Transmittal

Date: July 23, 2015 Reference No.: 086165-01-01

To:
Mr. Phil Richard
Wisconsin Department of Natural Resources
875 S 4th Avenue
Park Falls, Wisconsin 54552

Subject: Alternate Remedy Recommendation

No. of Copies	Description/Title	Drawing No./ Document Ref.	Issue
1	Alternate Remedy Recommendation	086165 (5)	
	Penta Wood Products Superfund Site - Siren Wisconsin		
	Report 5, dated July 22, 2015		

Issued for: ☐ Your information ☒ As requested ☐ Construction ☐ Quotation
☐ Your approval/comments ☐ Returned to you ☐ For re-submission

Sent by: ☐ Overnight courier ☐ Same day courier ☐ Mailed under separate cover ☒ Mail enclosed

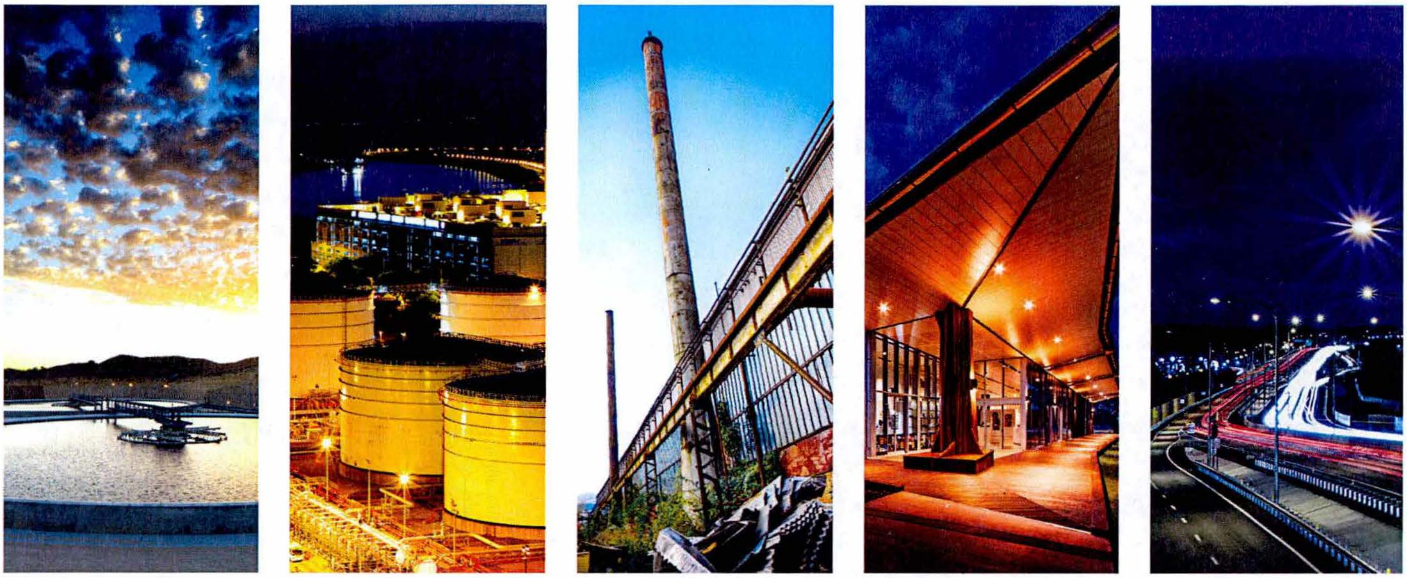
Remarks:

Copy to:

Completed by: Tim Ree
[Please Print]

Signed:

Filing: Correspondence File



Alternate Remedy Recommendation

Penta Wood Products Superfund Site
Siren, Wisconsin

Wisconsin Department of Natural Resources

1801 Old Highway 8 Northwest, Suite 114 St. Paul Minnesota 55112
086165 | Report No 5 | July 22 2015

Table of Contents

Figure Index

Table Index

Appendices

1. Introduction

GHD Services Inc. (GHD) prepared this Recommendation of Remedy Change for the Penta Wood Products Superfund Site (Site) in Siren, Wisconsin on behalf of Wisconsin Department of Natural Resources (WDNR). The Site location is shown on Figure 1.1, the Site plan is shown on Figure 1.2, and surrounding residential well locations are shown on Figure 1.3. This report presents:

- Introduction, background, and purpose (Section 1)
- Remedial action objectives (Section 2)
- LNAPL conceptual site model (Section 3)
- Significant changes (Section 4)
- Alternate remedy evaluation (Section 5)
- Recommended remedy (Section 6)
- Performance standards (Section 7)
- References (Section 8)

1.1 Purpose

The Record of Decision (ROD) issued by the United States Environmental Protection Agency (USEPA, November 1998) established remedial objectives to address the principal threat (i.e., light non-aqueous phase liquid (LNAPL) and soil contamination) and reduce risk through groundwater remediation. The ROD anticipated a point in time when active remediation could transition to Monitored Natural Attenuation (MNA). Extensive Site characterization data indicate that LNAPL has been remediated to the extent practicable and the residual LNAPL does not pose a principal threat. Natural attenuation can now effectively remediate residual contamination. GHD has reviewed the performance data and determined that active remediation has reached a point of diminishing returns over the past several years and is no longer required. Remediation can continue to be effective through Natural Source Zone Depletion (NSZD) to remediate residual LNAPL and MNA to remediate the remaining dissolve constituent plume in the groundwater. Either an Explanation of Significant Differences (ESD) or ROD Amendment is required to make this change.

The purpose of this document is to provide information to justify and recommend a change of the selected remedial action for the Site. This recommendation is based on significant changes in Site conditions because the active remedy has accomplished the goal. Also, there have been significant advances in the science and technical understanding of LNAPL remediation.

The ROD identified five potential remedial action alternatives (Alternatives 1 through 5). Alternative 3 was selected for the Site and consisted of the following components:

- Land use restrictions
- Building demolition
- Dismantle biopad and backfill onsite
- Grading, lagoon buttress, revegetation
- Excavation of hot spots, washout gully soils and sediments, and consolidation

- Soil cover over consolidated soils and sediments
- Insitu bioventing of vadose soils
- Insitu bioventing of dewatered smear zone
- LNAPL collection and offsite disposal
- Groundwater collection in LNAPL area
- Monitored natural attenuation – groundwater (outside of the LNAPL area)
- Granular activated carbon (GAC) adsorption
- Discharge of treated water via infiltration
- Environmental monitoring
- Maintenance of cover and erosion control
- Alternative water supply
- Five-year reviews

The recommended modified remedy proposed here (identified herein as Alternative 3A) would include:

- Land use restrictions through institutional controls
- MNA – groundwater
- NSZD – LNAPL
- Environmental monitoring
- Modified Performance Standards
- Maintenance of cover and erosion control
- Alternative water supply
- Five-year reviews

1.2 Background

A detailed background and history of the Site and associated actions is provided in the Five-Year Review Report (USEPA, January 2015). Historical Site data are presented in Appendix A of this report.

2. Remedial Action Objectives

The ROD specifies the following statutory and regulatory requirements (remedial action objectives) for the remedial action at the Site:

- Reduce/eliminate the potential risks to human health and ecological receptors associated with exposure to pentachlorophenol (PCP) and fuel oil components in surface water and groundwater, and PCP/fuel oil components and metals in the soil and sediment.
- Reduce/control the source of contaminants.

- Reduce the concentrations of these compounds in the groundwater plume to PALs (WDNR Preventive Action Limits).
- Satisfy Applicable or Relevant and Appropriate Requirements (ARARs).

The performance goals of the remediation system have been identified as:

- Remove LNAPL, to the extent practicable, to reduce a source of PCP to the groundwater.
- Extract and treat the most concentrated portions of PCP in the groundwater (exceeding 1,000 micrograms per liter (μg/L)), and reduce concentrations to a level that allows natural attenuation to achieve the Ch. NR 140, Wis. Adm. Code standards in a reasonable period of time.
- Lower the water table, to the extent practicable, to allow bioventing to promote natural degradation of the residual diesel range organics and PCP in the LNAPL smear zone.
- Comply with WPDES discharge criteria.

3. LNAPL Conceptual Site Model

A LNAPL Conceptual Site Model (LCSM) is a body of information describing aspects of the LNAPL and site setting necessary to satisfy the LNAPL remedial/management objectives (ASTM 2007, ITRC 2009). The LCSM is similar to a traditional Conceptual Site Model, which includes the source, pathway, and receptor, but the emphasis in the LCSM is on the LNAPL. The LCSM is comprised of some or all of the following scientific and technological information:

- Site setting
- Release history
- Remedial history
- Hydrogeological information
- LNAPL physical (e.g. density and viscosity) and chemical properties (e.g. constituents)
- LNAPL spatial distribution (vertical and horizontal delineation)
- LNAPL mobility and body stability/migration information
- LNAPL recoverability information
- Carbon footprint

3.1 Site Setting

The Site is a former wood treatment facility on an 82-acre property. The property is located in a rural and agricultural setting with residences located to the east, west, and south. Forested and wetland areas border the property to the north/northeast. The residential properties contain drinking water wells. The Site is situated on a hill with approximately 110 feet of drop in elevation toward the north/northeast. The Site layout and residential well locations are shown on Figures 1.2 and 1.3, respectively.

Future Site use will be controlled by institutional controls.

3.2 Release History

Contaminants were released to the subsurface during operation from 1953 to 1992. Raw timber was treated with a PCP and fuel oil solution or with a waterborne salt treatment chemical. The facility discharged wastewater from an oil/water separator through a gully into a lagoon located at the northeast corner of the property. Process wastes were discharged onto a wood-chip pile in the northwestern portion of the property. Beginning in the 1970s, WDNR observed several large spills, stained soils, fires, and poor operating practices. USEPA conducted a removal action during 1994 through 1996. Buildings were demolished and the remaining chemicals and sludge were disposed offsite. Highly contaminated soil was excavated and disposed offsite. Erosion control measures were implemented in 1998 to reduce washout of the contaminated wood debris from the lagoon into the wetlands. Thus a substantial portion of the source was removed. As such, there has been no on-going releases to drive further LNAPL migration at the Site for over 20 years. In addition, any residual LNAPL head that may have existed at the time of the previous actions would have long since dissipated or been eliminated through the various excavations and other remedial actions.

3.3 Remedial History

Extensive remedial actions have been conducted at the Site since USEPA issued the ROD in November 1998, including the following:

- Soil and sediment excavation and consolidation
- Bioventing
- Groundwater extraction and treatment
- LNAPL recovery
- Monitored natural attenuation of the remaining dissolved contaminant plume outside of the groundwater capture area

Initial operation of the remediation system started in October 2000. Due to the presence of emulsified oil in the extracted groundwater, additional pretreatment studies, design, and facility construction were conducted. The full treatment system operation including additional pretreatment began in March 2004 and operated through August 2014. In 2010, three additional extraction wells were installed in an effort to accelerate cleanup activities.

WDNR took over remediation system operations at the Site on September 1, 2014. During October 2014, the remediation system operation was modified to exclude the pretreatment portion of the system. In addition, LNAPL recovery was performed manually on a periodic basis.

3.4 Hydrogeology

The subsurface at the Site consists of unconsolidated soil and has been characterized with two aquifers, the unconfined aquifer (upper portion) and semiconfined aquifer (lower portion). The upper aquifer consists of sand and gravel with silt and clay to depths of 90 to 120 feet below ground surface. A glacial till, which separates the upper aquifer from the lower aquifer, consists of silt, silty sand, and sandy silts with gravel in a layer with thicknesses ranging between 3 to 45 feet. The till is present under most of the Site. The lower aquifer consists of sand and gravel. A general cross-section of the subsurface stratigraphy is shown on Figure 3.1.

The LNAPL is present within the unconfined aquifer at depths ranging between approximately 80 and 115 feet below ground surface. Based on historical groundwater level monitoring data and the observed groundwater level fluctuations, the LNAPL smear zone is approximately 7 feet thick and is located exclusively in the upper aquifer.

3.5 LNAPL Physical and Chemical Properties

The LNAPL is lighter than water with a density of approximately 0.95 grams per cubic centimeter. The viscosity of the LNAPL was measured at 9.7 centipoise, which is within the typical range (i.e., same order of magnitude) for weathered diesel fuel and kerosene. The LNAPL is a 5- to 7-percent PCP solution in a No. 2 fuel oil carrier.

3.6 LNAPL Extent

The areal extent of LNAPL based on measured in-well thicknesses is shown on Figure 3.2 and is less than 2 acres in size. The vertical distribution of LNAPL is localized within the unconfined aquifer. Based on historical groundwater level fluctuations, the smear zone is anticipated to be approximately 7 feet thick at the groundwater table. The plots of the well gauging data over time (Charts 1 and 2, Long-Term Remedial Action Report, CH2M HILL, November 2014) indicate that the predominant LNAPL behavior (i.e., how LNAPL thickness in wells changes with fluctuations in water table depth) is consistent with unconfined conditions in that in-well LNAPL thickness decreases with a rising water table and vice versa.

3.7 LNAPL Mobility and Body Stability

LNAPL migration is not occurring at the Site because there has not been an active LNAPL source to drive the migration in over 20 years. Given that a significant amount of the original LNAPL source has been aggressively removed through operation of the remediation system and the remaining LNAPL body is over 20 years old, the LNAPL body would have stabilized long ago. Most importantly, the footprint of where LNAPL is observed in wells has remained stable (i.e., LNAPL has not been observed outside of the LNAPL area) during historical monitoring. This provides a strong line of evidence that the Site LNAPL is predominantly present at immobile residual saturation levels.

3.8 LNAPL Recoverability

LNAPL recovery rates have reportedly ranged between approximately 3,000 and 5,000 gallons per year (8 and 14 gallons per day) under aggressive remediation since 2008, although there is some question as to whether these rates have been overestimated due to the way they were calculated historically (i.e., a fraction of the total fluids recovered was assumed to be LNAPL rather than specifically quantifying the volume of LNAPL). Regardless, based on a LNAPL body size/area of approximately 2 acres, this recovery rate is considered low at less than 10 gallons per day per acre. This low rate of recoverability is consistent with the viscosity and age of the LNAPL, which no longer has a driving source and localized saturations that have been progressively reduced due to remedial activities and smearing with groundwater level fluctuations.

LNAPL recovery is no longer considered technically feasible or required to stabilize the LNAPL given its well-stabilized state and calculated LNAPL transmissivity values less than the ITRC minimum threshold required for recovery (0.1 to 0.8 square feet per day). The remediation system has therefore achieved LNAPL recovery to the maximum extent practicable since a practical science-based end-point has been met.

3.9 Carbon Footprint

Based on the operation of the remediation system, the calculated a carbon footprint at the Site is approximately 1 million pounds of carbon dioxide per year. Much of the carbon dioxide load is associated with trucking and incinerating waste from the operation. Given the current Site conditions and comparing this carbon footprint with the most recent remedial system performance, it is likely that the operation of the current remedial system is producing a net environmental deficit.

4. Significant Changes

Conditions at the Site have changed significantly since remedial alternatives were evaluated and one alternative was selected in the ROD. In addition, advances in the science and technical understanding have changed LNAPL remediation. This section discusses these issues below.

4.1 Advances in the Science of LNAPL Remediation

The understanding of the science and behavior of LNAPL in the subsurface has significantly evolved since the ROD (1998) in large part based on the following guidance documents:

- American Petroleum Institute (API). August 2003. Models for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids. American Petroleum Institute Publication Number 4729.
- American Petroleum Institute (API). August, 2004. API Interactive LNAPL Guide, Version 2.0. American Petroleum Institute, Washington, District of Columbia.
- United States Environmental Protection Agency (USEPA). March 2005. EPA 542-R-04-011: A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL).
- American Society for Testing and Materials (ASTM). February 2007. E 2531-06: Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface.
- The Interstate Technology & Regulatory Council (ITRC). April 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL.
- The Interstate Technology & Regulatory Council (ITRC). December 2009. Evaluating LNAPL Remedial Technologies for Achieving Project Goals.
- Wisconsin Department of Natural Resouces (WDNR). February 2008. PUB-RR-787: Assessment Guidance for Sites with Residual Weathered Product.

As an example, the common understanding of LNAPL today is as follows:

- Most LNAPL bodies that have been in the ground for years (with no continuing source) are typically found to be stable (not migrating). The fraction of an LNAPL body that will be potentially mobile and/or recoverable will typically be quite low. API indicates that (API 2002): "*...for <u>most</u> of the hydraulic recovery cases evaluated from literature and in our own records, the <u>total LNAPL recovery was less than 30%</u> of the original volume in-place with the upper end being as high as 60%...The implication is that <u>for most sites, recovery of more than 30% of the LNAPL in-place would be the exception rather than the rule</u>.*" [underline added]. The longer the

LNAPL is in the ground, the smaller the potentially recoverable fraction becomes as LNAPL becomes increasingly disconnected and NSZD[1] processes progress. At sites where LNAPL has been in the ground for a number of years, as with the Penta Wood Products Superfund Site, it is GHD's experience that 10% or less is a reasonable expectation for the fraction of the LNAPL in-place that might be recoverable.[2]

- Many LNAPL bodies will be found to produce levels of dissolved and/or vapor phase contamination that are either undetectable or within risk-based screening levels. Even where dissolved and/or vapor phase contamination is unacceptably elevated, LNAPL recovery will do relatively little in terms of risk reduction since the vast majority of the LNAPL will remain (see previous point) and the mole fractions of constituents of concern will remain unchanged (i.e., no effect on volatilization or dissolution rates).
- Most LNAPL bodies will self-stabilize in a relatively short period of time following the cessation of active releases; therefore, LNAPL recovery will very often provide no significant added benefit in the mitigation or migration at sites where LNAPL has been in the ground for many years.

Further discussion on LNAPL occurrence, behavior and migration is presented as a series of technical appendices that form the basis for much of the commentary/interpretation provided in the remainder of this report:

- A list of common LNAPL-related terms and definitions is provided in Appendix B.
- A general discussion on LNAPL release dynamics, the creation of a multi-phase fluid system (i.e., LNAPL body), LNAPL saturation/residual saturation, mobility/body stability, chemical/physical properties, etc. is provided in Appendix C.
- A discussion of the analytical equations and models used to describe LNAPL occurrence, behavior and migration at the water table is presented in Appendix D.
- A discussion regarding the relevance and interpretation of LNAPL in-well thickness measurements is provided in Appendix E.

In 2013, the USEPA released a draft guidance document that speaks to the importance of establishing a plan to complete groundwater remediation within a reasonable time-frame. USEPA recognizes that groundwater remedies with long-term operation and maintenance do not always provide value. As such, USEPA is encouraging project managers to find cost-effective ways to reach Site closure. This report was prepared with consideration of USEPA's draft guidance.

4.2 System Performance

Approximately 242 million gallons of groundwater have been extracted, treated, and discharged through operation of the remediation system. Approximately 42,000 gallons of LNAPL have reportedly been recovered from the subsurface (Table 5-5, Long-Term Remedial Action Report, CH2M HILL, November 2014). Bioventing contributed to the degradation of contaminants in the vadose zone. These remedial actions represent significant changes that have occurred at the Site since before the remedy (Alternative 3) was selected and implemented and directly caused the change in conditions discussed in Section 4.3. LNAPL remediation has been effective at reducing

---

[1] See ITRC's Evaluating Natural Source Zone Depletion at Sites with LNAPL (April 2009)

[2] Based on soil/rock core petrophysical testing quantifying LNAPL saturations, residual saturations, and potentially recoverable fractions at numerous sites

the mobility/recoverability of the LNAPL to de minimis levels and has accomplished the goal for remediation of reducing the principal threat to groundwater to the extent practicable.

4.3 Current Conditions

4.3.1 Dissolved PCP Plume

The source remedy has resulted in a dramatic improvement in groundwater quality. Figure 4.1 shows that PCP concentrations at MW5 have declined significantly and have remained low for the past 3 years. Similarly, Figure 4.2 shows that PCP concentrations at MW10 have declined and remained low for the past 3 years.

As shown on Figures 8 through 11 of the Long-Term Remedial Action Report (CH2M HILL, November 2014), the dissolved PCP (primary constituent of concern at the Site) plume has decreased in size as follows:

- The area within the unconfined aquifer with PCP concentrations exceeding 1,000 ug/L decreased in size from approximately 5 acres (2008) to approximately 2 acres (2014).
- The area within the unconfined aquifer with PCP concentrations exceeding 1 ug/L decreased in size from approximately 10 acres (2008) to approximately 3 acres (2014) and is limited to within the Site property boundaries.
- The area within the semiconfined aquifer with PCP concentrations exceeding 1,000 ug/L was approximately 18 acres (1994). During 2009 through 2014, PCP was not detected in the semiconfined aquifer at concentrations exceeding 1,000 ug/L.
- The area within the semiconfined aquifer with PCP concentrations exceeding 1 ug/L decreased in size from larger than 20 acres (1994) to smaller than 2 acres (2014) and is limited to within the Site property boundaries.

At the Site, the initial purpose of groundwater remediation was to aggressively dewater to recover LNAPL and increase the smear zone available to bioventing. This work has been completed. In terms of PCP dissolution from the source zone to groundwater, the rate of dissolved phase which partitions from the LNAPL is small enough that MNA is effective as a groundwater remedy.

4.3.2 LNAPL Body

Based on the presence of LNAPL in wells at the Site, the size of the LNAPL body has remained stable from the time prior to implementing the remedy through more than 10 years of remediation system operation. The size of the LNAPL body is approximately 2 acres and is limited to within the Site property boundaries.

GHD also evaluated the trends in LNAPL thickness measurements at Site monitoring wells. Figures 4.3 and 4.4 show LNAPL measurements for MW10S and MW19, respectively. As shown, the LNAPL thickness varies and shows the common condition of thicker LNAPL in wells during low water tables (typical for unconfined conditions).

Four monitoring wells (MW10S, MW18, MW19, MW20) contain measurable LNAPL at thicknesses of less than 1 foot. Of the eleven extraction wells at the Site, six extraction wells (EW02, EW03, EW04, EW07, EW11, and EW13) do not contain LNAPL at measurable thicknesses. Three extraction wells (EW05, EW12, and EW14) contain LNAPL thicknesses less than 1 foot. Two extraction wells (EW06 and EW10) contain LNAPL thicknesses greater than 1 foot. The portion of the LNAPL body where LNAPL thicknesses are greater than 1 foot is less than approximately 0.5 acre. It is noted that in-well LNAPL thicknesses are generally not a good indicator of LNAPL mobility/recoverability and will generally not have any bearing on the stability of an old LNAPL body. Once an LNAPL body stabilizes, it will typically remain so even if significant in-well LNAPL thicknesses are observed within the areal extent of LNAPL impacts.

4.3.3 Soil excavation and consolidation

Soil, wood chips, sediment, biopad debris, and other selected debris throughout the Site were excavated and consolidated into a Corrective Action Management Unit (CAMU) located at the Site in 2000. Confirmation sampling documented residual soil contaminant concentrations met the target limits as reported by CH2M HILL (Remedial Action Report, September 2000).

4.4 LNAPL Mobility and Recoverability

During 2013 and 2014, CH2M HILL conducted a LNAPL mobility and recoverability evaluation at the Site as documented in the LNAPL Mobility and Recoverability Report (CH2M HILL, October 2014). Conclusions of this work included:

- The LNAPL extent has been delineated and is approximately the same as the dissolved PCP plume exceeding concentrations of 1,000 ug/L.
- The LNAPL body is stable and not migrating based on laboratory-measured low/residual LNAPL saturations.
- LNAPL is no longer recoverable using hydraulic and/or pneumatic means based on calculated LNAPL transmissivity values less than the ITRC minimum threshold required for recovery (0.1 to 0.8 square feet per day).

During operation of the system from 2004 through August 2014, approximately 42,000 gallons of LNAPL were reportedly recovered at the Site (Long-Term Remedial Action Report, CH2M HILL, November 2014). A decline curve analysis estimates a total recoverable LNAPL quantity of approximately 50,000 gallons. This provides another line of evidence that LNAPL has effectively been recovered to the maximum extent practicable.

Significant advances in the science, understanding and remedial approach to LNAPL have been made in recent years. In 2009, the Interstate Technology and Regulatory Council (ITRC) established new guidance on the science of mobile versus residual LNAPL (ITRC, 2009a). It is now understood that the quantities of LNAPL recovered from the subsurface at most sites represents a very small fraction of the overall LNAPL body and that the vast majority of the LNAPL remains in the aquifer formation as trapped/immobile/unrecoverable residual. This immobile LNAPL may or may not appear in monitoring wells depending on stratigraphy and hydraulic conditions. Also, in 2009, the ITRC established guidance on NSZD which recognizes that residual LNAPL can and in most cases will remain within the formation (ITRC, 2009b) and is compatible with MNA for groundwater remediation. Under a NSZD remedy, it is recognized that the threat of migration is no longer present. Further, NSZD studies have shown that on the order of 1,000 gallons per acre per year of LNAPL depletion is typically achieved via NSZD processes. At the Site, the LNAPL area is approximately 2 acres, which means that up to 2,000 gallons/year of LNAPL could conceivably be depleted by natural processes. Therefore, NSZD can replace active LNAPL removal and have similar effectiveness of the active remediation system at the Site. Since most of the LNAPL at old

LNAPL sites will be present as unrecoverable residual, this strategy is simply an acknowledgement that NSZD can and will be the dominant remedial process at these sites.

5. Alternate Remedy Evaluation

5.1 Description of Remedial Action Alternatives

The ROD identified five potential remedial action alternatives (Alternatives 1 through 5). Alternative 3 was selected for the Site and consisted of the following components:

- Land use restrictions
- Building demolition
- Dismantle biopad and backfill onsite
- Grading, lagoon buttress, revegetation
- Excavation of hot spots, washout gully soils and sediments, and consolidation
- Soil cover over consolidated soils and sediments
- Insitu bioventing of vadose soils
- Insitu bioventing of dewatered smear zone
- LNAPL collection and offsite disposal
- Groundwater collection in LNAPL area
- Monitored natural attenuation – groundwater (outside of the LNAPL area)
- Granular activated carbon (GAC) adsorption
- Discharge of treated water via infiltration
- Environmental monitoring
- Maintenance of cover and erosion control
- Alternative water supply
- Five-year reviews

The recommended remedy (identified herein as Alternative 3A) includes:

- Land use restrictions through institutional controls
- MNA – groundwater
- NSZD – LNAPL
- Environmental monitoring
- Modified performance standards
- Maintenance of cover and erosion control
- Alternative water supply
- Five-year reviews

5.2 Nine-Criteria Evaluation

An evaluation against the Superfund nine criteria for remedy selection is presented below. The existing remedy (Alternative 3) and recommended remedy (Alterative 3A) are evaluated below.

5.2.1 Overall Protection of Human Health and the Environment

This criterion examines the risk remaining after the remediation has been conducted. Also, short-term risks associated with each remedy are evaluated. To compare the remedial actions with respect to the overall protection of human health and the environment, each pathway of exposure is discussed below:

Residential Ingestion

Residential ingestion of contamination involves the inadvertent intake of contamination by persons living at or near the Site. Both Alternatives 3 and 3A will leave a portion of the LNAPL in place. However, in both cases the residual LNAPL is located within the Site property boundaries. As a result this exposure pathway is incomplete for both remedies, and residents at adjacent properties will not be exposed to contamination at levels exceeding regulatory criteria. Alternatives 3 and 3A are equally protective with respect to the residential ingestion criterion.

Groundwater Use

Groundwater is used as a non-potable water supply at the Site. Concentrations in the onsite supply well meet the ES. Both alternatives require institutional controls to ensure that groundwater at the Site is not used as a drinking water source. Groundwater sample analytical data indicates that groundwater at the nearby residential properties meets the ES. Alternatives 3 and 3A are equally protective with respect to the groundwater use criterion.

Residential Inhalation

Residential inhalation involves an evaluation of the potential for organic compounds to volatilize and migrate into buildings. Under both alternatives, the Site cannot be developed as a residential property. LNAPL would be reduced but some LNAPL would remain. The potential for volatile organic compound (VOC) migration into any future onsite buildings outside of the CAMU is extremely low based on the presence of LNAPL at depths more than 80 feet below ground surface. Alternatives 3 and 3A are equally protective with respect to the residential inhalation criterion.

Future Construction Workers

The risk to future construction workers arises from potential dermal contact and/or inhalation of contaminants during construction activities. The most common post-remediation construction activity would be the excavation for utilities or building foundations. The historical data demonstrates the LNAPL and the LNAPL smear zone are located more than 80 feet below the ground surface and poses no risk to future construction workers outside of the CAMU. Alternatives 3 and 3A are equally protective with respect to the future construction worker criterion.

Ecological Risk

Ecological risk is associated with the release of contamination to the ground surface, wetlands or surface water. Given that the LNAPL is subsurface and is stable, there are no completed pathways to the ground surface, surface water or wetlands. The natural groundwater flow direction is to the northeast toward the wetland. However, groundwater monitoring data collected downgradient of the LNAPL, demonstrate that neither the LNAPL nor the dissolved constituents are migrating toward the wetland. Hence, the groundwater pathway to ecological receptors is not complete. Alternatives 3 and 3A are equally protective with respect to the ecological risk criterion.

5.2.2 Compliance with Applicable or Relevant and Appropriate Requirements (ARARs)

As documented on page 44 in the ROD (USEPA, November 1998), USEPA determined that the current remedy complies with federal and state ARARs. The recommended remedy will meet federal and state ARARs through institutional controls and modified Performance Standards.

5.2.3 Long-Term Effectiveness and Permanence

Implementation of the selected remedy has permanently removed a portion of the contamination at the Site. Through advancement in LNAPL science and understanding, it is now recognized that it is not technically feasible to remove all LNAPL at remediation sites. Under either the current remedy or the recommended remedy, institutional controls in the form of groundwater use restrictions and land use restrictions would be required to address risks associated with residual contamination at the Site. Institutional controls will make the remedy effective long-term.

5.2.4 Reduction in Toxicity, Mobility, and Volume

As stated above (Section 4.0), the current remedy has significantly and permanently reduced the contamination in soil and groundwater at the Site. The recommended remedy will continue to reduce the toxicity, mobility, and volume at the Site. Through advancement in LNAPL science and understanding, it is now recognized that it is not technically feasible to remove all LNAPL at remediation sites. Accordingly, it is impracticable to reduce dissolved constituent concentrations to levels below the PAL or ES via engineered methods such as the current system or any other techniques that would typically be considered feasible at a site where there are no unacceptable exposure scenarios that cannot be effectively mitigated through institutional controls. As such, natural processes would be required to address residual contamination beyond what has been achieved to date and any other potential exposure scenarios would be managed through institutional controls.

5.2.5 Short-Term Effectiveness

Neither alternative has a short-term effectiveness impact since the alternatives do not require remedial construction. A two-year monitoring period of the recommended remedy will confirm that the short-term effectiveness will not be impacted.

5.2.6 Implementability

Continued implementation of the current remedy (Alternative 3) is possible. However, significant energy resources and manual labor would continue to be required to operate, maintain, and monitor the remediation system with much higher carbon footprint and little added remedial benefit expected over Alternative 3A. Implementation of the recommended remedy is also possible.

5.2.7 Cost

Annual remediation system operation and maintenance costs for the current remedy (Alternative 3) were approximately $1.1 million based on the summary table provided in Appendix A of the Five-Year Review Report (USEPA, January 2015). These actual costs are significantly more than estimated costs in the ROD, which were approximately $4.4 million (net present worth over a 30-year period). Costs associated with continued full remediation system operation are estimated to be approximately $1.1 million per year. Costs associated with the recommended remedial action (Alternative 3A) are estimated to be less than $0.1 million. Costs are summarized in Tables 5.1 and 5.2.

A comparison of the two cost estimates illustrates that the recommended remedial action can achieve remediation at a significantly lower cost than the current remedial action.

5.2.8 WDNR Acceptance

WDNR has reviewed this evaluation and with submittal of this report documents concurrence with the recommended remedial action.

5.2.9 Community Acceptance

Community acceptance of Alternative 3 was evaluated in the ROD based on comments received at the Public Meeting and during the public comment period. There were no comments and there was no opposition to Alternative 3. WDNR and GHD believe that the recommended remedy (Alternative 3A) would only require issuance of an Explanation of Significant Differences (ESD) by USEPA and would not require a ROD Amendment. If USEPA determines that only an ESD is required, public notice and a meeting with comment period would not be required.

6. Recommendations

The following actions are recommended for the Site:

- Discontinue operation of the groundwater extraction system.
- Discontinue manual LNAPL recovery.
- Discontinue operation of the bioventing system.
- Conduct semiannual groundwater monitoring and sampling and semiannual residential well sampling to evaluate dissolved plume conditions and confirm that migration does not occur while the remediation system is not operating.
- Conduct semiannual LNAPL thickness monitoring to evaluate LNAPL extent and confirm that LNAPL migration does not occur while the remediation system is not operating (e.g., the appearance of LNAPL in a well that never previously contained LNAPL).
- Submit semiannual reports
- Continue remediation through MNA and NSZD.
- Modify Performance Standards as appropriate (see Section 7.0).
- Implement institutional controls as appropriate.

The above actions would be performed over a two-year period and the results would be evaluated to determine whether a permanent shutdown of the remediation system and implementation of a passive remedy of monitored natural attenuation of groundwater and natural source zone depletion of LNAPL will achieve the modified Performance Standards at the Site. Following USEPA acceptance of this recommendation, a detailed scope of work during the two-year monitoring period would be developed for USEPA review and approval. If monitoring indicates the modified remedy is successful, institutional controls in the form of groundwater use restrictions and land use restrictions would be updated as appropriate to address risks associated with residual contamination at the Site.

7. Performance Standards

As discussed, below, the statutory and regulatory requirements (remedial action objectives) specified in the Record of Decision (USEPA, November 1998) have been met through implementation of the selected remedy (Alternative 3) or will be met through implementation of the recommended remedy (Alternative 3A):

- Reduce/eliminate the potential risks to human health and ecological receptors associated with exposure to PCP and fuel oil components in surface water and groundwater, and PCP/fuel oil components and metals in the soil and sediment.
    - This requirement was met following the soil excavation and consolidation work as documented in the Remedial Action Report (CH2M HILL, September 2000).
- Reduce/control the source of contaminants.
    - This requirement was substantially met through operation of the remediation system since 2004.
- Reduce the concentrations of these compounds in the groundwater plume to PALs (WDNR Preventive Action Limits).
    - The performance standard for each constituent of concern is recommended to be modified from the Preventative Action Limit (PAL) to the Enforcement Standard (ES) as identified in Ch. NR 140, Wis. Adm. Code. Ch. NR 140, Wis. Adm. Code establishes two types of groundwater quality standards to serve as basis for site closure: PALs and ESs. PALs are the promulgated cleanup goals applicable to all Wisconsin cleanup sites, to the extent technically and economically feasible. This is codified in s. NR 140.22(1), Wis. Adm. Code, and in s. NR 722.09(2)(b), Wis. Adm. Code. The ESs are generally numerically equivalent to the maximum contaminant levels (MCLs) under the federal Safe Drinking Water Act.
    - WDNR indicates that it has used the ES as the basis for eligibility for site closure since the mid-1990s. This eligibility criterion has been adopted in Ch. NR 726, Wis. Adm. Code. WDNR has concluded that groundwater quality compliance with PALs at contaminant discharge sites in Wisconsin is in many cases not technically or economically feasible and has granted PAL exemptions under s. NR 140.28(2), Wis. Adm. Code, at the time of closure. A PAL exemption can be granted when it is shown that groundwater contamination is stable or decreasing and groundwater standards will be met within a reasonable period of time as a result of natural attenuation. It is recommended that a PAL exemption under s. NR 140.28(2), Wis. Adm. Code, is approved for this Site.
- Satisfy Applicable or Relevant and Appropriate Requirements (ARARs).

