



Petroleum Site Management Update - A Roadmap to Closure

Introduction

Cleanup of sites contaminated with petroleum products including light non-aqueous phase liquid (LNAPL) remains a significant challenge for the U.S. Navy. In 2010, the NAVFAC LNAPL Site Management Handbook (NAVFAC, 2010) was developed to provide an overview of effective strategies to aid Navy Remedial Project Managers in managing these petroleum release sites to ensure protectiveness of human health and the environment, while simultaneously avoiding unnecessary and prolonged remedial efforts. This fact sheet emphasizes recent advances in management approaches, monitoring strategies, and remedial technologies since the handbook was developed. As shown in Figure 1, this fact sheet and the companion LNAPL Site Management Handbook provide a roadmap to closure for managing petroleum sites.

The management of LNAPL sites is shifting toward a more sustainable risk-based paradigm. Although Federal law (40 CFR 280.64) requires LNAPL to be recovered to the “maximum extent practicable,” implementing agencies have exercised some flexibility in

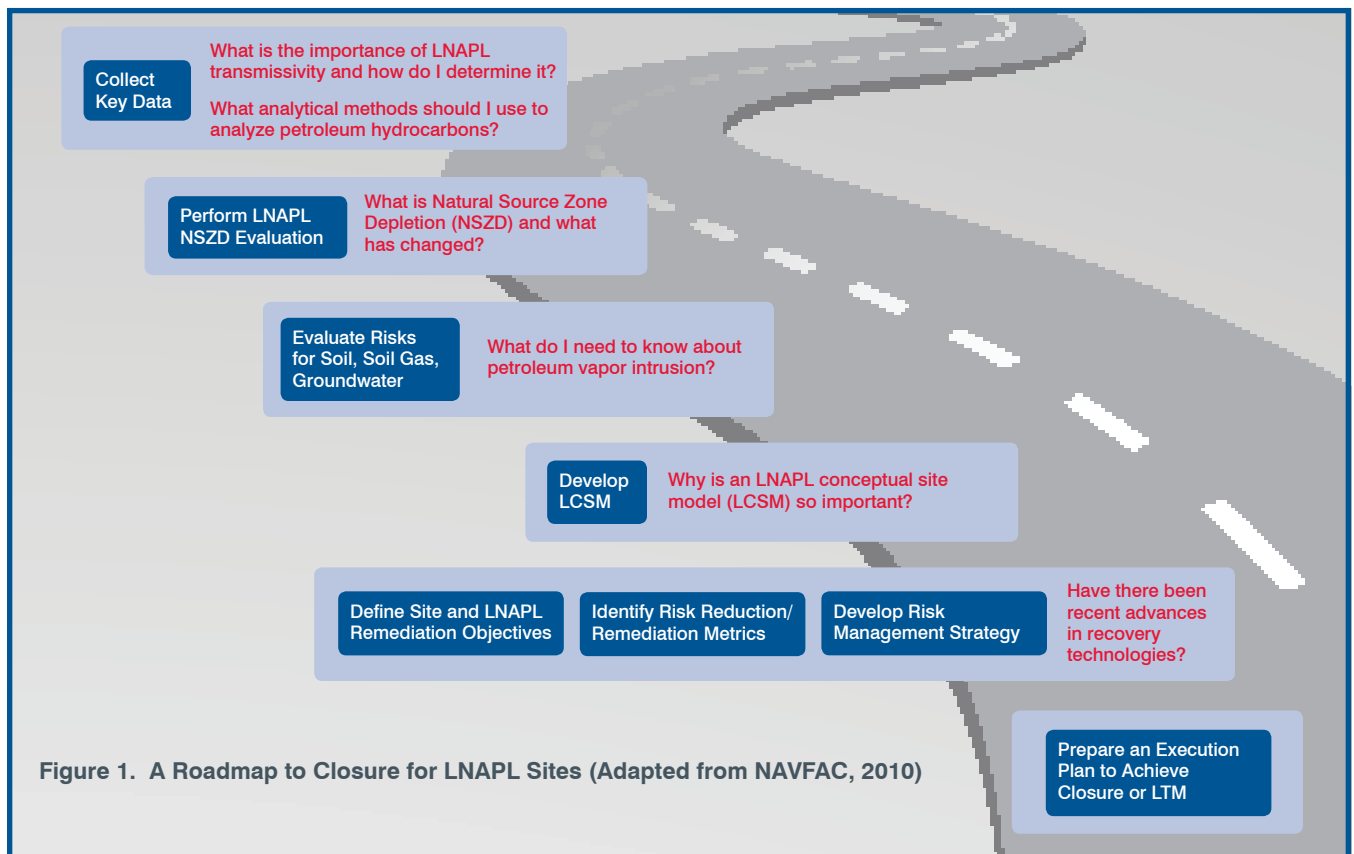


Figure 1. A Roadmap to Closure for LNAPL Sites (Adapted from NAVFAC, 2010)

defining the “extent practicable” on a state-by-state basis. In a number of states, policies have recently shifted to a risk-driven approach that considers LNAPL mobility and results in more cost-effective cleanups, while protecting human health and the environment. Although regulatory authorities require LNAPL recovery to the maximum extent practicable and some states may still require that any measurable LNAPL be recovered, a majority of states have re-assessed their interpretation of what is practicable. It is mostly acknowledged that recovering LNAPL until residual saturation is achieved (i.e., little or no LNAPL in wells) is not practical nor effective and relying on natural source zone depletion (NSZD) is equally protective and may provide the best balance of technical, societal, and cost considerations.

Regulatory authorities are shifting policy and guidance to adapt to a risk-based approach to LNAPL site management, and in many cases, are asking site owners to answer the following three questions:

- Is the LNAPL at risk of migrating?
- How much of the LNAPL is recoverable?
