille, 1970
coarse sand, medium sand	14,585	not reported	fuel oil	Schwille, 1970
medium sand, fine sand	24,324	not reported	fuel oil	Schwille, 1970
fine sand, silt	38,919	not reported	fuel oil	Schwille, 1970
coarse sand	26,002	32,936	gasoline	Hoag & Marley, 1986
medium sand	26,602	46,604	gasoline	Hoag & Marley, 1986
fine sand	32,936	104,009	gasoline	Hoag & Marley, 1986
well graded fine to coarse sand	79,741	102,276	gasoline	Hoag & Marley, 1986
glacial till	23,774	36,403	mineral oil	Pfannkuch, 1988
alluvium	37,642	not reported	mineral oil	Pfannkuch, 1988
coarse sand	23,774	not reported	paraffin oil	Convery, 1979
fine sediments	103,019	not reported	paraffin oil	Convery, 1979
Ottawa sand	21,792	39,870	paraffin oil	Convery, 1979
Saturated Zone Example Data From Mercer and Cohen Summary, 1990				
Soil Description/ Texture	Lower Measured Value of Residual Concentration (mg/kg)	Upper Measured Value of Residual Concentration (mg/kg)	Dil Type	Reference
92% sand, 5% silt, 3% clay	41,604	not reported	benzene	Lenhard & Parker
92% sand, 5% silt, 3% clay	45,071	not reported	benz alcohol	Lenhard & Parker
92% sand, 5% silt, 3% clay	27,736	not reported	p-cymene	Lenhard & Parker
92% sand, 5% silt, 3% clay	32,936	not reported	o-xylene	Lenhard & Parker
coarse Ottawa sand	39,004	69,340	1,1,1-trichlorethene	Anderson, 1988
coarse Ottawa sand	39,004	43,337	tetrachlorethene	Anderson, 1988
medium aeolian sand	46,566	50,271	karosene	Wilson, et al., 1990
medium aeolian sand	46,804	53,736	gasoline	Wilson, et al., 1990
medium aeolian sand	43,337	50,271	n-decane	Wilson, et al., 1990
medium aeolian sand	34,670	46,804	p-xylene	Wilson, et al., 1990
medium aeolian sand	67,606	50,271	tetrachlorethene	Wilson, et al., 1990
medium aeolian sand	43,585	64,139	solrol	Wilson, et al., 1990

Table 6 is from Ohio EPA-DERR Guidance for Assessing Petroleum Hydrocarbons in Soil (Ohio 2004)

Table 6 Total Petroleum Hydrocarbon Soil Saturation Concentrations (values are in mg/kg).

Petroleum Fraction	Residual Saturation Concentrations for:	Residual Saturation Concentrations for:	Residual Saturation Concentrations for:
	Sand and Gravel; Unknown Soil Type $K_v: 10^{-3} - 10^{-4}$ cm/s	Silty/Clayey Sand $K_v: 10^{-4} - 10^{-5}$ cm/s	Glacial Till and Silty Clay $K_v: < 10^{-5}$ cm/s
Light (C ₅ -C ₁₂)	1,000	5,000	8,000
Middle (C ₇ -C ₁₆)	2,000	10,000	20,000
Heavy (C ₁₈ -C ₃₈)	5,000	20,000	40,000

Where: "mg/kg" means milligrams per kilogram, "K_v" means vertical hydraulic conductivity of the unsaturated soil, "cm/s" means centimeters per second, and "C_x" means carbon chain length.

Residual soil concentration data is also summarized on Table 2 of Non-Aqueous Phase Liquid (NAPL) Mobility Limits in Soil (API 2000), but the table is too large to be reproduced in this document. It can be found with this link, [API 2000](#).