  - This requirement was met.

The performance goals of the remediation system have also been met as discussed below:

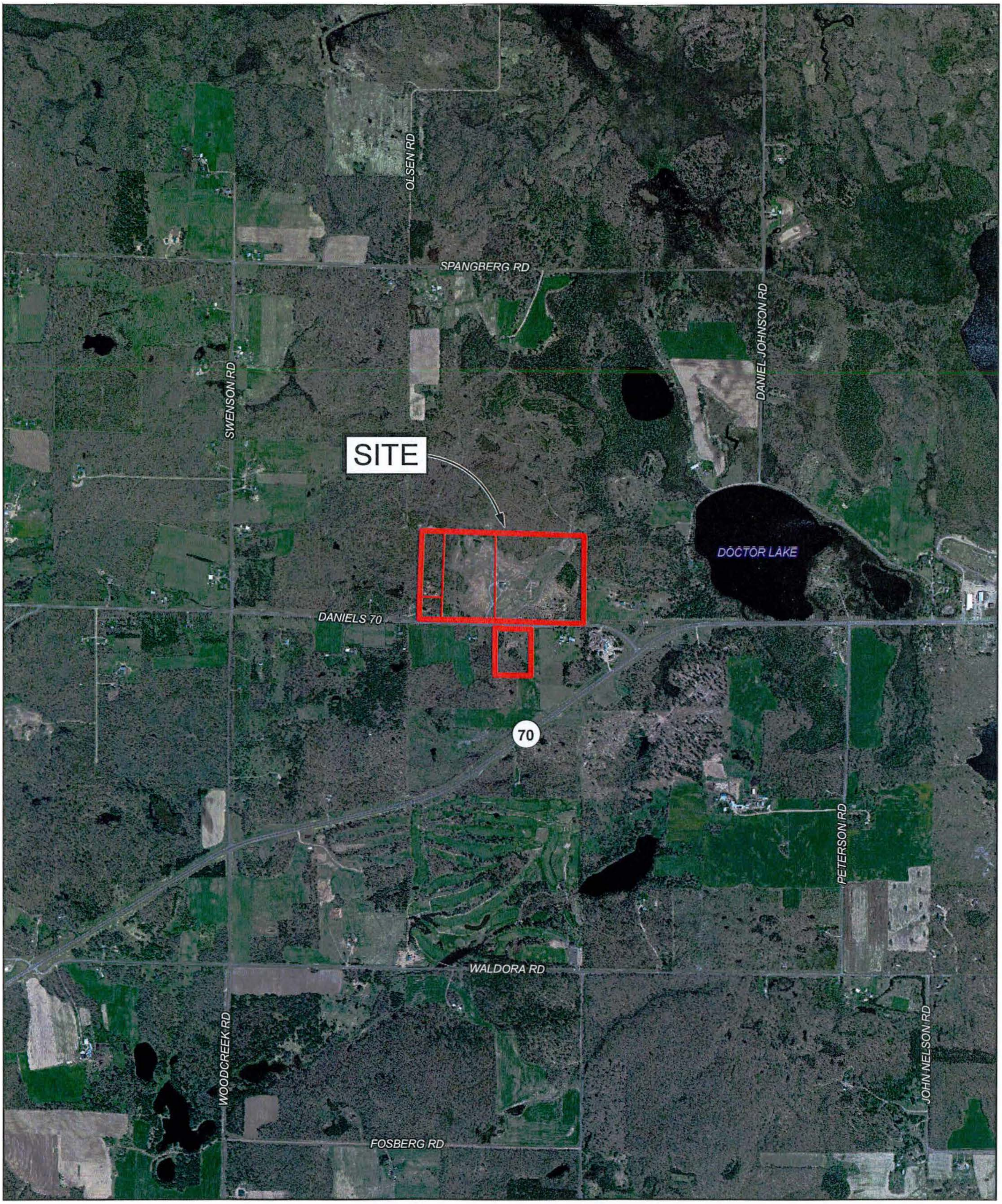
- Remove LNAPL, to the extent practicable, to reduce a source of PCP to the groundwater.
  - This goal was met by operation of the remediation system since 2004. LNAPL mobility and recoverability testing demonstrated that LNAPL has been recovered to the maximum extent practicable.
- Extract and treat the most concentrated portions (exceeding 1,000 micrograms per liter (μg/L)) of PCP in the groundwater, and reduce concentrations to a level that allows natural attenuation to achieve the NR 140 standards in a reasonable period of time.
  - This goal was substantially met by operation of the remediation system since 2004. The size of the dissolved plume has been significantly reduced. Dissolved concentrations will remain elevated in the immediate vicinity of the LNAPL body.
- Lower the water table, to the extent practicable, to allow bioventing to promote natural degradation of the residual diesel range organics and PCP in the LNAPL smear zone.
  - This goal was substantially met during operation of the remediation system since 2004.
- Comply with WPDES discharge criteria.
  - This goal was substantially met during operation of the remediation system since 2004.

8. References

The following key Site documents were referenced in preparation of this report:

- Record of Decision (USEPA, November 1998)
- Remedial Action Report (CH2M HILL, September 2000)
- Long-Term Remedial Action Report (CH2M HILL, November 2014)
- LNAPL Mobility and Recoverability Report (CH2M HILL, October 2014)

Figures



Source: DigitalGlobe 2011

0 1,000 2,000 ft

N

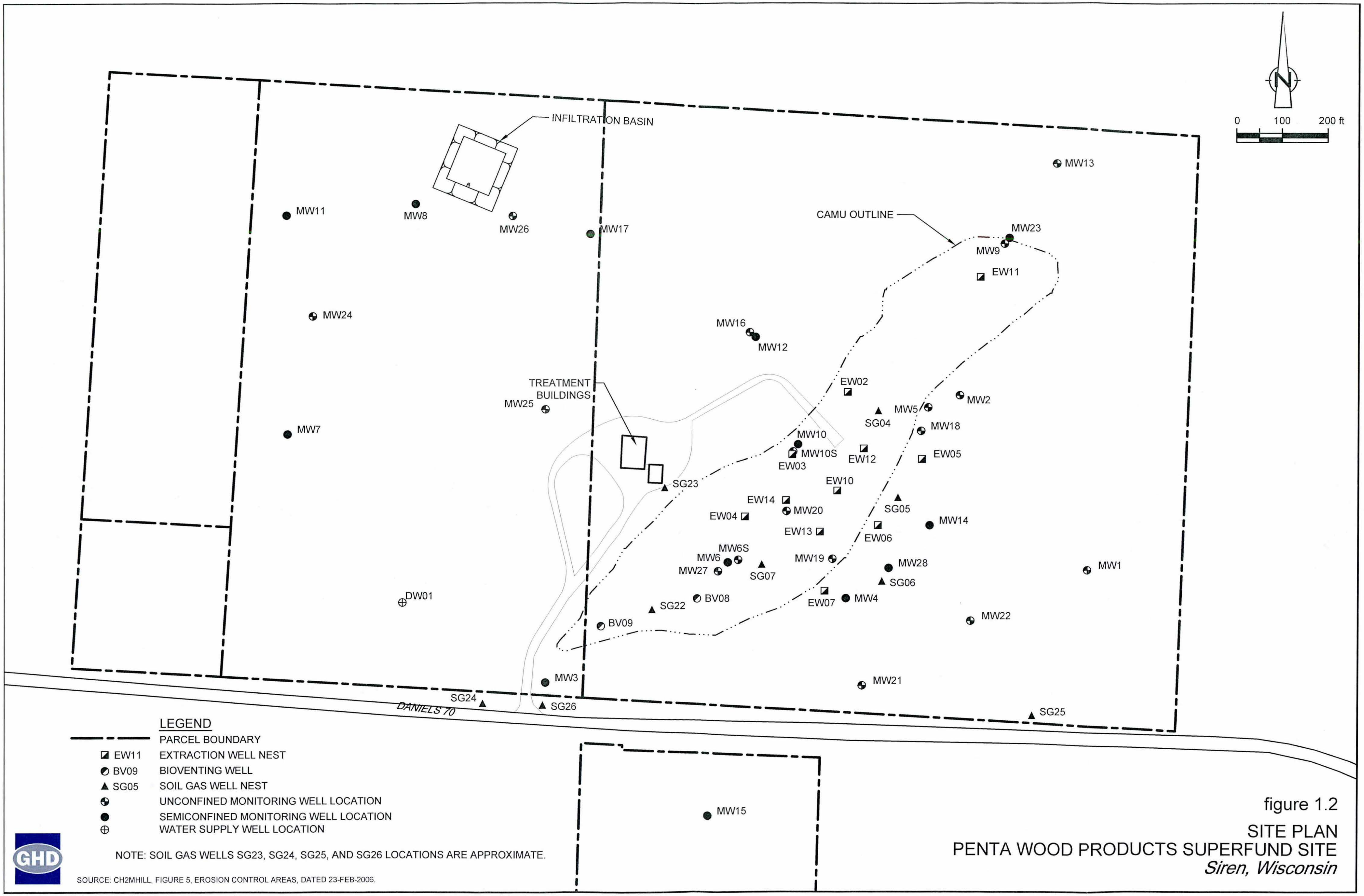
PENTA WOOD PRODUCTS
SUPERFUND SITE
SIREN, WISCONSIN

086165-01
Jul 22, 2015

SITE LOCATION

FIGURE 1.1

GIS File: I:\GIS\Projects\6-chars\08----\0861--\086165\086165-REPORTS\086165-01(005)\086165-01(005)GIS-SP001.mxd



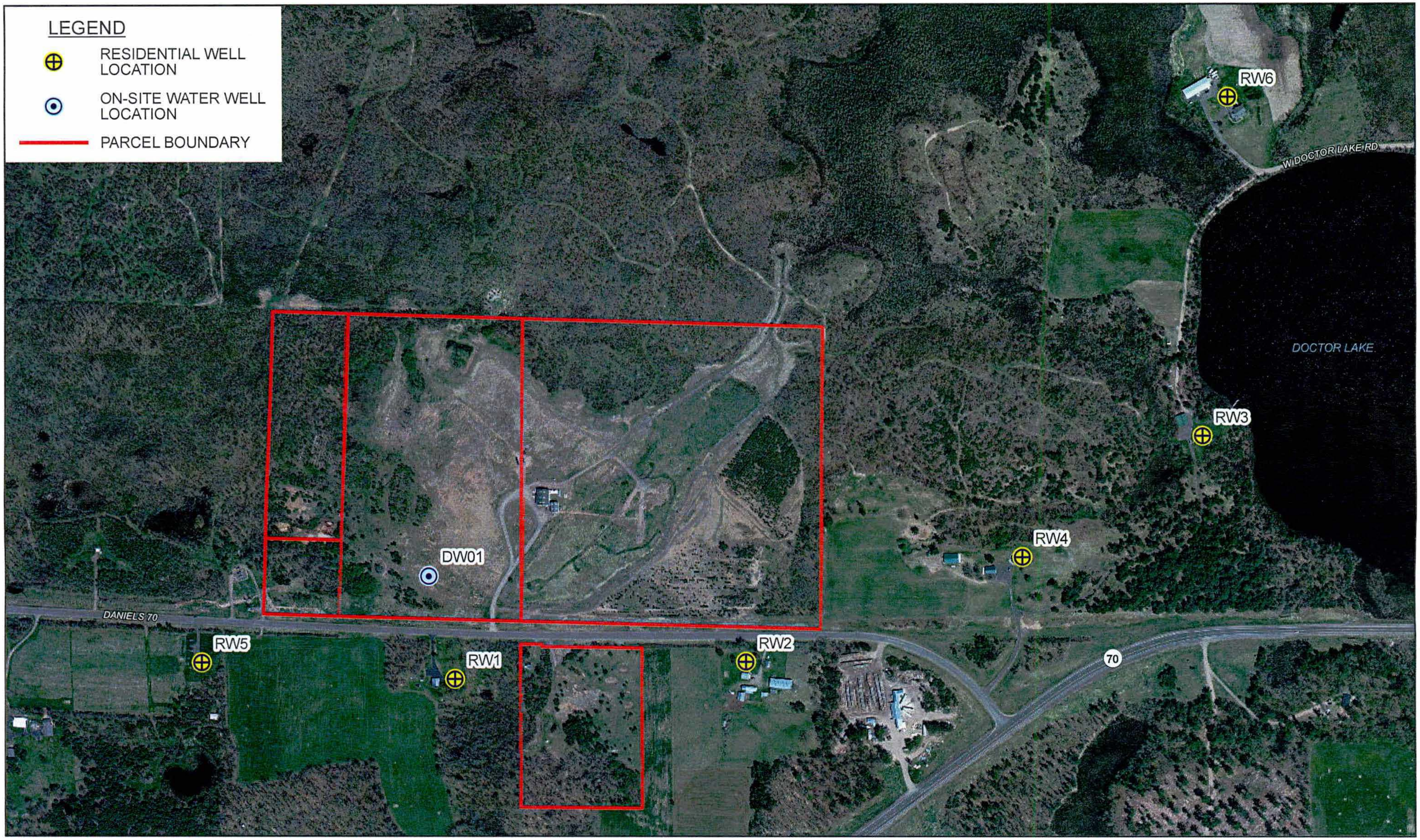
NOTE: SOIL GAS WELLS SG23, SG24, SG25, AND SG26 LOCATIONS ARE APPROXIMATE.

SOURCE: CH2MHILL, FIGURE 5, EROSION CONTROL AREAS, DATED 23-FEB-2006.

figure 1.2

SITE PLAN
PENTA WOOD PRODUCTS SUPERFUND SITE
Siren, Wisconsin

86165-01(005)GN-WA005 JUL 17/2015



0 200 400 600 ft

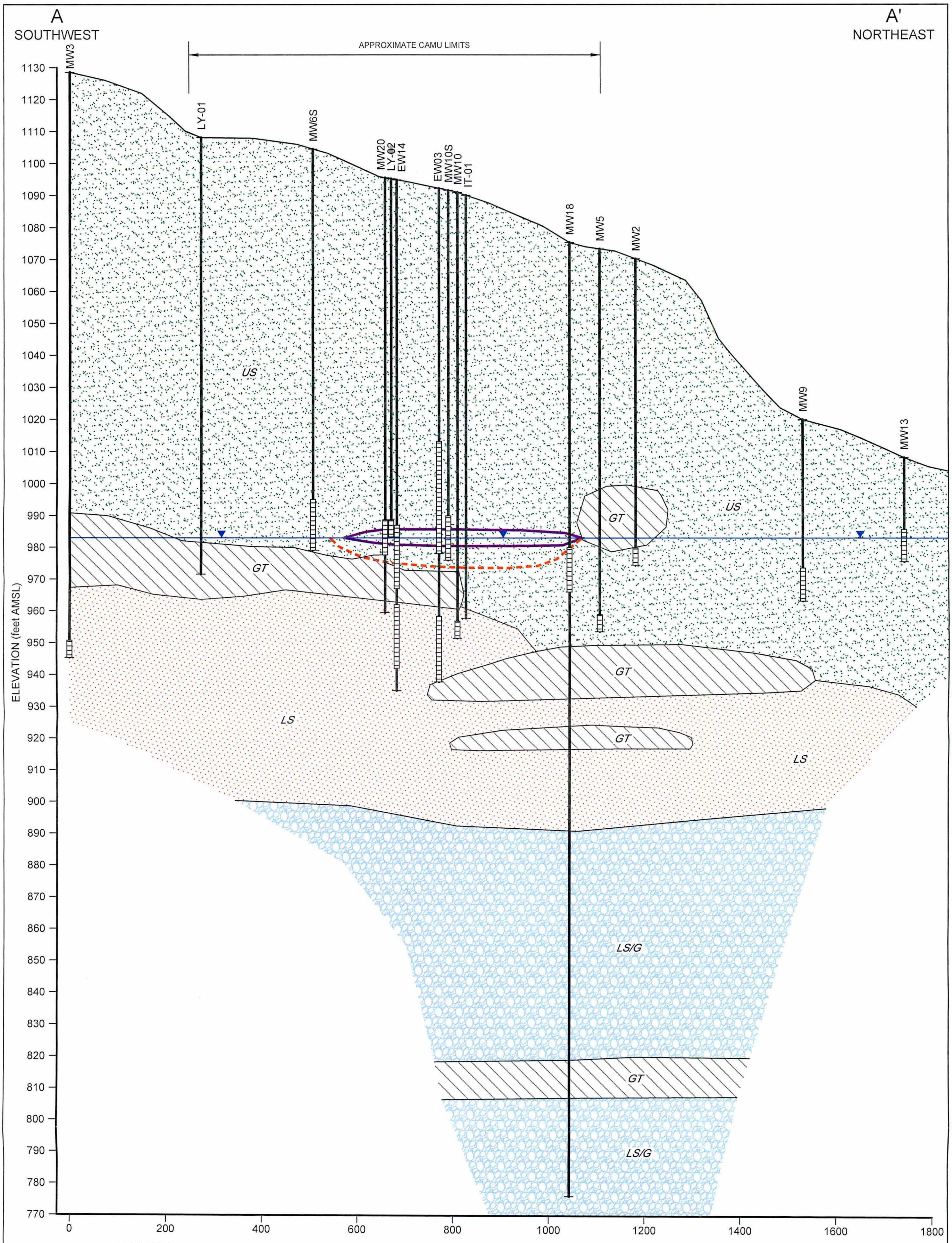
PENTA WOOD PRODUCTS SUPERFUND SITE
SIREN, WISCONSIN

086165-01
Jul 22, 2015

RESIDENTIAL WELL LOCATIONS

FIGURE 1.3

GIS File: I:\GIS\Projects\6-chars\08----\0861--\086165\086165-REPORTS\086165-01(005)\086165-01(005)GIS-SP002.mxd



LEGEND

MW-2 — WELL DESIGNATION
— GROUND SURFACE
— OBSERVATION WELL INSTALLATION
— STRATIGRAPHIC BOUNDARY
— SCREENED INTERVAL
— BOTTOM OF BORING
▼ APPROXIMATE WATER TABLE

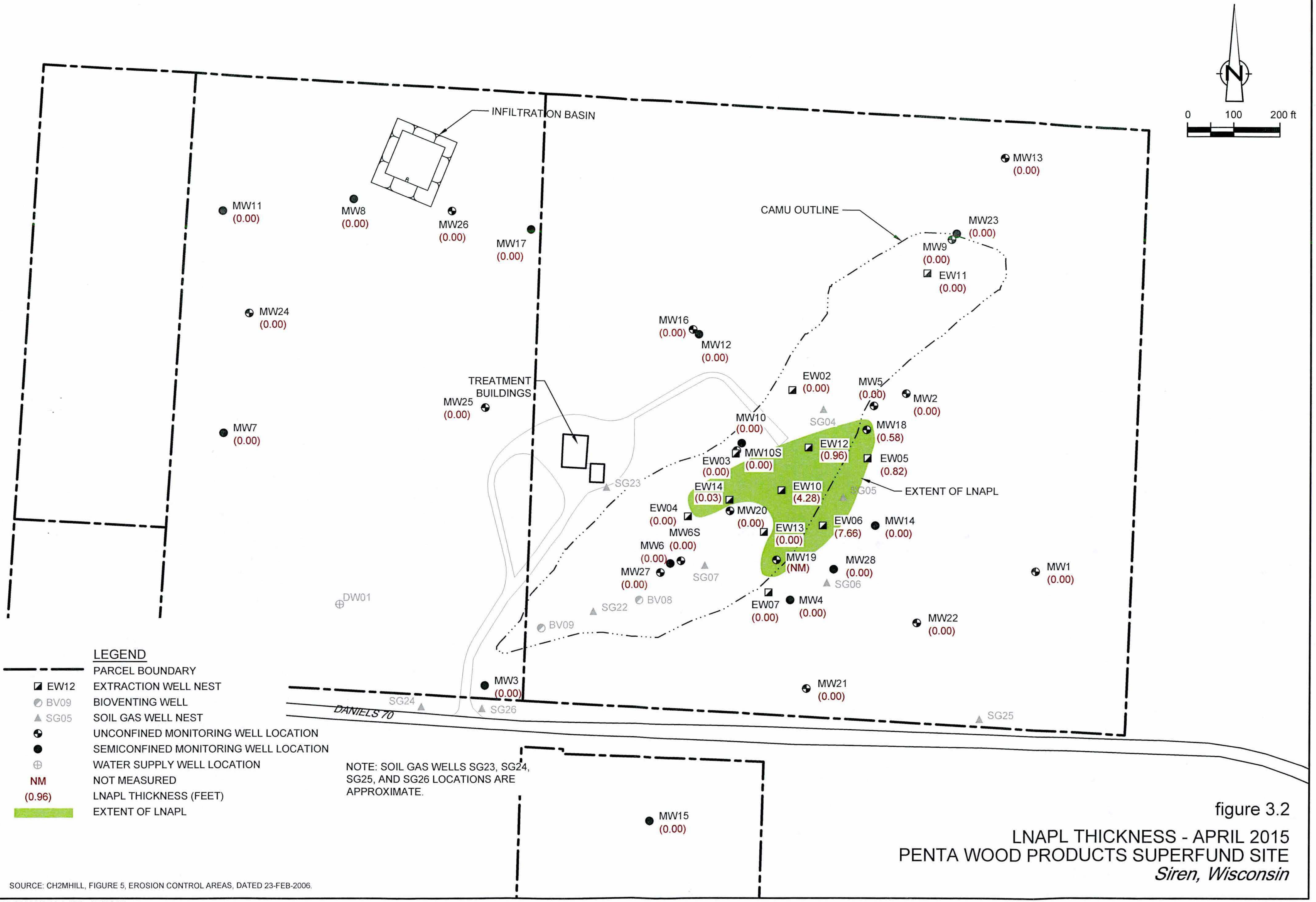
⁘	UPPER SAND (*US*) WELL GRADED SAND UNIT
▨	GLACIAL TILL (*GT*) SILTY SAND TO SANDY SILT WITH GRAVEL
⁘	LOWER SAND (*LS*) WELL GRADED SAND UNIT
⁘	LOWER SAND WITH GRAVEL (*LS/G*) WELL GRADED SAND WITH GRAVEL
—	APPROXIMATE LNAPL LIMIT
- - -	APPROXIMATE DISSOLVED PENTACHLOROPHENOL LIMIT

DISTANCE (feet)

SCALE: HORZ. 1" = 200'
VERT. 1" = 30'

figure 3.1

GENERAL CROSS-SECTION
PENTA WOOD PRODUCTS SUPERFUND SITE
Siren, Wisconsin



LEGEND

▬ · ▬	PARCEL BOUNDARY
◪ EW12	EXTRACTION WELL NEST
⊘ BV09	BIOVENTING WELL
▲ SG05	SOIL GAS WELL NEST
◕	UNCONFINED MONITORING WELL LOCATION
●	SEMICONFINED MONITORING WELL LOCATION
⊕	WATER SUPPLY WELL LOCATION
NM	NOT MEASURED
(0.96)	LNAPL THICKNESS (FEET)
🟩	EXTENT OF LNAPL

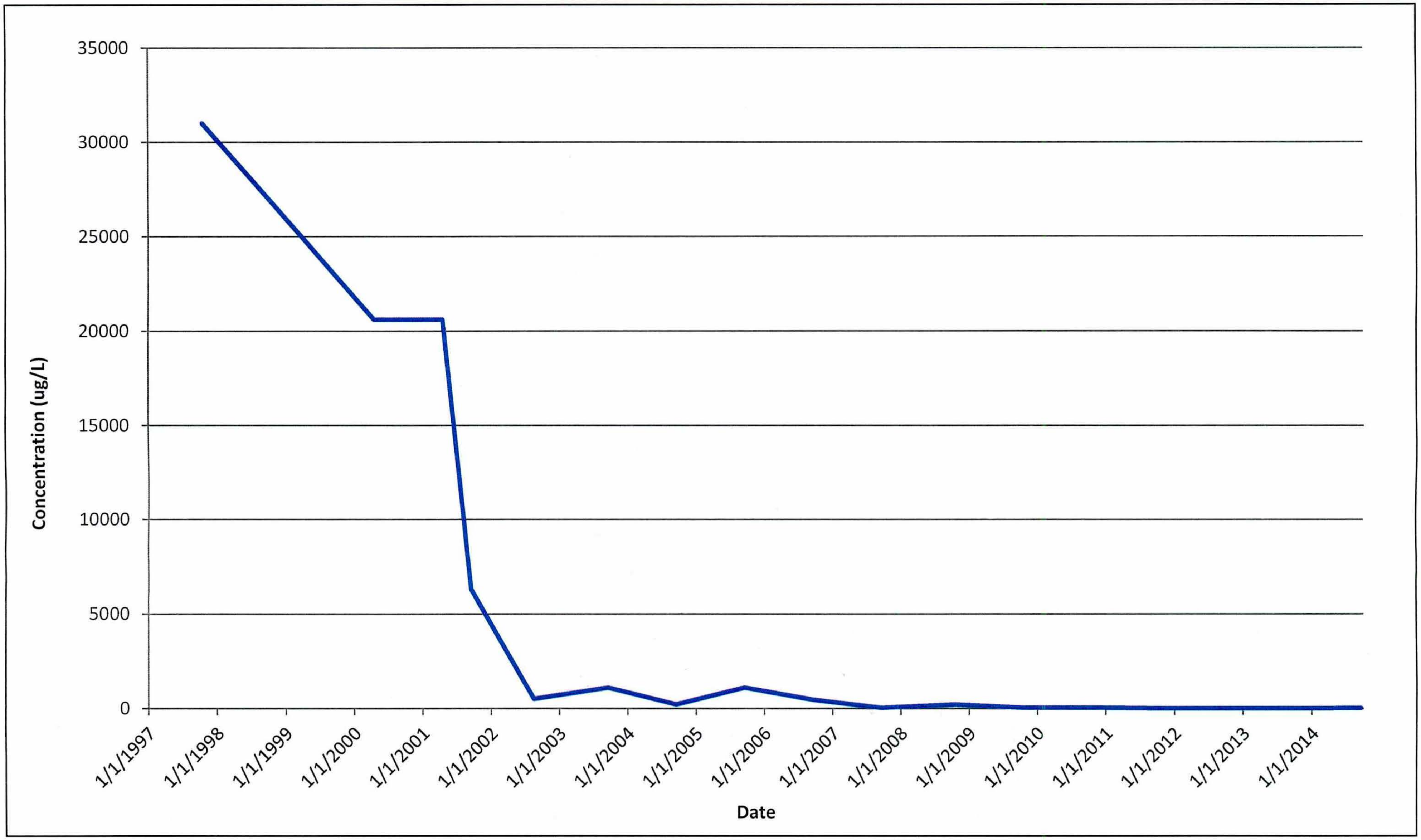
NOTE: SOIL GAS WELLS SG23, SG24, SG25, AND SG26 LOCATIONS ARE APPROXIMATE.

SOURCE: CH2MHILL, FIGURE 5, EROSION CONTROL AREAS, DATED 23-FEB-2006.

figure 3.2

LNAPL THICKNESS - APRIL 2015
PENTA WOOD PRODUCTS SUPERFUND SITE
Siren, Wisconsin

86165-01(005)GN-WA004 JUL 17/2015



LEGEND

▬ PCP CONCENTRATION

GHD

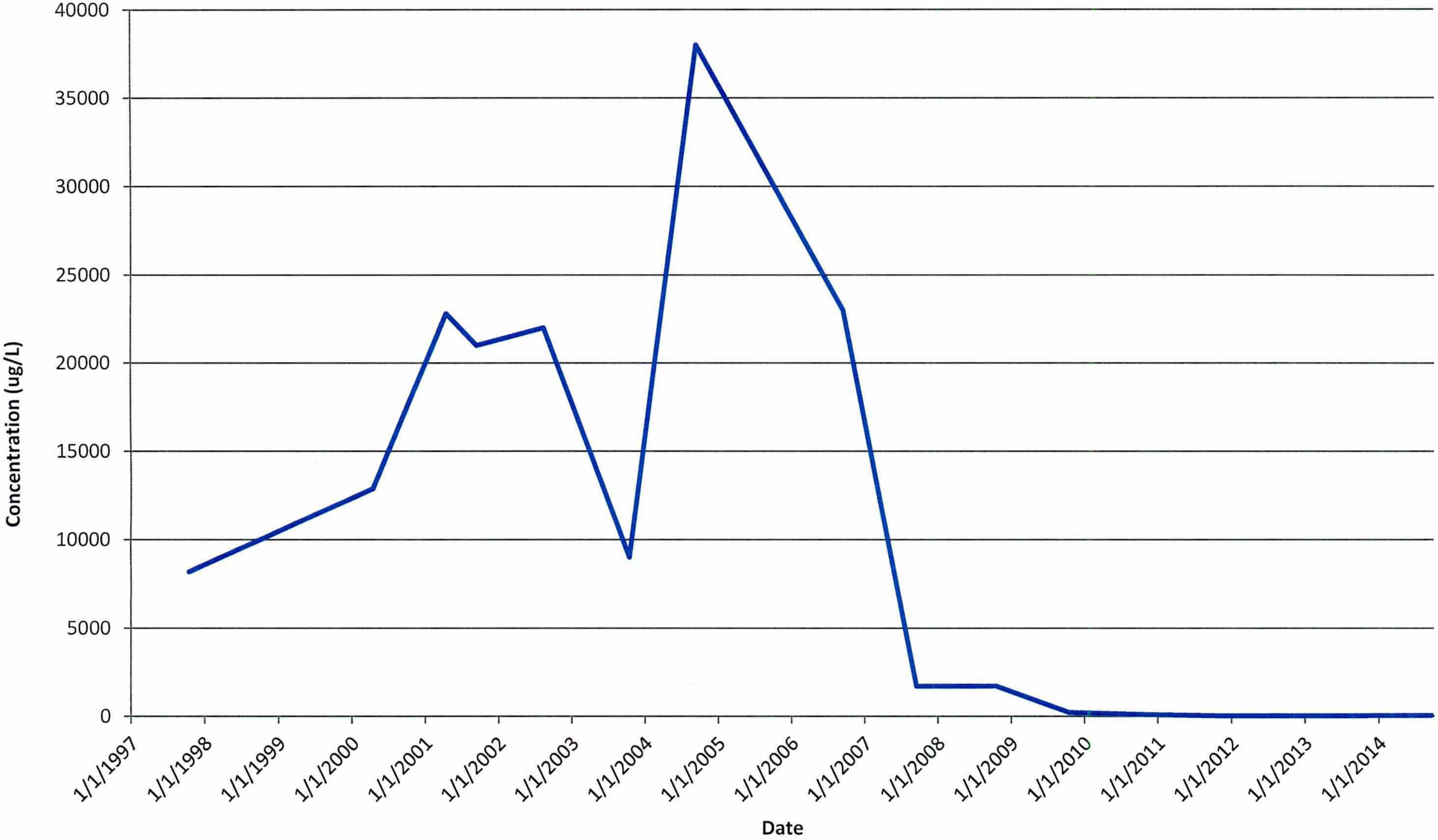
PENTA WOOD PRODUCTS SUPERFUND SITE
SIREN, WISCONSIN

PENTACHLOROPHENOL CONCENTRATION OVER TIME
MONITORING WELL MW-5

086165-01
Jul 22, 2015

FIGURE 4.1

GIS File: I:\GIS\Projects\6-chars\08----\0861--\086165\086165-REPORTS\086165-01(005)\086165-01(005)GIS-SP003.mxd