- Are there any potential risk exposure scenarios if LNAPL remains?

The LNAPL site management strategy must be designed to answer these three questions, address any risks that the site may present, and facilitate future decision-making. The benefits of implementing such a strategy include: (1) garnering regulatory approval for a site management approach that explicitly acknowledges the inherent challenge of LNAPL remediation and incorporates an adaptive remediation process; (2) recognizing the ability of intrinsic processes (e.g., NSZD) to contain or reduce LNAPL; and (3) helping to achieve a cost-effective and more environmentally sustainable remediation program.

What is the Importance of LNAPL Transmissivity and How Do I Determine it?

An important new development in LNAPL site management is the use of transmissivity to evaluate LNAPL recovery. LNAPL thickness in site wells has historically been used to estimate its recoverability and mobility. The old

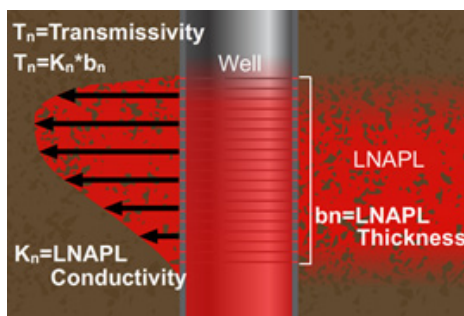


Figure 2. LNAPL Transmissivity

“pancake” saturation and distribution model assumed that LNAPL thickness in the formation was similar to that measured in site wells, which led to overestimates of LNAPL volume, recoverability, and risk. More recently, LNAPL transmissivity has been defined as the

volume of LNAPL through a unit width of aquifer per unit time per unit drawdown (see Figure 2). It has units of length²/time (L²/T) and is being used as a line of evidence to predict LNAPL recoverability. Unlike product thickness in a well, transmissivity is dependent on soil type and properties (e.g., porosity, conductivity), chemical and physical properties of the LNAPL (e.g., density, viscosity, composition), LNAPL saturation in the formation, as well as the thickness of the mobile LNAPL (Interstate Technology & Regulatory Council [ITRC], 2009a). This makes it a useful metric for estimating recovery.

LNAPL transmissivity is an important part of any LNAPL conceptual site model (LCSM). To determine transmissivity, soil lithology across the zone where LNAPL is present and the hydraulic conductivity within each interval must be known. Equilibrium fluid levels in wells and well construction details must also be known to establish baseline conditions. Calculation tools are available for estimating LNAPL transmissivity.