LEGEND

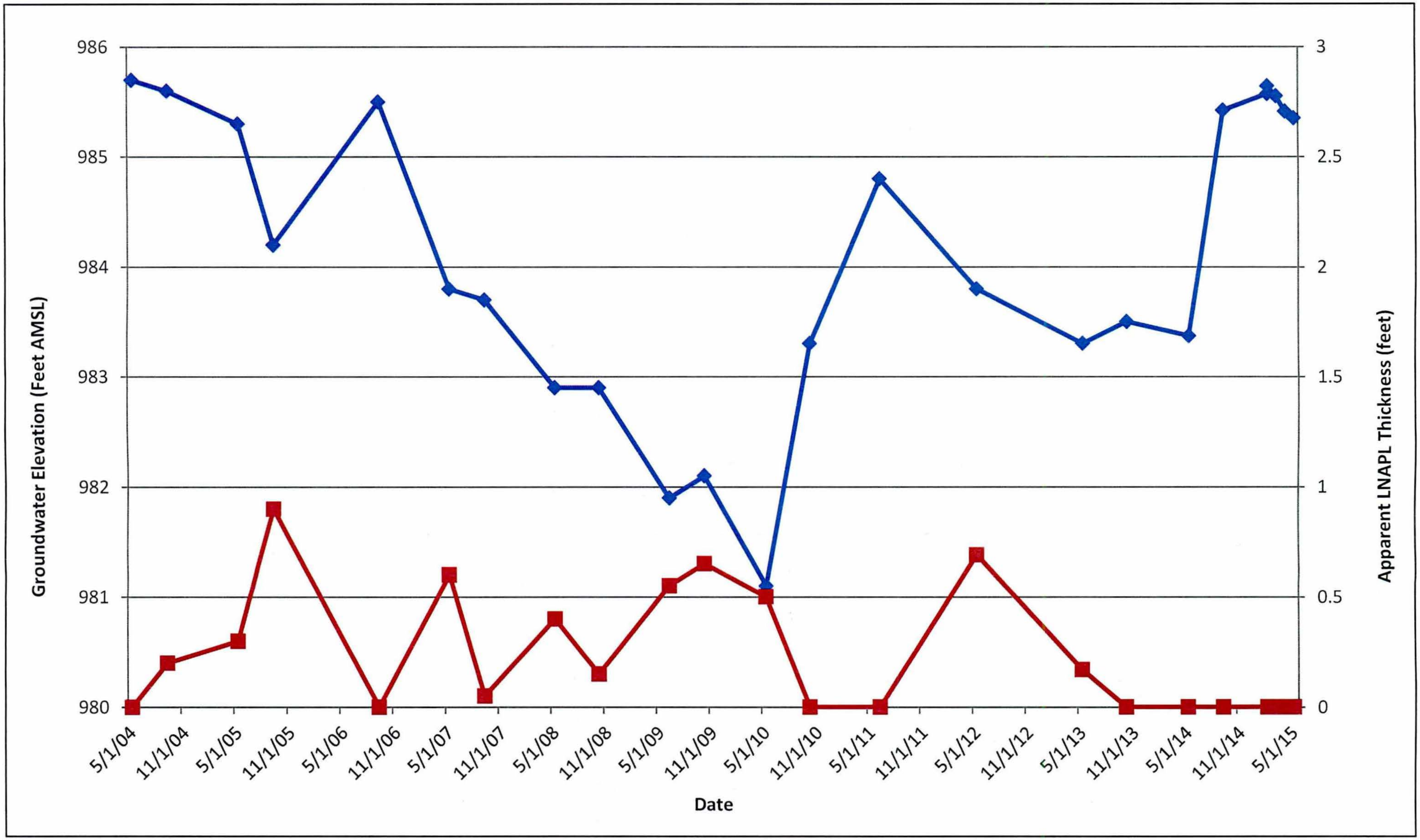
━ PCP CONCENTRATION

PENTA WOOD PRODUCTS SUPERFUND SITE
SIREN, WISCONSIN

PENTACHLOROPHENOL CONCENTRATION OVER TIME
MONITORING WELL MW-10

086165-01
Jul 22, 2015

FIGURE 4.2



LEGEND

◆	GROUNDWATER ELEVATION
■	LNAPL THICKNESS

GHD

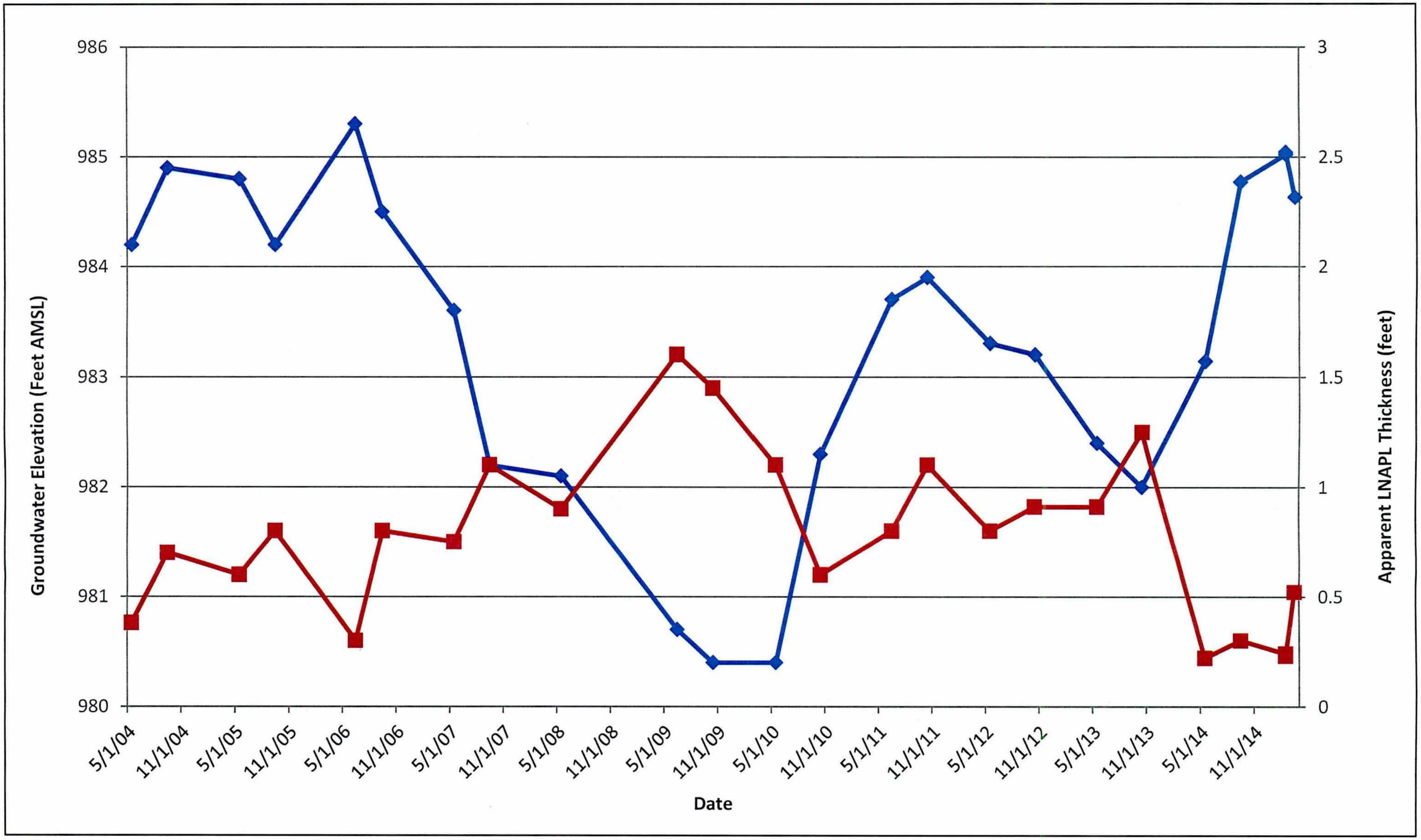
PENTA WOOD PRODUCTS SUPERFUND SITE
SIREN, WISCONSIN

086165-01
Jul 22, 2015

GROUNDWATER ELEVATIONS AND LNAPL THICKNESS
MONITORING WELL MW-10S

FIGURE 4.3

GIS File: I:\GIS\Projects\6-chars\08----\0861--\086165\086165-REPORTS\086165-01(005)\086165-01(005)GIS-SP005.mxd



LEGEND

- 🟦 GROUNDWATER ELEVATION
- 🟥 LNAPL THICKNESS

PENTA WOOD PRODUCTS SUPERFUND SITE
SIREN, WISCONSIN

086165-01

Jul 22, 2015

GROUNDWATER ELEVATIONS AND LNAPL THICKNESS MONITORING WELL MW-19

FIGURE 4.4

GIS File: I:\GIS\Projects\6-chars\08----\0861--\086165\086165-REPORTS\086165-01(005)\086165-01(005)GIS-SP006.mxd

Tables

Table 5.1

Current Remedy (Alternative 3) Cost Estimate
Penta Wood Products Superfund Site
Siren, Wisconsin

Task	*Description*	*Unit*	*Estimated Quantity*	*Unit Cost*	*Cost*
01	Remediation system operation and maintenance	Year	1	$ 571,189	$ 571,189
02	Waste characterization	Year	1	$ 9,064	$ 9,064
03	Waste disposal	Year	1	$ 292,270	$ 292,270
04	Housekeeping and grounds keeping	Year	1	$ 17,890	$ 17,890
05	Monthly soil gas monitoring	Month	7	$ 1,075	$ 7,525
06	WPDES Compliance Sampling/Analysis	Year	1	$ 17,040	$ 17,040
07	Semiannual groundwater/LNAPL level monitoring	Event	2	$ 894	$ 1,788
08	Groundwater monitoring well sampling (annual scope)	Event	1	$ 20,284	$ 20,284
09	Groundwater monitoring well sampling (semiannual scope)	Event	1	$ 8,511	$ 8,511
10	Semiannual residential well sampling/analysis	Event	2	$ 5,388	$ 10,776
11	Semiannual reporting	Report	2	$ 8,282	$ 16,564
12	Monthly status reporting	Report	12	$ 3,524	$ 42,288
13	Site plan updates	Year	1	$ 10,000	$ 10,000
Annual Subtotal					**$ 1,025,189**
Contingency				**10%**	**$ 102,519**
Annual Subtotal					**$ 1,127,708**
Total (30-Year Present Worth, 5%)				15.3725	**$ 17,335,690**

Table 5.2

Recommended Remedy (Alternative 3A) Cost Estimate
Penta Wood Products Superfund Site
Siren, Wisconsin

Task	*Description*	*Unit*	*Estimated Quantity*	*Unit Cost*	*Cost*
01	Remediation system operation and maintenance	Year	0	$ 571,189	$ -
02	Waste characterization	Year	0	$ 9,064	$ -
03	Waste disposal	Year	0	$ 292,270	$ -
04	Housekeeping and grounds keeping	Year	0	$ 17,890	$ -
05	Monthly soil gas monitoring	Month	0	$ 1,075	$ -
06	WPDES Compliance Sampling/Analysis	Year	0	$ 17,040	$ -
07	Semiannual groundwater/LNAPL level monitoring	Event	2	$ 894	$ 1,788
08	Groundwater monitoring well sampling (annual scope)	Event	1	$ 20,284	$ 20,284
09	Groundwater monitoring well sampling (semiannual scope)	Event	1	$ 8,511	$ 8,511
10	Semiannual residential well sampling/analysis	Event	2	$ 5,388	$ 10,776
11	Semiannual reporting	Report	2	$ 8,282	$ 16,564
12	Monthly status reporting	Report	0	$ 3,524	$ -
13	Site plan updates	Year	1	$ 10,000	$ 10,000
Annual Subtotal					**$ 67,923**
Contingency				**10%**	**$ 6,792**
Annual Subtotal					**$ 74,715**
Total (30-Year Present Worth, 5%)				15.3725	**$ 1,148,561**

Appendices

Appendix A
Historical Site Data

Appendix A.1

Historical Pentachlorophenol Concentrations
Penta Wood Products Superfund Site
Siren, Wisconsin

MW01		***MW02***		***MW03***		***MW04***		***MW05***		***MW06S***	
10/9/1997	2	10/9/1997	< 1	10/8/1997	< 1	10/9/1997	< 1	10/10/1997	31000	10/9/1997	< 1
4/24/2001	< 0.1	4/5/2000	< 0.5	4/4/2000	< 0.6	4/4/2000	< 0.5	4/7/2000	20600	4/26/2001	2.5
9/11/2001	0.5	6/18/2001	< 0.1	4/25/2001	< 0.11			4/26/2001	20600	9/12/2001	1.1
8/6/2002	0.067	9/12/2001	0.51	9/13/2001	J 0.092			9/13/2001	6300	8/7/2002	88
4/29/2003	< 0.1	8/6/2002	0.12	8/7/2002	0.11			8/7/2002	510	9/25/2003	0.33
9/24/2003	0.13	9/24/2003	0.28	9/23/2003	0.31			9/25/2003	1100	9/27/2006	0.21
5/4/2004	1.06	9/21/2004	1.26	9/21/2004	0.367			9/22/2004	214	9/20/2007	0.14
9/21/2004	0.442	9/28/2005	2.2	9/28/2005	0.20			9/28/2005	1100	10/23/2008	2.65
5/10/2005	0.12	9/26/2006	2.3	10/21/2008	< 0.10			9/26/2006	460	10/7/2010	< 0.1
9/29/2005	0.12	9/19/2007	3.7	10/7/2009	< 0.1			9/20/2007	31	10/19/2011	0.10
5/31/2006	J 0.049	10/21/2008	1.60	10/5/2010	< 0.1			10/22/2008	206	10/17/2012	0.10
5/8/2007	0.11	10/6/2009	2.21	10/18/2011	0.58			10/7/2009	33.3	10/9/2013	0.52
9/18/2007	< 0.093	10/6/2010	< 0.1	10/16/2012	0.46			10/6/2010	39.8	9/24/2014	0.27
10/21/2008	0.42	10/19/2011	0.097	10/8/2013	0.38			10/19/2011	0.97		
		10/16/2012	0.33	9/25/2014	0.35			10/17/2012	0.59		
		10/9/2013	0.94					10/10/2013	0.60		
		9/24/2014	0.32					9/24/2014	12.00		

Appendix A.1

Historical Pentachlorophenol Concentrations
Penta Wood Products Superfund Site
Siren, Wisconsin

MW07		MW08		MW09		MW10		MW10S		MW11	
10/14/1997	< 1	10/14/1997	< 1	10/8/1997	< 1	10/15/1997	8200	10/15/1997	30000	10/15/1997	< 1
4/4/2000	< 0.5	4/5/2000	< 0.5	4/5/2000	0.6	4/6/2000	12900	4/7/2000	J 56100	4/4/2000	< 0.6
4/25/2001	< 0.1	4/25/2001	0.2	4/23/2001	0.12	4/26/2001	22800	12/5/2000	3810	4/24/2001	< 0.11
9/11/2001	J 0.13	9/11/2001	J 0.062	9/12/2001	0.76	9/12/2001	21000	4/25/2001	49000	9/10/2001	J 0.091
8/7/2002	J 0.03	8/8/2002	< 0.04	8/6/2002	0.54	8/7/2002	22000	9/12/2001	82000	8/6/2002	< 0.04
9/24/2003	J 0.044	9/25/2003	< 0.11	9/25/2003	2.3	10/1/2003	9000	8/7/2002	390	9/23/2003	< 0.11
9/22/2004	9.18	9/23/2004	1.94	9/22/2004	2.92	9/23/2004	38000	9/25/2003	2200	9/21/2004	J 0.0656
9/27/2005	< 0.12	9/28/2005	< 0.12	10/18/2005	0.57	9/27/2006	23000	9/22/2004	9490	9/29/2005	< 740
9/26/2006	J 0.087	9/20/2007	< 0.093	9/21/2007	0.37	9/21/2007	1700	9/29/2005	< 0.11	9/27/2006	< 0.11
9/20/2007	< 0.093	10/22/2008	< 0.1	10/22/2008	< 0.1	10/23/2008	1720	9/26/2006	2700	9/20/2007	< 0.093
10/22/2008	< 0.1			5/18/2010	J 0.073	10/7/2009	220	9/21/2007	24	10/22/2008	0.27
10/7/2009	0.403			10/6/2010	< 0.1	10/7/2010	92.4				
10/6/2010	< 0.1			10/19/2011	0.098	10/20/2011	21				
10/19/2011	< 0.098			10/16/2012	0.39	10/17/2012	14				
10/17/2012	< 0.096			10/9/2013	0.41	10/10/2013	17				
10/9/2013	< 0.094			9/24/2014	1.6	9/25/2014	37				
9/23/2014	J 0.034										

Appendix A.1

Historical Pentachlorophenol Concentrations
Penta Wood Products Superfund Site
Siren, Wisconsin

MW12		*MW13*		*MW14*		*MW15*		*MW16*		*MW17*	
10/15/1997	13000	10/8/1997	J 0.7	10/9/1997	< 1	10/16/1997	< 1	10/14/1997	< 1	10/15/1997	< 1
4/6/2000	15000	4/5/2000	0.8	4/6/2000	< 0.5	4/4/2000	< 0.5	4/6/2000	< 0.5	10/28/1997	5
4/26/2001	1500	4/23/2001	0.18	6/19/2001	0.96	4/25/2001	< 0.11	4/23/2001	< 0.11	4/6/2000	< 0.5
9/13/2001	18000	6/19/2001	< 0.11			9/12/2001	J 0.077	9/10/2001	0.17	4/26/2001	0.72
5/14/2002	4300	9/10/2001	0.69			8/6/2002	< 0.04	8/6/2002	J 0.035	9/11/2001	< 0.059
8/8/2002	6400	8/5/2002	0.64			9/23/2003	< 0.1	9/23/2003	J 0.089	8/8/2002	J 0.032
4/29/2003	3000	9/23/2003	2.9			9/21/2004	0.279	9/21/2004	J 0.0962	9/25/2003	0.46
9/23/2003	10000	9/21/2004	4.67			9/29/2005	< 0.11	9/29/2005	< 0.11	9/22/2004	2.82
5/4/2004	11200	9/27/2005	0.85			9/27/2006	< 0.11	9/27/2006	< 0.046	9/27/2005	J 0.054
9/22/2004	9060	9/18/2007	0.53			9/19/2007	< 0.10	9/18/2007	0.20	9/26/2006	< 0.11
5/10/2005	8300	10/21/2008	0.31			5/20/2008	0.18	10/22/2008	J 0.08	9/19/2007	< 0.099
9/27/2005	8500	10/7/2009	0.16			10/21/2008	< 0.10	10/6/2009	< 0.1	10/22/2008	0.1
6/7/2006	6100					6/2/2009	< 0.1	10/5/2010	< 0.1	10/6/2009	< 0.1
9/26/2006	3100					10/7/2009	< 0.1	10/19/2011	J 0.095	10/5/2010	< 0.1
5/9/2007	3000					5/18/2010	< 0.1	10/16/2012	J 0.099	10/18/2011	< 0.095
9/19/2007	1100					10/7/2010	2.32	10/8/2013	J 0.029	10/16/2012	< 0.095
5/20/2008	2200					6/28/2011	< 0.1	9/23/2014	J 0.036	10/8/2013	< 0.095
10/21/2008	1670					10/18/2011	< 0.10			9/24/2014	< 0.097
6/2/2009	521					5/22/2012	J 0.024				
10/6/2009	295					10/16/2012	< 0.094				
5/19/2010	81.9					5/21/2013	J 0.025				
10/5/2010	43.7					10/8/2013	< 0.095				
6/29/2011	37					5/13/2014	< 0.095				
10/18/2011	37					9/23/2014	J 0.054				
5/22/2012	21					4/20/2015	< 0.094				
10/16/2012	26										
5/22/2013	24										
10/8/2013	28										
5/14/2014	19										
9/23/2014	24										
4/20/2015	16										

Appendix A.1

Historical Pentachlorophenol Concentrations
Penta Wood Products Superfund Site
Siren, Wisconsin

MW18		MW19		MW20		MW21		MW22		MW23	
10/10/1997	27000	10/16/1997	19000	10/15/1997	29000	2/9/1998	< 1	2/9/1998	< 1	2/26/1998	< 1
6/19/2001	27400	4/7/2000	11800	4/26/2001	36600	8/6/2002	J 0.035	8/6/2002	0.078	9/11/2001	0.49
		4/26/2001	25600	9/12/2001	83000	4/29/2003	0.15	9/24/2003	0.34		
		9/12/2001	400000	8/7/2002	30000	9/24/2003	J 0.063	9/21/2004	0.220		
		5/13/2002	14000	9/25/2003	13000	5/4/2004	0.135	9/28/2005	0.16		
		8/8/2002	11000	9/22/2004	133000	9/21/2004	0.474	9/18/2007	0.13		
		4/29/2003	4900	10/25/2005	63000	5/10/2005	0.33	5/20/2008	0.77		
		9/25/2003	15000	9/27/2006	44000	9/27/2005	J 0.046	10/21/2008	J 0.09		
		5/4/2004	70000	9/21/2007	9500	6/1/2006	J 0.023	6/2/2009	< 0.1		
		9/22/2004	111000	10/23/2008	41000	5/8/2007	< 0.098	10/6/2009	< 0.1		
		5/10/2005	45000			9/18/2007	0.13	5/18/2010	< 0.1		
		9/29/2005	13000			10/21/2008	< 0.10	10/6/2010	0.13		
		6/7/2006	17000					6/29/2011	< 0.1		
		9/27/2006	8200					10/18/2011	0.098		
		5/9/2007	11000					5/22/2012	J 0.084		
		9/21/2007	3500					10/16/2012	0.096		
		5/20/2008	23000					5/22/2013	0.11		
		10/24/2008	27900					10/8/2013	0.14		
		6/2/2009	18600					5/14/2014	J 0.093		
		10/7/2009	31800					9/24/2014	0.27		
		5/20/2010	26000					4/21/2015	J 0.072		
		10/7/2010	4470								
		6/29/2011	8880								
		10/20/2011	13000								
		5/22/2012	5300								
		10/17/2012	8100								
		5/22/2013	5800								
		10/10/2013	7900								
		5/14/2014	18000								

Appendix A.1

Historical Pentachlorophenol Concentrations
Penta Wood Products Superfund Site
Siren, Wisconsin

MW24		*MW25*		*MW26*		*MW27*		*MW28*		*DW01*	
2/8/1998	< 4	2/9/1998	1	4/24/2001	< 0.1	10/20/2011	0.17	10/20/2011	690	9/24/2003	J 0.05
4/24/2001	0.11			6/18/2001	1			10/17/2012	0.095	5/4/2004	0.102
				9/10/2001	J 0.16			10/9/2013	J 0.049	9/28/2004	1.08
				5/14/2002	0.1			9/25/2014	0.099	11/1/2004	< 0.0962
				8/5/2002	J 0.035					5/11/2005	J 0.033
				4/29/2003	< 0.11					9/27/2005	J 0.040
				9/23/2003	< 0.11					5/31/2006	J 0.039
				5/4/2004	0.242					9/26/2006	< 0.11
				9/23/2004	5.97					5/10/2007	J 0.074
				5/10/2005	< 0.11					9/19/2007	< 0.093
				9/27/2005	J 0.027					5/20/2008	< 0.094
				6/7/2006	< 0.11					10/23/2008	< 0.1
				9/26/2006	< 0.11					6/3/2009	< 0.1
				5/8/2007	< 0.095					10/8/2009	< 0.1
				9/19/2007	< 0.095					5/19/2010	< 0.1
				5/20/2008	< 0.096					10/7/2010	< 0.1
				10/22/2008	< 0.1					6/30/2011	< 0.1
				6/2/2009	< 0.1					10/18/2011	J 0.032
				10/6/2009	< 0.1					5/23/2012	J 0.028
				5/19/2010	0.13					10/18/2012	J 0.032
				10/5/2010	< 0.1					5/21/2013	J 0.029
				6/29/2011	< 0.1					10/8/2013	J 0.027
				10/19/2011	< 0.099					5/13/2014	J 0.057
				5/22/2012	< 0.10					9/25/2014	J 0.54
				10/16/2012	< 0.095					4/21/2015	J 0.023
				5/22/2013	< 0.094						
				10/8/2013	< 0.095						
				5/14/2014	< 0.095						
				9/24/2014	< 0.095						
				4/21/2015	< 0.094						
				4/21/2015	< 0.094						

Appendix A.1

Historical Pentachlorophenol Concentrations
Penta Wood Products Superfund Site
Siren, Wisconsin

RW1		*RW2*		*RW3*		*RW4*		*RW5*		*RW6*	
4/23/2001	< 0.1	4/24/2001	< 0.1	9/11/2001	J 0.1	4/23/2001	< 0.1	5/4/2004	< 0.0935	9/25/2014	< 0.095
9/11/2001	J 0.071	9/11/2001	9.5	9/28/2001	< 0.1	9/11/2001	J 0.073	9/22/2004	0.293	4/21/2015	< 0.095
9/28/2001	< 0.1	9/28/2001	< 0.1	5/14/2002	J 0.094	9/28/2001	< 0.1	11/1/2004	< 0.0962		
5/14/2002	0.23	5/14/2002	0.1	8/6/2002	< 0.04	5/14/2002	0.13	5/10/2005	< 0.11		
8/6/2002	0.04	8/6/2002	< 0.04	4/29/2003	< 0.11	8/6/2002	< 0.04	9/27/2005	< 0.11		
4/29/2003	J 0.1	4/29/2003	< 0.11	9/23/2003	< 0.11	4/29/2003	< 0.11	5/31/2006	< 0.11		
9/23/2003	0.28	9/24/2003	< 0.11	5/4/2004	< 0.0952	9/23/2003	< 0.11	9/25/2006	< 0.11		
11/20/2003	0.24	5/4/2004	J 0.0252	9/22/2004	2.18	5/4/2004	< 0.100	5/9/2007	< 0.092		
5/4/2004	0.140	9/22/2004	0.398	11/1/2004	< 0.0962	9/22/2004	0.266	9/18/2007	< 0.093		
9/22/2004	1.51	11/1/2004	< 0.0962	5/10/2005	< 0.11	10/1/2004	< 0.0962	5/20/2008	< 0.095		
11/1/2004	< 0.0952	5/10/2005	< 0.11	9/27/2005	< 0.11	5/10/2005	< 0.11	12/10/2008	< 0.1		
5/10/2005	J 0.068	9/27/2005	< 0.11	5/31/2006	< 0.11	9/27/2005	< 0.11	6/2/2009	< 0.1		
7/7/2005	J 0.043	5/31/2006	< 0.11	9/25/2006	< 0.11	5/31/2006	< 0.11	10/7/2009	< 0.1		
9/27/2005	J 0.050	9/25/2006	< 0.11	5/9/2007	< 0.092	9/25/2006	< 0.11	5/19/2010	< 0.1		
5/31/2006	J 0.055	5/9/2007	< 0.092	9/18/2007	< 0.093	5/9/2007	< 0.093	10/5/2010	< 0.1		
9/25/2006	< 0.11	9/18/2007	< 0.093	5/20/2008	< 0.097	9/18/2007	< 0.093	6/30/2011	< 0.1		
5/9/2007	J 0.048	5/20/2008	< 0.095	12/10/2008	< 0.1	5/20/2008	< 0.093	10/20/2011	< 0.095		
9/18/2007	0.27	12/10/2008	< 0.1	6/2/2009	< 0.1	12/10/2008	< 0.1	5/23/2012	< 0.095		
5/20/2008	J 0.066	6/2/2009	< 0.1	10/7/2009	< 0.1	6/2/2009	< 0.1	10/17/2012	J 0.030		
12/11/2008	< 0.1	10/7/2009	< 0.1	5/19/2010	< 0.1	10/7/2009	0.15	12/4/2012	< 0.095		
6/2/2009	< 0.1	5/19/2010	< 0.1	10/5/2010	< 0.1	10/20/2009	< 0.1	5/21/2013	< 0.095		
10/7/2009	< 0.1	10/5/2010	< 0.1	6/30/2011	< 0.1	5/19/2010	< 0.1	10/8/2013	< 0.098		
5/19/2010	< 0.1	6/30/2011	< 0.1	10/20/2011	< 0.095	10/5/2010	< 0.1	5/13/2014	< 0.095		
10/5/2010	< 0.1	10/20/2011	< 0.095	5/23/2012	< 0.097	6/30/2011	< 0.1	9/25/2014	< 0.096		
6/30/2011	< 0.1	5/23/2012	< 0.097	10/17/2012	J 0.015	10/20/2011	< 0.095	4/21/2015	< 0.095		
10/20/2011	J 0.040	10/17/2012	< 0.094	12/3/2012	< 0.095	5/23/2012	< 0.094				
12/16/2011	< 0.096	12/3/2012	< 0.095	5/21/2013	J 0.053	10/17/2012	J 0.071				
5/23/2012	J 0.019	5/21/2013	< 0.097	10/8/2013	< 0.096	12/3/2012	< 0.095				
7/11/2012	J 0.035	10/8/2013	< 0.094	5/13/2014	< 0.095	5/21/2013	< 0.094				
10/17/2012	J 0.045	5/13/2014	< 0.095	9/25/2014	< 0.095	10/8/2013	< 0.095				
12/3/2012	< 0.095	9/25/2014	< 0.096	9/25/2014	< 0.095	5/13/2014	J 0.023				
5/21/2013	J 0.031	4/21/2015	< 0.095	4/21/2015	< 0.097	9/25/2014	< 0.096				
10/8/2013	< 0.097					4/21/2015	< 0.094				
5/13/2014	J 0.051										
9/25/2014	J 0.043										
4/21/2015	< 0.095										

Appendix A.2

Historical LNAPL Thickness - Monitoring Wells
Penta Wood Products Superfund Site
Siren, Wisconsin

	Monitoring Well LNAPL Thickness (feet)			
Date	***MW10S***	***MW18***	***MW19***	***MW20***
Sep-01	0.01	0.27	0.51	0.11
May-02	0.00	0.29	0.23	0.00
Aug-02	0.00	0.33	0.22	0.00
May-03	0.00	0.00	0.00	0.00
Sep-03	0.00	0.32	0.24	0.04
May-04	0.00	0.45	0.36	0.35
Sep-04	0.21	0.54	0.67	0.52
May-05	0.29	0.48	0.63	0.36
Sep-05	0.87	0.06	0.83	1.15
May-06	0.00	0.00	0.29	0.00
Sep-06	0.00	0.05	0.80	0.69
Apr-07	0.58	0.04	0.74	1.22
May-07	0.58	0.03	0.54	1.20
Sep-07	0.04	0.16	1.07	0.00
May-08	0.40	1.19	0.90	1.71
Oct-08	0.14	0.04	0.00	0.00
Jun-09	0.54	1.58	1.60	1.45
Oct-09	0.63	1.92	1.46	1.02
May-10	0.51	2.01	1.10	0.85
Oct-10	0.00	0.57	0.59	0.00
Jun-11	0.00	0.42	0.79	0.00
Oct-11	0.00	0.53	1.07	0.00
May-12	0.69	0.79	0.80	2.17
Aug-12	0.04	0.43	0.89	0.30
Oct-12	0.00	0.45	0.91	0.88
Dec-12	0.02	0.44	1.06	0.95
May-13	0.17	0.53	0.94	1.08
Oct-13	0.00	0.70	1.25	0.81
May-14	0.00	0.79	0.22	0.22
Sep-14	0.00	0.56	0.30	0.00
2/13/15	0.00	0.56	0.24	0.00
2/20/15	0.00	0.53	0.23	0.00
3/24/15	0.00	0.34	0.52	0.00
4/16/15	0.00	0.58	NM	0.00
5/14/15	0.00	0.57	NM	0.00

Notes:

NM - Not Measured

Appendix A.3

Historical Groundwater Extraction Summary
Penta Wood Products Superfund Site
Siren, Wisconsin

Operation Period	*Volume of Groundwater Extracted (gallons)*
09/27/00 to 12/18/00	11,712,960
02/02/01 to 02/08/01	691,200
03/16/01 ro 06/10/01	9,288,000
06/15/01 to 09/27/01	6,822,720
02/27/04 to 12/31/04	18,548,154
01/01/05 to 12/31/05	21,374,796
01/01/06 to 12/31/06	14,759,392
01/01/07 to 12/31/07	16,551,336
01/01/08 to 12/31/08	18,118,696
01/01/09 to 12/31/09	18,533,648
01/01/10 to 12/31/10	18,561,632
01/01/11 to 12/31/11	17,796,668
01/01/12 to 12/31/12	23,051,892
01/01/13 to 12/31/13	29,793,563
01/01/14 to 12/31/14	18,415,098
01/01/15 to 06/30/15	6,282,127
Total Gallons Extracted	250,301,882

Appendix A.4

Historical Influent Pentachlorophenol Concentrations
Penta Wood Products Superfund Site
Siren Wisconsin

Date	*Influent PCP Concentration (ug/L)*
02/27/2004 to 12/31/2004*	9,227
01/01/2005 to 12/31/2005*	7,300
01/01/2006 to 12/31/2006*	6,425
01/01/2007 to 12/31/2007*	3,557
01/01/2008 to 12/31/2008*	3,255
March 2009	3,560
July 2009	3,140
September 2009	2,800
December 2009	2,030
March 2010	2050 J
June 2010	1,970
September 2010	1,830
December 2010	1,940
March 2011	2,470
June 2011	2,170
August 2011	1,700
October 2011	1,600
February 2012	2,600
May 2012	2,200
July 2012	1,900
October 2012	1,800
February 2013	1,100
May 2013	1,100
July 2013	1,800
October 2013	1,400
February 2014	1,800
May 2014	1,600
August 2014	2,100
September 2014	2,400
October 2014	2,400
November 2014	2,100
December 2014	4,600
January 2015	1,800
February 2015	480
March 2015	390
April 2015*	1,767
May 2015*	355
June 2015	550

Note:

* Average PCP influent concentration for that time period.

Appendix A.5

Historical Hazardous Waste Generation Summary
Penta Wood Products Superfund Site
Siren, Wisconsin

Date	*Filter Cake (lb)*	*Misc. Debris (lb)*	*Carbon (lb)*	*LNAPL (lb)*	*Water (gallons)*	*Yearly Total (lb)*
2000	0	200	6,000	5,009*	0	11,209
2001	0	400	56,100	6,166*	0	62,666
2002	0	1,400	48,000	10,790*	27,756	87,946
2003	0	600	0	3,083*	1,376	5,059
2004	155,960	3,200	102,000	53,522*	0	314,682
2005	178,784	1,290	104,860	23,847*	0	308,924
2006	112,640	1,200	136,520	52,892*	0	303,252
2007	174,020	2,200	245,377	77,615*	0	517,387
2008	211,402	3,176	70,007	28,036	0	312,621
2009	233,840	1,116	49,757	35,659	0	320,372
2010	210,940	0	81,227	34,937	0	327,104
2011	292,903	0	74,247	0	0	367,150
2012	182,280	0	65,420	25,493	0	273,193
2013	156,760	0	46,571	27,252	0	230,582
2014	110,754	13,513	65,995	11,720	0	201,982
2015	0	0	22,248	0	0	22,248

Note:

* - Volume shows the amount of waste disposed offsite and is estimated to be approximately 50 percent pure LNAPL and 50 percent mixture of water and emulsified LNAPL.

lb - pounds

Appendix B
Common LNAPL-Related Terms and Definitions

1. COMMON LNAPL-RELATED TERMS AND DEFINITIONS

Capillary Pressure: the difference between the fluid pressure in the non-wetting phase (typically LNAPL) and the pressure in the wetting phase (typically water) at a given reference point. This pressure may also be referred to as the “excess pressure”. The larger the capillary pressure, the greater the LNAPL saturation and the greater the potential for LNAPL mobility. For LNAPL movement or migration to occur, capillary pressure must exceed the resistive forces in the soil formation.

Confined Condition: a subsurface condition where pore fluids are under pressure at all reference points or elevations. In a confined condition, in-well LNAPL thickness varies directly with potentiometric surface elevation. Hence, an increase in the potentiometric surface elevation leads to an increase in in-well LNAPL thickness, and vice versa. LNAPL within the secondary porosity (fractures, fissures, seams) of fine textured soils (silts and clays) is often present in a confined condition. Confined conditions will often produce in-well LNAPL thicknesses that grossly over-represent the extent of impacts in the formation.

C_{sat}: the theoretical limit of a soil’s ability to effectively hold or contain a chemical constituent (or mixture) in the adsorbed, dissolved and vapor phases. Total soil concentrations in excess of a chemical constituent’s (or mixture’s) corresponding C_{sat} value will typically be assumed to indicate the presence of LNAPL. Published C_{sat} values will have limited use at LNAPL sites due to the site-specific nature of LNAPL composition and the difficulty in determining appropriate C_{sat} values for complex petroleum mixtures consisting of hundreds of individual chemical constituents.

Effective Solubility: different than pure-phase solubility, effective solubility describes the ability of a chemical constituent from a mixture to dissolve in water in the presence of other constituents in the mixture. It is a particularly important consideration for LNAPLs that are complex petroleum mixtures. Effective solubility is a function of the mole fraction of the constituent in the mixture, and is commonly orders of magnitude less than the constituent’s corresponding pure-phase solubility. Groundwater concentrations in excess of a petroleum constituent’s effective solubility will typically indicate the presence of LNAPL in the vicinity of a monitoring well.

Interfacial Tensions: the tension or attractive forces between two fluids along the interface of contact with one another. The interfacial tension between LNAPL and water in the subsurface tends to limit the ability of LNAPL to move.

Laser-Induced Fluorescence (LIF): a real-time LNAPL delineation technology that uses ultraviolet wavelengths of light to cause polycyclic aromatic hydrocarbons (PAHs) to fluoresce. All petroleum-based LNAPLs contain PAHs, allowing the use of LIF to detect the presence of LNAPL. LIF is employed in the field using direct-push techniques to delineate LNAPL impacts in the subsurface laterally and vertically (both above and below the water table). LIF also provides an indication of the intensity of impacts across an LNAPL body and the types of LNAPL encountered.

LNAPL: light non-aqueous phase liquid. LNAPLs are immiscible fluids that are less dense than water, and may be comprised of a pure chemical or solvent, or comprised of a complex mixture of chemicals, such as petroleum-based fuels. The term “LNAPL” most often refers to immiscible petroleum mixtures/fuels (i.e., gasoline, kerosene, diesel, crude oil, etc.).

LNAPL Body: the multi-phase fluid zone of LNAPL impacts in the subsurface. An LNAPL body is comprised of three fluids: air, LNAPL and water. Generally speaking, an LNAPL body is predominantly comprised of water, with a lesser amount of LNAPL, and the least amount of air.

LNAPL Conductivity: a hydrogeological term that helps describe the ability of LNAPL to move through the subsurface. LNAPL conductivity accounts for the LNAPL relative permeability, hydraulic conductivity, and the densities and viscosities of the fluids (water and LNAPL). LNAPL conductivity is a function of and varies directly with LNAPL relative permeability. Hence, an increase in LNAPL relative permeability results in an increase in LNAPL conductivity, and vice versa.

LNAPL Migration: a description of the expansion of the perimeter of an unstable LNAPL body in some or all directions (i.e., footprint of the overall LNAPL body or body periphery is continuing to grow). All migrating LNAPL is mobile; not all mobile LNAPL is migrating. Mobile LNAPL can be present within the interior of an LNAPL body that is not migrating.

LNAPL Mobility: a description of the potential for LNAPL to move at any point within an LNAPL body. LNAPL may be mobile where the LNAPL is continuous at saturations above residual saturation. Because LNAPL residual saturation within a LNAPL body varies from the vadose zone to the saturated zone, LNAPL mobility may also vary due to fluctuations in the water table elevation. The presence of mobile LNAPL within an LNAPL body does not necessarily mean that the LNAPL body as a whole is unstable or migrating.

LNAPL Pressure Head: the LNAPL pressure conditions at any point within an LNAPL body created by the release conditions. The pressure head can result from the vertical column of LNAPL due to accumulation at or in the vicinity of the water table from a surface or near-surface source (e.g., tank), or from other pressure conditions at the time of the release (e.g., pressure conditions of a subsurface pipeline release). The greater the pressure head, the more the LNAPL will penetrate into the water table (both vertically and laterally) and spread. Once the pressure head dissipates (i.e., source of release is terminated), the LNAPL will soon after cease to migrate and achieve a stable perimeter.

LNAPL Relative Permeability: a measure of the porous medium's (soil's) ability to enable movement of LNAPL in the subsurface in the presence of water. LNAPL relative permeability is a function of and varies directly with LNAPL saturation. Hence, an increase in LNAPL saturation results in an increase in LNAPL relative permeability, and vice versa.

LNAPL Residual Saturation: the LNAPL saturation level or threshold below which LNAPL will not flow under normal hydraulic conditions. LNAPL present at saturations that are less than or equal to residual saturation levels (i.e., within the residual range) will generally be considered to be immobile and unrecoverable. Conceptually speaking, LNAPL residual saturation represents the LNAPL saturation threshold where the LNAPL, due to its relatively low saturation, starts to break-up or become discontinuous in the form of droplets, stringers, ganglia, etc. As LNAPL saturation approaches or decreases to residual, the relative permeability of the LNAPL approaches zero, and the conductivity of the LNAPL approaches zero. The more LNAPL that initially saturates the soil pore space during a release, the higher the residual saturation will be (up to a theoretical maximum). Consequently, LNAPL residual saturation also varies continuously within an LNAPL body.

LNAPL Saturation: the percent of the soil pore space that is occupied by LNAPL. LNAPL saturation at a given point in the subsurface will be proportional to the capillary pressure at that point (i.e., the greater the capillary pressure, the greater the resulting LNAPL saturation). Because the capillary pressure varies throughout the impacted zone, the LNAPL saturation also varies accordingly. The larger the soil pore space, the greater the ability for the soil to hold LNAPL, the greater the LNAPL saturation, and vice versa.

LNAPL Stability: a description of the potential for the perimeter or footprint of an LNAPL body to move or expand over time. A LNAPL body that is moving or expanding (i.e., footprint of LNAPL body is growing) is deemed to be unstable or migrating. Conversely, a LNAPL body that is not moving or expanding with time is deemed to be stable, immobile, or non-migrating. Stable LNAPL bodies can contain localized areas of mobile LNAPL, with the overall footprint remaining unchanged over time.

LNAPL Velocity: the speed and direction at which the LNAPL can travel, based on Darcy flow principles. LNAPL velocity is based on the properties of the porous medium and fluids (water and LNAPL), pore fluid saturations, and the LNAPL gradient. LNAPL velocity only applies within the LNAPL body where there is continuous LNAPL at saturations above residual. There is no LNAPL velocity or movement within an LNAPL body where the LNAPL is not continuous and saturations are below residual. In addition, there is no LNAPL velocity or movement outside of a stable LNAPL body.

Non-Wetting Fluid: the fluid that does not preferentially coat the soil grains or particles in a multi-phase fluid system, but rather occupies the middle of the larger soil pores. In an air-water-LNAPL system (typical of an LNAPL body), both air (primarily in the unsaturated portion of the smear zone) and LNAPL (primarily in the saturated portion of the smear zone) tend to be the non-wetting fluids.

Pore Entry Displacement Pressure: the threshold pressure necessary for one fluid to enter into a porous medium occupied by another fluid, thereby displacing the fluid originally present. Pore entry displacement pressures may account for air displacing groundwater, LNAPL displacing groundwater, air displacing LNAPL, etc. In a water-saturated soil, the capillary pressure must equal or exceed the pore entry displacement pressure for the LNAPL to move and displace water.

Soil Resistive Forces: the forces that act to prevent the movement of LNAPL in a water-saturated porous medium. These forces, which are based on pore entry displacement pressure principles, account for the contact angle or wettability of the fluids (LNAPL and water), the interfacial tension between the fluids, and the soil pore size. LNAPL movement will only occur if the capillary pressure is sufficient to overcome the soil resistive forces.

Unconfined Condition: a subsurface condition with identical or similar pressure-related fluid characteristics to an unconfined aquifer or water table condition. LNAPL within the primary porosity of granular soils (sands and gravels) in a water table/phreatic surface setting is deemed to be in an unconfined condition. In an unconfined condition, in-well LNAPL thickness varies inversely with water table elevation. Hence, an increase in the water table elevation leads to a decrease in in-well LNAPL thickness, and vice versa.

van Genuchten Parameters: curve fitting parameters that describe how water drains from a given soil in response to increasing pressure conditions. These parameters serve as critical inputs for LNAPL modeling simulations.

Wetting Fluid: the fluid that preferentially coats the soil grains or particles in a multi-phase fluid system. In an air-water-LNAPL system (typical of an LNAPL body), water typically acts as the wetting fluid while air and LNAPL act as non-wetting fluids. The wetting fluid is typically the predominant fluid present in a multi-phase fluid system.

Appendix C
General LNAPL Discussion

Appendix C
General LNAPL Discussion

Table of Contents

Figure Index

Table Index

Preamble

This technical document was prepared by Conestoga-Rovers & Associates to present some of the basic principles describing the behavior and movement of light non-aqueous phase liquids (LNAPLs) in the subsurface. This document and the principles described herein are based on previous LNAPL-related publications, literature and guidance published by various groups including: American Petroleum Institute; ASTM International; Interstate Technology & Regulatory Council; USEPA Remediation Technologies Development Forum, etc. The concepts presented in this document have also been presented to the federal government of Canada (Environment Canada and Public Works & Government Services Canada) for use as technical guidance for the assessment and mobility of LNAPL / Free Product and associated dissolved phase plumes at federally owned/operated properties in Canada.

There are various approaches used to describe and demonstrate the behavior and movement of LNAPL in the subsurface. This document includes a discussion of the fundamentals of the behavior of hydrocarbons in the subsurface, specifically focusing on the aspects that relate directly to LNAPL mobility. This document also includes a discussion of the properties of fuels (density, viscosity, interfacial tension, capillary pressure, saturation, solubility etc); describes different soil types (silts, clay, sand, gravel) and the associated soil physical properties such as porosity, permeability, hydraulic conductivity etc.; phase distribution, vertical and horizontal distribution, groundwater flow/groundwater gradient. The discussion of fundamentals identifies key criteria that affect the accumulation and movement of LNAPL in the subsurface.
This document addresses the following key questions:

- How is LNAPL or “free product” defined?
- What are the site conditions under which an LNAPL body may be demonstrated to be immobile?
- What constitutes immobility of an LNAPL body? What may be used as evidence of immobility of an LNAPL body?
- What are the monitoring approaches that would be appropriate for demonstrating LNAPL immobility?
- How much monitoring data is required to demonstrate that the LNAPL body (and/or dissolved phase plume) is immobile?
- How is the dissolved phase plume mobility related to the mobility of the LNAPL body? What may be used as evidence of immobility of a dissolved phase plume?

This document focuses primarily on questions of LNAPL behavior and mobility. It does not evaluate the risks associated with LNAPL sites. Evaluation of human health and ecological risks is a separate exercise beyond the scope of this document. Further, this document does not consider any of the non-technical factors (cost, feasibility, socio-economic) that may be included in or used as the basis of a remedial action plan.

1. Introduction

The presence of light non-aqueous phase liquids (LNAPLs) or “free product” in the subsurface can present potential risks to the environment and human health in terms of exposure and other potential health and safety issues. Traditionally, the mere presence of LNAPL at a site was automatically perceived to be an unacceptable risk, requiring removal of all product or cleanup to some de minimis level based on a stipulated in-well LNAPL thickness threshold (for example, ⅛-inch, 0.01 feet, etc.). Research conducted over the past two decades, however, has lead to a better understanding and appreciation of the science governing the presence and behavior of LNAPL in the subsurface. In particular, our current understating of LNAPL behavior principles, backed up with almost two decades of “real world” experience at LNAPL-impacted sites, has demonstrated that the mere presence of LNAPL does not necessarily pose an adverse risk. Further, the sole reliance on in-well LNAPL thickness criteria as a regulatory trigger for initiating LNAPL recovery, or conversely, as a remediation goal for terminating LNAPL recovery, is now recognized to be a poor practice that is not consistent with current principles of LNAPL behavior and science or with a risk-based approach to LNAPL sites. Current LNAPL science indicates that a sound understanding of the environmental setting as well as the LNAPL spatial distribution, saturation, mobility and body stability plays a critical role in assessing the true risks associated with the presence of LNAPL. In situations where the LNAPL body and associated dissolved and vapor phase plumes can be shown to be stable/immobile and to pose no unacceptable risk to human health and the environment, the in-place management of the LNAPL, without the need for aggressive removal, may provide an acceptable LNAPL management strategy.

This document begins with a discussion of LNAPL basics, including what free product/LNAPL is, LNAPL physical and chemical properties, LNAPL fingerprinting and forensic testing, and effective solubilities from LNAPL mixtures. Next, the document progresses into the fundamentals of LNAPL behavior and provides a discussion on the development of a LNAPL Conceptual Site Model (LCSM). Finally, the document presents a detailed discussion on the potential lines of evidence for evaluating LNAPL mobility. The primary focus of this document is LNAPL mobility, and more specifically, what is required to demonstrate that the LNAPL body and associated dissolved phase plume are immobile. Hence, all sections of the document, including the LNAPL basics and fundamentals of LNAPL behavior sections, are considered necessary prerequisites for understanding and assessing LNAPL mobility.

This document specifically addresses LNAPL behavior at the water table (i.e., unconfined condition) and includes the vertical impacted soil zone typically referred to as the smear zone. The smear zone is where potentially mobile LNAPL may reside at sites where the source(s) of the LNAPL impacts have ceased for some time (i.e., no ongoing sources). The behavior of LNAPL in the vadose or unsaturated zone (above the smear zone) is not addressed here since LNAPL in these zones (particularly at older release sites) is often present at low saturations, and does not typically pose a potential for additional LNAPL migration at the water table. In addition, LNAPL behavior in the secondary porosity of fine textured soils (silts and clays) and fractured bedrock is not addressed in detail. There is very limited information available in the literature describing the evaluation of LNAPL mobility in macropores (e.g., fractures, fissures, root holes, etc.), and there is not currently any professional consensus on how this might be accomplished. However, references regarding LNAPL behavior in these situations are briefly discussed.

2. LNAPL Basics

2.1 What is Free Product / LNAPL?

Soil pore fluids in a subsurface setting are typically comprised of two types: water (deemed to be the wetting fluid); and air (deemed to be the non-wetting fluid). When a third, immiscible fluid (i.e., a fluid that does not readily dissolve in water) is present, the fluid is referred to as a Non-Aqueous Phase Liquid or NAPL. There are two primary types of NAPLs: (1) those with specific gravities (or densities) less than the specific gravity/density of water; and (2) those with specific gravities/densities greater than the specific gravity/density of water. Immiscible fluids with specific gravities less than water are referred to as “Light” NAPLs or LNAPLs. Immiscible fluids with specific gravities greater than water are referred to as “Dense” NAPLs or DNAPLs. DNAPLs, which will most often be comprised of chlorinated compounds or solvents, are not the subject of this document and will not be discussed further.

LNAPLs may be comprised of a single chemical or solvent, such as toluene or xylenes, or may be comprised of a complex mixture of chemicals or compounds, such as petroleum-based products (i.e., gasoline, kerosene, diesel, lube oil, crude oil, etc.). Generally speaking, most LNAPL-related impacts in an environmental setting are typically associated with petroleum-related materials, primarily due to the widespread use of petroleum products in society. Although single chemical/solvent releases can pose significant risk issues in terms of mobility, exposure and potential explosivity, their prevalence (i.e., frequency of occurrence) tends to be much less than petroleum-related LNAPLs. Consequently, the term LNAPL, for the remainder of this document, will only refer to petroleum products (i.e., mixtures), as opposed to pure chemicals or solvents.

Historically, the term “free product” has been used extensively as a synonym for LNAPL, particularly when used to describe the presence of gasoline or diesel LNAPLs in monitoring wells at retail petroleum facilities. Despite the fact that modern LNAPL science has demonstrated that well observations are not necessarily a reliable indicator of the presence of free product/LNAPL, many jurisdictions continue to define “free product” as some quantity of measureable petroleum product in a well greater than some minimum thickness criterion (e.g., greater than a sheen). Other similar terms and acronyms used to represent petroleum LNAPLs include “phase separated hydrocarbons” (PSH), “separate phase hydrocarbons” (SPH), “free phase hydrocarbons” (FPH), etc. For the purposes of this document, the term “LNAPL” will be used exclusively to refer to petroleum-related immiscible fluids. The acronym LNAPL has become a commonly accepted term used in most guidance documents to describe the behavior, management and remediation of petroleum-related immiscible fluids at environmental sites.

When a petroleum product is released to the subsurface, some of the constituents in the mixture will partition into the dissolved phase (groundwater), adsorbed phase (soil) and vapor phase (soil gas or pore air) in general accordance with equilibrium partitioning principles. If only a small amount of petroleum product is released, the product may be effectively “contained” within these three partitioned phases, with no real fourth “free phase” present. However, if sufficient quantity of petroleum product is released, the product will likely partition to the dissolved, adsorbed and vapor phases, to the maximum extent possible, with remaining product being present as a fourth “free” phase (i.e., LNAPL).

The American Petroleum Institute (API) and others have provided technical documents and publications with calculations (referred to as saturated soil or Csat equations) illustrating how individual petroleum constituents can partition, in accordance with equilibrium partitioning principles, from a LNAPL mixture into the dissolved, adsorbed and vapor phases (API, 2000). Partitioning of individual constituents from a complex mixture such as petroleum LNAPLs is based on Raoult’s Law, and incorporates the chemical composition of the mixture (mole fraction of the constituent), individual chemical properties, and other information to arrive at partitioned chemical concentrations in each of the three phases.

Partitioning calculations have also been reported for the general “bulk” category of hydrocarbons commonly referred to as Total Petroleum Hydrocarbons (TPH). However, the use of equilibrium partitioning principles to identify the amount of TPH that can be partitioned is more complex, since the partitioning calculation must either account for all petroleum constituents, or assume some “average” type of petroleum constituent (i.e., to represent the general properties of all constituents on a whole) to approximate the partitioned amount of TPH to each phase. Theoretically speaking, if the TPH soil concentration exceeds the corresponding TPH Csat value, then free phase LNAPL is likely to be present.

Understanding the partitioning of individual chemical constituents from a LNAPL mixture is an extremely important concept from both a LNAPL mobility and risk perspective.

The presence of LNAPL at a site has traditionally been determined by the presence of LNAPL in a monitoring well. In addition to the actual observation of LNAPL in a well, the presence of free product/LNAPL at a site can be inferred from other methods/data including:

- A positive Sudan IV jar/shake test
- Laboratory analysis of LNAPL saturations indicating values greater than 0%
- Petroleum constituent concentrations in groundwater in excess of the constituent’s effective solubility for the particular petroleum mixture
- Total petroleum hydrocarbon (TPH) concentrations in soil in excess of an appropriate TPH C_{sat} value
- Laser-Induced Fluorescence data exhibiting positive response levels (greater than background)

These methods are particularly useful where the presence of LNAPL is suspected, but it is not observed in wells. It is noted that these methods only allow an inference into the presence or absence of free product/LNAPL, and do not indicate whether or not the LNAPL is mobile. Evaluating the mobility of LNAPL is a more complex and highly site-specific exercise that will be discussed in depth throughout the remainder of this document.

There has been a paradigm shift over the past decade regarding the presence of LNAPL at environmental sites. Previously, most attention tended to be focused on whether or not LNAPL or free product was present (particularly in a well), and if present, how to remove it from the subsurface since it was perceived to represent an unacceptable risk by virtue of its very presence. Now, based on a current understating of the scientific principles governing LNAPL behavior, migration and remediation, the focus has shifted to understanding the quantity of LNAPL present (i.e., the LNAPL saturation), the type of LNAPL present, the spatial distribution, and potential risk and mobility issues to be used as a basis for LNAPL management and/or remediation. The remainder of this document will focus on LNAPL mobility, but will also present key related information and principles that ultimately play a role in and affect LNAPL mobility.

2.2 LNAPL Physical and Chemical Properties

2.2.1 LNAPL Physical Properties

The physical properties of LNAPL that are most often measured and used for LNAPL mobility and recoverability assessment include: density, viscosity and interfacial tensions. LNAPLs, being less dense than water, have specific gravities ranging from approximately 0.68 to just less than 1.0 (i.e., the density of water). Hence, in an open water environment, LNAPLs float on top of the water (which, as discussed in future sections, is generally not the case with LNAPL in the subsurface). Density can, however, be used to help distinguish one LNAPL from another. The following density ranges can be used to help characterize an LNAPL (API, 2004):

- Gasoline: 0.68 to 0.78 g/cm^3
- Diesel/No. 2 Fuel Oil: 0.80 to 0.85 g/cm^3
- Lube Oil: 0.83 to 0.88 g/cm^3
- Crude Oil: 0.70 to 0.98 g/cm^3

Other constituents or impurities within the LNAPL mixture may also have an effect on the LNAPL density (for example, LNAPL containing chlorinated compounds).

LNAPL viscosity is used to assess the “pumpability” of the LNAPL as well as the ability of the LNAPL to flow or migrate in the subsurface. Viscosity commonly refers to a fluid’s “thickness” or resistance to flow. Consequently, the higher the LNAPL viscosity, the more resistant the LNAPL is to flow, the less likely the LNAPL will be to migrate, and the harder the LNAPL will be to recover via pumping technologies. With the exception of a gasoline LNAPL, which has a viscosity lower than water, most petroleum-based LNAPLs are more viscous than water. The viscosity of LNAPL, along with LNAPL relative permeability, is accounted for in the determination of LNAPL conductivity, and often times yields a conductivity value one to two orders of magnitude lower than the conductivity of water (i.e., hydraulic conductivity). Typical room temperature viscosity values for various LNAPLs are (API, 2004):

- Gasoline: 0.62 cp
- Diesel: 2.7 cp
- JP-4 Fuel: 1 cp
- Crude Oil: 60 cp

Interfacial tensions between air/water, LNAPL/water and LNAPL/air play an important part in limiting or resisting the movement of LNAPL in the subsurface. In a multiphase system, the tension (or attraction) between different fluids in contact with one another will limit the ability for each respective fluid to flow.

2.2.2 LNAPL Chemical Properties

Petroleum-derived fuels (gasoline, kerosene, diesel, etc.) are complex mixtures of organic compounds (predominantly hydrocarbons) with varying compositions dependent upon the source of crude oil and the refining process (Thomas and Delfino, 1991). Petroleum hydrocarbons are the main components of fuels derived from crude oil. Crude oil is a mixture of paraffinic and aromatic hydrocarbons with a low percentage of sulphur and trace amounts of oxygen and nitrogen compounds. The paraffinic hydrocarbons are the most abundant compounds in crude oil. They include alkanes, which are saturated hydrocarbons with a straight carbon chain completely substituted with hydrogen atoms. The alkanes are typically very stable and unreactive as compared to their unsaturated counterparts. Crude oil contains alkanes with anywhere from one to more than 50 carbon atoms (C1-C50+). In general, C1-C4 alkanes exist as gases, while C5-C17 alkanes are liquids, and C18 and higher alkanes are solids at 20°C. Isoprenoids are branched chain paraffinic hydrocarbons that contain at least two methyl groups. Isoprenoids are often more volatile than the straight chain alkane compounds and make up a significant portion of fuels. Aromatic compounds include single ring (mono-aromatic) structures such as benzene, toluene, ethylbenzene and xylenes (collectively referred to as BTEX), and multi-ring (polycyclic) structures such as naphthalene, phenanthrene, anthracene, fluorine, pyrene and other polycyclic aromatic hydrocarbons (PAHs). The BTEX compounds are the most abundant mono-aromatic hydrocarbons in fuels (particularly gasoline), with smaller amounts of PAHs present (mostly the 2 and 3-ring species). All said, a typical petroleum-based LNAPL is comprised of hundreds of individual hydrocarbon compounds (straight chain and cyclic) as well as other non-hydrocarbon additives that may have been incorporated during the refining process.

Different LNAPLs behave differently based on their chemical composition. For example, a gasoline LNAPL, which is comprised of lighter (lower carbon chain molecules) hydrocarbons than diesel or fuel oil, is more apt to partition into both the vapor phase and dissolved phase, primarily due to the presence of greater quantities of volatile constituents such as BTEX. Due to the chemical and toxicological properties associated with BTEX, gasoline LNAPLs tend to pose more of a vapor and dissolved phase exposure risk than heavier LNAPLs. Further, gasoline LNAPLs may pose explosivity risks due to the abundance of volatile and combustible constituents in the LNAPL. In a given stratigraphy, the heavier (less volatile) petroleum products will typically exhibit a lower potential for mobility, a lower degree of recoverability, and less potential exposure issues than the lighter end/more volatile product types. Many LNAPL types that are heavier than gasoline will pose little to no risk in terms of vapor or dissolved phase impacts (particularly when degraded/weathered).

Depending on the source of the LNAPL, some LNAPLs may contain impurities or other ingredients not typically associated with petroleum LNAPLs. For example, LNAPLs at industrial manufacturing or chemical sites may contain other constituents of concern including chlorinated volatile organic compounds (CVOCs), polychlorinated biphenyls (PCBs), etc. The presence of these materials in the LNAPL may affect the mobility of the LNAPL as well as other issues including LNAPL handling, shipment, remediation, etc.

The chemical make-up or signature pattern of an LNAPL (and LNAPL age) can be determined using laboratory techniques, and is further discussed in the next subsection.

2.3 LNAPL Fingerprinting and Forensic Testing

The process of identifying the specific type of LNAPL (and sometimes the approximate age) via a laboratory process is referred to as LNAPL fingerprinting or LNAPL forensic testing. During this process, the laboratory generates a gas chromatograph of the LNAPL which effectively identifies the signature or pattern of carbon chain molecules in the LNAPL, starting from the lowest carbon chain (C4) up through molecules in excess of 30 carbon atoms (>C30). Various types of LNAPLs are predominantly comprised of specific ranges of hydrocarbon molecules as follows (Potter & Simmons, 1998):

- Gasoline: C4 to C12 range compounds
- Jet Fuel/Kerosene: C6 to C18 range compounds
- Diesel/No. 2 Fuel Oil: C8 to C21 range compounds
- Lube Oil: C18 to >C34 range compounds
- Crude Oil: C1 to >C34 range compounds

Various chromatographic markers and peak ratios are utilized to identify the type or types of LNAPL present, as well as provide an estimation of the level of degradation and/or approximate age. Laboratories may also use a boiling point evaluation to categorize the LNAPLs based on boiling point distillates.

The interpretation of laboratory fingerprinting data can be a difficult task, particularly when dealing with weathered LNAPLs or mixtures of various LNAPLs. For this reason, there is only a relatively small number of laboratories in North America with experienced petroleum forensic chemists that specialize in LNAPL characterization and interpretation of data.

2.4 Effective Solubilities from LNAPL Mixtures

The partitioning of individual constituents from a complex mixture such as petroleum LNAPLs is based on Raoult's Law, and incorporates the chemical composition of the mixture (mole fraction of the constituent), individual chemical properties, and other information to arrive at chemical concentrations in the dissolved, adsorbed and vapor phases. The ability for an LNAPL to yield an individual compound to groundwater via dissolution is a function of the mole fraction of the compound in the LNAPL mixture as well as the pure compound solubility. "Effective solubility" values for the components of various petroleum fuels are reported in the literature, or can be calculated according to Raoult's Law if site-specific LNAPL chemistry data are available (API, 2004):

$$C_i^{eq} = S_i \cdot MF_i$$

Where: C_i^{eq} = equilibrium aqueous concentration (or effective solubility) of hydrocarbon constituent i

S_i = pure phase solubility of hydrocarbon constituent i

MF_i = mole fraction of hydrocarbon constituent i in the LNAPL, approximately equal to the mass fraction

For example, the pure chemical solubility of benzene is approximately 1,760 milligrams per litre (mg/L) (API, 2004). Hence, a pure benzene solvent, in the presence of groundwater, has the ability to yield 1,760 mg of benzene per litre of water. Conversely, using the typical composition of benzene in a gasoline LNAPL and Raoult's Law, a gasoline LNAPL only has the ability to yield approximately 25 to 40 mg/L of benzene to groundwater (API, 2004). The reason for the difference is that petroleum hydrocarbon LNAPLs are comprised hundreds of individual hydrocarbon compounds, and these compounds must compete with each other when partitioning to the dissolved, adsorbed and/or vapor phases. As a result, the ability of each compound to partition into the dissolved, adsorbed and/or vapor phase from a complex petroleum mixture is much less than that of the pure solvent.

As previously mentioned, effective solubility information can be used to qualitatively assess the potential presence of LNAPL, even when no LNAPL has been identified in monitoring wells or boring logs. Using the benzene partitioning example above, if, at a suspected gasoline LNAPL release site, benzene was detected in the groundwater from a monitoring well at a concentration of 30 mg/L, this would suggest that gasoline LNAPL is likely in the immediate vicinity of the well. If benzene was detected at a much lower concentration (in the parts per billion range), it would suggest that gasoline LNAPL is not present in the vicinity of the well. Conversely, if benzene was detected at a much higher concentration (for example, 200 mg/L), this would suggest that the benzene resulted from some kind of pure solvent release, as opposed to a petroleum or gasoline LNAPL release.

For heavier LNAPLs, such as diesel, lube oil, etc., real world experience demonstrates that dissolved phase impacts associated with these LNAPLs are often times very limited or undetectable, as opposed to impacts associated with lighter LNAPLs such as gasoline.

3. Fundamentals of LNAPL Behavior

This section addresses LNAPL behavior at the water table (i.e., unconfined condition) and includes the vertical impacted soil zone typically referred to as the smear zone. The smear zone is where potentially mobile LNAPL may reside at sites where the source(s) of the LNAPL impacts have ceased for some time (i.e., no ongoing sources). The behavior of LNAPL in the vadose or unsaturated zone (above the smear zone) is not addressed here since LNAPL in these zones (particularly at older release sites) is often present at low saturations, and does not typically pose a potential for additional LNAPL migration at the water table. In addition, LNAPL behavior in the secondary porosity of fine textured soils (silts and clays) and fractured bedrock is not addressed in detail. There is very limited information available in the literature describing the evaluation of LNAPL mobility in macropores (e.g., fractures, fissures, root holes, etc.), and there is not currently any professional consensus on how this might be accomplished. However, references regarding LNAPL behavior in these situations are briefly discussed.

3.1 LNAPL Release Dynamics and The Creation of a Multi-Phase Fluid System

When an LNAPL release occurs, either directly in the subsurface (for example, from an underground tank or pipeline) or on a permeable surface, the LNAPL, if present in sufficient quantity, will percolate (or move under sufficient force, depending on the release conditions) vertically downward under the influence of gravity through the soil and eventually encounter the water table. During the downward movement of LNAPL toward the water table, the presence of confining layers and/or other subsurface heterogeneities may result in exaggerated and uneven lateral spreading and/or perching of LNAPL before the water table is encountered. Once at the water table, the LNAPL will penetrate vertically downward and laterally (including in the up-gradient direction) into the water table, displacing an amount of water proportional to the driving force of the vertical LNAPL column (or LNAPL head) created by the release. The displacement of groundwater will continue to occur as long as the downward force produced by the LNAPL head or pressure from the LNAPL release exceeds the upward force produced by the resistance of the soil matrix and the buoyancy force resulting from the density difference between LNAPL and groundwater. Once the release of LNAPL is terminated, the LNAPL footprint at the water table will continue to expand for a relatively short time, and eventually stop once the LNAPL head dissipates. The LNAPL eventually ceases to expand because the driving force (pressure or head) responsible for the LNAPL migration is no longer sufficient to overcome the resistive forces (see explanation below regarding resistive forces of soil) necessary to displace groundwater from the soil pores. When the LNAPL body reaches this state, the LNAPL body is referred to as stable or non-migrating. A conceptual schematic of a stable LNAPL body is provided in Figure 1.

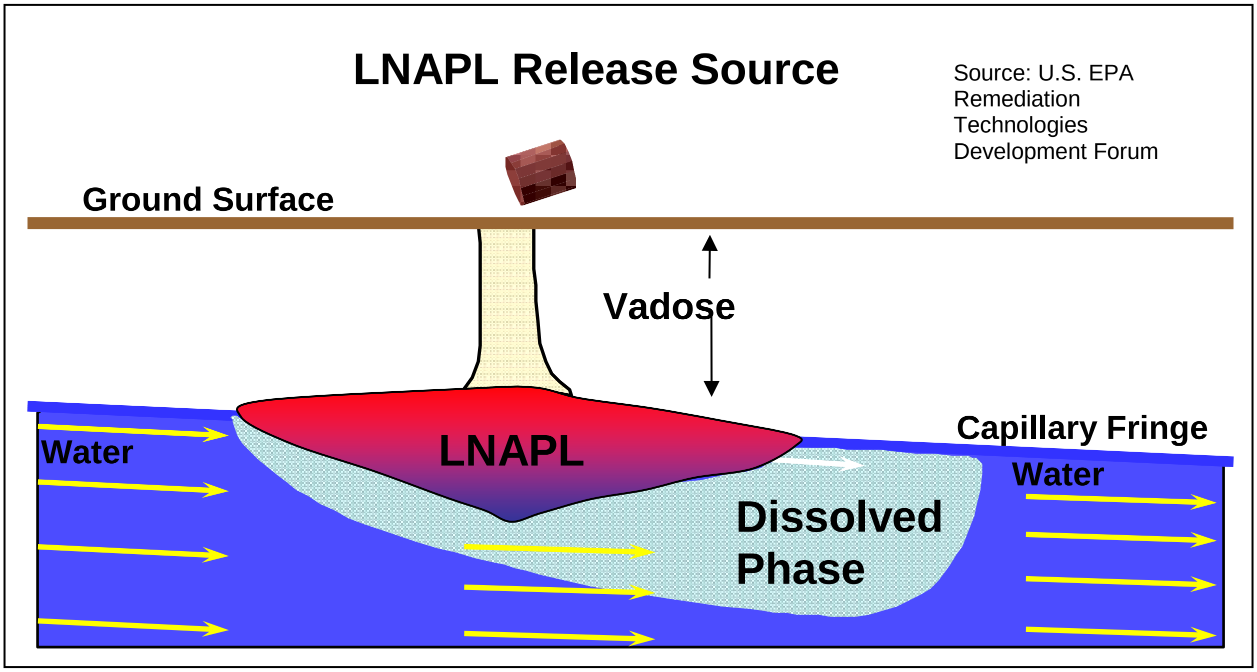
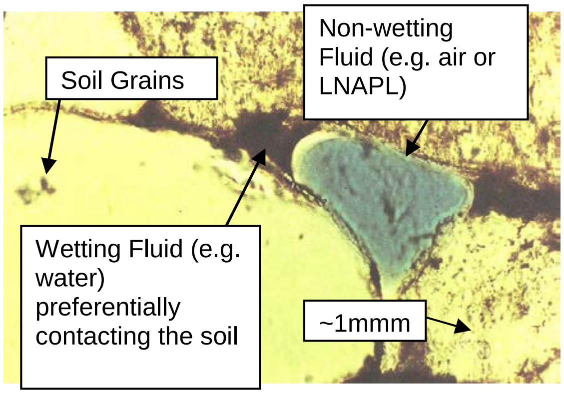


Figure 1: Typical LNAPL Release Scenario with Resulting LNAPL Body at Water Table

The concept of LNAPL penetrating vertically into the saturated zone (i.e., below the water table) during a release contradicts earlier beliefs that LNAPL completely “floats”, due to it being less dense than water, like a pancake (filling 100% of the soil pore space within the LNAPL impacted zone on top of the water table), with no portion of the LNAPL penetrating into the saturated zone. Recent LNAPL science and “real-world” experience shows that some LNAPL (and often times the majority of LNAPL at a given site) is commonly submerged beneath the theoretical water table surface. Further, LNAPL does not displace all groundwater from the soil pore space, but rather a portion of the groundwater that occupies the “largest” soil pore space only. Consequently, a typical LNAPL body consists of LNAPL filling much less of the soil pore space in a more highly variable distribution (that is much more discontinuous) than the historical assumption based on the “pancake” conceptualization would indicate. The LNAPL body at the water table is not comprised of a single fluid phase (LNAPL) but rather comprised of multiple fluids, both LNAPL and water. The top portion of the LNAPL body often includes a third fluid phase: air. Therefore, the term “LNAPL body” represents the spatial limits of LNAPL impacts, within which exists a multi-phase fluid system comprised of LNAPL, water and/or air in proportions that will vary throughout. Furthermore, because of the multi-phase nature of LNAPL occurrence in the subsurface, it is generally incorrect to refer to LNAPL as floating on the water table, and is more appropriate to think of an LNAPL body as a zone of LNAPL impacts, where the pore space contains varying quantities of LNAPL, groundwater and/or air both above and below the static water table elevation. Generally speaking, LNAPL bodies are predominantly comprised of water, followed by a lesser amount of LNAPL, with the smallest fraction of the pore space occupied by air. Figure 2 presents a pore-scale depiction of LNAPL and water co-existing in the soil pore space.

- LNAPL Co-exists with water in pore network
- Degree of saturation depends upon lithology and fluid properties
- LNAPL partially fills aquifer pore space



Source: U.S. EPA Remediation Technologies Development Forum

Figure 2: Current Conceptual Understanding of LNAPL in Multi-Phase Fluid System

LNAPL at the water table requires pressure to move. Unlike groundwater (including dissolved phase constituents), which typically forms a continuous system with flow velocity based on hydraulic gradients, LNAPL, being a non-wetting fluid, requires pressure to force it through the soil pores and displace the existing pore water. More specifically, LNAPL needs sufficient capillary pressure to overcome the resistive forces in the soil to enable the continued displacement of groundwater. In a multi-phase (LNAPL/water) fluid system, capillary pressure (also referred to as excess pressure), is the difference between the pressure in the non-wetting phase (LNAPL) and the pressure in the wetting phase (groundwater). The capillary pressure necessary to overcome the resistive forces for a non-wetting LNAPL to enter water-saturated media is called the pore entry displacement pressure (Mercer and Cohen, 1990). That is, if sufficient pressure is acting on the LNAPL, it will be able to enter a given pore space by forcing some portion of the groundwater out. Once the pore entry displacement pressure is achieved or exceeded, the LNAPL will continue to expand in a vertical and radial direction until there is insufficient LNAPL head or pressure to continue to displace water. The LNAPL head will usually become insufficient to displace water and enter non-impacted pore space shortly after the LNAPL release is terminated. Hence, soon after the LNAPL release is terminated, the LNAPL body eventually becomes stable (i.e., footprint no longer moving or expanding).