CALCULATION TOOLS

The American Petroleum Institute (API) provides a useful tool for calculating LNAPL transmissivity from baildown test data (API, 2012).

The American Society for Testing and Materials (ASTM) has developed standardized guidance (E2856-13) for estimating LNAPL transmissivity at a site (ASTM, 2013). The ASTM method provides procedures for estimating transmissivity by performing baildown tests, skimmer pump tests, performing continuous recovery with a treatment system, and by performing tracer tests.

State agencies are beginning to incorporate the concept of transmissivity into their regulations and guidance and encouraging its use to make sound LNAPL management decisions. For instance, the Michigan Department of Environmental Quality (MDEQ) states in its recently issued petroleum cleanup guidance that if LNAPL remaining at a site has a transmissivity greater than 0.5 ft²/day, it is likely that additional recovery would be beneficial and that the LNAPL may be recovered in a cost-effective and efficient manner (MDEQ, 2014). Similarly, the Massachusetts Department of Environmental Protection (MDEP) deems LNAPL recovery to be infeasible when LNAPL transmissivity in all recovery wells is less than 0.8 ft²/day or the total volume of LNAPL recovered at a site is less than 1 gallon in any 3 month period (MADEP, 2002).

What Analytical Methods Should I Use to Analyze Petroleum Hydrocarbons?

Analysis of total petroleum hydrocarbons (TPH) in soil and groundwater is not new; standard analytical methods have been in existence and utilized for several decades. However, it is important to stress that there are substantial differences

between various methods, the results of which can influence the LNAPL management strategy and one's ability to achieve site closure.

The most common method to analyze TPH in soil and groundwater is Environmental Protection Agency (EPA) Method 8015, which employs a gas chromatograph (GC) and a flame ionization detector (FID) for analysis. EPA Method 8015 can be used to analyze gasoline range organics (GRO) comprised of carbon range C_6 to C_{10} , covering a boiling point range of approximately 60 to 170 °C, and diesel range organics (DRO) comprised of carbon range of C_{10} to C_{28} , covering a boiling point range of approximately 170 to 430 °C (EPA, 1996). In addition to EPA Method 8015, various states have developed their own methods to evaluate the presence of TPH in soil and groundwater. Each of these methods has slight differences and may report data across slightly different carbon and boiling point ranges. Also, each state may have specific requirements for the analysis of individual TPH constituents depending on the nature of the LNAPL source (e.g., BTEX, naphthalene, MTBE, and TBA). Hence, it is important to consult with local regulatory agencies prior to identifying a particular analytical method for TPH.

A debated issue associated with the analysis of TPH is the use of silica gel to remove interferences that may contribute to an inaccurate TPH value. These interferences, which can include naturally occurring organic material and polar petroleum hydrocarbon degradation products such as aldehydes, ketones, alcohols, phenols and organic acids and esters, can result in reporting a TPH value that is substantially greater than the concentration due to the petroleum hydrocarbon itself. Silica gel cleanup has been successfully performed at Navy Base Realignment and Closure (BRAC) sites to better define the required footprint for excavation of petroleum impacted soils containing significant organic matter.

EPA Method 8015b provides an option for performing silica gel cleanup; however, specific state methods may require or prohibit silica gel cleanup. For instance, Florida Department of Environmental Protection (FDEP) FL-PRO method (FDEP, 1995) requires that a silica gel cleanup be performed to remove these interferences, whereas Washington State Department of Ecology (WSDOE) guidance (WSDOE, 2011) has been updated to state that silica gel should not be used unless naturally occurring organic matter is a significant portion of the TPH detected. The rationale for not performing silica gel cleanup stems from the possibility that some of the byproducts produced from the degradation of the parent petroleum hydrocarbon compounds may present a degree of toxicity, which had not been accounted for in historical risk assessments. However, recent research performed by analyzing these intermediate products and by performing aquatic toxicity testing indicate that these byproducts do not increase the toxicity of groundwater (Zemo et al., 2014).

What is Natural Source Zone Depletion and What Has Changed?

NSZD refers to naturally occurring processes including dissolution, volatilization, biodegradation, and sorption, which serve to attenuate LNAPL plumes. An NSZD evaluation helps to answer questions such as: 1) how long will LNAPL persist if not treated, 2) will active treatment help to achieve remedial action objectives in a reasonable time frame, and 3) are there portions of a site where treatment can cost-effectively increase depletion rates? The LNAPL Site Management Handbook (NAVFAC, 2010) describes NSZD, the importance of including it in the LCSM, and how it can be combined with other lines of evidence to provide strong technical support for the most appropriate LNAPL site management approach. Specific procedures and calculations to determine NSZD depletion rates can be found in the document *Evaluating Natural Source Zone Depletion at Sites with LNAPL* prepared by the ITRC (ITRC, 2009b). Key data and their use are presented in Table 1. A number of software modeling packages are available that can be used to evaluate various aspects of NSZD including mobility, dissolution, volatilization, and biodegradation.

New tools developed to gather data to evaluate NSZD include carbon dioxide (CO_2) traps (Environmental Security Technology Certification Program [ESTCP], 2014) and flux chambers. The CO_2 traps are passive adsorption devices that measure CO_2 in shallow points at or near grade. Because LNAPL is eventually converted into CO_2 through attenuation processes, multiple traps deployed across a site are an effective means of evaluating LNAPL depletion rates. Flux chambers use a mechanical method to circulate the chamber headspace through an internal manifold and gas analyzer. These devices are relatively inexpensive and easy to install with minimal training or site work. Carbon isotopes can also be analyzed to better differentiate between the degradation rates of petroleum hydrocarbons versus non-petroleum hydrocarbon fractions.

Table 1. Key Data to Evaluate NSZD

Data Need	Description
Groundwater	
Hydraulic conductivity, gradient, and source zone configuration	Estimate water flow through the source zone
Dissolved electron acceptor reactant (O ₂ , NO ₃ ⁻ , SO ₄ ²⁻) and product (Fe ²⁺ , Mn ²⁺ , CH ₄) up- and down-gradient of the source zone	Changes in values between up- and down-gradient wells are used to estimate hydrocarbon mass depletion rates and to provide evidence of biodegradation
Dissolved hydrocarbon concentrations up- and down-gradient of the source zone	Determine hydrocarbon source zone mass depletion rate due to dissolution not accounted for by biodegradation
Volume of water extracted and dissolved hydrocarbon and electron acceptor related data during active treatment	Coupled with an understanding of site hydrogeology to determine the fraction of flow passing through the source zone captured by extraction versus migrating down gradient, mass depletion resulting from extraction can be estimated
Vadose Zone (one method is sufficient)	
Soil gas profiles for hydrocarbons and respiration and biogenic gases (O ₂ , CO ₂ , CH ₄). Effective diffusion coefficient (can be stimulated using soil moisture and total porosity; or measured)	Depleted O ₂ is used to estimate NSZD; provides evidence of biodegradation Hydrocarbon and biogenic gas profiles demonstrate volatilization and vapor transport
CO ₂ surface flux measurements (chamber or CO ₂ trap methods)	Estimate mass depletion rate due to biodegradation. Provides a vadose zone mass depletion rate estimate independent of soil gas profiles and effective diffusion coefficient
If soil vapor extraction (SVE) or bioventing system is operating. Air extraction and/or injection rates couple with hydrocarbon, O ₂ and CO ₂ in extracted gas during operation of active remedy (e.g., soil vapor extraction, bioventing)	Extraction rates and gases are used to estimate mass removal rates, biodegradation and volatilization In situ respiration testing used to estimate biodegradation rates, required for bioventing, optional for SVE

What Do I Need to Know about Petroleum Vapor Intrusion?

Petroleum vapor intrusion (PVI) is the process by which vapors that volatilize from LNAPL, contaminated soils or groundwater migrate through the vadose zone into nearby buildings. The primary difference between PVI and chlorinated solvent vapor intrusion is that PVI is more readily mitigated due to extensive biodegradation that occurs in the vadose zone between the source of contamination and the building foundation. EPA is in the process of developing guidance for PVI at underground storage tank (UST) sites. Additional information regarding the status of the EPA guidance can be found at <http://www.epa.gov/oust/cat/pvi/>. In addition, ITRC has published a guidance document to help practitioners and regulators better understand when it is appropriate to use a screening method to evaluate PVI, how to investigate if a complete PVI risk pathway exists, and how to mitigate PVI if the pathway is potentially complete (ITRC, 2014).