Because the main mechanism for LNAPL spreading is the pressure/head of the release (during the release and until the LNAPL body stabilizes), the groundwater gradient will influence the direction of the LNAPL spreading to some extent, but groundwater flow will not typically induce additional LNAPL spreading or migration once stabilization has been achieved. It is also important to note that the radial component that is typical of LNAPL spreading can result in significant up-gradient and cross-gradient LNAPL spreading.

Notwithstanding the groundwater gradient discussion above, significant topographical changes (cliffs, bluffs, etc.) at the location(s) of LNAPL impacts can result in LNAPL seeps due to the excessively large gradient posed by the topography change. Further, these types of seeps often lead to unauthorized discharges of LNAPL into sensitive surface water receptors or bodies. Consequently, special attention must be given when significant topographical changes are in the near or immediate vicinity of LNAPL impacts.

Although LNAPL movement is not typically caused by horizontal hydraulic gradients (ASTM, 2007), LNAPL movement can be highly influenced by the presence of strong vertical gradients (i.e., the presence of a strong gradient in a downward direction). Case studies have shown that LNAPL, under the influence of a strong vertical gradient, can migrate significant distances down into the water table. For example, strong vertical gradients can be induced by municipal well fields actively pumping in lower aquifers. Consequently, when the site geology is comprised of multiple aquifers or water bearing zones, the potential for vertical gradients and deeply penetrating LNAPL should be assessed.

The porous media flow concepts that apply to groundwater systems (Darcy flow equations, etc.) also apply to LNAPL bodies, with two distinct differences. First, LNAPL conductivity (as opposed to water or hydraulic conductivity) includes a relative permeability term, which accounts for the negative influence of groundwater on the ability of LNAPL to flow, and the differences in density and viscosity between LNAPL and groundwater. Second, Darcy flow in an LNAPL body only applies where there is continuous LNAPL within the body. Hence, in any areas of discontinuous LNAPL within an LNAPL body or outside of a stable LNAPL body, there is no LNAPL flow or movement.

3.2 LNAPL Saturation

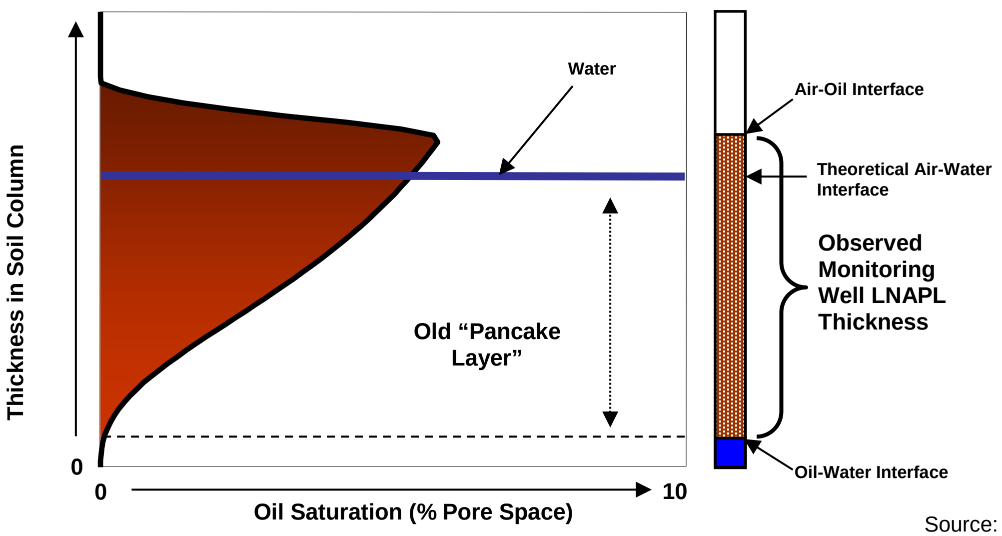
LNAPL saturation is defined as the percent of the soil pore space that is occupied by LNAPL. As previously discussed, LNAPL does not float on the water table like a pancake, but rather coexists with air and groundwater at varying saturations within the impacted soil zone, both above and below the water table. This is due to the fact that the saturation level of a given LNAPL at a given point in the subsurface will be proportional to the capillary pressure at that point (i.e., the greater the capillary pressure, the greater the resulting LNAPL saturation). Because the capillary pressure will vary throughout the impacted zone, the LNAPL saturation will also vary accordingly.

Geology plays an extremely important role with respect to LNAPL saturation (and mobility). The larger the soil pores in the primary porosity of the soil matrix, the greater the capacity for the soil to hold LNAPL, the greater the ease at which LNAPL can move, and the less pressure that is required for LNAPL to displace water and enter the pore space. Granular soils, such as sands and gravels, have large soil pores, relative to silts and clays, and can hold LNAPL at saturations upwards of 40 to 60% (although typical maximum saturations encountered in the field are usually in the 20 to 30% range). Conversely, silts and clays, which have extremely small soil pores relative to sands and gravels, will typically only allow LNAPL saturations on the order of 5 to 15%. The smaller soil pores not only limit the amount of LNAPL saturation, but also limit the flow or movement of LNAPL.

Soil porosity principles for LNAPL saturations and movement in overburden soil may also be applied to certain types of competent bedrock (i.e., bedrock that does not have secondary porosity in the form of fractures). For example, competent sandstone will enable LNAPL to behave in a similar manner as in a similar grain/pore sized sandy soil.

Secondary porosity also plays an extremely important role at LNAPL sites. Fine textured soils, such as silts and clays, are often comprised of a secondary porosity which may include macropores such as fractures, fissures, sand seams, etc. The same holds true for fractured bedrock. LNAPL movement through secondary porosity may occur at rates several orders of magnitude greater than the movement through the primary porosity. This is primarily due to the fact that the macropores generally have much larger pore sizes than the primary porosity, with a corresponding pore entry displacement pressure that is much lower. That is, LNAPL can displace water and move through macropores much more easily and to a greater extent than it can in the primary porosity of a fine-grained soil or rock matrix. Hence, the potential for LNAPL movement through secondary porosity must be considered when LNAPL impacts are present in fine textured soil and/or fractured bedrock.

Idealized LNAPL saturation profiles (in the vertical profile) can be generated (using LNAPL analytical models) based on in-well LNAPL thicknesses and the principles of capillary pressure. An idealized saturation profile used to illustrate the typical variation in LNAPL saturation above and below the theoretical water table in a homogenous granular soil with pore fluids at vertical equilibrium is shown in Figure 3.



Source: U.S. EPA Remediation Technologies Development Forum

Figure 3: Idealized LNAPL Saturation Profile Using Capillary Pressure Principles

The idealized LNAPL saturation profile in Figure 3 is based on the in-well LNAPL thickness identified in the monitoring well adjacent to the profile. Note that the saturation profile commences in the capillary fringe, above the corresponding air/LNAPL interface in the well, and continues down to the LNAPL/water interface in a non-linear manner. Note also that the highest degree of LNAPL saturation occurs in the formation at the approximate location of the air/LNAPL interface in the adjacent well. This type of saturation profile is also referred to as a capillary pressure prediction curve, and is based on the following critical assumptions: (1) the fluids (water and LNAPL) are in vertical equilibrium (i.e., not fluctuating up and down); and (2) the soil formation is homogeneous. These assumptions are required for the LNAPL saturation profile to accurately represent and correspond to the in-well LNAPL thickness. Figure 4 illustrates the conceptual depiction of pore scale fluid saturations through an LNAPL body, based on capillary pressure principles. Figure 5 shows how LNAPL saturation profiles can be depicted across an LNAPL body.

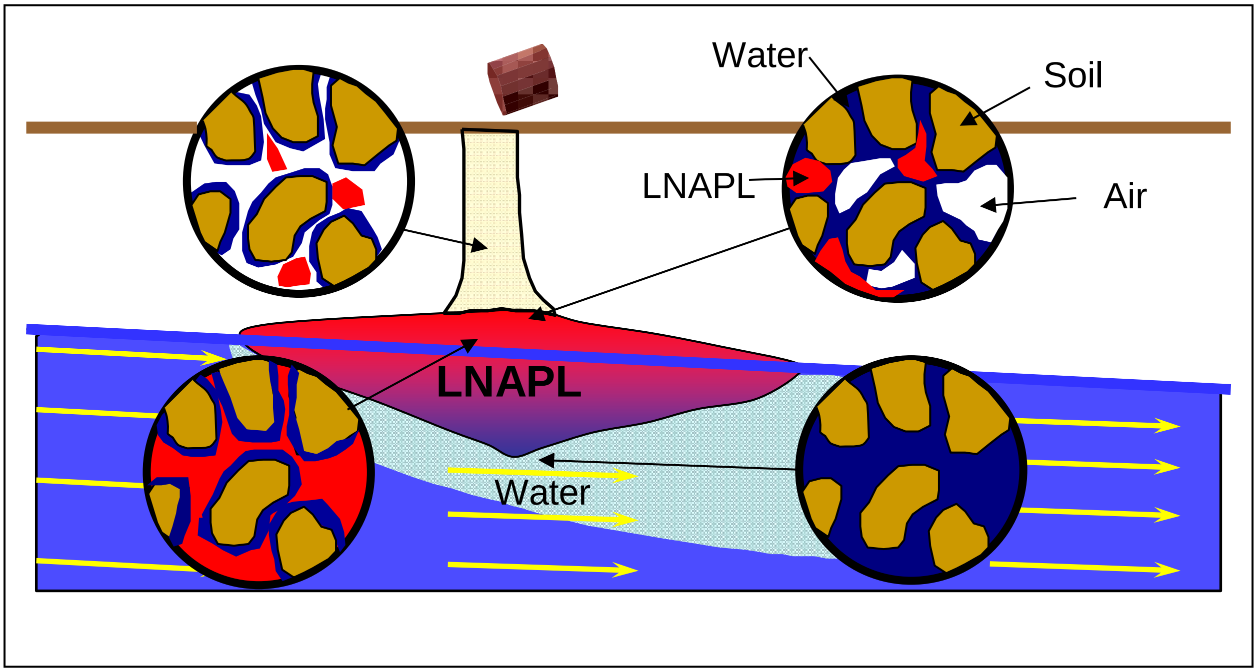


Figure 4: Pore Scale LNAPL Saturations with Respect to LNAPL Body Location

As previously discussed, geology plays an extremely important role with respect to LNAPL saturation. Figure 6 illustrates how LNAPL saturation profiles differ for varying types of soil (due to differences in soil pore size). Figure 7 illustrates how saturation profiles differ for a given soil with varying in-well LNAPL thicknesses.

Again, capillary pressure predictions for LNAPL saturation profiles are based on idealized assumptions. This idealized conceptualization is useful from a theoretical standpoint to illustrate the multi-phase model of LNAPL occurrence and behavior. However, these assumptions will not be met at many environmental sites, and in-well LNAPL thickness data will not typically provide an accurate depiction of the vertical extent of the LNAPL body in the adjacent soil. Where preferential pathways and/or other subsurface heterogeneities exist, LNAPL saturations can vary dramatically throughout an impacted zone and will be difficult or impossible to predict.

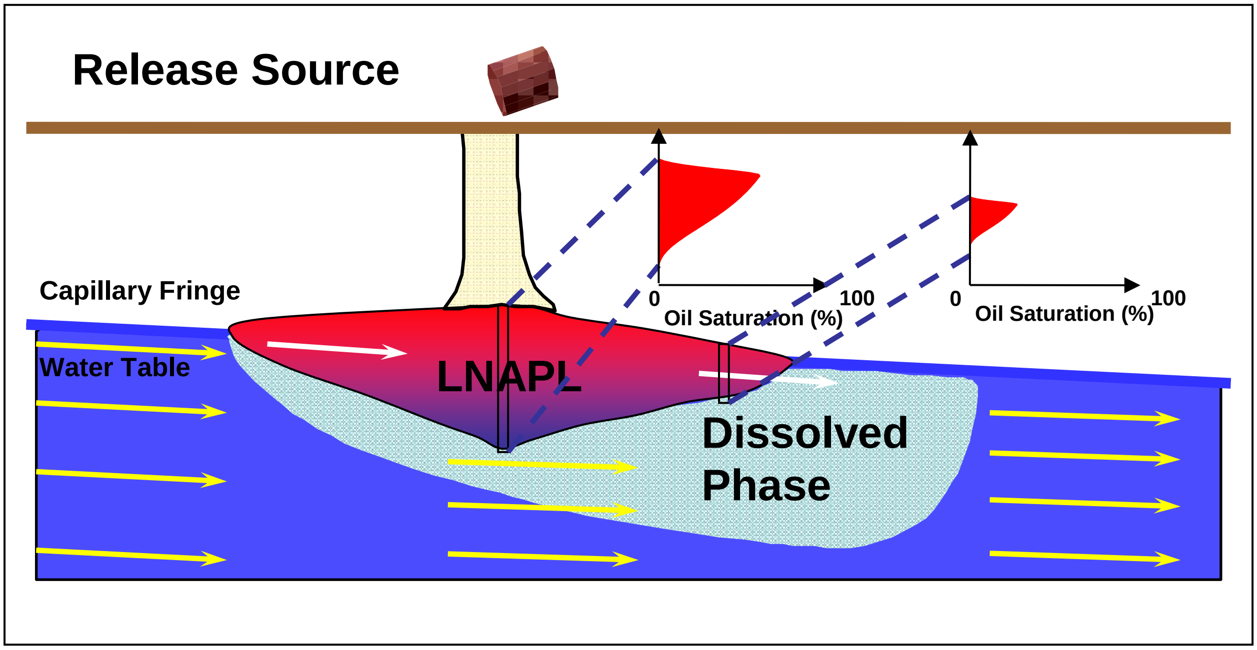


Figure 5: LNAPL Saturation Profile Changes with Respect to Location Within LNAPL Body

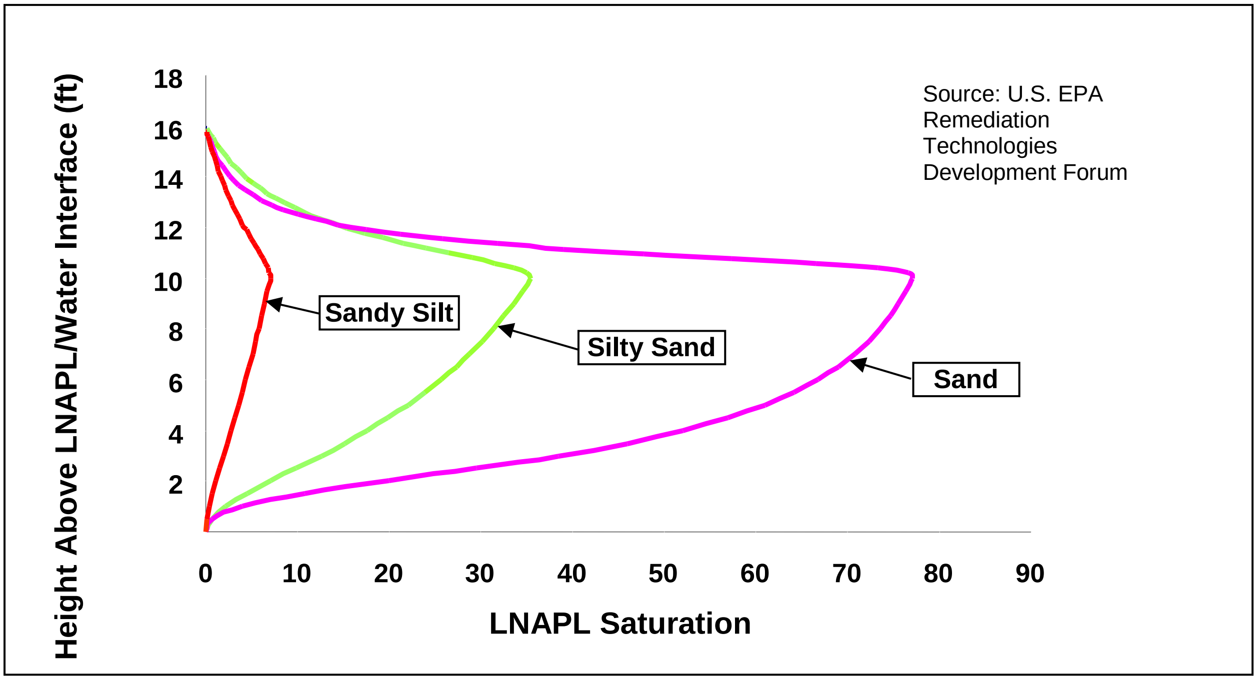


Figure 6: LNAPL Saturation Profiles for Varying Soil Types (10 Feet of In-Well Diesel LNAPL)

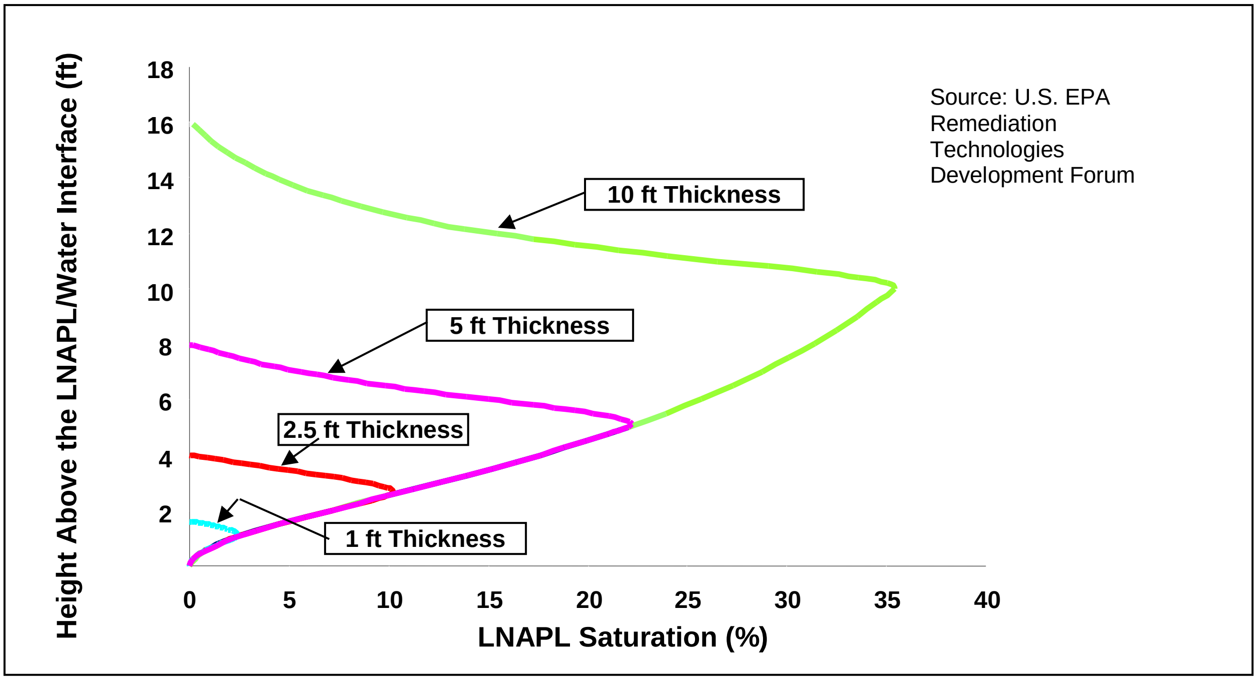


Figure 7: LNAPL Saturation Profiles for a Given Soil with Varying In-Well LNAPL Thicknesses

LNAPL saturations can be determined and/or measured by several methods:

1. Total petroleum hydrocarbon (TPH) soil concentrations can be converted to LNAPL saturations by the following calculation (ASTM International, 2007):

$$S_o = \frac{[TPH]}{10^{-6}} \cdot \frac{\rho_{fb}}{\rho_o} \cdot \Theta^{-1}$$

Where: S_o = LNAPL saturation (fraction of pore space filled with LNAPL)
$[TPH]$ = total petroleum hydrocarbon soil concentration (mg/kg)
ρ_{fb} = soil bulk density
ρ_o = LNAPL/oil density
Θ^{-1} = total soil porosity

2. LNAPL-saturated soil core samples can be collected and tested at certain specialized laboratories to directly determine LNAPL saturations (e.g., Dean-Stark extraction method); and/or

3. Various tools are available from the American Petroleum Institute (API) that can be used to estimate LNAPL saturations based on in-well LNAPL thickness observations (and soil and LNAPL physical properties). These are the Charbeneau spreadsheets, the LNAPL Dissolution and Transport Screening Tool (LNAST), and, most recently, the LNAPL Distribution and Recovery Model (LDRM).

Method 3 is widely used, but generally less reliable than Methods 1 and 2 as it is primarily dependant upon in-well LNAPL thickness observations. As previously discussed, conditions at most environmental sites (i.e., water table fluctuations, subsurface heterogeneties, etc.) make any accurate correlation between in-well LNAPL thicknesses and the actual impacted interval in the adjacent soil formation difficult (refer to Appendix F for a more detailed discussion on issues relating to the interpretation of in-well LNAPL thickness data).

LNAPL saturations are dynamic, and will change over time as LNAPL initially displaces water (during vertical and lateral migration following a release), and is then subsequently displaced as water refills some fraction of the pore space when water table elevation increases (API, 2004). LNAPL saturations can be expected to continue to change until such time as the LNAPL becomes sufficiently discontinuous, such that all saturations are at or below LNAPL residual saturation levels. A discussion of LNAPL residual saturation follows.

3.3 LNAPL Residual Saturation

LNAPL residual saturation is defined as the LNAPL saturation level or threshold below which LNAPL will not flow under normal hydraulic conditions. Consequently, LNAPL that is present at saturations that are less than or equal to residual saturation levels will generally be considered to be immobile and unrecoverable. Conceptually speaking, LNAPL residual saturation represents the LNAPL saturation threshold where the LNAPL, due to its relatively low saturation, starts to break-up or become discontinuous in the form of droplets, stringers, ganglia, etc. LNAPL residual saturation represents the amount of LNAPL trapped by capillary forces within the pore network that is hydraulically unable to move (Beckett, 2005). As LNAPL saturation approaches or decreases to residual, the relative permeability of the LNAPL approaches zero, and the conductivity of the LNAPL approaches zero. Figure 8 provides both a conceptual and pore scale illustration of LNAPL at residual saturation at a LNAPL body periphery.

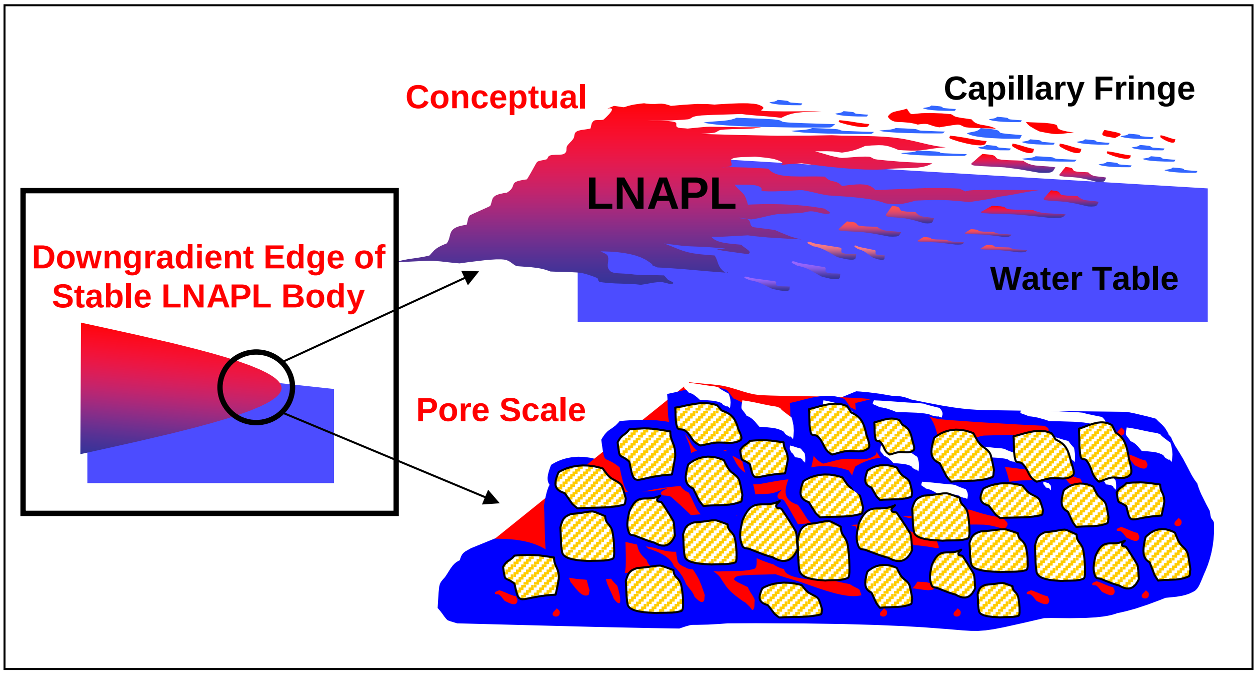
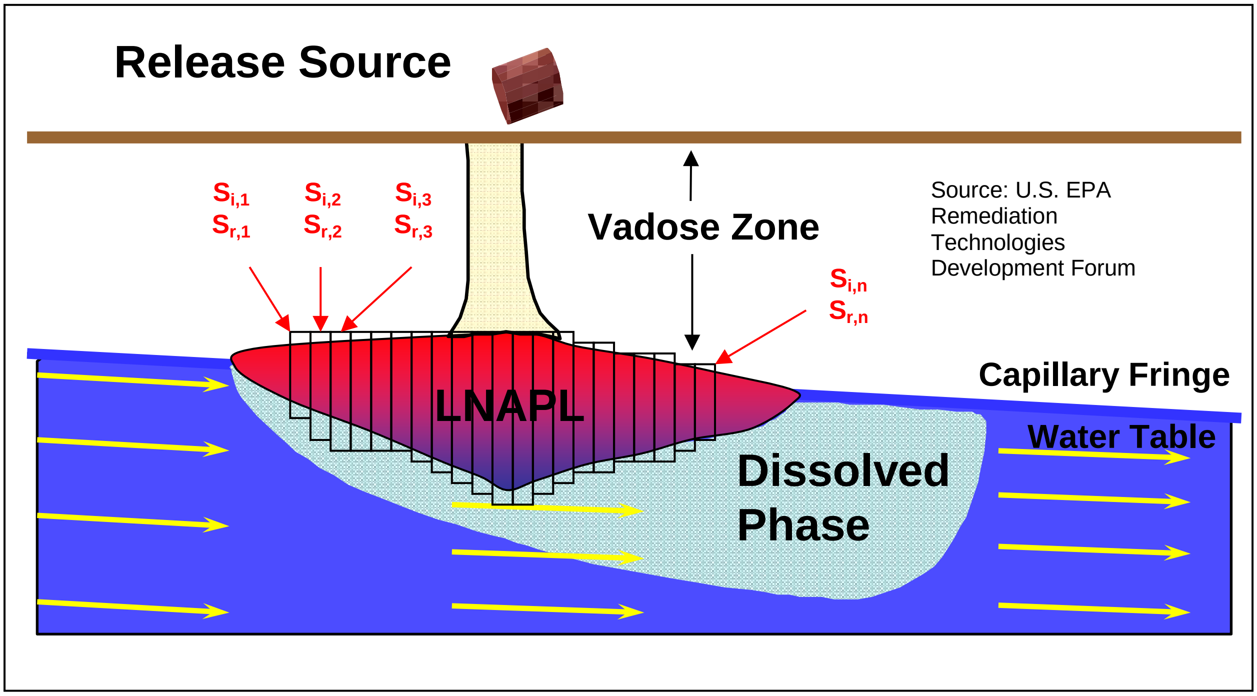


Figure 8: Conceptual and Pore Scale Illustration of LNAPL Residual Saturation

Recent research suggests that LNAPL residual saturation is a function of initial LNAPL saturation (Johnston, C.D. and Adamski, M., 2005). The greater the initial saturation at any point in an LNAPL body, the greater the residual saturation at that point. In other words, the more LNAPL that initially enters a pore space, the more that will become trapped and unable to move out of the pore space. Hence, an entire LNAPL body will be comprised of a variety of initial saturation and corresponding residual saturation values depending on the reference point or location within the body (refer to Figure 9). This concept contradicts earlier notions that there is only one single LNAPL residual saturation value for a given LNAPL and soil type.

LNAPL residual saturation may be characterized as a “range” of saturations less than the highest residual saturation threshold value. At any given location within the LNAPL body, if the LNAPL saturation is equal to or less than the residual saturation threshold (i.e., the upper limit of residual saturation) for that location, then the saturation is deemed to be in the “residual range” which may include any saturations above zero up to and including the residual saturation threshold. Under such conditions, the LNAPL would be deemed to be immobile.



Source: U.S. EPA Remediation Technologies Development Forum

Figure 9: LNAPL Residual Saturation as a Function of Initial Saturation

Residual LNAPL saturations can be determined by obtaining relatively undisturbed soil core samples from a site (maintained in a frozen state to prevent pore fluid drainage) and subjecting them to one of several different laboratory methods:

1. Oil/water drainage/imbibition capillary pressure testing: Involves spiking (via centrifuge) a sub-sample from the soil core with LNAPL up to its maximum saturation, then forcing water through under pressure to drain as much LNAPL as possible. Whatever LNAPL is left constitutes the residual LNAPL saturation.
2. Free product mobility testing via centrifuge at 1,000 times the force of gravity (Brady and Kunkel, 2005): Performed by taking a sub-sample from a soil core as-received (no pre-spiking with LNAPL) and spinning it in a centrifuge at 1,000 times the force of gravity (approximately equal to 40-50 psi applied to sample) for 1 hour. LNAPL remaining in the sample following the centrifuge represents the residual LNAPL saturation.
3. Water drive/flood testing: Involves forcing multiple (typically 10-15) pore volumes of water through a sub-sample from a soil core under 25 psi pressure. The LNAPL residual saturation is represented by the LNAPL that remains in the sample following the water drive.

Methods 1 and 2 both have aspects about the way the test is run that may result in residual saturation results that are unduly biased. In terms of Method 1, recall that recent research indicates residual LNAPL saturation is a function of initial LNAPL saturation (i.e., the more LNAPL that occupies the pore space initially, the higher the residual saturation). The initial spiking of the sample with LNAPL in Method 1 may therefore produce a residual saturation result that is biased high compared with what would be representative of an unspiked sample. With Method 2, the pressure applied during the test is so exceedingly high that it is far beyond the pressure conditions produced by typical hydraulic conditions at most sites. Furthermore, the elevated pressure utilized with Method 2 more often leads to the compression or collapse of the soil matrix during the test. When this occurs, one may not be able to conclude whether any LNAPL released from the sample during the test was the result of the applied gradient or the compression of the soil matrix "squeezing" LNAPL out of the sample. In either case, the results of Method 2 are likely to produce a residual saturation result that will be biased low and non-representative of actual site conditions. Method 3 also involves an applied pressure that is likely to be higher than conditions at a typical environmental site, however, because the pressure is much lower than Method 2 and the method does not involve any pre-spiking of LNAPL as in Method 1, it is the method that is likely to produce the most representative results.

It is important to note that LNAPL residual saturation for a given LNAPL and soil type at a given location within the LNAPL body varies greatly between the unsaturated (vadose) and saturated zones. Generally speaking, LNAPL residual saturations in the vadose zone are much lower than corresponding residual saturations in the saturated zone. This is true because of the difference in densities between an air/LNAPL pair versus a LNAPL/water pair, and because of the difference in interfacial tensions between an air/LNAPL pair versus a LNAPL/water pair. LNAPL in the vadose zone has a much greater ability to drain under the force of gravity and flow into a monitoring well, as opposed to LNAPL that is submerged beneath the water table. Put simply, much less pressure is required for LNAPL to push air out of the way to enter a pore than would be required for LNAPL to do the same to groundwater. This also plays a role in the appearance and disappearance of LNAPL in wells resulting from fluctuations of the water table elevation. Typical LNAPL residual saturations in the vadose and saturated zones for given soil types are as follows (ITRC, 2009c):

Table 1 Representative LNAPL Residual Saturation Values for the Vadose and Saturated Zones

Soil Type	Residual Saturation (Vadose)	Residual Saturation (Saturated)
Sand	3%	25%
Sandy Loam	5%	22%
Loam	7%	18%
Silty Loam	7%	16%
Sandy Clay	7%	10%
Silty Clay	4%	6%

Note that the "saturated" residual saturation of LNAPL in a coarse grained material (sand) is much higher than the corresponding "saturated" residual saturation in a silt or clay. As previously discussed, this is due to the fact that a coarse grained soil has a much greater capacity to hold LNAPL (due to larger soil pores) than a fine textured soil. Hence, the LNAPL saturations and corresponding residual saturations in a coarse grained soil are typically much higher than the LNAPL saturations and residual saturations in a fine textured soil. As previously noted, secondary porosity may control LNAPL flow in finer grained soils. Consequently, these typical values may or may not apply where this condition is present.

3.4 LNAPL Mobility and Body Stability

3.4.1 LNAPL Mobility

The mobility of LNAPL generally relates to its ability to move in a localized sense at any point within an LNAPL body, and does not necessarily represent a migrating LNAPL body. LNAPL mobility can be highly influenced by a fluctuating water table. The mobility of LNAPL is dependent on a variety of LNAPL properties (density, viscosity, interfacial tension) and soil properties (soil type(s) and drainage characteristics) and is often characterized in terms of LNAPL saturations (at any point within an LNAPL body) and the corresponding residual saturations. LNAPL saturations that exceed residual saturation levels indicate a potential for mobility, however, this does not necessarily indicate that the LNAPL body is migrating (ASTM International 2007, ITRC 2009).

Seasonal water table fluctuations have a direct impact on the mobility of LNAPL. A rising and falling water table creates a “smear zone” where mobile, continuous LNAPL becomes spread vertically and becomes discontinuous as water and LNAPL compete for pore space. Assuming a continuous source is not present, this interaction between water and LNAPL can effectively trap LNAPL as discontinuous, immobile droplets within the soil matrix (API, 2004). Consequently, during seasonal high water tables, some or all of the LNAPL in the smear zone (in an unconfined setting) can become submerged or trapped beneath the water table. This results in the submerged LNAPL losing much of its ability to flow through the soil matrix and/or into a monitoring well (due to a higher residual saturation in the saturated zone). In some situations, all LNAPL in a well can “disappear” with an increase in water table elevation.

The disappearance and reappearance of LNAPL in monitoring wells in response to fluctuating water table elevations is a relatively common occurrence. During a rising water table condition, there is a delay in the response or rising of the LNAPL in the formation as buoyancy forces attempt to move the LNAPL upward through the resistance presented by the soil formation (Oostrom et al, 2006). This delay is due to the resistance to LNAPL movement provided by the soil matrix and the fact that groundwater is less viscous than LNAPL and is able to move more easily through the soil than LNAPL. The LNAPL in a well, however, does not encounter the resistance to upward movement that the LNAPL in the formation does, and will rise on top of the water in the well more quickly than the LNAPL in the formation is able to rise through the soil matrix. This creates an LNAPL gradient from the well toward the formation, resulting in LNAPL flow out of the well and, in some situations, results in all LNAPL disappearing from the well. Conversely, during seasonal low water tables, more of the LNAPL in the smear zone becomes exposed, gaining the ability to drain from the newly unsaturated soil under gravity and flow in the soil and/or into a monitoring well (due to a lower residual saturation in the unsaturated zone). This explains the reappearance of LNAPL or increases in LNAPL thickness in wells during seasonal low water tables.

The rising and lowering of the water table has a direct influence on the inherent mobility of LNAPL within an LNAPL body, but does not necessarily create a migrating LNAPL body. Furthermore, at sites that do not have ongoing sources, changes in in-well LNAPL thickness that correlate with fluctuations in the water table elevation are more likely to be a result of localized vertical redistribution of LNAPL in and out of the well (as described above), as opposed to being representative of any significant lateral mobility (ITRC, 2009a).

As suggested above, LNAPL thickness in a monitoring well varies inversely with water table elevation in an unconfined setting or condition. Hence, an increase in water table elevation results in a decrease in in-well LNAPL thickness. Conversely, a decrease in water table elevation results in an increase in in-well LNAPL thickness. In a confined setting (including LNAPL present in the secondary porosity of silts, clays and possible fractured rock), in-well LNAPL thickness tends to vary directly with potentiometric surface elevation. Hence, an increase in potentiometric surface elevation results in an increase in in-well LNAPL thickness, and vice versa.

It is important to note that LNAPL mobility, on its own, only defines the potential for LNAPL movement or migration, and does not explicitly define movement/migration. To define LNAPL migration, the LNAPL gradient is required in addition to LNAPL mobility (API, 2004). Further, and as previously indicated, Darcy flow in an LNAPL body only applies where there is continuous LNAPL within the body. Hence, in any areas of discontinuous LNAPL (i.e., LNAPL saturations below residual) within an LNAPL body, or outside of a stable LNAPL body, there is no LNAPL flow or movement.

3.4.2 LNAPL Body Stability

LNAPL stability relates to the ability or inability of an LNAPL body to migrate (i.e., whether or not the perimeter or extent of an LNAPL body is expanding/advancing over time). If the perimeter of an LNAPL body is growing or moving over time, the body is typically referred to as migrating or unstable. If the LNAPL body remains essentially the same size and in the same location over time (i.e., same overall footprint over time), the body is referred to as stable or non-migrating. Generally speaking, most historical LNAPL bodies, where the source of the release has been terminated, are stable. LNAPL bodies are spatially self-limiting (due to the capillary pressure principles previously discussed) unless continually supplied from an on-going release, thus distinguishing LNAPLs from dissolved and vapor plumes that may migrate significant distances (API, 2004). Typically, once the release of LNAPL stops, LNAPL in the water table region will eventually cease to move as the resistive forces in the saturated soils balance the driving forces in the LNAPL pool (API, 2002; Huntley and Beckett, 2001). Often times, the following factors combine to produce a stable plume that is not spreading or migrating (U.S. EPA, 2005a):

- LNAPL fluid properties
- LNAPL relative permeability
- Conductivity of the porous media
- Hydraulic gradient
- Pore throat displacement entry pressure
- Fluctuating water table

For an entire LNAPL body, LNAPL can be found to be mobile near the center of the body, where LNAPL saturations are highest (in excess of residual saturation), and immobile at the outer body fringes where saturation decreases to residual. Hence, parts of the LNAPL body may exhibit some localized potential for mobility, whereas the overall body remains stable.

Figure 10 provides a conceptual drawing of an LNAPL body that is continuing to expand or migrate. The expanding body is represented at the periphery by bold “force” arrows, indicating that the LNAPL has sufficient pressure or head to continue displacing groundwater. Conversely, Figure 11 shows a stable LNAPL body with “force” arrows in equilibrium with the resisting force of soil and groundwater.

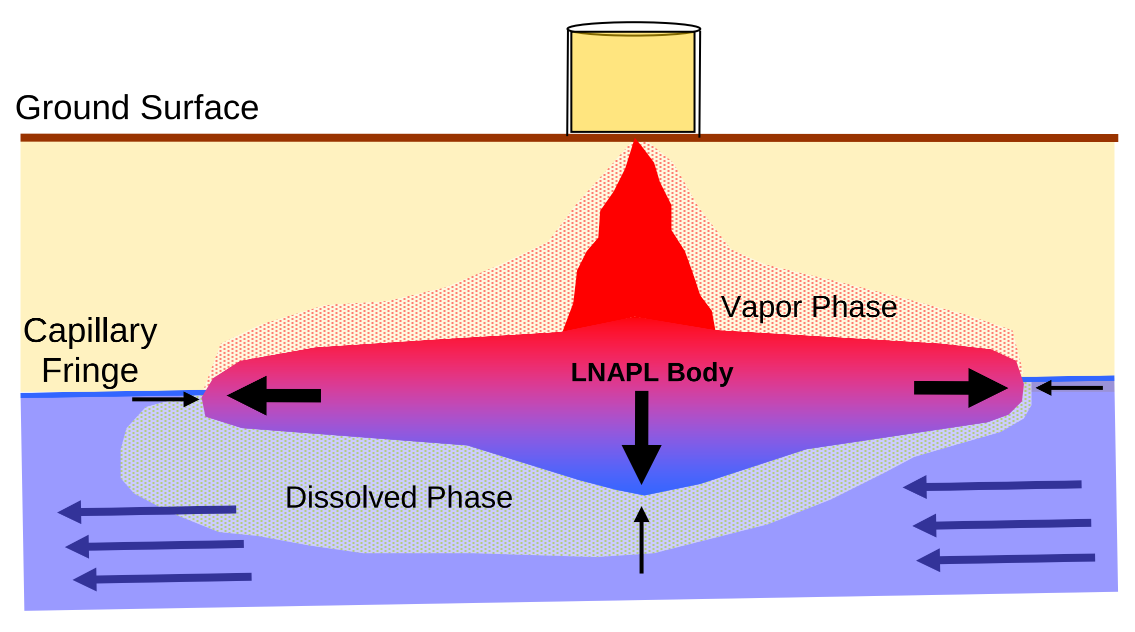


Figure 10: Expanding/Migrating LNAPL Body (Thick Force/Pressure Arrows Within Body Indicate Continued LNAPL Body Migration in all Directions)

Water table fluctuations in a stable LNAPL body may cause immobile LNAPL to become mobile and flow or drain into an immediately adjacent monitoring well. However, although there may be some limited LNAPL drainage and vertical redistribution or smearing, the LNAPL body is still likely to be stable and non-migrating. Hence, at a site with a stable LNAPL body (i.e., no continuing LNAPL release), the disappearance of LNAPL from a monitoring well for months and/or years, followed by the reappearance of LNAPL does not necessarily mean that the LNAPL is migrating.

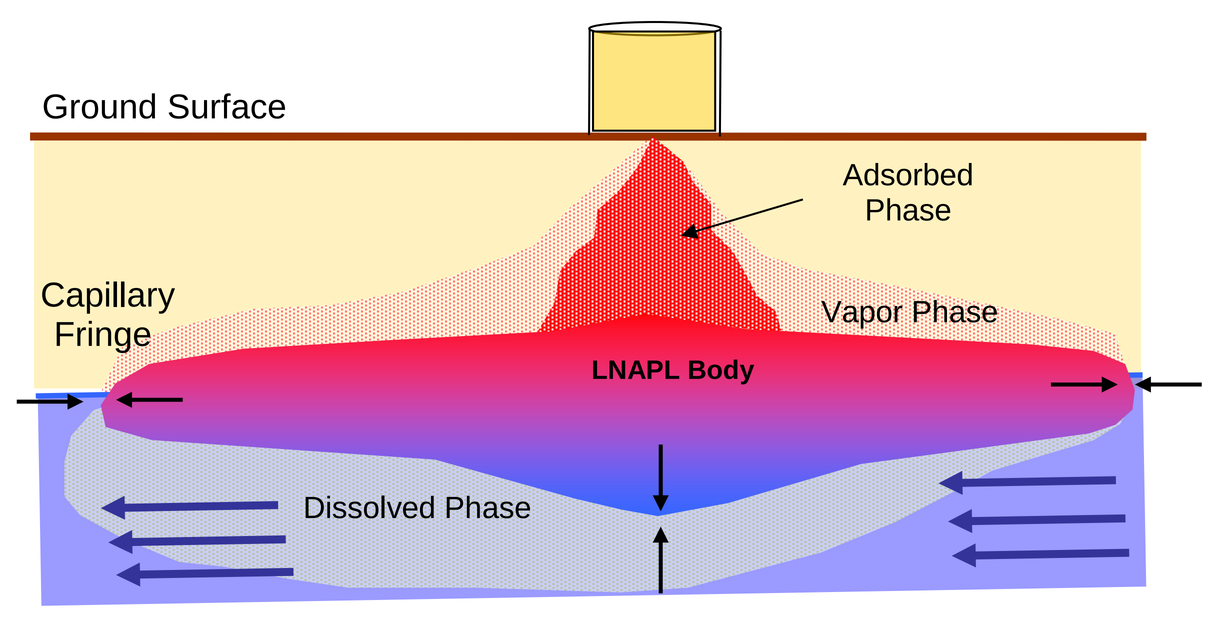
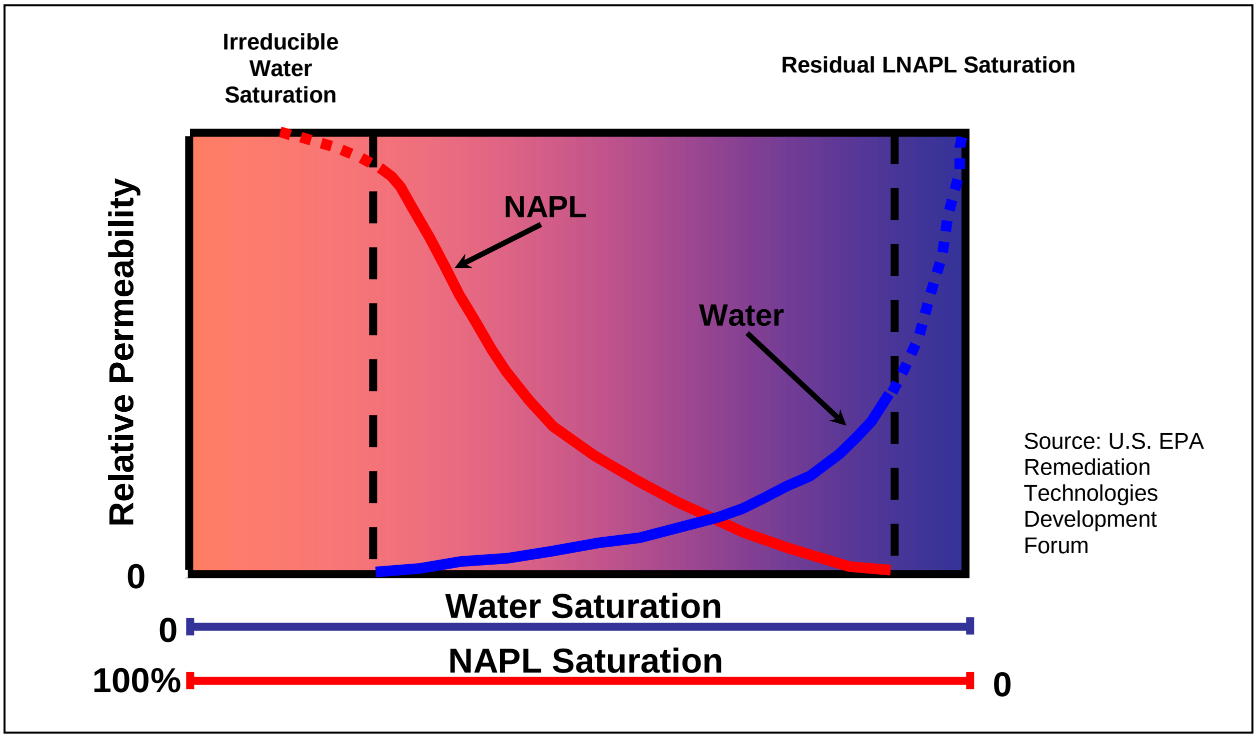


Figure 11: Stable/Non-Migrating LNAPL Body (Arrows Within and Outside of LNAPL Body Indicate Opposing Forces/Pressures are at Equilibrium)

3.5 LNAPL Relative Permeability

Relative permeability is the term used to quantify and describe the potential of one fluid phase to move in the presence of a second immiscible fluid phase. It may also be characterized as the ability of the soil or porous medium to transmit one fluid in the presence of another. In an LNAPL and groundwater setting, LNAPL relative permeability describes the ability of the LNAPL to move in the presence of water. LNAPL relative permeability is a function of and varies directly with LNAPL saturation. Hence, an increase in LNAPL saturation results in an increase in LNAPL relative permeability, and vice versa.

Figure 12 presents the relationship between water saturation, LNAPL saturation and relative permeability for both water and LNAPL. In terms of the LNAPL relative permeability, of particular interest is the fact that when LNAPL saturations decrease to residual, LNAPL relative permeability effectively decreases to zero. This has broad implications since LNAPL conductivity and velocity are dependent on LNAPL relative permeability. Hence, as LNAPL relative permeability approaches zero, LNAPL conductivity and velocity also approach zero.



Source: U.S. EPA Remediation Technologies Development Forum

Figure 12: Relative Permeability as a Function of Water and LNAPL Saturation

Figures 13, 14 and 15 present a series of illustrations showing how LNAPL relative permeability relates to LNAPL mobility and body stability. In Figure 13, an expanding LNAPL body is shown to exhibit LNAPL saturations above residual at varying locations throughout the body. In this figure, the LNAPL body is continuing to expand or migrate due to the ongoing release of LNAPL from the tank/source, and due to the relatively high LNAPL saturations and pressure conditions. In Figure 14, the source of the LNAPL release has been terminated, and the LNAPL body has ceased to migrate (i.e., is stable) due to the lack of pressure head and low saturations at the body periphery. Hence, despite having higher LNAPL saturations in the interior of the body, which represent areas of inherent mobility, the low saturations and pressure conditions at the body periphery are not sufficient to overcome the resistive forces in the soil and displace groundwater. In Figure 15, the LNAPL has been repeatedly smeared over time due to ongoing fluctuations in the water table. The smearing has reduced the LNAPL saturations throughout the entire LNAPL body to the extent that all saturations are less than residual. In this scenario, the LNAPL is both immobile and stable.

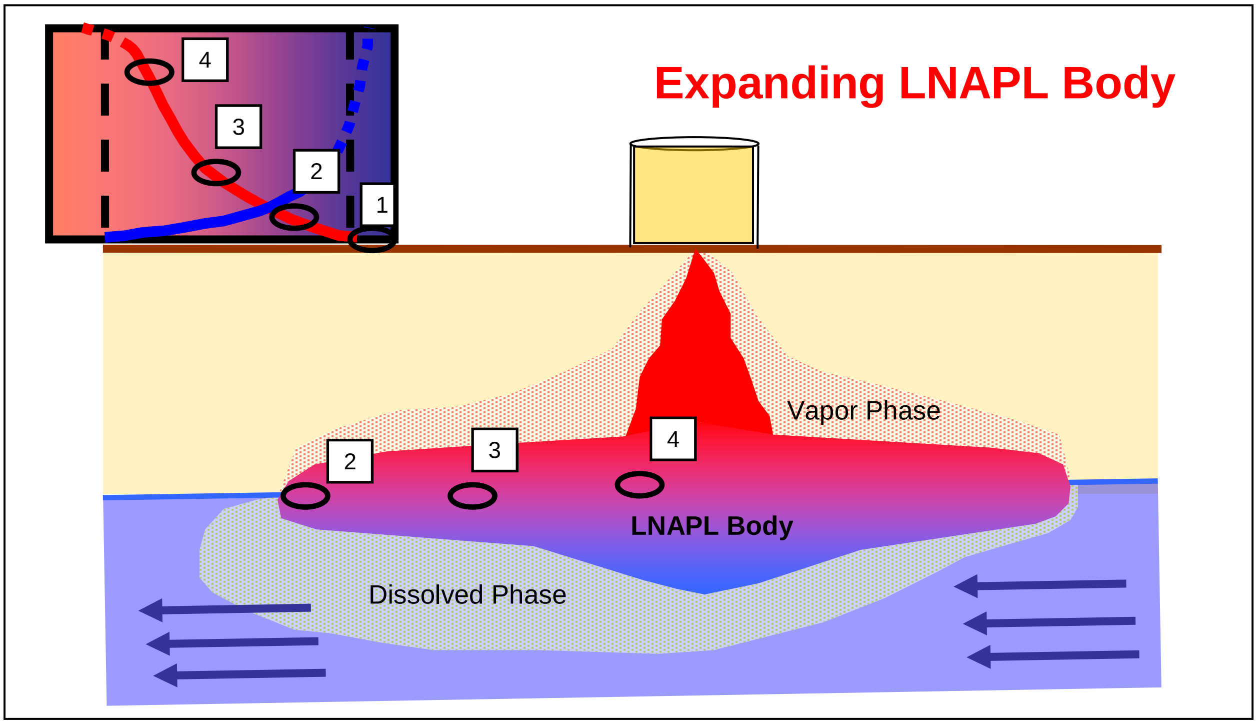


Figure 13: Expanding LNAPL Body as a Function of Relative Permeability

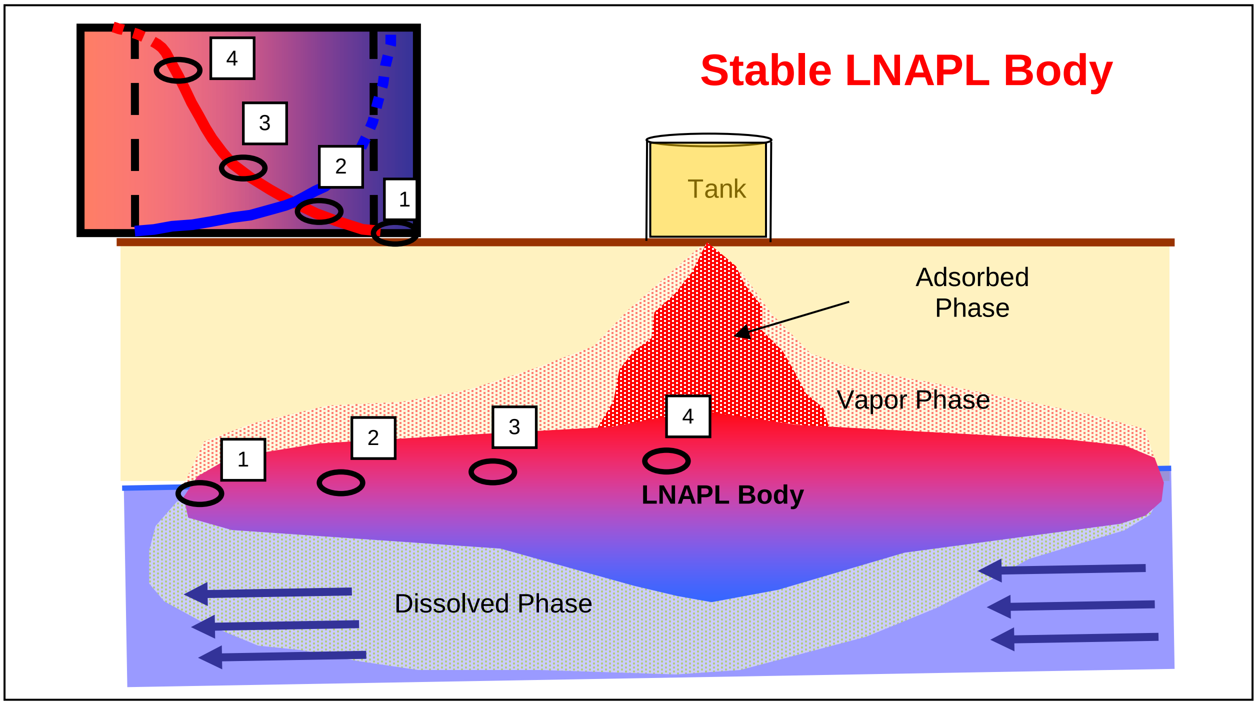


Figure 14: Stable LNAPL Body as a Function of Relative Permeability

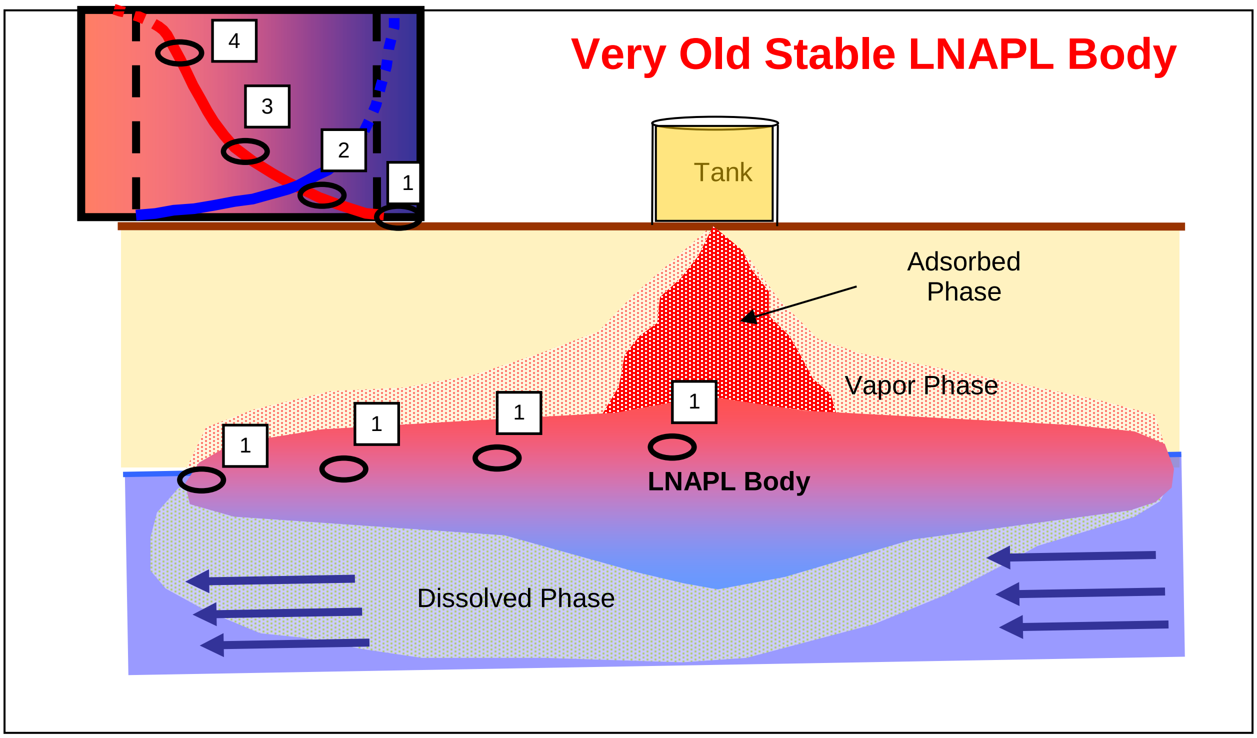


Figure 15: Very Old "Smeared" Stable LNAPL Body (All LNAPL Saturations Below Residual)

3.7 LNAPL Conductivity and Velocity

LNAPL conductivity is a function of the fluid properties (LNAPL and water) as well as the porous medium properties. It includes the LNAPL relative permeability term, the hydraulic conductivity and the densities and viscosities of the fluids. Using Darcy flow principles, the LNAPL specific discharge is equal to the product of the LNAPL conductivity and LNAPL gradient. The LNAPL velocity in turn, is equal to the LNAPL specific discharge divided by the effective free LNAPL porosity (which is defined by the product of the LNAPL saturation and total soil porosity).

Any calculated LNAPL velocity values exceeding the de minimis value of 10-6 cm/s (ASTM International, 2007) suggest a potential for mobile LNAPL. Conversely, any calculated velocities less than 10-6 cm/s suggests that the LNAPL is effectively immobile.

4. LNAPL Conceptual Site Model (LCSM)

The LNAPL Conceptual Site Model (LCSM) is the body of information describing aspects of the LNAPL and site setting necessary to satisfy the LNAPL remedial/management objectives (ASTM, 2007; ITRC, 2009a). The LCSM is similar to a Conceptual Site Model, which includes the source, pathway, and receptor, but the emphasis in the LCSM is on the source component (i.e., the LNAPL). An LCSM includes both “scientific” information regarding the LNAPL, soil and site conditions/setting, and “other considerations and factors” that are necessary to establish the true remedial drivers (risk-based or non-risk factors) for the LNAPL/site. The remedial drivers, in turn, are used to establish the overall LNAPL remedial/management objectives, and follow-up technology-specific goals, metrics and endpoints, where applicable. The discussion presented in this section focuses on the LCSM concepts and components that relate directly to the evaluation of LNAPL mobility and LNAPL body stability.

The LCSM may be comprised of some or all of the following scientific and technological information:

- Site setting (historical and current)
- Geological and hydrogeological information/setting
- LNAPL physical (density, viscosity, interfacial tensions) and chemical properties (fingerprinting, constituents, mole fractions, etc.) characteristics
- LNAPL spatial distribution (vertical and horizontal delineation)
- LNAPL mobility and body stability/migration information
- LNAPL recoverability information
- Associated dissolved-phase and vapor-phase plume information
- LNAPL natural depletion processes

The level of detail required for a given LCSM is site-specific and based on the complexity of environmental conditions at each site, the regulatory framework, and the overall LNAPL site management objectives. In certain situations, where the size of the LNAPL body is relatively small and a presumptive remedy such as soil excavation is adequate to satisfy the LNAPL site management objectives, the LCSM may be limited, with a primary focus on LNAPL delineation or spatial distribution. In other situations, where a presumptive remedy such as excavation is not feasible, the LCSM will need to be developed in adequate detail, particularly in terms of hydrogeology, LNAPL spatial distribution and mobility. With the distribution and mobility aspects understood, the recoverability aspects become more straightforward to select and manage.

LNAPL mobility and body stability are typically evaluated using various lines of evidence (refer to Section 5.0 for further discussion on lines of evidence) including the following:

- Historical LNAPL-related data (depth to LNAPL/water levels, in-well thicknesses, stable or shrinking dissolved-phase plume, recovery data, etc.)
- Site-specific laboratory data (TPH profiling, LNAPL saturations in soil cores, etc.)
- Dye tracer testing
- LNAPL modeling (analytical and/or numerical) simulations
- Combinations of the above

The extent to which one particular line of evidence may be needed for the LCSM is dependent on the other available lines of evidence. For example, at a site where there is little to no historical data or where the data sets are extremely sparse, there will be a stronger need for extensive site-specific laboratory data with follow-up modeling to adequately characterize LNAPL mobility and body stability issues. Conversely, at a site with an abundance of historical data covering the full range of water table fluctuations, there may be less need to engage in a comprehensive laboratory program or modeling effort to complete the LCSM.

Associated dissolved-phase and vapor-phase information can provide additional lines of evidence pertaining to the overall stability or instability of the LNAPL body. A stable dissolved-phase plume also suggests that the LNAPL body is stable (i.e., not expanding or moving with time). Conversely, a migrating dissolved-phase plume suggests that the LNAPL body may not be stable.

ASTM International (ASTM) advocates (ASTM, 2007) the development of an LCSM to evaluate LNAPL sites in a manner consistent with the risk-based corrective action (RBCA) process. ASTM identifies three tiers of LCSMs based on site complexity: Tier 1, Tier 2 and Tier 3 (with site complexity and LCSM requirements increasing with increasing Tier level). Generally speaking, the LCSM for a given site is deemed adequate (in terms of level of detail) when the collection of additional information regarding the site/LNAPL will not enhance decision making associated with potential corrective action/management as they pertain to the site management objectives.

LNAPL mobility evaluations may also be characterized into the three Tier levels described above, with increasing complexity for each increase in Tier level. Example components of Tier 1, Tier 2 and Tier 3 LNAPL mobility evaluations are provided in Table 2 (ITRC, 2009a). It is noted that the elements identified in Table 2 are intended as examples of mobility evaluation components, and may or may not need to be included in all evaluations.

The LCSM is used as the “scientific basis” for all LNAPL remedial and/or management decisions and strategies. However, “other considerations and factors” must also be evaluated to: (1) establish the true remedial drivers for the LNAPL/site; (2) establish relevant and appropriate LNAPL remedial/management objectives; and (3) evaluate potential remedial/management strategies (including the development of technology –specific goals, metrics and endpoints, where applicable). These “other considerations and factors” include:

- LNAPL risk issues (current and potential future)
- LNAPL-specific regulatory requirements
- Additional considerations (business, stakeholder, community, etc.)

For more information and discussion regarding these “other considerations and factors”, the reader is referred to the Interstate Technology & Regulatory Council (ITRC) 2009 TechReg Guidance (ITRC, 2009a).

Table 2 LNAPL Mobility Evaluation Tiers[1,2]

Mobility Tier	What	Why	How
Tier 1: (Based on relatively standard field and lab data)	**Field Data**: may include geology/hydrogeology; soil and groundwater analytical results; depth to LNAPL/water measurements; in-well LNAPL thicknesses; existing recovery data.	To understand the type of LNAPL present, the general spatial distribution of LNAPL across the site, the response of in-well thicknesses to changes in water table elevation, the potential for LNAPL recovery, and potential risk issues associated with the LNAPL body and associated dissolved and vapor phases.	Typical field methods
	Lab Data: may include LNAPL fingerprinting/characterization; density; viscosity.		Common laboratory methods
	Modeling Data: use of analytical models with in-well LNAPL thickness data.	To generate LNAPL saturation profiles and preliminary estimates of LNAPL mobility based on in-well thicknesses.	Analytical models
Tier 2: (May require the collection of numerous soil samples along the vertical profile or the collection of LNAPL-saturated soil cores for laboratory testing and/or modeling purposes)	**Field Data**: in addition to Tier 1 data, may include: - LNAPL baildown testing; - more sophisticated LNAPL delineation techniques such as Laser Induced Fluorescence (LIF); - the collection of multiple soil samples (per location) for vertical TPH profiling purposes; and/or - the collection of LNAPL-saturated soil cores for subsequent lab mobility testing.	To achieve a much more defined spatial distribution of LNAPL in the subsurface (both above and below the water table). This information may be used to: (1) assess the potential volume of LNAPL present; (2) determine strategic locations for the collection of LNAPL-saturated soil cores for subsequent mobility testing; and/or (3) determine strategic locations for the placement of potential monitoring/recovery wells/screens.	Specialty vendors providing LIF services
	Lab Data: in addition to Tier 1 data, may include:		
	- TPH analysis of multiple soil samples along the vertical profile;	To convert TPH soil concentrations into LNAPL saturations and create a laboratory generated LNAPL saturation profile based on actual TPH sample results.	Typical field sampling methods
	- core photography in both white light and ultraviolet light;	White light photo used to evaluate soil texture and pore structure, and to identify changes in stratigraphy. Ultraviolet (UV) light photo used to identify the presence of LNAPL at specific locations in the soil	ASTM D5079/API RP40

Table 2 LNAPL Mobility Evaluation Tiers [1,2]

Mobility Tier	What	Why	How
		core. This information can be used to select sub-samples of the soil core to undergo LNAPL mobility testing.	
	- LNAPL saturation and residual saturation testing;	To determine the potential for LNAPL mobility at specific test locations. The greater the LNAPL saturation above LNAPL residual saturation for a given test location, the greater the potential for LNAPL mobility at that location. LNAPL saturation and residual saturation measurements may also be used in subsequent modeling efforts to generate LNAPL saturation profiles and calculate LNAPL relative permeability, conductivity, mobility and velocity values.	Pore fluid (LNAPL and water) saturations by Dean-Stark, API distillation extraction method using toluene (API RP40)
	- Air/water capillary pressure testing;	To generate a residual water saturation (also referred to as the irreducible water saturation) value and van Genuchten curve fitting parameters to be used as inputs in subsequent modeling efforts to generate LNAPL saturation profiles and calculate LNAPL relative permeability, conductivity, mobility and velocity values.	ASTM D6836/API RP40
	- LNAPL density and viscosity;	To be used as an input in subsequent modeling efforts to generate LNAPL saturation profiles and calculate LNAPL relative permeability, conductivity, mobility and velocity values.	LNAPL Density: ASTM D1481
	- Interfacial tensions (LNAPL/water, air/water, LNAPL/air).	To be used as an input in subsequent modeling efforts to generate LNAPL saturation profiles and calculate LNAPL relative permeability, conductivity, mobility and velocity values.	ASTM D971
	Modeling Data: may include:		
	- Use of commercially available software to analyze LNAPL baildown test	To calculate LNAPL transmissivity and conductivity values (which may be used	Commercially available software (AQTEsolv)

Table 2 LNAPL Mobility Evaluation Tiers [1,2]

Mobility Tier	What	Why	How
	data/observations	to evaluate LNAPL recovery, calculate LNAPL velocity, etc.)	
	- Use of API or other analytical models	To generate LNAPL saturation profiles, calculate LNAPL specific and recoverable volumes, calculate LNAPL relative permeability profiles (as a function of LNAPL saturation), and calculate LNAPL conductivity, mobility and velocity values.	API Interactive LNAPL Guide software (Calculation Tools) API LNAPL Distribution and Recovery Model (LDRM) Others
Tier 3: (May require extensive "data density" and the use of sophisticated numerical models)	**Field Data**: more detailed site and LNAPL data than Tier 2	To generate an extremely detailed understanding of the current LNAPL characteristics, spatial distribution and setting, and to enable detailed predictions about potential future LNAPL migration and behavior. May be required in situations where sensitive receptors are located in close proximity to the site and/or when proposed future changes in land use may present additional risk issues. This type of LCSM is only expected to be needed in rare circumstances.	
	Lab Data: more comprehensive lab data than Tier 2		
	Modeling Data: likely requires the use of numerical (either finite difference or finite element) models		Commercially available numerical models

Notes:

(1) This table is meant to show example components of a Tier 1, Tier 2 and Tier 3 LNAPL mobility evaluation. Not all mobility evaluations will require use of all components. Rather, the type and extent of mobility evaluation required will be based site-specific project needs and data gaps.

(2) This table was modified from Appendix C of ITRC (2009a).

5. References

API (American Petroleum Institute). 2000. *Non-aqueous phase liquid (NAPL) mobility limits in soil*. Soil & Groundwater Research Bulletin, No. 9, June 2000. Prepared by Edward J. Brost and George E. DeVaull, Equilon Enterprises LLC, Westholow Technology Center, Houston, Texas.

API (American Petroleum Institute). 2003. *Models for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids*. API Publication Number 4729, August 2003.

API (American Petroleum Institute). 2004. *API Interactive LNAPL Guide, Version 2.0*. American Petroleum Institute, Washington, District of Columbia, August 2004.

API (American Petroleum Institute). 2007. *LNAPL Distribution and Recovery Model, Volume 1: Distribution and Recovery of Petroleum Hydrocarbon Liquids in Porous Media*. API Publication Number 4760, January 2007.

ASTM (ASTM International). 2007. *E 2531-06: Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface*. ASTM Committee E50 on Environmental Assessment, Risk management and Corrective Action, ASTM International, West Conshohocken, PA, February 2007.