A comprehensive LNAPL site management plan must evaluate the potential risks present due to PVI and provide a strategy

to mitigate them should they be found to exist. The principal question that must be answered is: does a complete PVI pathway exist (accounting for biodegradation)? ITRC's PVI guidance document (ITRC, 2014) provides a simple screening method that examines the vertical distance between the petroleum contamination and the building foundation to estimate if the PVI pathway is complete or not. In general, it is recommended that if the vertical separation distance between the building foundation and the LNAPL source is greater than 15 and 18 ft for petroleum storage tank sites and petroleum industrial sites, respectively, and the vertical distance between the building foundation and the water table is greater than 5 ft, then additional evaluation is not necessary (ITRC, 2014). However, detailed site characterization may be needed if results of preliminary screening are inconclusive or if precluding factors such as preferential pathways, on-going release of source material, presence of volatile fuels (e.g., gasoline), or soil conditions that inhibit biodegradation of petroleum hydrocarbons are present. ITRC provides useful guidance for performing a more detailed investigation based on several site-specific scenarios (ITRC, 2014), which can be found at

<http://www.itrcweb.org/PetroleumVI-Guidance/>. If screening or additional characterization demonstrates that there likely is a complete pathway for PVI, then the LNAPL site management plan should include some form of mitigation, which could consist of institutional controls, passive or active mitigation at the building, and active remediation.

Why Is an LNAPL Conceptual Site Model So Important?

It is necessary to re-emphasize the importance of the LCSM. The LCSM provides the basis from which all management decisions are made, and hence, to the extent possible, should provide an accurate and detailed assessment of the LNAPL and its residual, dissolved, and vapor phase constituents at a site. Management decisions based solely on the thickness of LNAPL measured should be avoided since past experience has demonstrated that the thickness does not correlate well with risk or recoverability. Better metrics include mobility of free-phase LNAPL, stability of the plume body, and the source strength, all of which have a direct impact on risk. A mass balance approach can be used to quantify NSZD. LNAPL mass in the saturated zone and the vadose zone may be determined and compared to mass reduction processes including dissolution, biodegradation, and volatilization. Reduction in source strength, quantified as a rate (lbs/yr) or flux (lbs/ft²/yr) may be compared to reductions estimated for active remediation to determine if a proposed remedy provides a significant benefit. Several resources that address these metrics and provide further guidance for developing comprehensive LCSMs for risk-based decision-making include:

- ASTM E2531-06E1 Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface (ASTM, 2006)
- *Evaluating LNAPL Remedial Technologies for Achieving Project Goals* (ITRC, 2009a)
- *Evaluating Natural Source Zone Depletion at Sites with LNAPL* (ITRC, 2009b)
- Environmental Cleanup Best Management Practices: Effective Use of the Project Life Cycle Conceptual Site Model (EPA, 2011)

Developing the LCSM is an iterative process. As additional information is gathered, the LCSM is refined and may change. At some sites, at which risk is known to be limited, little additional site-specific data may be required. However, at sites where risk is either unknown, and/or where it is necessary to reduce uncertainties, additional site characterization may be required. Techniques such as high resolution site characterization (HRSC) including multi-level sampling, optical screening technologies such as laser-induced fluorescence (LIF), membrane interface probe (MIP), geophysics, and other

enhanced characterization techniques may be considered. Resources for advanced characterization techniques include:

- High Resolution Site Characterization Remediation Innovative Technology Seminar (RITS) (NAVFAC, 2014a)
- High Resolution Site Characterization for Groundwater Factsheet (NAVFAC, 2014b)

Have There Been Recent Innovations in LNAPL Remediation?

There has been little change in LNAPL remediation technologies. Existing technologies, described in the LNAPL Management Handbook (NAVFAC, 2010), are still applied routinely at sites. Vendors continue to formulate new amendments and develop proprietary equipment (e.g., specialized skimmers) to facilitate LNAPL recovery or in situ destruction. However, the efficacy of these innovations is largely unproven for a wide range of site conditions. Nonetheless, researchers continue to investigate new technologies and approaches to improve LNAPL remediation, especially at complex sites where conditions impede the successful application of conventional technologies. For instance, a novel approach is being tested to treat long-chain viscous LNAPL contamination (e.g., creosote, Bunker C, Navy Special Fuel Oil). The technology applies an ignition source and introduces air into the aquifer to propagate a thermal front, which oxidizes the LNAPL. Because heat is not applied continuously as with other thermal technologies, the cost of energy is minimized. Limited applications of this technology have been performed to date; therefore, its benefits and limitations have not been fully defined. Demonstrations are planned at two Navy facilities including Naval Air Station North Island and the Fleet and Industrial Supply Center, Defense Fuel Supply Point Yorktown. Additional details regarding this and other innovative technologies will be provided through Technology Transfer (T2) e-mails as it becomes available.

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Resources

- American Petroleum Institute (API). (2012). User Guide for the API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis. API Publication. September.
- American Society for Testing and Materials (ASTM). (2006). Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface. Publication E2531-06e1.
- American Society for Testing and Materials, West Conshohocken, PA.
- American Society for Testing and Materials (ASTM). (2013). Standard Guide for Estimation of LNAPL Transmissivity. Publication E2856-11E01. American Standard Testing Material International, West Conshohocken, PA.
- Environmental Protection Agency (EPA). (1996). Method 8015b Nonhalogenated Organics Using GC/FID. Revision 2. December.
- Environmental Protection Agency (EPA). (2011). Environmental Cleanup Best Management Practices: Effective use of the Project Life Cycle Conceptual Site Model. Office of Superfund Remediation and Technology Innovation. EPA-542-F-11-011. July.
- Environmental Security Technology Certification Program (ESTCP). (2014). Frequently Asked Questions about Monitored Natural Attenuation in Groundwater, FAQ 15. What are CO₂ traps and how do they help me show attenuation? Prepared by David Adamson and Charles Newell. February.
- Florida Department of Environmental Protection (FDEP). (1995). Florida Petroleum Residual Organic (FL-PRO) - an Alternative Method to Total Recoverable Petroleum Hydrocarbons by 418.1 or 9073. Revision 1. November.
- Interstate Technology & Regulatory Council (ITRC). (2009a). Evaluating LNAPL Remedial Technologies for Achieving Project Goals. LNAPL-2. Washington, D.C.: Interstate Technology & Regulatory Council, LNAPLs Team.
- Interstate Technology & Regulatory Council (ITRC). (2009b). Evaluating Natural Source Zone Depletion at Sites with LNAPL. LNAPL-1. Interstate Technology & Regulatory Council, Washington, D.C.
- Interstate Technology & Regulatory Council (ITRC). (2014). Petroleum Vapor Intrusion, Fundamentals of Screening, Investigation, and Management. Interstate Technology & Regulatory Council, Washington, D.C. October.
- Massachusetts Department of Environmental Protection (MADEP). 2002. Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the VPH/EPH Approach; Policy #WSC-02-411.
- Michigan Department of Environmental Quality (MDEQ). (2014). Non-Aqueous Phase Liquid (NAPL) Characterization, Remediation, and Management For Petroleum Releases. Prepared by the Michigan DEQ Remediation and Redevelopment Division. RRD Resource Materials-25-2014-01. June.
- Naval Facilities Engineering Command (NAVFAC). (2010). LNAPL Management Handbook. November.
- Naval Facilities Engineering Command (NAVFAC). (2014a). High Resolution Site Characterization RITS.
- Naval Facilities Engineering Command (NAVFAC). (2014b). High Resolution Site Characterization for Groundwater Factsheet
- Washington State Department of Ecology (WSDOE). (2011). Guidance for Remediation of Petroleum Contaminated Sites. Toxics Cleanup Program
Publication No. 10-09-057. September.
- Zemo, Dawn, Rachel Nohler, Asheesh Tiwary, Kirk O'Reilly, Renae Magaw, Catalina Espino-Devine, and Karen Sunowiec. (2014). Nature and Estimated Toxicity of Polar Metabolite Mixtures in Groundwater Quantified as Extractable "TPH" at Biodegrading Fuel Release Sites. Presented at the NEBC Technical Seminar. October.