Beckett, G.D. 2005. *Pro Tools for LNAPL Decision Making*. A Workshop Presented by the American Petroleum Institute, August 17, 2005, Costa Mesa, California.

Brady, M.M. and L.A. Kunkel. 2005. *A screening method for determining free product mobility.* Presented at – 2005 Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Prevention, Assessment, and Remediation Conference, August 18-19, 2005, Costa Mesa, California.

Brooks, R.H. and A.T. Corey. 1964. *Hydraulic properties of porous media*, Hydrol. Pap. 3, Colo. State Univ., Fort Collins.

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

Charbeneau, R.J., Johns, R.T., Lake, L.W. and M.J. McAdams III. 1999. *Free-product recovery of petroleum hydrocarbon liquids*, American Petroleum Institute Publication Number 4682, Washington D.C., June 1999.

Huntley, D. and G.D. Beckett. 2001. *Evaluating hydrocarbon removal from source zones: tools to access concentration reduction*. Submitted for API Review.

Huntley, D. and G.D. Beckett. 2002. *Persistence of LNAPL Sources and Relation to Risk.* Department of Geological Sciences, San Diego State University, 2002.

ITRC (Interstate Technology & Regulatory Council). 2009a. *Evaluating LNAPL Remedial Technologies for Achieving Project Goals.* LNAPL-2. Washington, D.C.: Interstate Technology & Regulatory Council, LNAPLs Team. www.itrcweb.org.

ITRC (Interstate Technology & Regulatory Council). 2009b. *Evaluating Natural Source Zone Depletion at Sites with LNAPL.* LNAPL-1. Washington, D.C.: Interstate Technology & Regulatory Council, LNAPLs Team. www.itrcweb.org.

ITRC (Interstate Technology & Regulatory Council). 2009c. *Part 1, An improved understanding of LNAPL behavior in the subsurface - state of science vs. state of practice.* Internet-Based Training 1 (IBT-1), LNAPLs Team, www.clu-in.org/live/archive.

ITRC (Interstate Technology & Regulatory Council). 2009d. *Part 2, LNAPL characterization and recoverability – improved analysis - do you know where the LNAPL is and can you recover it.* Internet-Based Training 2 (IBT-2), LNAPLs Team, www.clu-in.org/live/archive.

ITRC (Interstate Technology & Regulatory Council). 2009e. *Part 3, Evaluating LNAPL remedial technologies for achieving project goals.* Internet-Based Training 3 (IBT-3), LNAPLs Team, www.clu-in.org/live/archive.

Johnson, J.A., and M. Ling. 2005. *Evaluating the reliability of LNAPL thickness measurements and the conditions that produce non-representative values*. Presented at - Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Prevention, Assessment, and Remediation Conference, August 18-19, 2005, Costa Mesa, California, pp. 44-56.

Johnston, C.D. and M. Adamski. 2005. *Relationship between initial and residual LNAPL saturation for different soil types*. Presented at - 2005 Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Prevention, Assessment, and Remediation Conference, August 18-19, 2005, Costa Mesa, California, pp. 29-42.

Mercer, J.W. and Cohen, R.M. 1990. *A review of immiscible fluids in the subsurface: properties, models, characterization and remediation.* J. Contaminant Hydrology, v. 6, pp. 107-163.

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

Oostrom, M., Hoftsee, C., and T.W. Weistsma. 2006. *Behavior of Viscous LNAPL Under Variable Water Table Conditions*. Soil & Sediment Contamination, Volume 15, pp. 543-564.

Potter, T.L. and K.E. Simmons. 1998. *Total Petroleum Hydrocarbon Criteria Working Group Series Volume 2: Composition of Petroleum Mixtures*. Amherst Scientific Publishers, Amherst, Massachusetts.

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

Science Advisory Board for Contaminated Sites in British Columbia. 2006. *Report on: approaches and methods for evaluation of light non-aqueous phase liquid mobility – hydrogeological assessment tools project.* Prepared by Golder Associates Ltd. and Submitted to British Columbia Ministry of Environment, February 2006.

Texas Commission on Environmental Quality (TCEQ). 2008. *TCEQ Regulatory Guidance, Risk-Based NAPL Management*. Remediation Division, RG-366/TRRP-32, February 2008.

Thomas, D.H., and J.J. Delfino. 1991. *A gas chromatographic/chemical indicator approach to assessing ground water contamination by petroleum products*. Ground Water Monitoring Review 11, no. 4: 90-100.

U.S. Environmental Protection Agency. 2005a. *A decision-making framework for cleanup of sites impacted with light non-aqueous phase liquids (LNAPL)*. Remediation Technologies Development Forum, NAPL Cleanup Alliance, Office of Solid Waste and Emergency Response, EPA 542-R-04-011, March 2005. www.clu-in.org.

U.S. Environmental Protection Agency. 2005b. *The basics, understanding the behavior of light non-aqueous phase liquids (LNAPLs) in the subsurface*. Remediation Technologies Development Forum, U. S. Environmental Protection Agency Technology Innovation and Field Services Division. February 2005 course notes, 111 p.

van Genuchten, M.T. 1980. *A closed form equation for predicting the hydraulic conductivity of unsaturated soil*, Soil Sci. Soc. Am. J., vol. 44, pp. 892-898.

WDOE and WDNR. 2008. *Assessment Guidance for Sites with Residual Weathered Product*. Wisconsin Department of Commerce and Wisconsin Department of Natural Resources, PUB-RR-787, February 2008.

Appendix D

LNAPL Behavior Equations and Models

Appendix D
LNAPL Behavior Equations and Models

Table of Contents

Figure Index

List of Symbols/Acronyms

α	van Genuchten α
α_{ow}	Capillary Pressure Head Parameter – Oil/Water (ft^{-1})
α_{ao}	Capillary Pressure Head parameter – Air/Oil (ft^{-1})
b_o	LNAPL Thickness (ft)
ϕ	Total Soil Porosity
ϕ_{eff}	Effective Porosity (Effective Free Oil Porosity)
g	Gravitational Constant (kg m/s^2)
h	Water Pressure Head in van Genuchten Drainage Model
h_c	Critical height/head of LNAPL
i	Reference Point Along Vertical LNAPL Saturation Profile
i_w	Water Hydraulic Gradient (assumed equal to oil gradient)
k	Soil Permeability (cm^2)
k_{ro}	LNAPL Relative Permeability
k_{ro-b}	LNAPL Relative Permeability from Burdine Equation
k_{ro-m}	LNAPL Relative Permeability from Mualem Equation
K_w	Hydraulic Conductivity Water (cm/s or ft/day)
K_o	LNAPL Conductivity (cm/s)
λ	Model Fitting Parameter
μ_o	LNAPL Viscosity (cp)
μ_w	Water Viscosity (cp)
M	Model Fitting Parameter
M_o	LNAPL Mobility (cm/s or ft/day)
n	Number of Equally Spaced Points on the Z-Axis
N	van Genuchten N
ρ_o	LNAPL Density (g/cm^3)
ρ_w	Water Density (g/cm^3)

P_C	Capillary Pressure
P_D	Pore Displacement Entry Pressure
P_o	Oil/LNAPL Pressure
P_R	Resistive Soil Pressure/Force
P_w	Water Pressure
q_o	LNAPL Specific Discharge (cm/s or ft/day)
r	Radius of Curvature at Fluid Interface
σ_{aw}	Air-Water Interfacial Tension (dynes/cm)
σ_{ow}	Oil-Water Interfacial Tension (dynes/cm)
σ_{ao}	Air-Oil Interfacial Tension (dynes/cm)
S_o	LNAPL Saturation
S_{or}	LNAPL Residual Saturation
S_{ors}	LNAPL Residual Saturation – Saturated Zone
S_{orv}	LNAPL Residual Saturation – Vadose Zone
S_t	Total (LNAPL plus Water) Saturation
S_w	Water Saturation
S_{wr}	Water Residual (Irreducible) Saturation
θ	Contact Angle between Fluid Interface and Soil Particle
T_o	LNAPL Transmissivity (cm^2/s or ft^2/day)
V_o	LNAPL Specific Volume (ft^3/ft^2)
υ_o	LNAPL Velocity (cm/s or ft/day)
z	Reference Elevation on the Vertical LNAPL Saturation Profile (ft)
z_{ao}	Air-Oil Elevation (ft)
z_{aw}	Air-Water Elevation (ft)
z_{ow}	Oil-Water Elevation (ft)
$z_{\max}$	Maximum Elevation of LNAPL (above residual saturation) in Smear Zone (ft)

1. Introduction to LNAPL Behavior Equations / Theory

This Appendix presents some of the basic LNAPL concepts and mathematical expressions or equations that describe the occurrence, behavior and migration of LNAPL in the subsurface. Specifically, this section addresses LNAPL behavior at the water table and includes the vertical impacted soil zone typically referred to as the smear zone. The smear zone is where potentially mobile LNAPL may reside at sites where the source(s) of the LNAPL impacts have ceased for some time (i.e., no ongoing sources). The behavior of LNAPL in the vadose or unsaturated zone (above the smear zone) is not addressed here.

The analytical equations/models presented herein are based on a number of assumptions including: the fluids (LNAPL and water) are in vertical equilibrium and the soil conditions are homogeneous. These conditions are required for in-well or apparent LNAPL thicknesses to be considered representative of the spatial (vertical) distribution of LNAPL in the formation. Situations where these conditions are not met include sites with:

- Water table fluctuations
- Confined conditions
- Sump wells in a perched setting
- On-going LNAPL release(s)
- Heterogeneous conditions

Although in a real world setting, there are often times when vertical equilibrium of liquids and homogeneous soil conditions do not exist; LNAPL analytical equations and models may still be used to generate qualitative information about LNAPL behavior. The degree to which model results are quantitatively valid and defensible will be based on actual site conditions and the accuracy of the LNAPL Conceptual Site Model (LCSM). Where possible, the use of site-specific model inputs (as determined from field and/or laboratory testing) is preferred over the use of default literature look-up values.

2. Pressure Conditions Necessary for LNAPL Movement

LNAPL requires pressure to move in the subsurface at the water table. More specifically, the capillary pressure must be sufficient to overcome the soil resistive forces to enable the displacement of groundwater from unimpacted saturated soil pores. The following sections provide a discussion regarding capillary pressure, soil resistive forces and pore entry displacement pressure. A figure illustrating the idealized relationship between LNAPL in a well versus LNAPL in a formation, based on the principles of capillary pressure and LNAPL saturation, is provided in Figure 1.

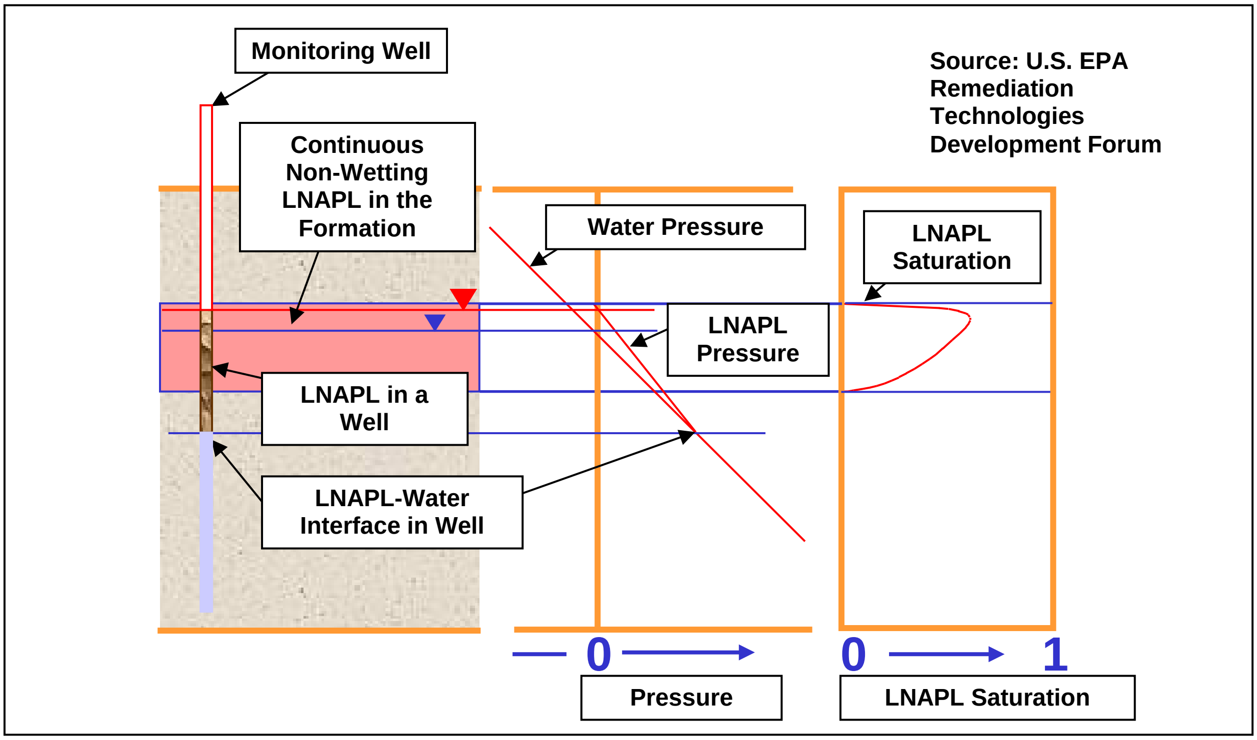


Figure 1: Idealized Relationship Between In-Well LNAPL Thickness and Formation Thickness

2.1 Capillary Pressure

Capillary pressure, which is sometimes referred to as “excess pressure”, is defined as the difference between the fluid pressure in the non-wetting phase (typically LNAPL) and the pressure in the wetting phase (typically water) at a given reference point. The larger the capillary pressure (i.e., pressure difference between the two fluids), the greater the LNAPL saturation, and the greater the potential for LNAPL mobility. For LNAPL movement or migration to occur, LNAPL capillary pressure must exceed the resistive forces in the soil formation.

Any object submerged in a fluid is subject to a fluid pressure based on the depth of submersion beneath the top of fluid (or air/fluid interface). The greater the depth of submersion, the greater the pressure at that point. The fluid pressure is a function of the density of the fluid, the depth of submersion, and the gravitational constant. In a subsurface environment, LNAPL and water exhibit pressures depending on the depth beneath the fluid or phreatic surface. As shown in the middle panel in Figure 1, LNAPL pressure is zero at the top surface of the LNAPL, and increases in a linear manner with increasing depth below the surface. Similarly, water pressure is zero at the top surface of the water, and increase linearly with increasing depth. The prime difference, however, is that the tops of the fluid (LNAPL and water) surfaces are at different elevations, based on the density differences between the fluids. Figure 2 provides the pressure graph from Figure 1 along with the elevation or depth scale for the fluids, with the zero reference being at different locations for the LNAPL and water.

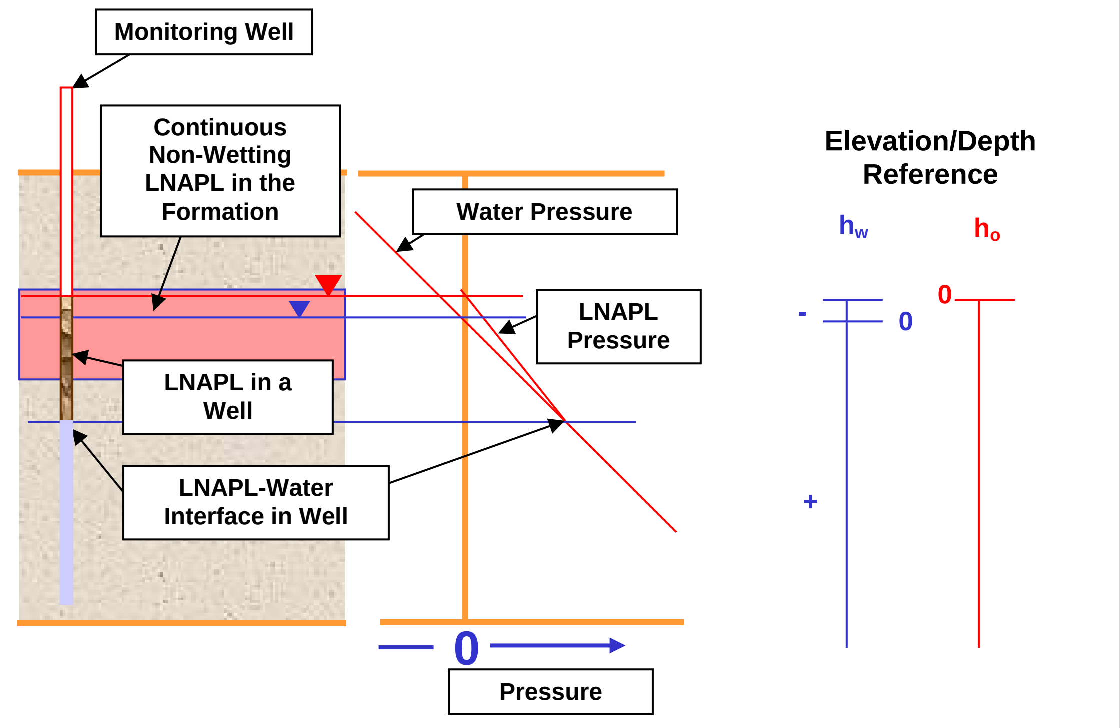


Figure 2: Pressure Graph with Reference Elevations/Depths for LNAPL and Water

As shown above in Figure 2, the LNAPL and water pressures are equal at the elevation of the LNAPL/water interface in the adjacent monitoring well. Graphically, the capillary pressure represents the difference between the LNAPL and water pressure lines, for a given reference point or elevation/height.

As shown on the left hand panel in Figure 2, the LNAPL within the well extends below the LNAPL in the formation. This occurs because the well behaves as a large macropore, and the LNAPL at the bottom of the well lacks the necessary capillary pressure at this elevation to displace water in the adjacent formation. The degree to which the LNAPL in a well extends below the LNAPL in the formation is more pronounced in fine textured soils (silts and clays) (USEPA, 2005).

It is important to note that the water pressure line extends up into the capillary fringe, where the elevation reference becomes negative, resulting in a negative pressure or vacuum. This vacuum represents the negative pressure experienced in the water phase within the capillary fringe. Hence, the zero pressure at the surface of the LNAPL minus the negative pressure of the water in the capillary fringe, still results in a positive capillary pressure.

The capillary pressure is represented mathematically by the following equation:

$$P_C = P_o - P_w \qquad (2.1)$$

Where:

P_C = Capillary pressure at reference point below fluid surface

P_o = Oil/LNAPL pressure at reference point below LNAPL surface

P_w = Water pressure at reference point below (or above) water surface

The pressure of the fluid in each fluid phase is a function of the following:

$$P = \rho gh \quad (2.2)$$

Where:

ρ = Density of the fluid

g = Gravitational constant

h = Height or depth of fluid with respect to reference point

Hence, capillary pressure can be expressed as:

$$P_C = (\rho_o gh) - (\rho_w gh) \quad (2.3)$$

$$P_C = (\rho_o - \rho_w) gh \quad (2.4)$$

2.2 Soil Resistive Forces

For LNAPL to enter a water-saturated porous media and displace water from the pore space, the LNAPL (and more specifically, the capillary pressure) must exert sufficient pressure to overcome the resistive forces of the soil. The resistive forces of the soil are based on the soil pore size, the interfacial tension between the LNAPL and water at the fluid interface, the curvature formed between the fluids at the fluid interface, and the contact angle between the fluid interface and soil particles. When two fluids are in contact with one another in small confines, the fluid interface forms a curvature based on the properties of the fluids. The smaller the confines, the greater the curvature of the interface. Hence, on a microscopic pore scale level, the smaller the effective soil pore size, the greater the curvature of the fluid interface, and the smaller the radius of curvature. The pressure conditions created when two fluids are present in the soil pore space can be represented by the equation (API, 2003):

$$P_R = \frac{2\sigma_{ow}}{r} \quad (2.5)$$

Where:

P_R = Resistive pressure

σ_{ow} = Oil/LNAPL-water interfacial tension

r = Effective soil pore size/radius of curvature of interface between fluids

This resistive pressure effectively works to prevent or resist the movement of one fluid in the presence of the other. As inferred from Equation 2.5, soils with very small pore sizes (i.e., silts and clays) will have fluid interfaces with very small radii of curvature resulting in very large resistive pressures working to prevent LNAPL movement. Conversely, soils with larger pore sizes will have larger radii of curvature resulting in lower resistive pressures working to prevent LNAPL movement.

At the source of a release, where LNAPL has migrated down to and penetrated vertically into the water table, the downward movement of LNAPL in the saturated zone results in the lateral displacement of water. The horizontal component of the displacement is based on the contact angle between the fluid interface and the soil particles. Figure 3 provides a conceptual drawing illustrating the primary forces and contact angles involved during the displacement of water by LNAPL.

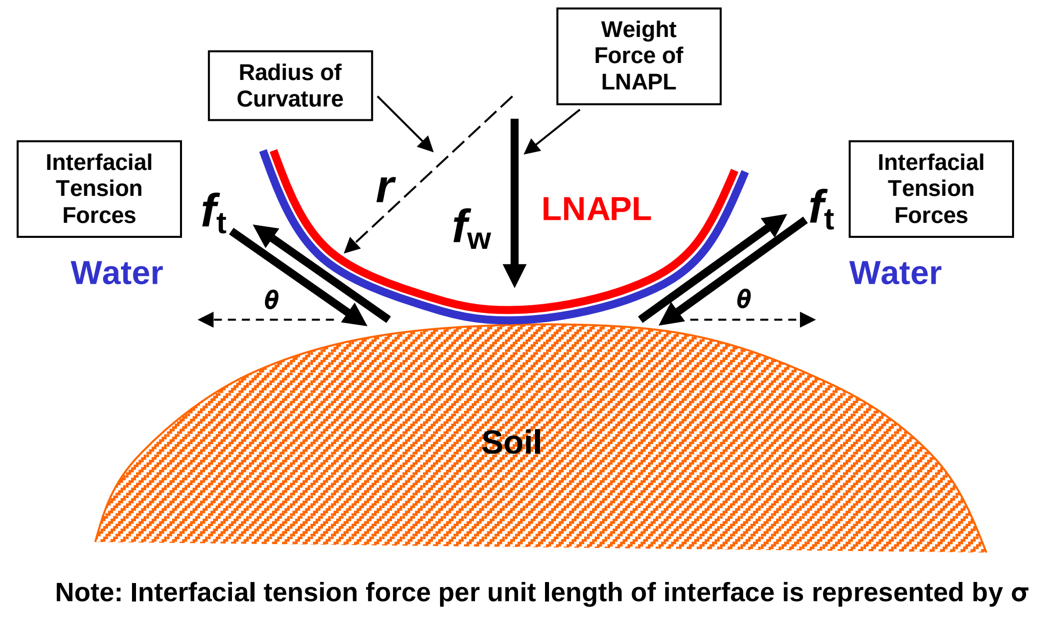


Figure 3: Soil Resistive Forces for LNAPL Displacement of Pore Water

From Figure 3, the soil resistive force or pressure working to prevent LNAPL from displacing water can be expressed as:

$$P_R = \frac{2\sigma \cos\theta}{r} \qquad (2.6)$$

Where:

θ = Contact angle between the two fluids (based on degree of fluid wettability)

$\cos\theta$ = Perpendicular or horizontal component of the resistive force/pressure

The doubling of the forces in the numerator is to account for the mirror image of interfacial tension forces shown in Figure 3 on both the right and left-hand sides.

The following expressions may therefore be used to summarize when LNAPL movement into a water-saturated porous medium may or may not occur:

- If $P_C > P_R$, LNAPL will displace water from soil pore
- If $P_C \leq P_R$, LNAPL will not displace water from soil pore

2.3 Pore Entry Displacement Pressure

The pore entry displacement pressure represents the specific threshold pressure necessary for one fluid to enter into a porous medium occupied by another fluid, thereby displacing the initial fluid (Mercer and Cohen, 1990). Pore entry displacement pressures may account for air displacing groundwater, LNAPL displacing groundwater, air displacing LNAPL, etc. In a water-saturated soil, the capillary pressure must equal or exceed the pore entry displacement pressure, for the LNAPL to move into the pore and displace water.

The specific capillary pressure threshold necessary for LNAPL to displace water in a water-saturated porous medium can be established by setting the capillary pressure equal to the soil resistive forces equation above as follows (API, 2007, Adamson, 1982):

$$P_C = \frac{2\sigma_{ow}\cos\theta}{r} \qquad (2.7)$$

Using the conceptual drawings in Figures 1 and 2, the capillary pressure threshold necessary to displace pore water is identified in Figure 4.

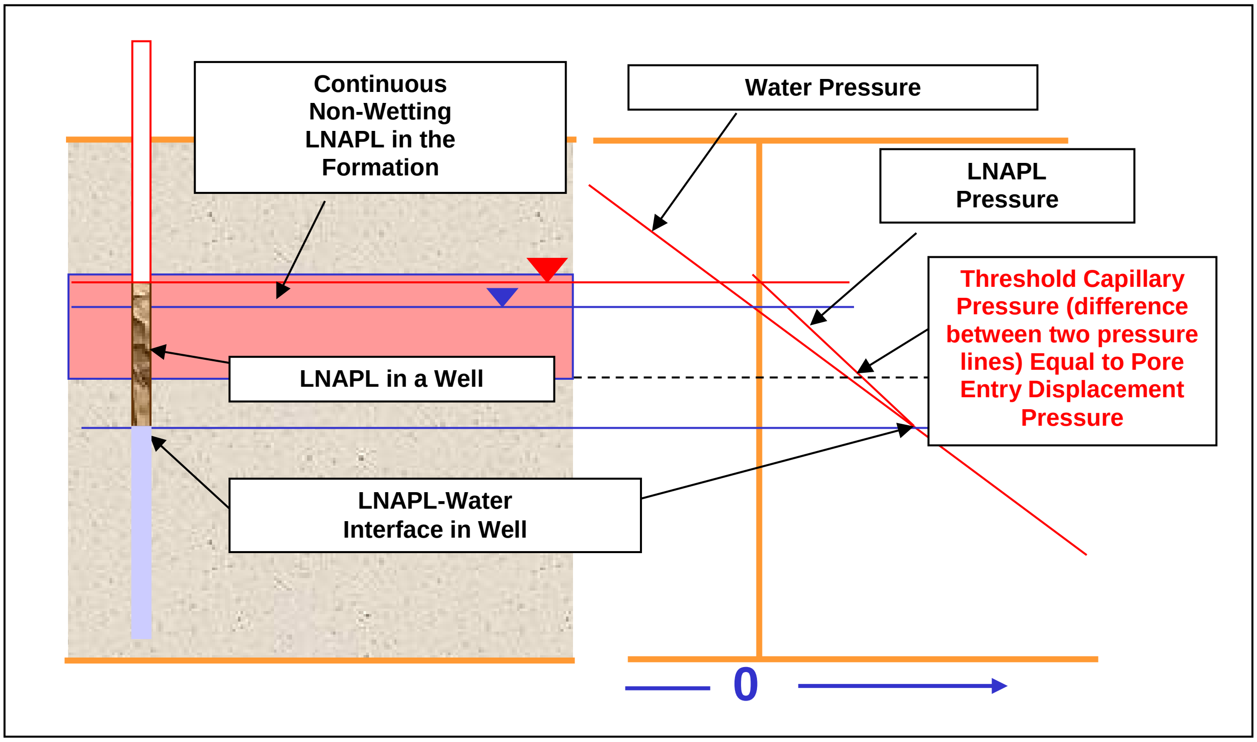


Figure 4: Threshold Capillary Pressure Equal to Pore Entry Displacement Pressure

Although the situation illustrated in Figure 3 was for LNAPL migrating vertically into the water table, Equations 2.6 and 2.7 may also be used to assess the potential for horizontal LNAPL migration in the saturated zone at the periphery or leading edge of the LNAPL body. Further, Equations 2.6 and 2.7 may be used to determine the critical height or head of LNAPL necessary to exceed the pore entry displacement pressure and result in the displacement of groundwater.

Combining Equations 2.4 and 2.7 yields the following expression:

$$(\rho_o - \rho_w)gh = \frac{2\sigma_{ow}\cos\theta}{r} \qquad (2.8)$$

Equation 2.8 can be rearranged to solve for the critical height (or head) of LNAPL necessary for displacement of water to occur, as follows:

$$h_c = \frac{2\sigma_{ow}\cos\theta}{rg\left|(\rho_o - \rho_w)\right|} \qquad (2.9)$$

Where:

h_c = Critical height of LNAPL necessary to generate a capillary pressure equal to the pore entry displacement pressure, whereby LNAPL will displace water

It is important to note that the expressions used to describe capillary pressure, soil resistive forces, and the pore entry displacement pressure identified above are simplified analytical expressions used to describe LNAPL movement in an idealized situation (i.e., homogeneous soil with fluids at vertical equilibrium). This expression of critical head will often be compared to in-well LNAPL thickness data to assess the potential for LNAPL mobility. However, fluctuations in the water table elevation and heterogeneous soil conditions have a significant effect on in-well LNAPL thickness. Therefore, caution must be used when attempting to use the expressions above in relation to in-well LNAPL thickness to assess the potential for LNAPL movement or migration.

3. Soil Drainage Characteristics

Two primary models are used to represent soil drainage characteristics with respect to LNAPL mobility. The first is the Brooks and Corey (1964) soil characteristic model which assumes that some minimum amount of threshold pressure buildup is necessary to initiate the drainage of water from a saturated soil. The threshold pressure is the pore entry displacement pressure (Mercer and Cohen, 1990) discussed in Section 2.0 as it applies to an air/water setting. The second is the van Genuchten model, which assumes that drainage or fluid displacement will occur (albeit at a minor amount) as soon as a pressure is applied by one fluid to the other. The difference between the models is shown conceptually in Figure 5.

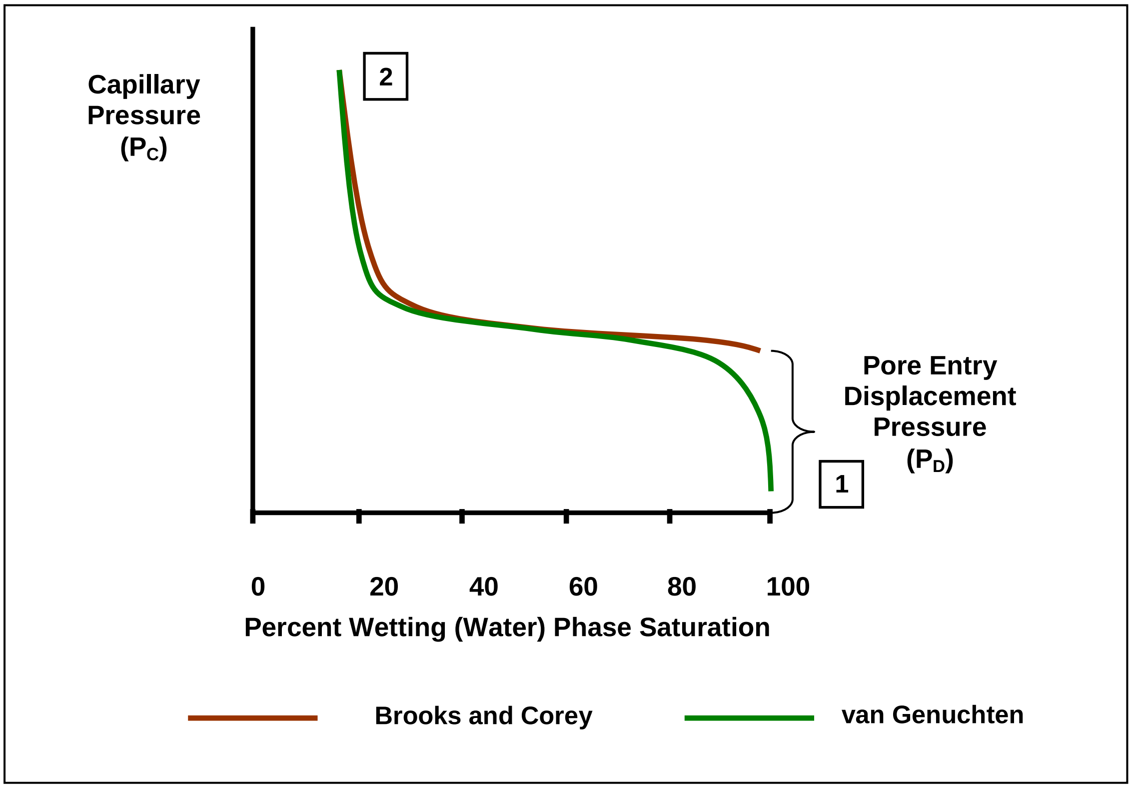


Figure 5: Soil Drainage Characteristic Models

According to the van Genuchten (1980) model, the water saturation S_w is related to the suction pressure head *h* by the following expression (API, 2003):

$$S_w(h) = S_{wr} + (1 - S_{wr})\left[\frac{1}{1+(\alpha h)^N}\right]^M \qquad (3.1)$$

Where:

S_w = Water saturation (as percent of soil pore space)

S_{wr} = Residual (or irreducible) water saturation

h = Water pressure head

α, M, N = Model or curve fitting parameters (refer to Section 4.0)

The Brooks and Corey (1964) model may be expressed as (API, 2007):

$$S_e = \left(\frac{P_D}{P_C}\right)^\lambda \quad ; \quad P_C > P_D \qquad (3.2)$$

$$S_e = 1 \quad ; \quad P_C < P_D \qquad (3.3)$$

Where:

S_e = Wetting (water) phase saturation for capillary pressures greater than displacement pressure

P_D = Displacement pressure head

P_C = Capillary pressure head

λ = Brooks and Corey pore size distribution parameter

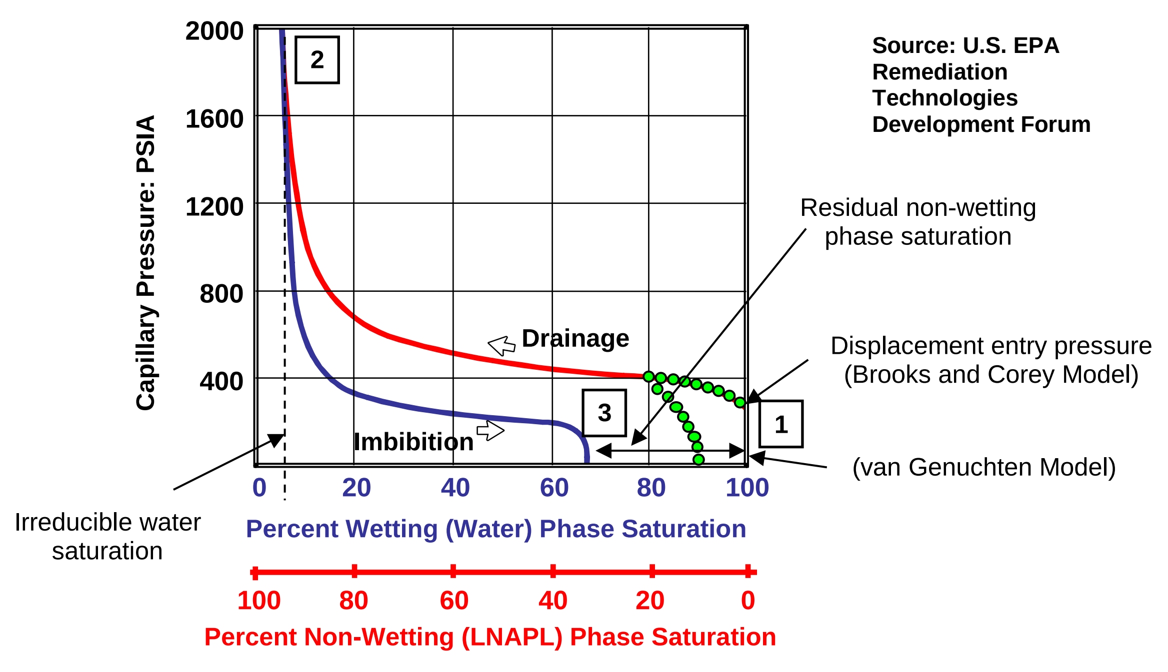
Equation 3.2 can be further expressed as (API, 2001):

$$S_e = \left[\frac{S_w - S_{wr}}{1 - S_{wr}} \right] \tag{3.4}$$

The soil drainage characteristic curves in Figure 5 are based on air displacing water, and are generated in an air-water drainage capillary pressure test. Capillary pressure tests are typically conducted in a laboratory with the use of a centrifuge. For an air-water capillary pressure test, the test commences with a fully water saturated soil core (see point “1 “in Figure 5). The core is placed in the centrifuge and spun at increasing speeds to induce increasing pressure conditions. As the core is spun, the water drains out of the core, under the influence of the centrifugal force/pressure, and is replaced with air. The mass of water released is recorded for each distinct pressure condition (to be added to the final water saturation at the conclusion of the test to determine water saturations at each point in the test). The test concludes when no more water drains from the core, despite increases in pressure. The remaining water at this point (see point “2” in Figure 5) is referred to as the irreducible water saturation or the residual water saturation.

As shown in Figure 5, the primary difference between the Brooks and Corey model versus the van Genuchten model occurs only at very high water saturations, with the Brooks and Corey drainage of water not commencing until the pore entry displacement pressure is obtained.

Capillary pressure tests may also be conducted for LNAPL and water as illustrated in Figure 6.



Source: U.S. EPA Remediation Technologies Development Forum

Figure 6: Capillary Pressure Test for LNAPL-Water

As shown in Figure 6, the LNAPL-water capillary pressure test consists of three parts. The test commences with a fully water saturated soil core (again, placed in a centrifuge – see point “1”). As the core is spun, water drains from the core and is replaced by LNAPL (hence, the water and LNAPL saturation scales on the x-axis). The LNAPL displacing water is represented by the red line in Figure 6. The term “Drainage” refers to the phase of the test when the wetting fluid (water) is being drained from the core during the initial spin phase. Spinning continues until no further water drainage occurs with increased pressure (see point “2”). At this point, spinning ceases and water is reintroduced as the displacing fluid. The second spin phase results in LNAPL being drained from the core and being replaced by water, and is represented by the blue line in Figure 6. This phase of the test is referred to as “Imbibition”, which refers to the wetting fluid (water) being imbibed or reintroduced into the core. Spinning continues until no further LNAPL drainage occurs with increasing pressure. The LNAPL saturation at this point is referred to as the LNAPL residual saturation (Note: The capillary pressure test is only one method for determining the LNAPL residual saturation).

As shown in Figure 6, the Drainage curves (red line) for both the Brooks and Corey and van Genuchten model are essentially the same, except at very low LNAPL saturations. In practice, the differences in the estimates provided by the different methods will most often be negligible.

The Brooks and Corey and van Genuchten equations shown above may be used for other fluid combinations if appropriate scaling relationships for density and interfacial tensions are introduced (API, 2001, 2003, 2007). These equations, as well as the concepts discussed in Section 2.0, are used in Section 4.0 to generate expressions for LNAPL saturation (refer to right-hand panel in Figure 1) and relative permeability, which in turn are used to determine LNAPL conductivity, mobility and velocity. For additional information pertaining to capillary pressure scaling relationships, refer to API 2001, API 2003 and API 2007.

The API models provided in the LNAPL Interactive Guide (API, 2004) allow for the use of either the Brooks and Corey or van Genuchten models. However, the more recent API LDRM model (API, 2007) relies solely on the van Genuchten model. The van Genuchten model has found wide use because it provides a smooth function in predicting the vertical saturation distribution and may readily be fit to both laboratory and field data (API, 2007). However, the van Genuchten model is contrary to the fact that a positive capillary pressure is required for LNAPL to displace groundwater in previously unimpacted soil pores, which is accounted for in the Brooks and Corey model. Hence, the van Genuchten model is considered appropriate for LNAPL migration in LNAPL impacted areas, whereas the Brooks and Corey model is considered more appropriate for potential LNAPL migration into previously unimpacted soil areas (API, 2007).

4. LNAPL Mobility and Velocity Equations

4.1 LNAPL Mobility Equations

As described in the API Interactive LNAPL Guide (API, 2004), inherent oil mobility was defined by Parker (1996) and others as the ratio of free oil transmissivity to specific oil volume at a given location. These two parameters can be measured with core analyses or estimated through baildown test analyses. The oil transmissivity is the product of the oil conductivity and the thickness of the free oil zone. The specific volume is the product of oil saturation, total porosity, and the thickness of the free oil zone. The inherent oil mobility is expressed as:

$$M_o = \frac{T_o}{V_o} \qquad (4.1)$$

Where:

M_o = inherent oil mobility (ft/day)

V_o = specific oil volume per unit area (ft^3/ft^2)

T_o = oil transmissivity (ft^2/day)

The specific oil volume is a function of the oil saturation along the vertical profile and is expressed as:

$$V_o = \int_{z_1}^{z_2} \phi S_o \, dz \qquad (4.2)$$

Where:

ϕ = total porosity (dimensionless)

S_o = oil saturation (dimensionless)

z = vertical thickness of oil impacts where z_1 is typically considered to be the oil-water interface elevation and z_2 is considered to be the maximum elevation of LNAPL above the air-oil interface (ft)

Oil saturation is a function of capillary pressure (the difference between the pressure in the non-wetting phase and the pressure in the wetting phase) and varies across the vertical impacted zone in a non-linear manner as shown in Figure 7.

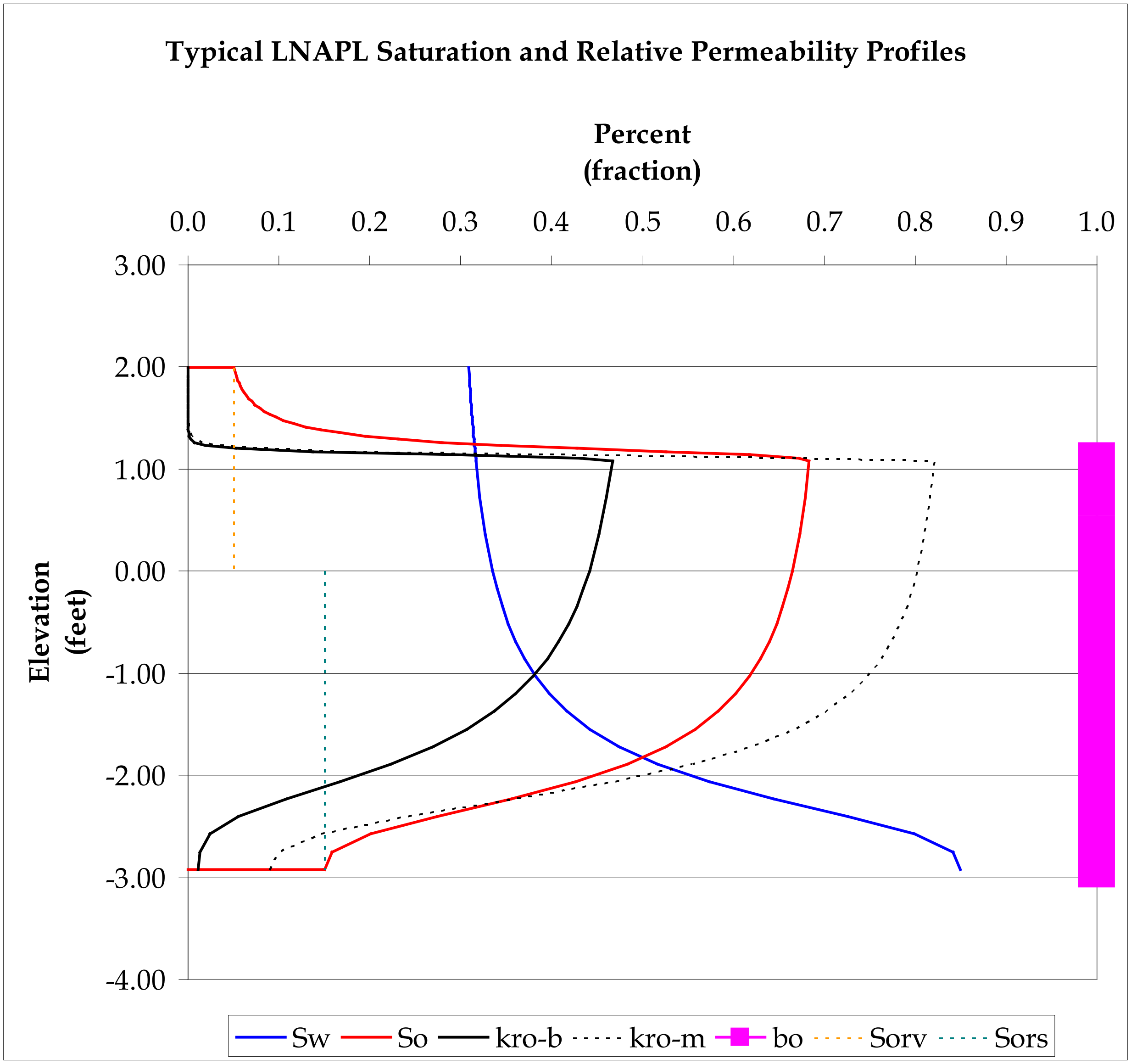


Figure 7: Idealized LNAPL Saturation and Relative Permeability Profiles

Sw = Water Saturation Profile

So = Oil/LNAPL Saturation Profile

kro-b = Oil/LNAPL Relative Permeability Profile using Burdine Calculation

kro-m = Oil/LNAPL Relative Permeability Profile using Mualem Calculation

bo = In-Well Oil/LNAPL Thickness

Sorv = Oil/LNAPL Residual Saturation in the Vadose Zone

Sors = Oil/LNAPL Residual Saturation in the Saturated Zone

Note: the “Elevation” axis is referred to as the z-axis, with the theoretical water table elevation set at 0.00 feet, and the following elevation references:

zmax/z2 = Maximum Oil/LNAPL Elevation in the Capillary Fringe

zow/z1 = Minimum Oil/LNAPL Elevation, equivalent to the Oil/Water Elevation in Well

zao = Maximum Oil/LNAPL Elevation in the Well, or the Air/Oil Interface Elevation

Hence, Equation 4.2 cannot be evaluated analytically. However, a simplified expression of the specific oil volume averaged across the vertical LNAPL saturation profile can be expressed as (API, 2004):

$$\overline{V_o} = b_o \phi \overline{S_o} \tag{4.3}$$

Where:

$\overline{V_o}$ = mean oil specific volume averaged across the saturation profile (ft^3/ft^2)

b_o = vertical extent of LNAPL impacts (ft)

$\overline{S_o}$ = mean oil saturation averaged across the saturation profile (dimensionless)

The oil transmissivity is expressed as:

$$T_o = \frac{\rho_o}{\rho_w} \frac{\mu_w}{\mu_o} \int_{z_1}^{z_2} k_{ro} K_w dz \tag{4.4}$$

Where:

ρ_o = oil density (g/cm^3)

ρ_w = water density (g/cm^3)

μ_o = oil viscosity (cp)

μ_w = water viscosity (cp)

k_{ro} = oil relative permeability (dimensionless)

K_w = water hydraulic conductivity (cm/s)

Oil relative permeability is a function of oil saturation and varies across the vertical impacted zone in a non-linear manner as shown in Figure 7. Hence, Equation 4.4 cannot be evaluated analytically. However, a simplified expression of the free oil transmissivity averaged across the vertical LNAPL saturation profile can be expressed as (API, 2004):

$$\overline{T_o} = b_o \overline{K_o} \tag{4.5}$$

Where:

$\overline{T_o}$ = mean oil transmissivity averaged across the saturation profile (ft^2/day)

$\overline{K_o}$ = mean oil conductivity averaged across the saturation profile (ft/day)

Substituting Equations 4.3 and 4.5 into Equation 4.1 results in a simplified expression to determine inherent mobility at any location within an LNAPL body:

$$\overline{M_o} = \frac{b_o \overline{K_o}}{b_o \phi \overline{S_o}} = \frac{\overline{K_o}}{\phi \overline{S_o}} \qquad (4.6)$$

Where:

$\overline{M_o}$ = mean inherent oil mobility (ft/day)

Therefore, the mean inherent oil mobility is equivalent to the ratio of the average oil conductivity to the effective free oil porosity (API, 2004).

It is important to recognize that the inherent LNAPL mobility only defines the potential for LNAPL movement (API, 2004). Although described in terms of "length per time" (feet per day, centimeters per second), it does not explicitly define LNAPL migration. <u>To determine the movement of a LNAPL requires defining the oil gradient in addition to inherent mobility, both of which are needed to evaluate LNAPL body stability</u>.

Equation 4.6 is expressed as a function of "mean" or "average" saturation and oil conductivity to yield a mean mobility value. A mean value is typically used for mobility calculations because LNAPL saturation, conductivity and relative permeability vary across the vertical LNAPL impacted zone both above and below the water table. The use of mean or average values for LNAPL saturation, relative permeability and conductivity is deemed to represent the inherent mobility of LNAPL on a macro-scale or plume-scale.

The mean oil conductivity is expressed as:

$$\overline{K_o} = \frac{\rho_o}{\mu_o} \overline{k_{ro}} k g \qquad (4.7)$$

Where:

$\overline{K_o}$ = mean oil conductivity (ft/day)

$\overline{k_{ro}}$ = mean oil relative permeability (dimensionless)

k = soil permeability (ft^2)

g = gravitational constant (ft/day^2)

The permeability of the soil is expressed as:

$$k = \frac{K_w \mu_w}{\rho_w g} \qquad (4.8)$$

Consequently, Equation 4.7 can be re-written as:

$$\overline{K_o} = \overline{k_{ro}} K_w \frac{\rho_o \mu_w}{\rho_w \mu_o} \qquad (4.9)$$

The density and viscosity values for water are close to one, and therefore may be eliminated from Equation 4.9.

The relative permeability of LNAPL represents the ability of the LNAPL to flow in the presence of water. Assuming that the LNAPL residual saturation in both the vadose zone and saturated zone are zero, LNAPL relatively permeability can be expressed as a function of LNAPL saturation and water saturation based on the following three phase integration of the Burdine (1953) equations and Brooks and Corey (1964) soil characteristic model (API, 2003):

$$k_{ro}(S_w, S_o) = S_o^2 \left[\left(\frac{S_t - S_{wr}}{1 - S_{wr}} \right)^{\frac{\lambda+2}{\lambda}} - \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{\frac{\lambda+2}{\lambda}} \right] \qquad (4.10)$$

Where:

S_w = water saturation (dimensionless)

S_o = oil saturation (dimensionless)

S_t = total saturation ($S_w + S_o$)

λ = pore size distribution index (dimensionless)

S_{wr} = water residual (or irreducible) saturation (dimensionless)

The pore distribution size index is expressed as (API, 2003):

$$\lambda = \frac{M}{1-M}(1 - 0.5^{1/M}) \qquad (4.11)$$

Where:

M = model fitting parameter (dimensionless)

M is determined from the expression (API, 2003, 2007):

$$M = 1 - \frac{2}{N} \quad ; \quad N > 2 \qquad \text{Burdine} \qquad (4.12)$$

$$M = 1 - \frac{1}{N} \quad ; \quad N > 1 \qquad \text{Mualem (see below)} \qquad (4.12)$$

Where:

N = van Genuchten model fitting parameter (dimensionless)

Alternatively, LNAPL relative permeability can be expressed as a function of LNAPL saturation and water saturation based on the following three phase integration of the Mualem (1976) equation with van Genuchten's soil characteristics function (Parker et al., 1987; API, 2003):

$$k_{ro}(S_w, S_o) = S_o^{1/2} \left\{ \left[1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{1/M} \right]^M - \left[1 - \left(\frac{S_t - S_{wr}}{1 - S_{wr}} \right)^{1/M} \right]^M \right\}^2 \qquad (4.13)$$

Equations 4.10 and 4.13 predict different distributions of LNAPL relative permeability for the same set of fluid saturation values, with Equation 4.10 generally predicting smaller values for LNAPL relative permeability. Generally speaking, the Mualem equation (Equation 4.13) is believed to better predict LNAPL relative permeability in fine-grained soils (e.g., clays), whereas the Burdine equation (Equation 4.10) is believed to better predict LNAPL relative permeability in sands (U.S. EPA, 2005).

The mean (or effective) relative permeability of the LNAPL may be calculated from:

$$\overline{k_{ro}} = \frac{1}{b_o}\int_{z_1}^{z_2} k_{ro}\,dz \qquad (4.14)$$

Equation 4.14 cannot be evaluated analytically. However, the mean oil relative permeability may be approximated from the relative oil permeability profile (graph) by:

$$\overline{k_{ro}} = \frac{1}{n}\sum_{i=1}^{n} k_{roi} \qquad (4.15)$$

Where:

n = number of equally spaced points between z_1 and z_2 (on z-axis) where the oil relative permeability is read off the relative permeability graph

k_{roi} = LNAPL relative permeability value (dimensionless) at point '*i*' on the LNAPL relative permeability profile

i = the specific point number on the relative permeability profile

Alternatively, the mean oil relative permeability may be approximated using a piecewise linear function (Note: some computer models including the API Interactive LNAPL Guide software calculate a mean oil relative permeability value).

As shown in Figure 7, LNAPL or oil saturation varies as a function of depth across the vertical LNAPL impacted zone. Assuming vertical equilibrium of the LNAPL and water, the water saturation across the LNAPL impacted zone may be expressed as (API, 2003):

$$S_w(z) = S_{wr} + (1 - S_{wr} - S_{ors})\left[\frac{1}{1 + (\alpha_{ow}(z - z_{ow}))^N}\right]^M \qquad (4.16)$$

Where:

S_{ors} = oil residual saturation in the saturated zone (dimensionless)

α_{ow} = capillary pressure head parameter between LNAPL and water (1/ft)

z_{ow} = elevation of the oil-water interface in a monitoring well (ft)

The capillary pressure head between LNAPL and water is scaled appropriately to reflect the densities and interfacial tensions of the two fluids and is expressed as (API, 2003):

$$\alpha_{ow} = \left(1 - \frac{\rho_0}{\rho_w}\right)\left(\frac{\sigma_{aw}}{\sigma_{ow}}\right)\alpha \qquad (4.17)$$

Where:

σ_{aw} = air-water interfacial tension (dynes/cm)

σ_{ow} = oil-water interfacial tension (dynes/cm)

α = van Genuchten model fitting parameter (dimensionless)

The total liquid saturation (LNAPL plus water) across the LNAPL impacted zone is expressed as (API, 2003):

$$S_t(z) = S_{wr} + S_{orv} + (1 - S_{wr} - S_{orv})\left[\frac{1}{1 + (\alpha_{ao}(z - z_{ao}))^N}\right]^M \qquad (4.18)$$

Where:

S_{orv} = oil residual saturation in the vadose zone (dimensionless)

α_{ao} = capillary pressure head parameter between air and LNAPL (1/ft)

z_{ao} = elevation of the air-oil interface in a monitoring well (ft)

The capillary pressure head between air and LNAPL is scaled appropriately to reflect the densities and interfacial tensions of the two fluids and is expressed as (API, 2003):

$$\alpha_{ao} = \frac{\rho_o}{\rho_w}\left(\frac{\sigma_{aw}}{\sigma_{ao}}\right)\alpha \qquad (4.19)$$

Where:

σ_{ao} = air-LNAPL interfacial tension (dynes/cm)

Hence, the LNAPL saturation is obtained from the expression (API, 2003):

$$S_o(z) = S_t(z) - S_w(z) \qquad (4.20)$$

A typical LNAPL saturation profile (as determined by Equations 4.16 through 4.20), and relative permeability profile (as determined by Equations 4.10 through 4.13), corresponding to an in-well LNAPL thickness of 4.0 feet in a sandy soil, is illustrated in Figure 7.

The mean oil saturation may be calculated from:

$$\overline{S_o} = \frac{1}{b_o}\int_{z_1}^{z_2} S_o dz \qquad (4.21)$$

Equation 4.21 cannot be evaluated analytically. However, the mean oil saturation may be approximated from the oil saturation profile (graph) by:

$$\overline{S_o} = \frac{1}{n}\sum_{i=1}^{n} S_{oi} \qquad (4.22)$$

Where:

n = number of equally spaced points between z_1 and z_2 (on z-axis) where the oil saturation is read off the oil saturation graph

S_{oi} = LNAPL saturation value (dimensionless) at point '*i*' on the LNAPL saturation profile

i = the specific point number on the saturation profile

Alternatively, the mean oil saturation may be approximated using a piecewise linear function (Note: some computer models including the API Interactive LNAPL Guide software calculate a mean oil saturation value).

As shown in Figure 7, the LNAPL saturation varies across the LNAPL impacted zone. For the purposes of calculating LNAPL mobility, one can use "mean" or "average" values for relative permeability, conductivity and saturation to calculate (using Equation 4.6) the average LNAPL mobility across the vertical LNAPL impacted zone. Alternatively, if one determines the maximum LNAPL saturation value, either through calculation or a combination of field and laboratory techniques, then an approximate "worst-case" scenario for LNAPL mobility may be calculated using Equation 4.6.

4.2 LNAPL Specific Discharge and Velocity Equations

As previously mentioned, to determine the movement of a LNAPL requires defining the oil gradient in addition to inherent mobility, both of which are needed to evaluate LNAPL body stability. The LNAPL specific discharge is expressed as:

$$\overline{q_o} = \overline{K_o} i_o \qquad (4.23)$$

Where:

$\overline{q_o}$ = mean oil specific discharge (ft/year)

i_o = oil gradient (often assumed to be equal to the water table gradient)

The seepage velocity of the LNAPL is based on the specific discharge while correcting for the effective porosity of the formation. The seepage velocity is the potential average velocity of the LNAPL within connected or continuous pore throats and is expressed as:

$$v_o = \frac{\overline{q_o}}{\phi_{eff}} \tag{4.24}$$

Where:

v_o = oil seepage velocity (ft/year)

ϕ_{eff} = effective porosity (dimensionless)

The effective porosity of the oil or the free oil porosity is expressed as:

$$\phi_{eff} = \phi\overline{S_o} \tag{4.25}$$

Consequently, equation 4.24 may be re-written as:

$$v_o = \frac{\overline{K_o}}{\phi\overline{S_o}} \cdot i_o \tag{4.26}$$

Which represents the inherent oil mobility (M_o) from Equation 4.6, multiplied by the LNAPL gradient.

4.3 LNAPL Immobility

LNAPL bodies are spatially self-limiting unless continually supplied from an on-going release, thus distinguishing LNAPLs from dissolved and vapor plumes that may migrate significant distances (API, 2004). Typically, once the release of free product stops, LNAPL in the water table region will eventually cease to move as the resistive forces in the saturated soils balance the driving forces in the LNAPL pool (Huntley and Beckett, 2001). The endpoint of this movement is when the LNAPL reaches field residual saturation, a condition where effective hydraulic conductivity of the LNAPL is zero (Huntley and Beckett, 2001).

The LNAPL velocity from Equation 4.26 does not account for the resistive forces impeding LNAPL movement at the body periphery (i.e., it does not recognize the fact that the Darcy flow equations for multi-phase fluid flow do not apply outside of a stable LNAPL body). This may lead to misleading calculations of LNAPL velocities that are not evident in the field.

When evaluating LNAPL velocities within the confines of a stable LNAPL body and/or at the periphery of a migrating LNAPL body, it is recommended that a lower limit to velocity potential be used as a screening value. For instance, landfill liners may have allowable seepage potentials of 1 x 10^{-6} cm/s (ASTM, 2005). Hence, an LNAPL velocity of 1 x 10^{-6} cm/s or less can be used as a *de minimis* mobility level for LNAPL (ASTM, 2007).

5. LNAPL Specific Volume and Recoverable Volume

The specific volume of LNAPL defined by Equation 4.2 represents the area beneath (to the left of) the LNAPL saturation curve (see Figure 7) multiplied by the total soil porosity. As previously stated, Equation 4.2 cannot be evaluated analytically. However, Equation 4.3 provides an expression to solve for the mean oil specific volume (averaged across the saturation profile) as a function of mean LNAPL saturation, vertical extent of LNAPL impacts, and soil porosity. Mean LNAPL saturation can be determined graphically as defined by Equation 4.22. Once the mean LNAPL saturation is calculated, the LNAPL specific volume may be determined using Equation 4.3. Alternatively, the LNAPL specific volume may be determined graphically from the expression:

$$\overline{V_o} = \left(z_{\max} + \left|z_{ow}\right|\right)\frac{1}{n}\sum_{i=1}^{n}\phi S_{oi} \qquad (4.27)$$

Where:

V_o = LNAPL specific volume (ft^3/ft^2)

z_{max} = z_2, representing maximum elevation of LNAPL above the air-oil interface (ft)

z_{ow} = elevation of LNAPL/water interface (ft)

n = number of equally spaced points between z_1 and z_2 (on z-axis) where the oil saturation is read off the oil saturation graph

S_{oi} = LNAPL saturation value (dimensionless) at point '*i*' on the LNAPL saturation profile

i = the specific point number on the saturation profile

ϕ = total soil porosity

Equation 4.27 is approximately equal to the simplified expression for specific volume provided in Equation 4.3.

It is important to note that the LNAPL specific volume includes both the recoverable LNAPL (at saturations above residual saturation) and non-recoverable LNAPL (at saturations equal to or less than residual saturation). Recoverable LNAPL includes only LNAPL at saturations above residual saturation. On the LNAPL saturation profile (Figure 7), the recoverable LNAPL is represented by that portion of the area beneath (to the left of) the saturation curve and to the right of the vertical residual saturation lines (vadose and saturated). When residual saturations (vadose and saturated) are set equal to zero, the LNAPL specific volume is equal to the LNAPL recoverable volume.

LNAPL recoverable volume is equal to the LNAPL specific volume minus the volume of LNAPL at saturations less than residual. Hence, the LNAPL recoverable volume is defined by:

$$\overline{V_r} = \left(z_{\max} + \left|z_{ow}\right|\right)\frac{1}{n}\sum_{i=1}^{n}\phi S_{oi} - \left\{z_{\max}\left(S_{orv}\right)\phi + \left|z_{ow}\right|\left(S_{ors}\right)\phi\right\} \qquad (4.28)$$

or:

$$\overline{V_r} = \overline{V_o} - \left\{z_{\max}\left(S_{orv}\right)\phi + \left|z_{ow}\right|\left(S_{ors}\right)\phi\right\}$$

Where:

V_r = LNAPL recoverable volume (ft^3/ft^2)

If the approximate dimensions of an LNAPL body are known (length and width), then the approximate total volume of LNAPL may be determined by multiplying the area of the body by the LNAPL specific volume. Similarly, the recoverable volume of LNAPL may be determined by multiplying the area of the body by the LNAPL recoverable volume. However, it is important to note that the calculations of total and recoverable LNAPL volumes are based on vertical equilibrium assumptions for the fluids and homogeneous soils (refer to Section 1.0), and may not be indicative of actual site conditions. Hence, LNAPL specific volume and recoverable volume calculations should be viewed, at best, as rough order of magnitude approximations for qualitative screening purposes.

6. References

Adamson, A.W. 1982. Physical Chemistry of Surfaces. 4th Edition, Wiley-Interscience, New York.

American Petroleum Institute (API). July 2001. Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and recovery Models. American Petroleum Institute Publication Number 4711, prepared by Tom Sale, Ph.D., Research Scientist, Department of Chemical and Bioresource Engineering, Colorado State University.

American Petroleum Institute (API). August 2003. Models for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids. American Petroleum Institute Publication Number 4729, prepared by Randall J. Charbeneau, Ph.D., Environmental and Water Resources Engineering Program, College of Engineering, The University of Texas at Austin.

American Petroleum Institute (API). August, 2004. API Interactive LNAPL Guide, Version 2.0. American Petroleum Institute, Washington, District of Columbia.

American Petroleum Institute (API). January 2007. LNAPL Distribution and Recovery Model (LDRM). American Petroleum Institute Publication Number 4760, prepared by Randall J. Charbeneau, Ph.D., Environmental and Water Resources Engineering Program, College of Engineering, The University of Texas at Austin.

Brooks, R.H. and A.T. Corey. 1964. *Hydraulic properties of porous media*, Hydrol. Pap. 3, Colo. State Univ., Fort Collins.

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

Huntley, D. and G.D. Beckett. 2001. *Evaluating hydrocarbon removal from source zones: tools to access concentration reduction*. Submitted for API Review.

Mercer, J.W. and Cohen, R.M. 1990. *A review of immiscible fluids in the subsurface: properties, models, characterization and remediation.* J. Contaminant Hydrology, v. 6, pp. 107-163.

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

Parker, J.C., R.J. Lenhard, and T. Kuppusamy. 1987. *A Parametric Model of Constitutive Properties Governing Multiphase Flow in Porous Media*. Water Resources Research, vol. 23, no. 4, pp. 618-624.

U.S. Environmental Protection Agency. 2005. *The basics, understanding the behavior of light non-aqueous phase liquids (LNAPLs) in the subsurface*. Remediation Technologies Development Forum, U. S. Environmental Protection Agency Technology Innovation and Field Services Division. February 2005 course notes, 111 p.

van Genuchten, M.T. 1980. *A closed form equation for predicting the hydraulic conductivity of unsaturated soil*, Soil Sci. Soc. Am. J., vol. 44, pp. 892-898.

Appendix E
In-Well LNAPL Thickness Interpretation

1. In-Well LNAPL Thickness Interpretation

Many State agencies place a significant regulatory emphasis on the presence of LNAPL in a well, or the in-well LNAPL thicknesses observed at a given site. In-well LNAPL thicknesses, when used properly, provide valuable information relating to the spatial distribution of LNAPL in the subsurface. However, the relevance of in-well LNAPL thicknesses is often misunderstood. We (meaning both the regulators and the regulated environmental community in general) have often used in-well LNAPL thicknesses for far more than they “scientifically” represent. For example, we tend to solely use in-well LNAPL thicknesses to determine:

- Whether LNAPL exists in an area
- If there has been a new or subsequent LNAPL release(s)
- Whether the LNAPL is mobile
- Whether the LNAPL is recoverable (and the extent to which it can be recovered)
- How a LNAPL recovery program is progressing
- When the LNAPL remediation is completed

Unfortunately, these uses are not necessarily based on the scientific principles governing LNAPL behavior in the subsurface and often times lead to poor decision-making. Here are <u>some</u> common examples (with follow-up explanations) where in-well LNAPL thicknesses are inappropriately used or misunderstood:

- The absence of LNAPL in a monitoring well means that LNAPL is not present at that location

  Not necessarily true: the presence of LNAPL in a well in an LNAPL-affected area is highly dependent on the water table elevation, in relation to the LNAPL impacts, as well as many other factors relating to the characteristics of the LNAPL and soil. In an unconfined setting, in-well LNAPL thicknesses often vary inversely with water table elevation. Hence, an increase in water table elevation typically results in a decrease in in-well LNAPL thickness. Sometimes, during high water tables, the LNAPL becomes entirely submerged and no LNAPL remains in the well. However, as the water table elevation decreases over time, the LNAPL re-appears in the well. In a confined setting, in-well LNAPL thickness varies directly with potentiometric surface elevation. Hence, as the potentiometric surface elevation increases, in-well LNAPL thicknesses also tend to increase.

- LNAPL showing up in a well(s) where it hasn’t been detected in an extended period of time (months or years) suggest that the plume is migrating or that a new release has occurred.

  Not necessarily true: water table elevations/fluctuations may prevent LNAPL from appearing in a given well for months or years. The LNAPL has not necessarily moved away, it may simply be submerged and does not have the ability to displace water and flow into the well screen.

- In-well LNAPL thicknesses are a good indicator of remedial progress. Decreasing in-well LNAPL thicknesses over time (during active LNAPL recovery) indicate that the remedial system is working.

  Not necessarily true: a decrease in in-well LNAPL thickness <u>may or may not</u> be attributed to the LNAPL recovery system. As indicated above, in-well LNAPL thicknesses are highly influenced by water table elevation. High water tables may prevent LNAPL from showing up in wells for extended periods of time, making it appear as though the LNAPL has been recovered.

- The greater the in-well LNAPL thickness, the more LNAPL you should be able to recover from the well.

  Not necessarily true: the potential to recover LNAPL from a given well is a function of LNAPL transmissivity (which in turn is a function of the soil/LNAPL properties) rather than in-well thickness. Often times, the greatest in-well LNAPL thicknesses are found in fine textured soils (silts and clays) with sand seams, fractures, fissures, etc. that contain LNAPL under pressure. If the monitoring well (which is essentially a large macropore) intercepts the seam/fracture, the LNAPL fills the well to the extent that the pressures equilibrate. Hence, you could have a large in-well thickness resulting from a relatively small LNAPL saturated seam/fracture. LNAPL recovery in this situation may be very poor. Conversely, small in-well LNAPL thicknesses in transmissive formations may yield much greater LNAPL recoveries.

- If LNAPL exists in a well, the LNAPL must be mobile and migrating.

  Not necessarily true: LNAPL mobility and migration are functions of LNAPL saturation, relative permeability and other soil and LNAPL properties. The mere presence of LNAPL in a well does not necessarily mean that the LNAPL has the potential to migrate.

The proper use of in-well LNAPL thickness information requires an examination of LNAPL thickness changes over time in response to fluctuating water table elevations and other potential contributing factors (including whether or not active LNAPL recovery is being conducted in the area). In an unconfined setting, the greatest in-well LNAPL thicknesses (and the best indication of the spatial distribution of the LNAPL) tend to occur during the lowest water table conditions. When used properly, in-well thicknesses measured over time can provide a good general depiction of LNAPL spatial distribution. However, when used inappropriately or misunderstood, decisions based on in-well thickness may not have a sound scientific basis.

Some regulatory requirements/guidance associated with LNAPL indicate that project/site closure may be obtained if no LNAPL, or less than some minimum threshold thickness of LNAPL, is identified in monitoring wells over a stipulated period of time. Numerous projects/sites have been closed by regulators on the basis that the stipulated in-well LNAPL thickness requirements have been met. However, in some of these situations, the LNAPL has not diminished in presence or been recovered, but rather, has been submerged by a high water table, thereby preventing its occurrence in monitoring wells. In these situations, the LNAPL will likely reappear in the well when the water table elevation drops. Hence, the stipulated regulatory requirement for project/site closure does not reflect and is not based on the LNAPL “science” and can result in the closure of projects/sites where the true risks associated with the LNAPL may not be understood. This dilemma, in part, has caused some regulatory agencies to move away from the “perception” of LNAPL risks based on in-well thicknesses, and toward the LNAPL “science” and the development of a technically sound LNAPL Conceptual Site Model (LCSM).